I. THE REDUCTION OF MOLECULAR NITROGEN IN BINUCLEAR DINITROGEN COMPLEXES OF TITANIUM AND ZIRCONIUM.

II. HYDROGEN REDUCTION OF CARBON MONOXIDE PROMOTED BY MONONUCLEAR CARBONYL AND HYDRIDE COMPLEXES OF BIS(PENTAMETHYL-CYCLOPENTADIENYL) ZIRCONIUM.

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to Marcela and Ignacio

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Abstract

I. The Reduction of Molecular Nitrogen in Binuclear Dinitrogen Complexes of Titanium and Zirconium.

II. Hydrogen Reduction of Carbon Monoxide Promoted by Mononuclear Carbonyl and Hydride Complexes of Bis(pentamethylcyclopentadienyl)Zirconium.

PART I

The synthesis and characterization of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ (1), $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (2), $\{(\eta^5C_5Me_5)_2Zr(CO)\}_2N_2$ (3), and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ (4) are described. 1 is prepared from lithium pentamethylcyclopentadienide and zirconium tetrachloride. Sodium amalgam reduction of 1 under N_2 yields 2. 3 and 4 are prepared by substitution of the two terminal dinitrogen ligands by CO and PF_3, respectively. In solution 2 (and 4) exhibits fluxional behavior. The dynamics of 2 in solution as studied by ^1H and ^{15}N NMR shows that 2 undergoes $[\eta^5\text{-}C_5Me_5]$ ring site exchange as a result of the lability of the terminal dinitrogen ligands. A re-investigation of the titanium system analog in solution showed that the complex, originally assigned the formula $(\eta^5\text{-}C_5Me_5)_2TiN_2$, is in fact analogous to the zirconium complex i.e. $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$ (5). The product distribution (N_2H_4, NH_3) for the reaction of 2, 3, 4, 5, and $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (6) with anhydrous HCl in toluene is reported. Hydrazine obtained in high yields obtained

from the reaction of 2 and 5 with HCl. 6 also gives hydrazine but in much lower yield. Under the same conditions the reaction with HCl for the complexes 3 and 4 results in the quantitative release of the dinitrogen and partial reduction of the terminal ligands. The product distribution for the reaction of 2 with HBr, HCl, and H_2SO_4 each being carried out in toluene, diethyl ether and methanol is also reported. 2-$(^{15}N_2)_3$ exchanges only terminal dinitrogen ligands with free $^{14}N_2$ in toluene solution at -23°. Treatment of 2 which is labelled with $^{15}N_2$ exclusively in the bridge position yields 1.5 mols $^{14}N_2$, 0.5 mol $^{15}N_2$, 0.5 mol $^{14}N_2H_4$, and 0.5 mol $^{15}N_2H_4$. The implications of these data with regard to the N_2 reduction sequence are discussed.

The reactions of 2, 3, 4, and 6 with $LiAlH_4$ are reported. 2 gives hydrazine (0.5 mol) and ammonia (1 mol) after hydrolysis of the reaction products with HCl. 6 also gives hydrazine and ammonia but in lower yield. Under the same conditions the reaction of 3 and 4 results in the evolution of most of the dinitrogen. A study of the reaction of 2 labelled with $^{15}N_2$ exclusively in the bridge position showed that the hydrazine and ammonia originate from the bridge position.

PART II

The synthesis and characterization of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (1), $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2), and $]C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ prepared from

$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ are described. Both 1 and $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ react with H_2 forming $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$(4) in high yield. 2 reacts with CO and PF_3 at -80° to yield $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$ (3) and $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(PF_3)$. 3 dimerizes to $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2$ (μ-OCH=CHO) above -50°. In the presence of 2, 3 may be reduced to 4. These observations are interpreted in terms of a reaction sequence mediated by the formyl hydride complex $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ derived from 3 via migratory insertion. The reaction of 2 with formaldehyde on an equal molar basis produces a mixture of 4 and $(\eta^5\text{-}C_5Me_5(_2Zr(OCH_3)_2$. The implications of these results with respect to the possible intermediacy of formaldehyde in the formation of 4 and the plausible mechanisms for the formation of 4 and $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(\mu\text{-}OCH=CHO)$ are discussed. The synthesis of $(\eta^5\text{-}C_5Me_5)_2HfCl_2$ and $(\eta^5\text{-}C_5Me_5)_2HfH_2$ are reported. A comparison of the bis(pentamethylcyclopentadienyl) hydrides of group IV with the bis(cyclopentadienyl) hydrides of groups V, VI, and VII is made. The possible determining factor in the rearrangement of 3 to $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ is discussed.

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Preparation of:

CHAPTER I

Introduction

Dinitrogen complexes are coordination compounds which contain the N_2 molecule as a ligand. The possibility of the existence of such complexes was predicted on theoretical grounds in 1960, both by Orgel[1] and Ruch[2], but it was not until 1965 that Allen and Senoff[3] in an attempted synthesis of an amine complex from $RuCl_3$ and hydrazine hydrate found that the expected $[Ru(NH_3)_6]^{+2}$ ion was not formed, but instead the stable complex $[(NH_3)_5RuN_2]Cl_2$.

About the same time as this discovery, Volpin and Shur[4] made the observation that Ziegler-Natta systems and similar combinations of transition metal compounds and organometallic reducing agents take up gaseous nitrogen at room temperature and pressures from 1 to 150 atm. After hydrolysis of these mixtures, the nitrogen is collected as NH_3.

Both discoveries, together with the fact that it was known, long before, that the part played by transition metals in the activation of this inert molecule in enzyme systems and in the Haber-Bosch process, almost certainly involved the formation of a metal-dinitrogen complex, led in the last decade to an intensive search for simple chemical systems that would mimic the reductive fixation of N_2 by living systems.

The result of this search was, on one hand, the preparation of a considerable number of new transition metal dinitrogen

complexes (today more than 100 are known) and, on the other hand, that several transition metal compounds in combination with or without a reducing agent were able to convert N_2 to ammonia or hydrazine.

Attempts to reduce the complex bound N_2 ligand in well characterized dinitrogen complexes proved to be, until recently, quite disappointing, and usually resulted in the liberation of the coordinated dinitrogen. In the case of the complexes of type trans-$[M(N_2)_2Ph_2PCH_2CH_2PPh_2]$ (M=Mo, W), one N_2 ligand is eliminated and the other N_2 ligand is reduced to the hydrazido ($M{\equiv}N\text{-}NH_2$) or diazene form ($M \leftarrow N(H)=NH$) from which the release and/or further reduction of the N_2H_2 moiety could not be realized[5, 6].

The N_2-reducing systems proved to be much more fruitful; however, what the chemist wanted was a defined system in which he could follow the reduction of the N_2 molecule step by step, isolate and unambiguously characterize the compounds involved in the system. The combination bis(cyclopentadienyl)titanium dichloride/ethyl magnesium bromide in ether was one of the first N_2-reducing systems with which Volpin and Shur[7] observed the fixation and reduction of nitrogen in 1964. The intermediacy of bis(cyclopentadienyl) titanium(II) in titanocene-based N_2-reducing systems was shown by several workers[8, 9, 10, 11]. Thus for example, it has been shown that solutions of a metastable form of titanocene, $[(C_5H_5)_2Ti]_2$, prepared from different sources absorb N_2 in situ

to yield a binuclear dinitrogen complex $[(C_5H_5)_2Ti]_2N_2$. Yet in no case has it been possible to obtain this dinitrogen complex as a uniform crystalline material, and the chemical and physical properties of $[(C_5H_5)_2Ti]_2N_2$ appear to be different depending on its mode of preparation. The instability of the metastable species $[(C_5H_5)_2Ti]_2$ with respect to rearrangement to titanium hydride complexes via a ring α - hydrogen shift[9,12,13,14] is undoubtedly contributory to the above disparities.

In order to eliminate the occurrence of an α-hydrogen shift, the synthesis of permethyltitanocene, $[C_5(CH_3)_5]_2Ti$, was undertaken[9]. These efforts resulted in the isolation of a stable derivative of titanocene and the isolation of a stable dinitrogen complex $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$[8,15]. Although the dinitrogen in the above complex remained inert toward reduction, $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ was able to pick up more dinitrogen in solution to give another dinitrogen complex, which could not be isolated, but released hydrazine in moderate yields upon treatment with HCl.

About the same time of this discovery, we began to investigate the analogous zirconium system with the hopes of obtaining a dinitrogen complex with similar reactivity and an enhanced stability. The results of this investigation are shown in the following pages.

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Part A

Preparation of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and Protonation Leading to Stoichiometric Reduction of Dinitrogen to Hydrazine

Abstract

The synthesis and characterization of $[C_5(CH_3)_5]_2ZrCl_2$ 1 and $\{[C_5(CH_3)_5]_2Zr\}_2(N_2)_3$ 2 are described. 1 is prepared from lithium pentamethylcyclopentadienide and zirconium tetrachloride. Sodium amalgam reduction of 1 under N_2 yields 2. Treatment of 2 with excess HCl at -80° yields 1, 2 mols of N_2, and $N_2H_4 \cdot 2\,HCl$ in near stoichiometric yield.

Sir:

In connection with our studies of dinitrogen complexes of Group IV transition metal cyclopentadienyls, we have prepared a dinitrogen complex of permethylzirconocene via the following sequence:

$$ZrCl_4 + 2Li[C_5(CH_3)_5] \longrightarrow \underset{1}{[C_5(CH_3)_5]_2ZrCl_2} + 2\,LiCl \quad (1)$$

$$2\underset{1}{[C_5(CH_3)_5]_2ZrCl_2} + 4Na(Hg) \xrightarrow{N_2} \underset{2}{\{[C_5(CH_3)_5]_2Zr\}_2(N_2)_3} + 4\,NaCl \quad (2)$$

Lithium pentamethylcyclopentadienide is prepared from 1,2,3,4,5-pentamethylcyclopentadiene and n-butyllithium in 1,2-dimethoxy-

ethane, then treated in situ with freshly sublimed zirconium tetrachloride. Permethylzirconocene dichloride, 1, is isolated in good yield (50-60%) by a procedure similar to that for the analogous titanium derivative.[1,2] Pale yellow crystalline 1 so obtained analyzes satisfactorily[3] and exhibits a singlet nmr absorption at 1.99 ppm ($CDCl_3$), nearly identical in position to that observed for permethyltitanocene dichloride.[1]

Reduction of 1 with excess sodium amalgam in toluene under 1 atm of N_2 leads, over the period of two days at room temperature, to a dark permanganate-red dinitrogen complex, 2. 2 is isolated in moderate yields (30-40%) as large, well-formed, metallic green[4] crystals by removal of toluene, extraction and subsequent recrystallization from pentane under 1 atm of nitrogen. 2 is moderately soluble in toluene, but only slightly soluble in pentane or diethyl ether. At room temperature in solution, 2 reversibly releases its dinitrogen in vacuo over a period of several hours. Quantitative measurements of the N_2 released (eq. 3) as well as elemental analyses[5] are in good agreement with the stoichiometry $\{[C_5(CH_3)_5]_2Zr\}_2(N_2)_3$.

$$\underset{2}{\{[C_5(CH_3)_5]_2Zr\}_2(N_2)_3} \rightleftharpoons 2\underset{3}{[C_5(CH_3)_5]_2Zr}^{6} + 3N_2 \qquad (3)$$

The molecular weight determined cryoscopically for a solution containing 53.3 mg 2 per g benzene was 820±100, indicating a binuclear solution structure as suggested by its stoichiometry (807 is

calculated for 2). The ^{1}H-nmr spectrum[7] for 2 in toluene-d_8 at 25° shows a single, somewhat broadened resonance centered at δ 1.75 ppm. Below ca. 5° this signal splits into two resonances of nearly equal intensity at 1.74 and 1.76 ppm, indicative of the presence of two isomers of 2 which are in rapid equilibrium on the nmr time scale above this temperature. The full details of this equilibrium are presently under investigation utilizing ^{13}C and ^{15}N nmr and ir spectroscopy and will be reported in a forthcoming full paper. The infrared spectrum of 2 (nujol mull) exhibits, in addition to those bands characteristic of [η^5-$C_5(CH_3)_5$] rings, two strong bands at 2041 and 2006 cm^{-1} and a band of medium intensity at 1556 cm^{-1} which shift upon substitution of doubly labelled $^{15}N_2$[8] to 1972, 1937, and 1515 cm^{-1}, respectively. These three bands are thus attributed to NN stretching frequencies for 2. The 1556 cm^{-1} band, the position of which suggests a major reduction in the N≡N bond order, could possibly be due to a bridging N_2 in a non-centrosymmetric structure, e.g.,

$$[C_5(CH_3)_5]_2Zr\begin{array}{c}\diagdown\\ N_2\end{array}\!\!-\!N\equiv N\!-\!\begin{array}{c}\diagup\\ N_2\end{array}\!\!Zr[C_5(CH_3)_5]_2 \ .$$

The X-ray crystal structure determination for 2, in progress at the time of this writing, should settle the questions concerning the mode(s) of Zr-N_2 bonding in this dimer.

Treatment of 2 with a ten-molar excess of HCl at -80° in toluene yields, after subsequent warming to room temperature, a

mixture of $\underset{\sim}{1}$, N_2, H_2 ($Zr:N_2:H_2$ = 1.000:0.998:0.158),[9] and a white crystalline solid identified as pure $N_2H_4 \cdot 2\,HCl$.[10] Equation 4 is consequently implicated as a major reaction pathway wherein the four reducing equivalents available in the dimer are utilized in the reduction of one of the three mols of N_2 to N_2H_4.

$$\{[C_5(CH_3)_5]_2Zr\}_2(N_2)_3 + 4\,HCl \longrightarrow$$

$$2\,[C_5(CH_3)_5]_2ZrCl_2 + 2N_2 + N_2H_4 \qquad (4)$$

At present $\underset{\sim}{2}$ appears to be the best characterized dinitrogen complex capable of liberating reduced N_2 on simple protonation[11,12] and thus represents a first stage of dinitrogen activation well-suited for further study. We are presently investigating the essential features of this reaction with respect to whether di-imide is an intermediate in hydrazine formation and/or whether the reduction involves a μ-dinitrogen.

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3. Calculated for $C_{20}H_{30}Cl_2Zr$: C 55.56, H 6.94, Cl 16.40, Zr 21.10; found: C 55.57, H 6.99, Cl 16.36, Zr. 21.21.
4. The metallic green color of these large crystals appears to be associated with a very high index of refraction. When dissolved in toluene or petroleum ether, even at -80°, dark permanganate-red solutions are observed. Furthermore, the powder obtained by grinding these large green crystals appears red to transmitted but metallic green to reflected light. On the basis of these observations we conclude that the permanganate-red and metallic green compounds are compositionally identical.
5. Calculated for $C_{20}H_{30}N_3Zr$: C 59.54, H 7.44, N 10.41, Zr 22.61; found: C 59.75, H 7.36, N 10.18, Zr 22.77.
6. Although 3 has not been completely characterized at present, its nmr spectrum strongly suggests that the predominant species in solution has the structure $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$, apparently formed via a reversible ring methyl hydrogen abstraction by the Zr center for the tautomer $[\eta^5\text{-}C_5(CH_3)_5]_2Zr$. A completely analogous tautomeric behavior has recently been established for $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ (ref. 2).

7. Spectra were recorded on a Varian HR-220 (CW) spectrometer. ^{1}H chemical shifts were calculated from their positions relative to the residual aromatic protons in toluene-$\underline{d}_8$ and converted to values relative to (and downfield of) TMS at δ 0.

8. Bio-Rad "$N_2{}^{15}$" with a composition (mass spectrum) of $^{15}N\equiv N^{15}$, 93.3%; $^{15}N\equiv N^{14}$, 6.3%; $^{14}N\equiv N^{14}$, 0.37%.

9. Identical treatment of $\underset{\frown}{3}$ with HCl yields only $\underset{\frown}{1}$ and H_2 in a 1.00:0.996 mol ratio, respectively.

10. Isolated via extraction of the residue (after removal of toluene) with 6 M HCl and identified by its infrared spectrum and a mixed melting point determination.

11. Chatt and co-workers have previously observed protonation of one of the ligated dinitrogens in complexes of the type trans-$[M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2]$, M = Mo, W; however the release and/or further reduction of the resulting $[N_2H_2]$ moiety has not been realized. J. Chatt, G.A. Hea and R.L. Richards, Chem. Commun., 1010 (1972).

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Part B

Reduction of Molecular Nitrogen to Hydrazine. Structure of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II) and an ^{15}N Labeling Study of its Reaction with Hydrogen Chloride

Abstract

The structure of $[(C_5Me_5)_2ZrN_2]_2N_2$, 1, has been determined by single crystal x-ray diffraction methods and by ^{1}H and ^{15}N nmr spectroscopy. The binuclear structure consists of two $(\eta^5\text{-}C_5Me_5)_2ZrN{\equiv}N$ moieties bridged by a third dinitrogen ligand, terminal and bridging dinitrogen ligands are bound end-on with essentially linear Zr-N≡N and Zr-N≡N-Zr arrangements. 1-$(^{15}N_2)_3$ exchanges only terminal dinitrogen ligands with free $^{14}N_2$ in toluene solution at -23°. Treatment of 1 which is labelled with $^{15}N_2$ exclusively in the bridge position yields 1.5 mols $^{14}N_2$, 0.5 mol $^{15}N_2$, 0.5 mol $^{14}N_2H_4$, and 0.5 mol $^{15}N_2H_4$. The implications of these data with regard to the N_2 reduction sequence are discussed.

Sir:

We recently reported the synthesis and isolation of a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II), $[(C_5Me_5)_2ZrN_2]_2N_2$, 1, and noted further that on treatment with HCl one of the three N_2 ligands was reduced to hydrazine in 86% yield according to eq. 1.[1] The ready protonation and reduction of

$$[(C_5Me_5)_2ZrN_2]_2N_2 + 4\,HCl \longrightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4 \qquad (1)$$

N_2 in $\underset{\wedge}{1}$ is of considerable interest in view of a general lack of such reactivity for other isolated dinitrogen complexes.[2] Accordingly we have investigated the structure of $\underset{\wedge}{1}$ and have carried out an ^{15}N labeling study to determine which dinitrogen ligand is reduced to hydrazine in the reaction with HCl.

The structure of $\underset{\wedge}{1}$ as recently determined by single crystal x-ray diffraction methods is illustrated in Figure 1. The binuclear structure consists of two $(\eta^5\text{-}C_5Me_5)_2ZrN{\equiv}N$ moieties bridged by a third dinitrogen ligand. Terminal and bridging dinitrogen ligands are bound end-on with essentially linear Zr-N≡N and Zr-N≡N-Zr arrangements; NN distances are 1.116(8), 1.114(7), and 1.182(5) Å, respectively.

The ^1H nmr spectrum of $\underset{\wedge}{1}$ at 5° (toluene-$\underline{d}_8$) shows the expected two singlets attributable to the pairwise equivalent $(\eta^5\text{-}C_5Me_5)$ rings.[1] ^{15}N nmr data for $[(C_5Me_5)_2Zr(^{15}N_2)]_2$ ($^{15}N_2$) also support a solution structure for $\underset{\wedge}{1}$ identical to that in the crystalline state. Thus at -28° (toluene-$\underline{d}_8$), the 18.25 MHz ^{15}N nmr spectrum for $\underset{\wedge}{1}\text{-}(^{15}N_2)_3$ consists of two doublets attributable to the two ^{15}N nuclei of the two equivalent terminal dinitrogen ligands ($^1J_{^{15}N\text{-}^{15}N}$ = 6.2 Hz) centered 89.8 and 160.4 ppm upfield of a third singlet resonance due to the two ^{15}N nuclei of the $\mu\text{-}N_2$. The ^{15}N nmr spectrum for $\underset{\wedge}{1}\text{-}(^{15}N{\equiv}N^{14})_3$ exhibits the same spectrum with the exception that the two upfield doublets now appear as the expected singlets. The results of a variable temperature ^1H and ^{15}N nmr study of $\underset{\wedge}{1}$ will be reported in a forthcoming full paper.[3]

We have also investigated the possibility that the terminal dinitrogen ligands are substitutionally more labile than the μ-N_2. Table I summarizes the results of our studies of the exchange of free $^{14}N_2$ with $\underset{\wedge}{1}$-$(^{15}N_2)_3$. In a typical experiment ca. 0.1 mmol $\underset{\wedge}{1}$ was dissolved in 8.0 ml toluene in vacuo over a 15 min period at 0°. This solution was then cooled to -23°, natural $^{14}N_2$ admitted, and the system quickly closed off. After a period of stirring at -23° the exchange was quenched by rapid cooling to liquid nitrogen temperature. The gas phase was then transferred to a sample bulb by means of a Toepler pump and analyzed by mass spectrometry for $^{14}N{\equiv}N^{14}$, $^{14}N{\equiv}N^{15}$, $^{15}N{\equiv}N^{15}$.

The first three entries in Table I demonstrate that after 15 min exposure to free $^{14}N_2$, the composition of the gas phase above the solution is in close agreement with that predicted for complete exchange of two of the three dinitrogen ligands of $\underset{\wedge}{1}$. This observation requires that under these conditions exchange occurs between free N_2 and only the two equivalent terminal dinitrogen ligands. Incomplete exchange is observed after 5 min, permitting an estimate of the terminal N_2 exchange half life of 2.6(1) min ($\tilde{p}_{N_2}$ =1 atm). On the basis of the experiment conducted at reduced pressure the exchange rate appears proportional to free N_2 concentration ($t_{\frac{1}{2}}$ = 5.0(3) min, $\tilde{p}_{N_2}$ = 0.50 atm).

The results of these exchange experiments allow an accurate assessment of the extent of ^{15}N labeling in both terminal and bridge positions for $\underset{\wedge}{1}$, and thus should allow a determination of which of

the three dinitrogen ligands of $\underset{\sim}{1}$ is reduced to hydrazine in the reaction with HCl. Following exchange of free $^{14}N_2$ with the terminal positions of $\underset{\sim}{1}$-$(^{15}N_2)_3$, a 20 M excess of HCl was condensed onto the frozen toluene solution of the resulting complex. This mixture was warmed slowly to -80° whereupon an immediate reaction accompanied melting (<10 sec to completion) as evidenced by a color change from intense red to pale yellow. After warming slowly to room temperature, N_2 was collected (1.93(6) mol N_2/mol $\underset{\sim}{1}$), a small amount of H_2 (0.13(2) mol H_2/mol $\underset{\sim}{1}$) removed by passage through CuO at 320°, and a sample analyzed by mass spectrometry for $^{14}N{\equiv}N^{14}$, $^{14}N{\equiv}N^{15}$, and $^{15}N{\equiv}N^{15}$. Hydrazine was extracted from the residue with 0.1 M HCl and oxidized with 0.1 M KIO_3 to N_2, which was collected via a Toepler pump and also analyzed for $^{14}N{\equiv}N^{14}$, $^{15}N{\equiv}N^{14}$, and $^{15}N{\equiv}N^{15}$.[4]

The results (Table II) clearly indicate that the dinitrogen ligand which is reduced to hydrazine is not exclusively the μ-N_2 as might be anticipated. Rather the composition of both evolved N_2 and hydrazine are in close agreement with that expected for the reaction proceeding according to eq. 2.[5,6] Furthermore, we have also observed that treatment of

$$[(C_5Me_5)_2Zr(N_2{}^t)]_2(N_2{}^b) + 4\,HCl \longrightarrow 2(C_5Me_5)_2ZrCl_2 + \tfrac{3}{2}\,N_2{}^t + \tfrac{1}{2}\,N_2{}^b + \tfrac{1}{2}\,N_2{}^t\,H_4 + \tfrac{1}{2}\,N_2{}^b\,H_4 \qquad (2)$$

$[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]_2N_2$,[7] $\underset{\sim}{2}$, with HCl under identical conditions

yields $(C_5Me_5)_2ZrCl_2$, CO (1.29 mol/mol 2), H_2 (1.19 mol/mol 2), and N_2 (1.02 mol/mol 2).[8] Thus no reduction of the μ-N_2 of 2 is observed, an indication that the terminal dinitrogen ligands are playing roles beyond that of mere spectators in the reaction of 1 with HCl.

The data require a reaction sequence mediated by a symmetric species in which one terminal N_2 and the μ-N_2 have become equivalent.[9] While a number of mechanisms satisfying this requirement could be formulated, we favor one involving protonation of a terminal dinitrogen of 1, loss of the other terminal N_2, and generation of the symmetric reaction intermediate $(C_5Me_5)_2Zr(N_2H)_2$, 3.[10] Consistent with the labeling experiments, 3 would then lead to one mol each of N_2 and N_2H_4 (eq. 3).

$$(C_5Me_5)_2Zr(N_2H)_2 + 2\,HCl \longrightarrow (C_5Me_5)_2ZrCl_2 + N_2H_4 \qquad (3)$$

Generation of the neutral, monomeric species 3 from 1 would require a formal two-electron transfer to the N_2-bearing Zr accompanied by release of the other zirconium in the fully oxidized state, i.e., as $(C_5Me_5)_2ZrCl_2$. Strong electronic coupling of the two Zr(II) centers through the μ-N_2 of 1 as suggested by its structural features, ir, and visible spectra should facilitate such a Zr-to-Zr charge transfer.

Acknowledgement

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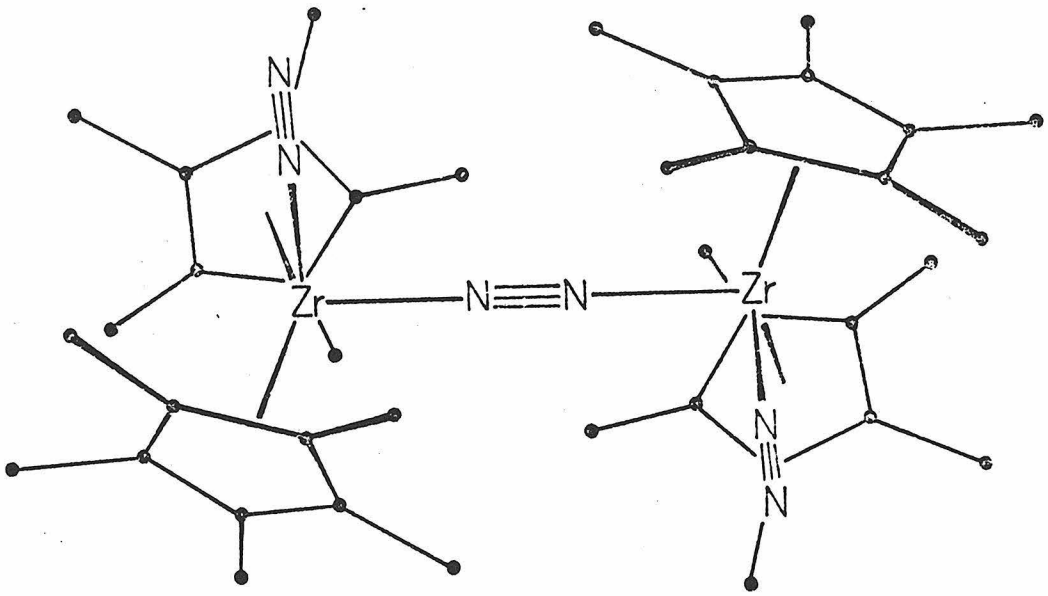

Figure 1. The molecular structure of 1.

Table I. Results of N_2 Exchange of $[(C_5Me_5)_2Zr(^{15}N_2)]_2(^{15}N_2)$ (99.36% $^{15}N\equiv{}^{15}N$) with free natural N_2 (99.66% $^{14}N\equiv{}^{14}N$) in Toluene at -23° (estimated standard deviations).

$[(C_5Me_5)_2Zr)^{15}$-$N_2)]_2(^{15}N_2)$ (mmol)	$^{14}N_2$ added (mmol)	$\tilde{p}N_2$ (atm)	Exposure time (min)	$\chi(^{14}N_2)$ calcd[a] / $\chi(^{15}N_2)$	$\chi(^{14}N_2)$ obsd / $\chi(^{15}N_2)$	mol N_2 exchanged per mol dimer
0.1255 (2)	2.106 (1)	1.0	15	0.887 / 0.106	0.886 (1) / 0.107 (1)	2.02 (2)
0.1906 (2)	2.164 (1)	1.0	30	0.844 / 0.149	0.841 (1) / 0.152 (1)	2.04 (2)
0.1091 (2)	2.338 (1)	1.0	60	0.908 / 0.0848	0.906 (1) / 0.0863 (10)	2.04 (2)
0.1217 (2)	2.154 (1)	1.0	5	0.892 / 0.101	0.921 (1) / 0.0728 (10)	1.44 (2)
0.1141 (2)	1.130 (1)	0.50	15	0.826 / 0.167	0.846 (1) / 0.147 (1)	1.77 (2)

[a] Mol fractions $^{14}N\equiv{}^{14}N$ and $^{15}N\equiv{}^{15}N$ expected in gas phase for complete exchange of terminal N_2 ligands only.

Table II. Results of N_2 Labeling Experiments for the Reaction: $[(C_5Me_5)_2ZrN_2]N_2 + 4HCl \longrightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$ (estimated standard deviations)

$X(^{15}N_2)$ in two positions of $[(C_5Me_5)_2ZrN_2]_2N_2$		$X(^{15}N_2)$ in N_2 evolved on HCl addition		$X(^{15}N_2H_4)$ in hydrazine obtained on HCl addition	
Terminal	Bridge	Calcd[a]	Obsd[b]	Calcd[a]	Obsd[b]
0.107 (5)	0.9936 (1)	0.328 (4)	0.388 (1)	0.550 (3)	0.528 (1)
0.152 (5)	0.9936 (1)	0.362 (4)	0.388 (1)	0.573 (3)	0.547 (1)
0.086 (5)	0.9936 (1)	0.313 (4)	0.329 (1)	0.540 (3)	0.488 (1)
0.349 (5)	0.9936 (1)	0.510 (4)	0.580 (1)	0.671 (3)	0.665 (1)
0.264 (5)	0.9936 (1)	0.446 (4)	0.526 (1)	0.629 (3)	0.634 (1)
0.388 (5)	0.9936 (1)	0.539 (4)	0.619 (1)	0.691 (3)	0.682 (1)
0.079 (5)[c]	0.9936 (1)[c]	0.308 (4)[c]	0.335 (1)[c]	0.536 (3)[c]	0.522 (1)[c]

[a] Calculated for reaction proceeding 100% according to eq. 2. [b] No $^{15}N\equiv^{14}N$ was formed in reaction.

[c] DCl substituted for HCl.

References

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2. Notable exceptions are complexes of the type $ML_4(N_2)_2$ (M = Mo, W; L = PMe_2Ph, $PMePh_2$), which have recently been shown to liberate up to 1.8 mol of ammonia in acid methanol. J. Chatt, A.J. Pearman, and R.L. Richards, Nature, 253, 39 (1975); J. Chatt, J. Organometal. Chem., 100, 17 (1975).

3. J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan, and J.E. Bercaw, manuscript in preparation.

4. Colorimetric determinations of ammonia (indophenol; J.A. Russell, J. Biol. Chem., 156, 457 (1944)), and hydrazine (p-dimethylaminobenzaldehyde; I.D. Snell and C.T. Snell, "Colorimetric Methods of Analysis," Vol. IIA, D. Van Nostrand Company, Inc., New York, N.Y., 1959, p. 707), indicate that the reduced N_2 consists of 0.86 mol N_2H_4 and 0.24 mol NH_3 per mol of 1. Treatment of 1 with anhydrous N_2H_4 in toluene at -80° (instantaneously) yields N_2 (3 mols) and NH_3 (2 mols), thus indicating that ammonia could arise from interference of this reaction during the latter stages of the reaction with HCl.

5. A small correction for residual N_2 trapped in the frozen toluene (0.0185 mmol as determined by a blank) was made

in calculating the expected fraction of $^{15}N_2$ evolved on the addition of HCl.

6. Since (1) the reaction proceeds only 86% according to eq. 2 (footnote 4), and (2) iodate oxidizes N_2H_4 but not NH_3 to N_2, hydrazine labelling should be somewhat more reliable.

7. $\underset{\sim}{2}$ is prepared by treatment of $\underset{\sim}{1}$ with CO at -23° and isolated as metallic green crystals. On the basis of analytical data, ir: ν(CO) 1902(ms), 1860(s); ν(NN) 1682(ms), and nmr (toluene, $\underline{d_8}$): s, δ 1.80 (30H); s δ 1.82 (30H), the structure of $\underset{\sim}{2}$ is believed to be identical to $\underset{\sim}{1}$ with carbonyl substituted for the terminal dinitrogen ligands.

8. Apparently some carbon monoxide is reduced when $\underset{\sim}{2}$ is treated with HCl. The identity of the reduction product(s) is presently under investigation.

9. This intermediate need only be symmetric on the reaction time scale, so that a monoprotiated species such as $[(C_5Me_5)_2Zr(N_2)(N_2H)]^-$ is a possibility, providing proton transfer between dinitrogen ligands is sufficiently rapid. No significant variation in X ($^{15}N_2$) was observed with DCl (Table 2), so that if this is the case such a proton transfer cannot be so slow as to be comparable to the rate of subsequent reaction steps.

10. Our data do not exclude the possibility that this symmetric intermediate could, in fact, be dimeric (<u>e.g.</u>, $[(C_5Me_5)_2Zr(\mu\text{-}N_2H)_2Zr(C_5Me_5)_2]^{2+}$, $[(C_5Me_5)_2Zr(\mu\text{-}N_2H_2)_2Zr(C_5Me_5)_2]^{4+}$);

however, in view of the high charges necessarily associated with such dimers, we favor the neutral monomer $\hat{3}$.

Part C

Solution Structure and Dynamics of Binuclear Dinitrogen Complexes of Bis (pentamethylcyclopentadienyl) titanium (II) and Bis (pentamethylcyclopentadienyl) zirconium (II)*

Abstract

The synthesis and characterization of $\{(\eta^5\text{-}C_5(CH_3)_5)_2 ZrN_2\}_2N_2$(1), $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (2) and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$(3) is described. In solution 1 and 3 exhibit fluxional behavior. The dynamics of 1 in solution as studied by ^1H and ^{15}N NMR shows that 1 undergoes $[\eta^5\text{-}C_5(CH_3)_5]$ ring exchange as a result of the lability of the terminal dinitrogen ligand. A re-investigation of the titanium system analog in solution showed that the complex, originally assigned the formula $(\eta^5\text{-}C_5Me_5)_2TiN_2$, is in fact the zirconium analog $\{(\eta^5\text{-}C_5Me_5)_2 TiN_2\}_2 N_2$(4).

Introduction

Bis (pentamethylcyclopentadienyl) derivatives of titanium and zirconium have proven to be useful congeners to their bis (cyclopentadienyl) analogos by virtue of enhanced stability, solubility, and crystallizability.

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* The NMR interpretation does not belong to me. The following pages form part of a manuscript in preparation which carries the title by the following authors: Juan M. Manriquez, Donald R. Mc Alister, Edward Rosenberg, Alan M. Shiller, Kenneth L. Williamson, Sunney I. Chan and John E. Bercaw.

Dinitrogen complexes of $(\eta^5\text{-}C_5Me_5)_2Ti$ and $(\eta^5\text{-}C_5Me_5)_2Zr$ are of particular interest in view of the ready protonation and reduction to hydrazine of their ligated N_2.[1-6] The solid-state structures of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$[5] and $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2$[6] N_2 have been recently reported. Here are reported the results of an NMR and ir study of the solution structure and dynamics of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, its carbonyl and PF_3 derivatives, and the titanium analog.

Experimental

Physical Measurements. ^1H NMR spectra were recorded on a Varian 220 (CW) spectrometer. ^{15}N NMR spectra were obtained at 18.25 MHz on a Bruker WH 180 (FT) spectrometer. Computer simulated spectra were obtained by A.M. Shiller and Professor S.I. Chan from this department. Infrared spectra were obtained on Perkin-Elmer 180, 255, and 457 and Beckman IR-12 spectrophotometers.

Materials. All manipulations were performed on a vacuum line, in a glove box which was evacuated to <0.1 Torr and filled just prior to use with either prepurified argon or nitrogen, or in a Vacuum Atmospheres glove box under nitrogen. Nitrogen used in the experiments was prepurified grade rendered rigorously oxygen and water free by passage over MnO on vermiculite[7] and activated 4A molecular sieves. Toluene, benzene, and 30-60°

petroleum ether were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[8] 1,2,3,4,5-Pentamethylcyclopentadiene and $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ were prepared as described earlier.[2,8] $^{15}N\equiv{}^{14}N$ was prepared in aqueous solution from $(^{15}NH_4)_2SO_4$ (Merck, Sharpe and Dohme) and $NaNO_2$; nitric oxide was removed with $FeSO_4$, then $^{15}N\equiv{}^{14}N$ was collected via a Toepler pump. Both $^{15}N\equiv{}^{14}N$ and $^{15}N\equiv{}^{15}N$ were rendered rigorously water and oxygen free by contact with solid $\{(C_5(CH_3)_5\}\{C_5(CH_3)_4CH_2\}Ti$,[2] and finally examined by mass spectroscopy.[9]

Procedures

1. $(C_5Me_5)_2ZrCl_2$. 300 ml 1,2 dimethoxyethane was vacuum transferred from $LiAlH_4$ to a 500 ml 3-neck flask. 20.4 g (150 mmols) $C_5(CH_3)_5H$, then 70 ml (150 mmols) n-butyllithium were added at -80° via syringe. This mixture was warmed slowly to room temperature and stirred for 30 min. The mixture was cooled again to -80°, and 15.3 g (63 mmols) freshly sublimed $ZrCl_4$ were added. This mixture was warmed to R.T., then heated at reflux for 3 days. Solvent was removed under reduced pressure to leave a thick pale-brown residue, which was taken up in 250 ml $CHCl_3$ and 100 ml 6 M HCl. The aqueous layer was separated and washed with $CHCl_3$. The combined chloroform layers were washed once with distilled water, dried over Na_2SO_4, then concentrated to approximately 50 ml. Two hundred ml 90-100° petroleum ether were added and solvent slowly removed

by rotary evaporation. The residual solution (~ 50 ml) was cooled, the product filtered off, and washed with cold petroleum ether. Yield 15 g of pale yellow crystals (55%).

Analysis: Calc. for $C_{20}H_{30}Cl_2Zr$: C 55.56, H 6.94, Cl 16.40, Zr 21.10; found: C 55.57, H 6.99, Cl 16.36, Zr 21.21. NMR (chloroform, $\underline{d}_1$): s, δ 2.00.

2. $\{(C_5Me_5)_2ZrN_2\}_2N_2$. To 5.0 g $(C_5Me_5)_2ZrCl_2$, 20 ml Hg and 80 ml benzene were added 2.5 ml of 40% Na/Hg (2.5g Na) under N_2 with stirring and cooling. This mixture was stirred vigorously at R.T. for 3 days under 1 atm. N_2. The resultant dark red solution was decanted from the bulk of the amalgam and filtered. The amalgam was washed with 20 ml fresh benzene, which was also filtered. The combined filtrates were reduced in volume as quickly as possible to approximately 10 ml, 40 ml 30-60° petroleum ether added, and the resulting solution allowed to stand under N_2 for 20 hr. The product was then filtered off, washed three times at low temperature with 10 ml portions of 30-60° petroleum ether, dried in vacuo and finally transferred to a storage ampoule in a nitrogen filled glove box.

Yield: 2.36 g of metallic green crystals (51%).

Analysis: Calc. for $C_{40}H_{60}N_6Zr_2$: C 59.54, H 7.44, N 10.41, Zr 22.61; Found: C 59.75, H 7.36, N 10.18, Zr 22.77.

3. $\{(C_5Me_5)_2ZrN_2\}_2N_2$ labeled with $^{15}N\equiv{}^{15}N$ or $^{15}N\equiv{}^{14}N$. Toluene and N_2 were slowly removed from a solution of $\{(C_5Me_5)_2ZrN_2\}_2N_2$ over a 3 hr period at R.T., yielding a red-orange

crystalline mass of $\{C_5(CH_3)_5\}\{C_5(CH_3)_4CH_2\}ZrH$.[3] This complex was dissolved in 15 ml 30-60° petroleum ether, a small amount of yellow precipitate filtered off, and either $^{15}N\equiv{}^{15}N$ or $^{15}N\equiv{}^{14}N$ admitted. After 20 hr the product was filtered, washed and dried as before. ^{15}N NMR samples were prepared in toluene-$\underline{d}_8$, filtered into 10 mm diameter NMR tubes, and sealed under approximately 1 atm $^{15}N\equiv{}^{15}N$ or $^{15}N\equiv{}^{14}N$.

4. $\{(C_5Me_5)_2Zr(CO)\}_2N_2$. To 139 mg (0.172 mmol) $\{(C_5Me_5)_2ZrN_2\}_2N_2$ was added 8 ml toluene and 1.060 mmol CO at liquid nitrogen temperature. The mixture was warmed to -23° and stirred vigorously for 1 hr. After cooling the dark red solution to -80° the residual gas mixture (1.025 mmol) was collected by means of a Toepler pump. CO was oxidized to CO_2 by circulation through CuO at 320° and trapped at liquid nitrogen temperature. Residual N_2 (0.337 mmol, 1.95 mmol N_2/mmol dimer) was collected and discarded, then CO_2 was collected from the trap at -80° (corresponding to 0.683 mmol residual CO). The amount of CO absorbed was thus 0.377 mmol (2.18 mmol CO/mmol dimer). In a separate experiment 674 mg $\{(C_5Me_5)_2ZrN_2\}_2N_2$ in toluene was treated with excess CO at -23° for 1 hr. Toluene was then removed slowly in vacuo at -20°C, petroleum ether added, and the resulting green crystalline product filtered, washed, and dried as before.

Analysis: Calc. for $C_{42}H_{60}N_2O_2Zr$: C 62.48, H 7.49, N 3.47; Found: C 59.88, H 7.25, N 3.24.

5. $\{(C_5Me_5)_2Zr(PF_3)\}_2N_2$. To 112 mg (0.139 mmol) $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ was added 8 ml toluene and 0.536 mmols PF_3 at -80°. The mixture was warmed to -23° and stirred for 15 min at this temperature. After cooling the solution back to -80°, N_2 (0.257 mmol, 1.86 mmol/mmol dimer) was collected through a series of three liquid nitrogen-cooled traps, then discarded. The traps were warmed to -80° and residual PF_3 (0.272 mmol) was collected. The amount of PF_3 absorbed was thus 0.264 mmol (1.90 mmol/mmol dimer). $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ was isolated as green microcrystalline solid using the procedure for $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$. Note: $\{(C_5Me_5)_2Zr(PF_3)\}_2N_2$ as a solid decomposes at R.T. and must be kept at ≤ -20°.

Results

^{1}H NMR spectra $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, **1**, in toluene-$\underline{d}_8$ at various temperatures are shown in Figure 1, and the results summarized in Table I. The spectrum at -26 is readily interpreted on the basis of the structure determined by x-ray diffraction methods, figure 2. Thus the two singlets are attributed to the equivalent pairwise $[\eta^5\text{-}C_5(CH_3)_5]$ rings, although the difference in their chemical shifts is quite small, amounting to only 3.4 Hz at 220 MHz. In the range -26° to +50° the two signals first broaden, then coalesce at approximately +11°, and finally give rise to a single line which narrows to a limiting half-width of 1.9 Hz at +50°.

These spectra imply that the two types of $[\eta^5\text{-}C_5(CH_3)_5]$ rings undergo mutual site exchange on the time scale of the NMR. A possible mechanism for simultaneous interchange of all four ring environments would involve simple 180° rotation about one or both of the $Zr\text{-}\mu\text{-}N_2$ bonds of the dimer via either a cis or trans intermediate.

The people who know nuclear magnetic resonance attempted to fit the spectra; however, line shapes could not be fit to this model. However; since the $[\eta^5\text{-}C_5(CH_3)_5]$ protons exhibited temperature-dependent chemical shift variations comparable to peak separations, one could not rule out the rotation mechanism. ^{15}N NMR experiments were therefore undertaken. The 18.25-MHz ^{15}N NMR spectrum for $\underset{\wedge}{1}\text{-}(^{15}N_2)_3$ at -28° (toluene-d_8) (Figure 3) is readily interpreted on the basis of the solid-state structure. Thus the singlet 185 ppm downfield of HNO_3 is attributed to the two equivalent ^{15}N nuclei of $\mu\text{-}N_2$ and the two doublets centered 86 ppm and 17 ppm downfield of HNO_3 to the two ^{15}N nuclei of the two equivalent terminal dinitrogen ligands ($^1J_{^{15}N\equiv^{15}N}$ = 6.2Hz). The ^{15}N NMR spectrum $\underset{\wedge}{1}\text{-}(^{15}N\equiv^{14}N)_3$ (figure 3) exhibits the same spectrum except the two upfield doublets now appear as the expected singlets.

On the basis of the rotation mechanism no temperature dependence of the ^{15}N NMR spectrum for $\underset{\wedge}{1}$ is predicted, since two equivalent nitrogen magnetic environments, those for the two enantomeric forms of $\underset{\wedge}{1}$, would be averaged.

As can be seen; however, on warming $\underset{\wedge}{1}\text{-}(^{15}N_2)_3$ from -28°

to +50°, the signals due to the two terminal dinitrogen ligands steadily broaden; the singlet attributable to the μ-N_2 remains sharp over the entire temperature range[10] (figure 4).

It was suggested that mutual site exchange between the proximal and distal positions relative to zirconium for the two nitrogen nuclei of the two terminal dinitrogen ligands would account for the observed temperature dependence of the ^{15}N NMR spectra. Further more, they found that the rate of this process, as estimated from line width data, was comparable to the rate of $[C_5(CH_3)_5]$ ring site exchange. It therefore appeared that the mechanism for mutual site exchange of nitrogen atoms of the terminal dinitrogen ligands should also allow $[\eta^5$-$C_5(CH_3)_5]$ site exchange.

They found that one process satisfying this requirement was the one shown in figures 5 and 6. The first step (figure 5) involves dissociation of one of the terminal dinitrogen ligands of $\underset{\sim}{1}$. The resulting intermediate may be expected to rearrange, taking on a planar trigonal arrangement of $[\eta^5$-$C_5(CH_3)_5]$ ring centroids and the μ-N_2 at the coordinatively unsaturated zirconium center, a local ligand geometry about Zr entirely analogous to that established for $\{(\eta^5$-$C_5Me_5)_2Ti\}_2N_2$.[6] $\underset{\sim}{1}$ is regenerated by addition of N_2 to either side of the unsaturated zirconium center. In the fast exchange limit this process would average the ^{15}N chemical shifts for the proximal and distal positions of the terminal N_2 ligands, and, providing there is a rapid equilibration with free N_2 in solution, a third weighted component would be added due to the chemical

shift of free N_2 in toluene-$\underline{d}_8$, which was independently measured to be 65.5 ppm upfield of HNO_3.

As can be seen (figure 5 and 6), "inversion" at one zirconium center for $\underset{\wedge}{1}$ effects $[\eta^5\text{-}C_5(CH_3)_5]$ ring exchange between the two sites (α, eclipsed with N_2, and β) only at the other Zr. Thus at least two such sequences involving each of the two terminal dinitrogen ligands are required to effect complete site exchange for all four $[\eta^5\text{-}C_5(CH_3)_5]$ rings (figure 6). If the assumption is made that addition of N_2 to the coordinatively unsaturated Zr center for the intermediate $(\eta^5\text{-}C_5Me_5)_2(N_2)\text{-}N_2\text{-}Zr(\eta^5\text{-}C_5Me_5)_2$ occurs equally from either side, then on a purely statistical basis the rate of N_2 dissociation is expected to be eight times faster than the rate of site exchange for all four $[\eta^5\text{-}C_5(CH_3)_5]$ rings.

Estimating a free N_2 concentration of 5 mM and $[\underset{\wedge}{1}] \cong 50$ mM, computer simulated spectra could satisfactorily be fit to both the observed ^1H and ^{15}N NMR spectra, assuming the above mechanism.

^1H NMR spectra for $\underset{\wedge}{1}$ under 0.5 atm N_2 or for samples prepared under argon showed no significant difference from those measured under 1 atm N_2; in particular, coalescence occurs at the same temperature. This result suggests that the rate determining step in the mechanism is dissociation of a terminal dinitrogen ligand from $\underset{\wedge}{1}$.

The lability of the terminal dinitrogen ligands of $\underset{\wedge}{1}$ has been further substantiated by N_2 substitution experiments carried out with $1\text{-}(^{15}N_2)_3$.[4] When this complex was treated with natural

$^{14}N_2$ in toluene, complete exchange of two of the three dinitrogen ligands was found after 15 min at -23°. This observation requires that under these conditions exchange occurs between free N_2 and only two equivalent terminal dinitrogen ligands of 1.

Treatment of 1 with CO or PF_3 yields $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (2) and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ (3), respectively (equations 1 and 2). Both were isolated as metallic green cyrstalline materials.

$$\{(\eta^5\text{-}C_5Me_5)_2Zr\,N_2\}_2N_2 + 2\,CO \rightarrow \{(\eta^5\text{-}C_5Me_5)_2\,Zr(CO)\}_2N_2 + 2\,N_2 \quad (1)$$

1 2

$$\{(\eta^5\text{-}C_5Me_5)_2\,Zr\,N_2\}_2N_2 + 2\,PF_3 \rightarrow \{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2 + 2N_2 \quad (2)$$

1 3

On the basis of their characteristic color, their ir spectra (Table II), and ^1H NMR spectra (see below), 2 and 3 appear to have structures identical to 1 with CO and PF_3 substituted for the terminal dinitrogen ligands. 2 exhibits a ^1H NMR spectrum (toluene-d_8) consisting of two singlets of equal intensity at 1.80 and 1.82 ppm at -48°. Except for small chemical shift variations, this spectrum is maintained up to +64° (further heating results in sample decomposition). $[\eta^5\text{-}C_5(CH_3)_5]$ ring site exchange for 2 is thus much slower than for 1, indicating lower lability for the terminal carbonyls.

Unlike 1 and 2, 3 exhibits low stability in solution,

decomposing over a period of several minutes at R.T., thus precluding an accurate NMR study. However, at -76° the ^{1}H NMR spectrum of 3 (toluene-$\underline{d}_8$) exhibits the expected two singlets of equal intensity at 1.79 and 1.81 ppm. These two signals coalesce at approximately -35° and give rise to a single line which narrows steadily to -6° where decomposition sets in. While this behavior could be taken to indicate a higher lability of PF_3 relative to N_2, this is difficult to reconcile considering the ability of PF_3 to quantitatively displace* the two terminal dinitrogen ligands of 1. In view of this unexpected behavior and the fact that the decomposition mechanism and product(s) for 3 are as yet undefined, we hesitate to interpret these NMR data in terms of a specific reversible dynamic process.

The definition of the solution structure and dynamics of 1 serves to clarify the structure of its titanium analog, $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$ (4), which was originally assigned the formula $(\eta^5\text{-}C_5Me_5)_2TiN_2$.** [1,2] On the basis of its infrared

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* Of course this displacement requires only that the equilibrium constant (K_{on}/K_{off}) be larger for PF_3 than for N_2; however, we see no obvious reason for a faster addition of PF_3 (relative to N_2) to the coordinatively unsaturated Zr center.

** On the basis of H^1 and ^{15}N NMR, ir data and stoichiometry in vacuo, this unstable complex was interpreted to exist in both end-on, $(\eta^5\text{-}C_5Me_5)_2Ti(\eta^1\text{-}N_2)$, and edge-on $(\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}N_2)$, forms in solution. The stoichiometry has been subsequently re-examined under the same experimental conditions that the ^{1}H and ^{15}N NMR and ir spectra were taken, that is 1 atm of N_2. Thus by measuring the change in pressure (Δp) in the reaction of $(\eta^5\text{-}C_5Me_5)_2$ Ti with N_2 values between 1.38 and 1.41 mmols N_2/Ti (theoretically 1.5) were obtained, consistent with the formula $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$.

spectrum (Table II) and its ^{1}H and ^{15}N NMR spectra, there can be little doubt that the structure of $\underset{\sim}{4}$ is entirely analogous to that for $\underset{\sim}{1}$. The ^{1}H NMR spectrum for $\underset{\sim}{4}$ (toluene-$\underline{d}_8$) exhibits two singlets of equal intensity at 1.55 and 1.63 ppm at -78°, which coalesce at approximately -42°. At higher temperatures this signal loses intensity and further broadens due to the onset of dissociative exchange with two paramagnetic species $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ and $(\eta^5\text{-}C_5Me_5)_2Ti$ (eq. 3). In view of these complications no attempt was made to analyze these ^{1}H NMR data for $\underset{\sim}{4}$ using the model shown in figures 4 a and b. The high lability of the dinitrogen ligands for $\underset{\sim}{4}$ and its ^{1}H NMR spectra over the temperature region -78° to -42° are, however, in full accord with this mechanism for $[\eta^5\text{-}C_5Me_5]$ ring exchange.

$$2(\eta^5\text{-}C_5Me_5)_2Ti \overset{N_2}{\rightleftharpoons} \{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2 \overset{2N_2}{\rightleftharpoons} \{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2 \qquad (3)$$

Discussion

These studies have shown that complexes of the type $\{(\eta^5\text{-}C_5Me_5)_2ML\}_2N_2$ (M = Ti, Zr; L = N_2, CO, PF_3) can exhibit fluxional behavior in solution where by the pairwise equivalent $[\eta^5\text{-}C_5(CH_3)_5]$ rings undergo site exchange, if the terminal ligand is labile. While we cannot rule out the possibility that rotation about one (or both) of the M-N_2-M bonds also occurs in solution, we can state that it must be much slower. Indeed, the barrier to 180° rotation must be greater than ~10 kcal/mol for $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$, since no ring site exchange (by either mechanism) is observed by ^{1}H NMR up to +64°. Judging

from the lower NN stretching frequency for the μ-N_2, this barrier should be even higher for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$. Although steric crowding of $[\eta^5\text{-}C_5(CH_3)_5]$ rings may make some contribution, we feel that this high barrier to rotation is for most part due to considerable π character between Zr centers and the bridging dinitrogen ligand. This situation whereby $\underset{\frown}{1}$ is locked firmly in the gauche configuration is entirely consistent with the qualitative MO picture of the $Zr\text{-}N_2$ bonding presented earlier.[5]

While the lability of the terminal dinitrogen ligands of $\underset{\frown}{1}$ inferred from the ^1H and ^{15}N NMR experiments has been demonstrated by N_2 substitution experiments carried out with $\underset{\frown}{1}\text{-}(^{15}N_2)_3$, the rate of free $^{14}N_2$ exchange with the terminal dinitrogen positions of $\underset{\frown}{1}\text{-}(^{15}N_2)_3$ is $\sim 10^4$ times slower than the site exchange for the terminal dinitrogen ligands measured by ^{15}N NMR. This large discrepancy could be taken to indicate that the terminal N_2 ligands rotate while bonded to the zirconium (e.g., via an edge-on $Zr(\eta^2\text{-}N_2)$ intermediate) at a rate greater than dissociation (Indeed such linkage isomerization has been demonstrated for $[(NH_3)_5RuN_2]^{+2}$ by Armor and Taube[11]. It is, however, difficult to envision how this process could be coupled to $[\eta^5\text{-}C_5(CH_3)_5]$ ring site exchange. Furthermore, satisfactory fits to the observed ^{15}N NMR data could be obtained only by including the $\sim 10\%$ contribution due to free $^{15}N_2$ in toluene-d_8 in the ^{15}N chemical shifts for the terminal dinitrogen ligands. In light of this requirement and the satisfactory agreement obtained between the predicted and observed ratio of rates measured by ^1H and ^{15}N NMR, we discount

this possibility in favor of mechanism shown in figure 4 a and b.

Whatever the true explanation of the discrepancy in these rates, it must account for the observations that the faster process measured by NMR is independent of the pressure of added N_2, while the rate of $^{14}N_2$ substitution for the terminal N_2 positions of $\underset{\wedge}{1}$-$(^{15}N_2)_3$ exhibits a first order dependence in $\tilde{p}N_2$.[4] Thus the rate determining step in the two mechanisms are, in fact, different. We can only surmise at this point that the rate of exchange of N_2 in the gas phase with the terminal N_2 positions of $\underset{\wedge}{1}$ must be limited by the rate of N_2 diffusion from the gas phase into the solvent cage containing $\underset{\wedge}{1}$.

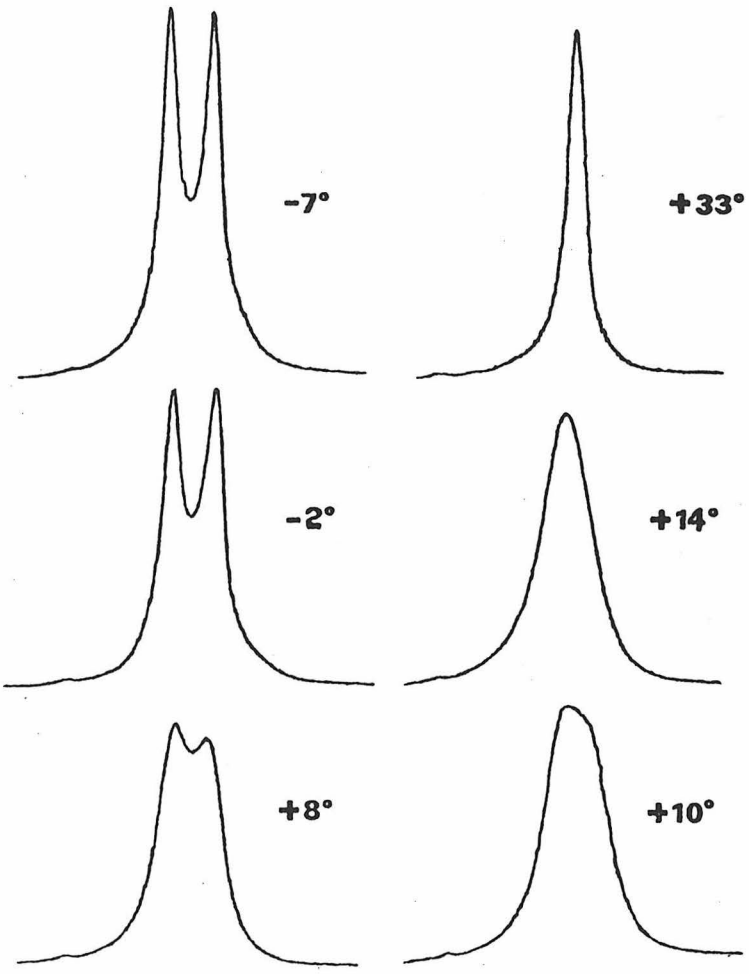

Figure 1. ^{1}H NMR spectra of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (toluene-$\underline{d}_8$) at various temperatures.

Table I. Summary of ^{1}H NMR data for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (toluene-$\underline{d}_8$)

T(°C)	δ_1 (line width, Hz)	δ_2 (line width, Hz)
-26°	1.77 (2.4)	1.79 (3.0)
-20°	1.77 (2.4)	1.79 (2.7)
-7°	1.77 (2.7)	1.79 (2.7)
-2°	1.77 (3.0)	1.79 (2.8)
+4°	1.79	1.80
+8°	1.80	
+11°	1.80 (6.8)	
+14°	1.80 (5.8)	
+20°	1.80 (4.0)	
+33°	1.80 (2.2)	
+50°	1.80 (1.9)	

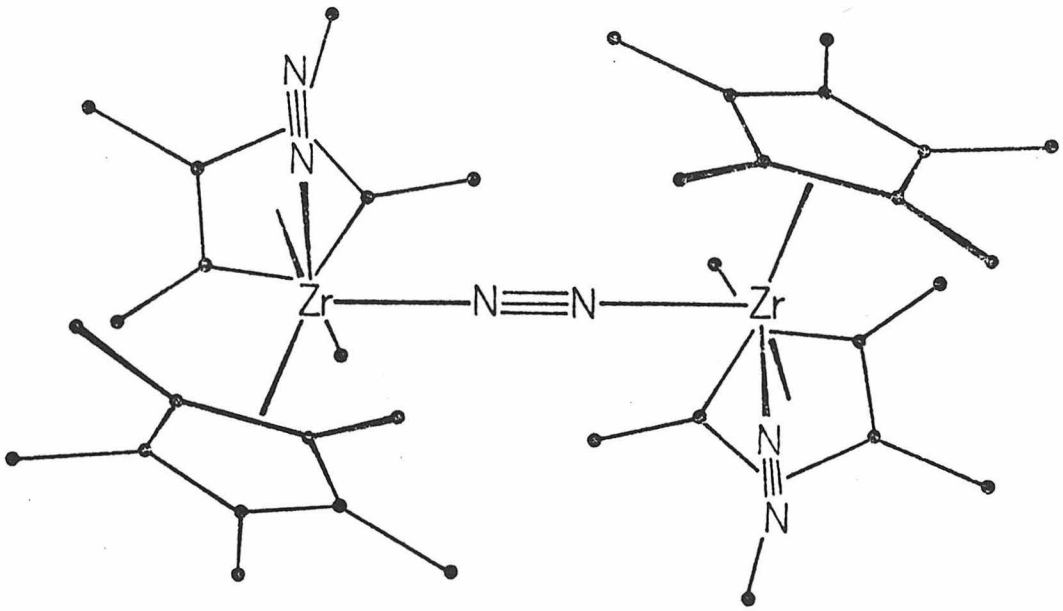

Figure 2. The molecular structure of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$

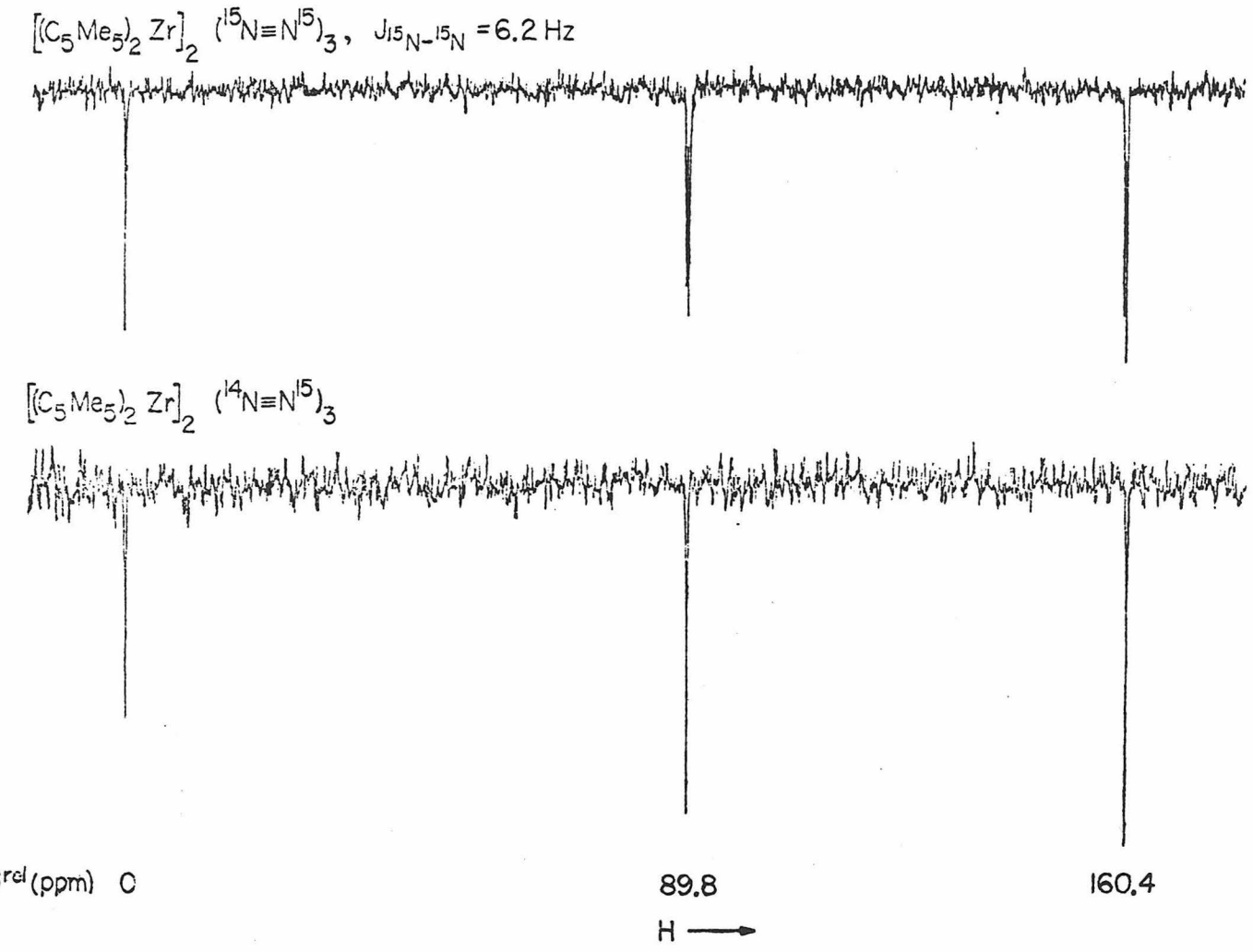

Figure 3. 18.25 MHz ^{15}N NMR Spectra for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (toluene-$\underline{d}_8$) at -28°.

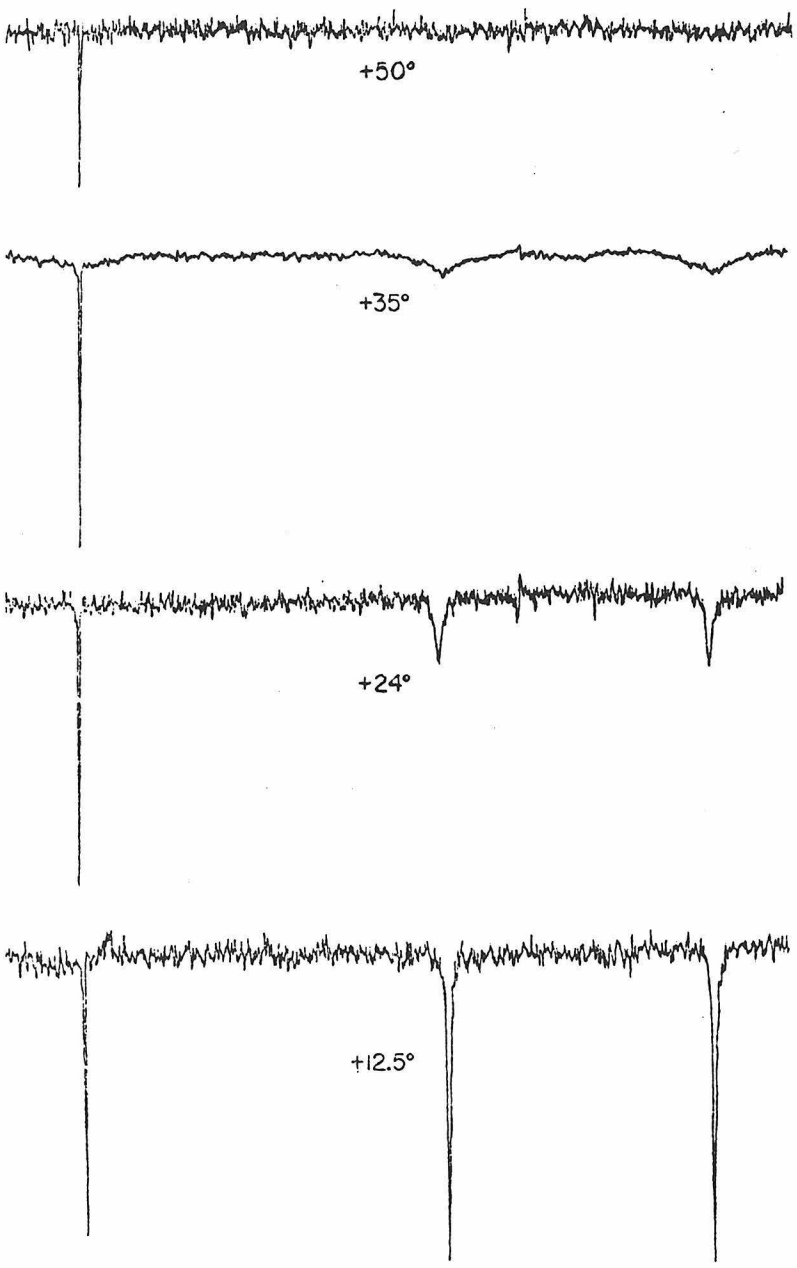

Figure 4. ^{15}N NMR spectra of $[(C_5Me_5)_2Zr]_2$ ($^{15}N \equiv {}^{15}N)_3$ (toluene-$\underline{d}_8$) at various temperatures.

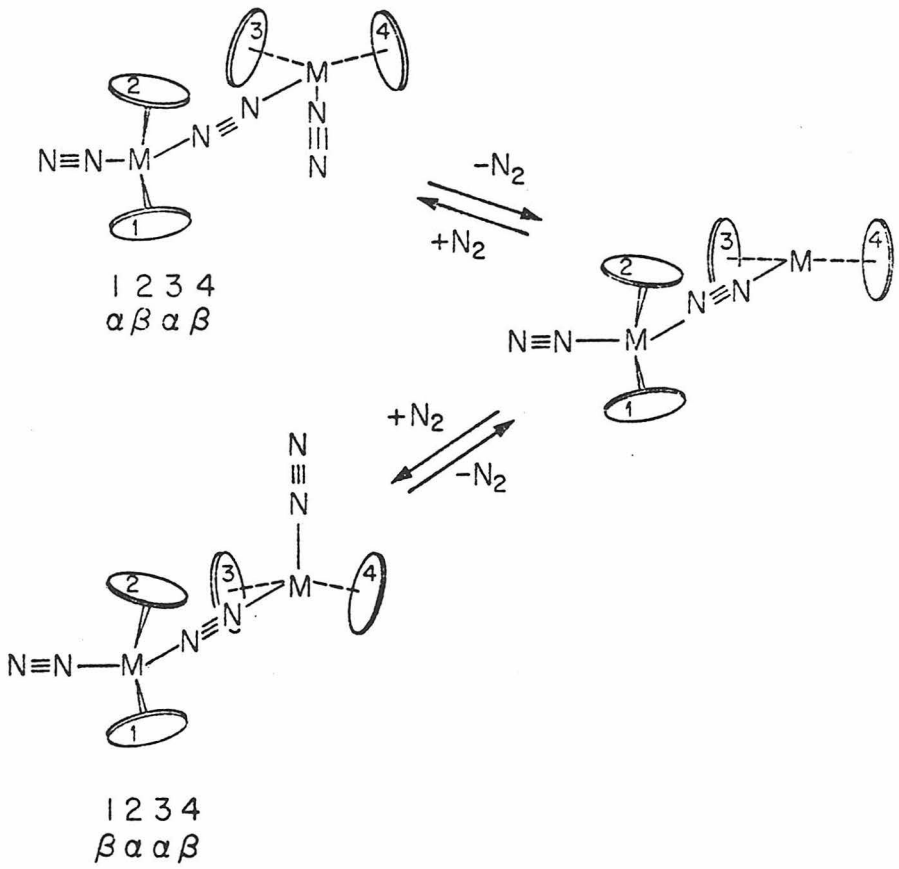

Figure 5. Rearrangement for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ which exchanges $[(\eta^5\text{-}C_5(CH_3)_5]$ rings 1 and 2 between two types of sites (α and β).

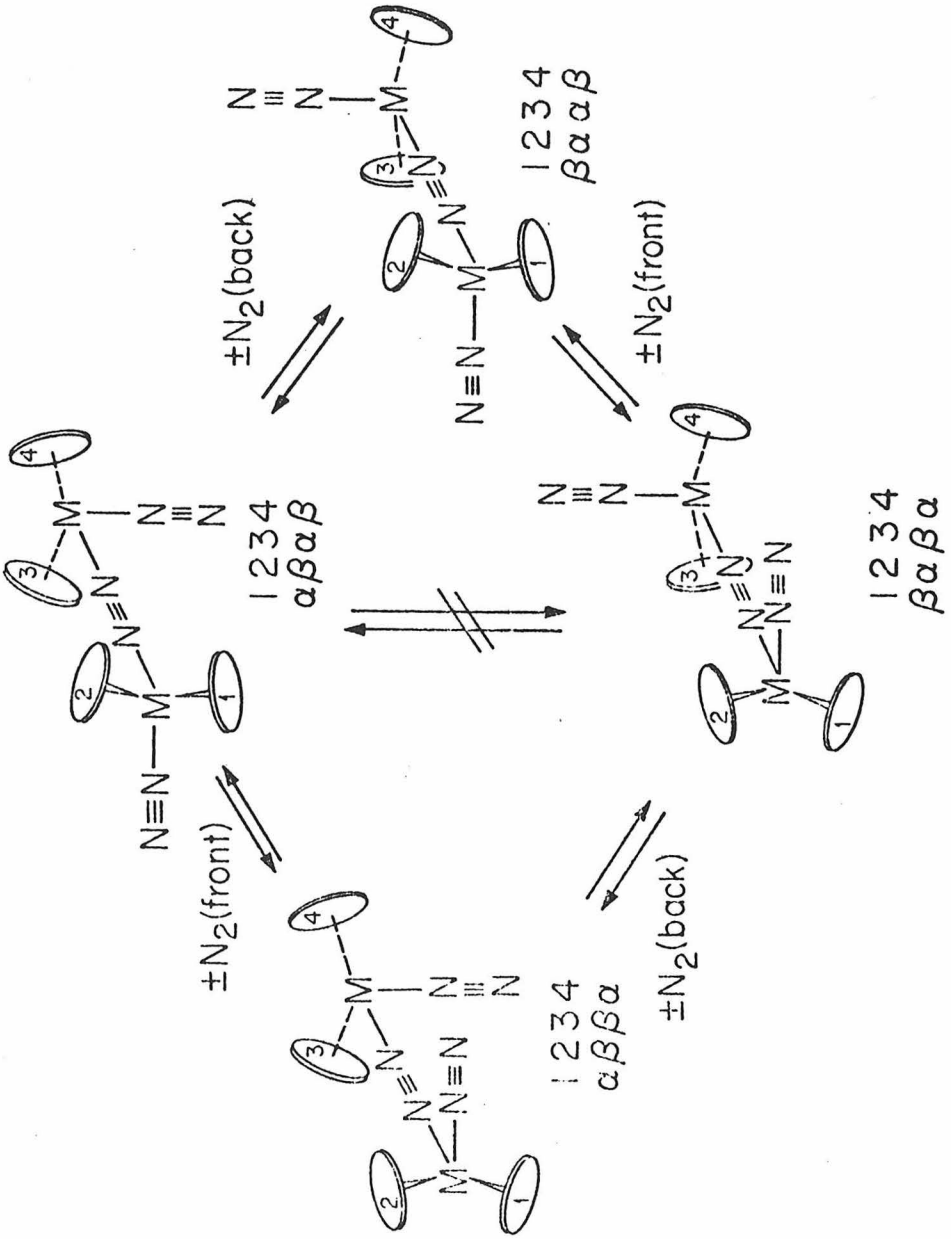

Figure 6. Sequence which interchanges all four (η^5-C_5Me_5) rings for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$.

Table II. Infrared Data.

	Sample form	ν(NN), cm^{-1}	ν(CO), cm^{-1}
$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$	KBr pellet	2040(m) 2003(s) 1578(m)	
	nujol mull	2041(m) 2006(s) 1556(m)	
	pentane solution	2047(m) 2014(s) ...[a]	
$\{(\eta^5\text{-}C_5Me_5)_2Zr(^{14}NN^{15})\}_2(^{14}NN^{15})$	nujol mull	2006(m) 1970(s) 1530(m)	
$\{(\eta^5\text{-}C_5Me_5)_2Zr\,^{15}N_2\}_2\,^{15}N_2$	nujol mull	1972(m) 1937(s) 1515(m)	
	toluene-$\underline{d}_8$ solution	1975(s) 1937(vs) ...[a]	

Table II. Continued

$\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$	nujol mull	1682(m)	1902(m) 1860(s)
$\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$	nujol mull	1655(vw)	
$\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$	nujol mull	2058(m) 2020(s) 1711(m)	
	heptane solution	2056(m) 2023(s) ...[a]	

[a] Cut-off below $\sim$1800 cm^{-1} due to cell window (sapphire) and solvent absorptions.

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9. Biorad "$^{15}N_2$": $^{15}N\equiv{}^{15}N$, 93.4%; $^{15}N\equiv{}^{14}N$, 6.3%; $^{14}N\equiv{}^{14}N$, 0.3%; "$^{15}N\equiv{}^{14}N$": $^{15}N\equiv{}^{15}N$, 1.9%; $^{15}N\equiv{}^{14}N$, 89.6%; $^{15}N\equiv{}^{14}N$, 8.5%.
10. Sample decomposition above +50° precluded measuring spectra at higher temperatures.
11. J.A. Armor and H. Taube, J. Amer. Chem. Soc., 92, 2560 (1970).

Part D

Binuclear Dinitrogen Complexes of Bis(pentamethylcyclopentadienyl)-titanium (II) and Bis(pentamethylcyclopentadienyl) zirconium (II). Reaction with Acids.

Abstract

The product distribution (N_2H_4, NH_3) for the reactions of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ (1), $[(\eta^5\text{-}C_5Me_5)_2TiN_2]_2N_2$ (2), and $[(\eta^5\text{-}C_5Me_5)_2ZrN_2]_2N_2$ (3) with anhydrous HCl in toluene are reported. Hydrazine is obtained in high yields from the reaction of 2 and 3 with HCl. 1 also gives hydrazine but in much lower yield. Under the same conditions the reaction with HCl for the complexes $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (4) and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ (5) results in the quantitative release of the dinitrogen and partial reduction of the terminal ligands. The product distribution for the reaction of 3 with HBr, HCl, and H_2SO_4 each being carried out in toluene, diethyl ether and methanol is also reported. The possible mechanisms for the reduction of the N_2 to hydrazine are discussed.

Experimental

Physical Measurements. ^1H NMR spectra were recorded on a Varian T-60 and A-60-A spectrometers. Mass spectra were obtained from a Dupont model 21-492-B Mass Spectrometer.

Analyses. Ammonia was determined by indophenol reagent according with the procedure of: J.A. Russel, J. Biol. Chem., 156, 457 (1944), and hydrazine by p-dimethylaminobenzaldehyde reagent according with the procedure of: I.D. Snell and C.T. Snell, "Colorimetric Methods of Analysis", Vol IIA, D. Van Nostrand, New York, N.Y., 1959, p. 707.

Materials. All manipulations were performed either on a vacuum line or in a glove box which was evacuated to <0.1 torr and filled just prior to use with either prepurified argon or nitrogen. Nitrogen used in the experiments was prepurified grade rendered rigorously oxygen and water free by passage over MnO on Vermiculite[2] and activated 4A molecular sieves. All hydrocarbon and ether solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[3] 1,2,3,4,5-Pentamethylcyclopentadiene and $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ were prepared as described earlier.[1,3] $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$, and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ were prepared as described in part Ic.

Procedures

1. Reaction of $[(C_5Me_5)_2Ti]_2N_2$ with HCl. To $[(C_5Me_5)_2Ti]_2N_2$ (129.6 mg, 0.195 mmol) were added 9 ml of toluene in vacuo at liquid nitrogen temperature. 3.9 mmols HCl (20 M excess) were condensed onto the frozen toluene solution. This mixture

was warmed slowly to -80° whereupon an immediate reaction accompanied melting, and the purple-blue color faded to purple-brown with gas evolution. The gases were passed through a series of liquid nitrogen cooled-traps and the N_2/H_2 mixture collected via a Toepler pump. $N_2 + H_2$ amounted to 0.337 mmol. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O, which was removed in a liquid nitrogen cooled-trap. N_2 (0.153 mmol, 0.785 mmol/mmol dimer) remained. Thus H_2 evolved was 0.184 mmol, 0.944 mmol/mmol dimer. To the residue after evaporation of the toluene were added 10 ml of $CHCl_3$ and extracted 4 times with 10 ml portions of 0.1 N HCl. The 0.1 N HCl-soluble products were diluted to an appropriate volume and colorimetric determinations for ammonia and hydrazine were carried out. Analysis showed that the reduced N_2 consists of N_2H_4 = 0.116 mmol/mmol dimer and NH_3 = 0.073 mmol/mmol dimer.

2. Reaction of $[(C_5Me_5)_2TiN_2]_2N_2$ with HCl. To $[(C_5Me_5)_2Ti]_2N_2$ (118.8 mg; 0.179 mmol) were added 8 ml of toluene in vacuo at liquid nitrogen temperature. This mixture was warmed to room temperature and exposed to 1 atm N_2, with stirring, the solution was cooled gradually to -80° over a 60 min period in order to convert $[(C_5Me_5)_2Ti]_2N_2$ into $[(C_5Me_5)_2TiN_2]_2N_2$. This solution was then cooled to liquid nitrogen temperature and after the residual N_2 had been removed 3.6 mmols HCl (20M excess) were condensed onto the frozen toluene solution. The mixture was

warmed slowly to -80° whereupon an immediate reaction accompanied melting. The N_2/H_2 mixture was fractionated from HCl, collected, and analyzed as described above. A small correction for residual N_2 trapped in the frozen toluene (0.0185 mmol as determined by a blank) was made in calculating the N_2 evolved in the addition of HCl. N_2 evolved 0.400 mmols, 2.236 mmol/mmol dimer; H_2 evolved 0.044 mmols, 0.245 mmol/mmol dimer. The residue after evaporation of the toluene was treated as described above. Composition of $CDCl_3$-soluble portion of the residue (nmr): ~90% $(C_5Me_5)_2TiCl_2$, ~10% $(C_5Me_5)TiCl_3$. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consist of: N_2H_4 = 0.656 mmol/mmol dimer and NH_3 = 0.052 mmol/mmol dimer.

3. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with HCl. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (147.0 mg; 0.182 mmol) were added 8 ml of toluene in vacuo at liquid nitrogen temperature. 3.6 mmols HCl (20 M excess) were condensed onto the frozen toluene solution. This mixture was warmed slowly to -80° whereupon an immediate reaction accompanied melting as evidenced by a color change from intense red to pale yellow. The N_2/H_2 mixture was fractioned from HCl, collected, and analyzed as described in 1. Composition of $CDCl_3$-soluble portion of the residue (nmr): 100% $(C_5Me_5)_2ZrCl_2$. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and

hydrazine showed that the reduced N_2 consist of: N_2H_4 = 0.750 mmol/mmol dimer and NH_3: 0.226 mmol/mmol dimer.

4. Reaction of $[(C_5Me_5)_2ZrCO]_2N_2$ with HCl. To $[(C_5Me_5)_2ZrCO]_2N_2$ (80.4 mg; 0.100 mmols) were added 8 ml of toluene in vacuo at liquid nitrogen temperature. 2 mmols HCl (20 M excess) were condensed onto the frozen toluene solution. This mixture was warmed slowly to -80°. A fast reaction took place with the formation of a brown oily ppt. As no further change was observed the mixture was warmed slowly to room temperature. At ~-30° a fast reaction took place as evidenced by the disappearance of the brown-oily ppt. and a color change from brown to pale yellow. The gases were passed through a series of liquid nitrogen-cooled traps, and the N_2, H_2, CO mixture collected via a Toepler pump. $N_2 + H_2 + CO$ amounted to 0.348 mmol. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O and CO to CO_2, which was removed in a liquid nitrogen cooled-trap. N_2 (0.101 mmols, 1.010 mmol/mmol dimer) remained. Then, the liquid nitrogen cooled-trap was changed by a dry-ice-acetone trap in order to separate CO_2 from water. CO_2 (0.128 mmol/mmol dimer). Thus H_2 evolved was 0.118 mmol, 1.18 mmol/mmol dimer. The residue after evaporation of the toluene was treated as described in 1. Composition of $CDCl_3$-soluble portion of the residue (nmr): 100% $(C_5Me_5)_2ZrCl_2$. The 0.1 N HCl-soluble products gave a negative test with Nessler's reagent.

5. Reaction of $[(C_5Me_5)_2 Zr PF_3]_2 N_2$ with HCl. To $[(C_5Me_5)_2 ZrN_2]_2 N_2$ (82.1 mg; 0.102 mmol) were added 8 ml of toluene at -80° in vacuo. This mixture was warmed to 0° and stirred over a 10 min period at this temperature in order to dissolve the complex. This solution was submerged in a CCl_4 slush bath (-23°) and allowed to equilibrate under stirring for 5 min. PF_3 (0.412 mmol) was introduced and after 30 min, under stirring at this temperature the system was cooled to -80°. The N_2 was fractionated from PF_3 by passage through a series of liquid nitrogen cooled-traps and collected via a Toepler pump. N_2 collected 0.197 mmol, 1.937 mmol/mmol dimer. Then the liquid nitrogen cooled-traps were replaced by dry ice-acetone cooled traps in order to collect the PF_3. PF_3 collected 0.202 mmol; thus PF_3 consumed was 0.210 mmol, 2.059 mmol/mmol dimer. To the above solution of the complex, $[(C_5Me_5)_2 Zr(PF_3)]_2N_2$, 2 mmols HCl (20 M excess) were introduced. A fast reaction took place as evidenced by a color change from red to white yellow. The N_2/H_2 mixture was fractionated from HCl/PF_3 by passage through a series of liquid nitrogen cooled-traps and analyzed as described in 1. N_2 evolved 0.079 mmol, 0.775 mmol/mmol dimer; H_2 evolved 0.135 mmol, 1.324 mmol/mmol dimer. After the PF_3 was fractionated from HCl by condensing the PF_3/HCl mixture into a flask with previously degassed pyridine, warming to room temperature under stirring and Toepler pumped residual gas through a series of dry ice acetone cooled traps. PF_3

collected 0.101 mmol, 0.990 mmol/mmol dimer (confirmed by its mass spectrum). The amount of N_2 in the complex as determinated by a blank: 2.750 mmols/mmol dimer.

6. Reaction of $[(C_5Me_5)_2 ZrN_2]_2 N_2$ with HCl in diethyl ether. To $[(C_5Me_5)_2 ZrN_2]_2N_2$ (109.5 mg; 0.136 mmol) were added 8 ml of diethyl ether in vacuo at liquid nitrogen temperature. 2.7 mmols HCl (20 M excess) were condensed onto the frozen diethyl ether solution. This mixture was warmed slowly to room temperature whereupon an immediate reaction accompanied by melting took place. Even though this reaction is fast, several hours are required for completion due to the insolubility of the dinitrogen complex in diethyl-ether. The N_2 /H_2 mixture was fractionated from HCl, collected, and analyzed as described in 1. N_2 evolved 0.355 mmols, 2.618 mmol/mmol dimer; H_2 evolved 0.209 mmol, 1.543 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.142 mmol/mmol dimer and NH_3: 0.091 mmol/mmol dimer.

7. Reaction of $[(C_5Me_5)_2 ZrN_2]_2N_2$ with HCl in methanol. To $[(C_5Me_5)_2 ZrN_2]_2 N_2$ (128.2 mg; 0.159 mmol) were added 8 ml of methanol (degassed and dried over molecular sieves) in vacuo at liquid nitrogen temperature. 3.2 mmol HCl (20 M excess) were condensed onto the frozen methanol solution. This mixture was warmed slowly to room temperature whereupon

an immediate reaction accompanying melting took place. Similar to the above case this reaction is fast, but it takes several hours to completion due to the insolubility of the dinitrogen complex in methanol. The N_2/H_2 mixture was fractionated from HCl, collected, and analyzed as described in 1. N_2 evolved 0.353 mmol, 2.220 mmol/mmol dimer; H_2 evolved 0.079 mmol, 0.495 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.433 mmol/mmol dimer and NH_3: 0.430 mmol/mmol dimer.

8. Reaction of $[(C_5Me_5)_2 ZrN_2]_2 N_2$ with HBr in toluene. To $[(C_5Me_5)_2 ZrN_2]_2 N_2$ (104.2 mg; 0.129 mmol) were added 8 ml of toluene in vacuo at liquid nitrogen temperature. 2.6 mmols HBr (20 M excess) were condensed onto the frozen toluene solution. This mixture was warmed slowly to -80° whereupon an immediate reaction accompanied melting as evidenced by a color change from intense red to yellow. The N_2/H_2 mixture was fractionated from HBr, collected, and analyzed as described in 1. N_2 evolved 0.258 mmol, 2.000 mmol/mmol dimer; H_2 evolved 0.018 mmol, 0.142 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.795 mmol/mmol dimer and NH_3 = 0.125 mmol/mmol dimer.

9. Reaction of $[(C_5Me_5)_2 ZrN_2]_2N_2$ with HBr in diethyl ether. To $[(C_5Me_5)_2 ZrN_2]_2 N_2$ (98.6 mg; 0.122 mmol) were added 8 ml of diethyl ether at liquid nitrogen temperature. 2.4 mmols HBr (20 M excess) were condensed onto the frozen diethyl ether solution. This mixture was warmed slowly to room temperature whereupon an immediate reaction accompanied melting. After 1-2 hours the N_2/H_2 mixture was fractionated from HBr, collected, and analyzed as described in 1. N_2 evolved 0.269 mmol, 2.205 mmol/mmol dimer; H_2 evolved 0.049 mmol, 0.402 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.675 mmol/mmol dimer and NH_3 = 0.122 mmol/mmol dimer.

10. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with HBr in Methanol. To $[(C_5Me_5)_2 ZrN_2]_2$ (95.9 mg; 0.119 mmol) were added 8 ml of methanol (degassed and dried over molecular sieves) in vacuo at liquid nitrogen temperature. 2.4 mmols HBr (20 M excess) were condensed onto the frozen methanol solution. This mixture was warmed slowly to room temperature whereupon an immediate reaction accompanied melting. After 1-2 hours the N_2/H_2 mixture was fractionated from HCl, collected, and analyzed as described in 1. N_2 evolved 0.261 mmol, 2.193 mmol/mmol dimer; H_2 evolved 0.066 mmol, 0.555 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists

of: N_2H_4 = 0.501 mmol/mmol dimer and NH_3 = 0.324 mmol/mmol dimer.

11. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with H_2SO_4 in toluene.

This reaction was performed in the apparatus showed in figure 1. Concentrated sulfuric acid (98%, 0.2 ml) were placed via syringe in the bulb A, evacuated, and 2 ml of toluene were condensed into bulb A in vacuo at -80° . The stopcock was then closed and connected to the reaction flask as shown in figure 1. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (95.9 mg; 0.119 mmol) were condensed 6 ml of toluene at -80° C. The H_2SO_4 (~30 M excess) in toluene was added by opening the stopcock of the bulb A. This mixture was warmed slowly to room temperature. At ~ -40° a fast reaction took place as evidenced by a color change from dark red to white-yellow (~10 min to completion). The N_2/H_2 mixture was collected and analyzed as described in 1. N_2 evolved 0.280 mmol, 2.353 mmol/mmol dimer; H_2 evolved 0.107 mmol, 0.899 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.455 mmol/mmol dimer and NH_3 = 0.198 mmol/mmol dimer.

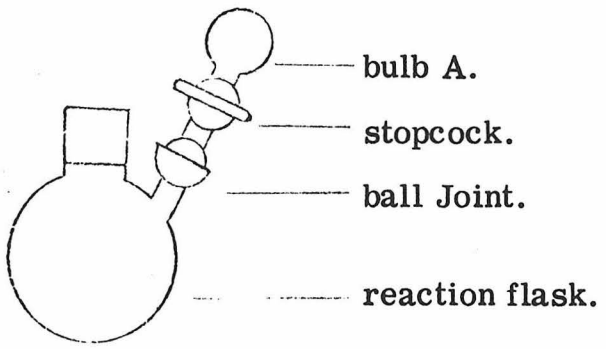


Figure 1.

12. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with H_2SO_4 in diethyl ether. This reaction was carried out in the same way as above, with the difference that toluene was substituted by diethyl ether. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (86.1 mg; 0.107 mmol) were condensed 6 ml of diethyl ether under vacuo at -80°. 3.7 mmols H_2SO_4 (~35 M excess) in 2 ml of diethyl ether were added by opening the stopcock of the bulb A. This mixture was warmed slowly to room temperature. At ~ -40° a fast reaction took place. After 1-2 hours the N_2/H_2 mixture was collected and analyzed as described in 1. N_2 evolved 0.205 mmol, 1.916 mmol/mmol dimer; H_2 evolved 0.012 mmol, 0.112 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.923 mmol/mmol dimer and NH_3 = 0.140 mmol/mmol dimer.

13. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with H_2SO_4 in methanol. This reaction was carried out in the same way as 11, with the difference that toluene was substituted by methanol. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (77.4 mg, 0.096 mmol) were condensed 6 ml of methanol in vacuo at liquid nitrogen temperature. 3.7 mmols H_2SO_4 (~40 Mol excess) in 2 ml of methanol were added by opening the stopcock of the bulb A. This mixture was warmed slowly to room temperature. At ~ -40° a fast reaction took place. After 2 hrs the N_2/H_2 mixture was collected and analyzed as described in 1. N_2 evolved 0.205 mmol, 2.135 mmol/mmol

dimer; H_2 evolved 0.031 mmol, 0.323 mmol/mmol dimer. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consists of: N_2H_4 = 0.516 mmol/mmol dimer and NH_3 = 0.414 mmol/mmol dimer.

Results

In table I are summarized the reactions of the binuclear dinitrogen complexes of bis(pentamethylcyclopentadienyl) titanium (II) and zirconium (II) with anhydrous HCl in toluene at -80°. From table I we see that treatment of $\{(C_5Me_5)_2TiN_2\}_2N_2$(2) or $\{(C_5Me_5)_2ZrN_2\}_2N_2$(3) with HCl yields $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ or $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, respectively, N_2, N_2H_4, and a small amount of NH_3 and H_2. The stoichiometry for the reaction with 3 is in close agreement with equation (1), wherein the four reducing equivalents available in the dimer have been utilized in the reduction of one of the three dinitrogen ligands to N_2H_4.

$$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2 + 4\,HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2\,N_2 + N_2H_4 \quad (1)$$

3

Identical treatment of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$(1) with HCl also leads to hydrazine, but in much lower yield. However, treatment of $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$(4) or $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$(5) with HCl yields $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, 1 mol of N_2 (no N_2H_4 or NH_3 is detected), approximately one half of the expected amount of

free, terminal ligand, and H_2. The stoichiometry for both reactions is not in disagreement with equation (2), but, since the product(s) of this reaction have not been characterized and the reaction of $\underset{\sim}{5}$ with HCl has been carried out only once, it is not yet clear whether a maximum of 1L is reduced as written in equation 2.

$$\{(\eta^5\text{-}C_5Me_5)_2ZrL\}_2N_2 + 4HCl \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrCl_2 + N_2 + H_2 + L + \text{"}(LH_2)_n\text{"} \quad (2)$$

$\underset{\sim}{4}$ or $\underset{\sim}{5}$

In table II are summarized the product distributions for the reaction of $\underset{\sim}{3}$ with HBr, HCl, and H_2SO_4, each being carried out in toluene, diethyl ether, and methanol. We can see that the efficiency of HBr and HCl in the reduction of one of the three dinitrogen ligands to N_2H_4 in toluene and methanol is very similar; however, in diethyl ether HBr is much more efficient than HCl (68% N_2H_4 vs. 14% N_2H_4, respectively). The solvent substantially effects the reaction with a given acid. For the three solvents examined the order for HCl (to produce highest yield in hydrazine) is: toluene > methanol > diethyl ether, and for HBr is: toluene > diethyl ether > methanol. In the case of sulfuric acid a still different behavior is observed. Diethyl ether, which was not the best solvent for HBr and HCl, surprisingly, gives the record yield of hydrazine for H_2SO_4, up to 0.92 mol N_2H_4 per mol of dimer. Toluene, which was the best

solvent for HCl and HBr, is the worst for H_2SO_4. For sulfuric acid the order in the solvents (to produce highest yield in hydrazine) is diethyl ether > methanol > toluene. For toluene and diethyl ether regardless of acid used, the yields in ammonia are quite low, whereas in CH_3OH, ammonia yields are consistently higher. Furthermore in methanol all the acids investigated give comparable yields of ammonia and hydrazine.

Discussion

The studies of the product distribution for the reaction of $\underset{\sim}{3}$ as a function of the acid and the solvent have shown that for a given acid the solvent substantially effects the reaction. These observations have been noted also for complexes of the type $M(N_2)_2L_4$, where M = Mo, W and L = PMe_2Ph.[4,5] The implications are at present, however, difficult to interpret. As mentioned above, all the acids in methanol give comparable yields of ammonia and hydrazine. It is interesting to note that on the basis of the number of reducing equivalents utilized in the reduction of dinitrogen to hydrazine and ammonia (see Table II last column), methanol is a good solvent for all the acids investigated. In part Ib, we saw that the formation of ammonia in the reaction of $\underset{\sim}{3}$ with HCl in toluene is believed to arise from interference of a reaction of hydrazine with $\underset{\sim}{3}$. The consistently high yields of ammonia observed in methanol can be rationalized, if one considers that the reaction proceeds

slowly at -40° over a period of 1-2 hrs, due to the insolubility of the complex in methanol. This fact and the higher solubility of protonated hydrazine in methanol undoubtedly favor the side reaction leading to ammonia.

From the studies of the reaction of the dinitrogen complexes of titanium and zirconium with HCl in toluene it is clear that reduction of N_2 to N_2H_4 occurs only in high yields in $\underset{\sim}{2}$ and $\underset{\sim}{3}$; that is, when terminal dinitrogen ligands are present. The reaction of $\underset{\sim}{1}$ with HCl, where only a bridging dinitrogen is present, also leads to hydrazine but in much lower yield. However, since $\underset{\sim}{1}$ reacts with more N_2 at low temperature to yield $\underset{\sim}{2}$, it is likely that the small yield of ammonia and hydrazine formed in this reaction result from $\underset{\sim}{2}$ formed from $\underset{\sim}{1}$ and liberated N_2 during the reaction.

The above results, and the fact that the bridging N_2 in $\underset{\sim}{4}$ and $\underset{\sim}{5}$ is not reduced, suggest a special role for the terminal dinitrogen ligands in the reduction sequence.

In part Ib were reported the results of the labelling study of the reaction of $\underset{\sim}{3}$ with HCl in toluene at ~ -95°. The data required a reaction sequence mediated by a symmetric species in which one terminal N_2 and the μ-N_2 have become equivalent. While a number of mechanisms satisfying this requirement could be formulated, we favor one involving protonation of a terminal dinitrogen of $\underset{\sim}{3}$, loss of the other terminal N_2, and generation of the symmetric reaction intermediate $(\eta^5\text{-}C_5Me_5)_2Zr(N_2H)_2$ $\underset{\sim}{6}$

(Scheme I). Consistent with the labelling experiments, 6 would lead to 1 mole each of N_2 and N_2H_4. Generation of the neutral, monomeric species 6 from 3 would require a formal two-electron transfer to the N_2-bearing Zr accompanied by release of the other Zr in the fully oxidized state, i.e., as $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. Strong electronic coupling of the two Zr (II) centers through the $\mu\text{-}N_2$ of 3, as indicated by its structure, ir, and visible spectra, should facilitate such Zr-to-Zr charge transfer. A further evidence in support of this strong electronic coupling can be inferred from the infrared spectrum of 5.[6]

The NMR studies reported in part Ic demonstrate that 3 retains its integrity, since no exchange of terminal and bridging dinitrogen ligands is observed by ^{15}N NMR, even at +50°. On the other hand, an extrapolation of our data to -95° gives an estimated half life for terminal dinitrogen dissociation of approximately 15 sec., which, within reasonable error limits, is comparable to the visually-estimated half life of the reaction of 3 with a 20 M excess of HCl at this temperature. This result presents the possibility that 6 could be generated from the coordinatively unsaturated species $(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\text{-}N_2\text{-}Zr(\eta^5\text{-}C_5Me_5)_2$ (7) by initial protonation of the terminal dinitrogen of 7, attack of the Cl^- at the unsaturated zirconium center of 7 and finally generation of the symmetric reaction intermediate 6 by addition of a second HCl at the $Zr\text{-}\mu\text{-}N_2$ bond (Scheme IIa). It is interesting to note that protonation of the terminal dinitrogen

ligand in 7, is even more plausible than in 3, since dissociation of one terminal dinitrogen ligand would result in an increase of the basicity of the other terminal dinitrogen.

A third possible mechanism would involve addition of HCl across the Zr-μ-N_2 bond of the coordinatively unsaturated zirconium center of 7, then by addition of the second molecule of HCl the reaction intermediate (6) could be generated (Scheme IIb).

Of the three mechanisms, I, IIa and IIb, our experimental evidence is not enough to favor any one of them. However, based on the observations that (1) there is up to now no well characterized binuclear dinitrogen complex containing only bridging dinitrogen where the reduction of the N_2 has been achieved unequivocally and (2) reduction of the N_2 has been shown to occur in dinitrogen complexes containing either only terminal dinitrogen ligands or both, one would tend to favor I or IIa.

A further point which was also investigated, although the results are yet inconclusive, was the mechanism by which 6 decomposes to N_2 and N_2H_4.

An easy pathway to visualize is one in which diimine (2 mols) is an intermediate, which then disproportionates to N_2 and N_2H_4 (1 mol each) (Scheme IIIa). A second mechanism, where diimine is not an intermediate in the reaction, would involve, for example, a kind of "acid catalyzed disproportionation" of the bis (diazenido) intermediate (6) to an hydrazido

complex (7), which further generates hydrazine by addition of two HCl molecules (Scheme IIb).

We carried out two experiments in order to detect diimine. The first was based on the observed competitive H_2 inhibition of N_2 reduction and the N_2 catalized HD formation from D_2 by nitrogenase.[8,9] However, we found no change in the stoichiometry of the reaction of 3 with HCl in toluene at -80° under 1 atm of H_2. In the second experiment we attempted to trap diimine with azobenzene, by carrying the reaction of 3 with HCl at -80° in the presence of azobenzene, but again, no change in the stoichiometry was observed. Nevertheless, the above results do not rule out Scheme IIIa, because both reactions were carried out at -80° C. If the activation energies for the above reactions are much higher than that of disproportionation of diimide, no change in the stoichiometry would be expected. Unfortunately H_2 and azobenzene react with 3 at higher temperature, thus precluding experiments at a temperature where more conclusive results could be obtained.

Even though our experimental evidence at present does not allow us to have a preference for either of the above mechanisms (IIIa and IIIb), we can make an analogy to the finding of Chatt and coworkers where the diazenido complexes $[MX_2(N_2H)(Ph_2PCH_2CH_2PPh_2)]$ (M=Mo or W, X=Cl or Br), obtained by deprotonation of the respective hydrazido complexes $[MX_2(N_2H_2)(dpe)_2]$ by mild alkali, revert quantitatively to the parent N_2H_2 complexes

on treatment with one mole of halogen acid.[5] Because diimine is not an intermediate in Chatt's systems one might favor a Scheme like IIIb.

Table I. Products of the reaction with HCl of Binuclear complexes of bis(pentamethylcyclopentadienyl) titanium II and zirconium II in toluene. All the values are mmol/mmol dimer.

complex	N_2 evolved/ dimer	N_2 missing/ dimer	CO or PF_3 evolved/dimer	CO or PF_3 missing/dimer	H_2 evolved/ dimer	NH_3/ dimer[d]	N_2H_4/ dimer[d]	product of the reaction.
$[(C_5Me_5)_2Ti]_2N_2$	0.785	0.215	---	---	0.944	0.073	0.116	$(C_5Me_5)_2TiCl_2$ ~90%
$[(C_5Me_5)_2TiN_2]_2N_2$	2.236	0.764	---	---	0.245	0.052	0.656	$(C_5Me_5)_2TiCl_2$ ~90%
$[(C_5Me_5)_2ZrN_2]_2N_2$	2.060	0.840[b]	---	---	0.203	0.226	0.750	$(C_5Me_5)_2ZrCl_2$ 100%
$[(C_5Me_5)_2Zr(CO)]_2N_2$	1.010	0	1.280	0.720	1.180	---	---	$(C_5Me_5)_2ZrCl_2$ 100%
$[(C_5Me_5)_2Zr(PF_3)]_2N_2$	0.965[a]	0.035[c]	0.990	1.010	1.324	---	---	$(C_5Me_5)_2ZrCl_2$ 100%

[a] Based on the N_2 missing per dimer (see c).

[b] Determined by substracting N_2 evolved in the reaction with HCl from the real amount of N_2 in the complex as determined by a blank.

[c] Determined by substracting the N_2 of the exchange + the N_2 evolved in the reaction with HCl from the real amount of N_2 in the complex as determined by a blank.

[d] NH_3 determined by indophenol reagent, N_2H_4 by p-dimethylaminobenzaldehyde reagent.

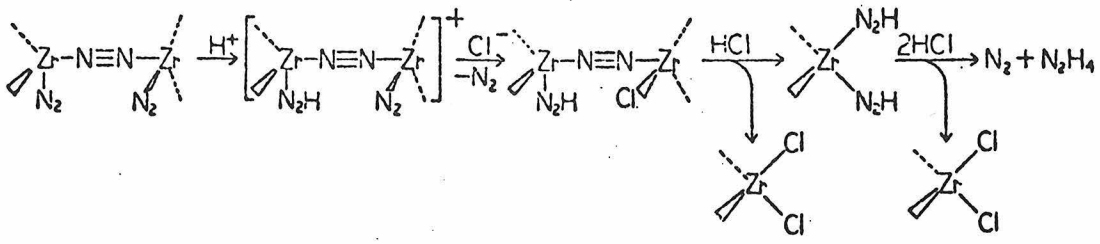
Table II. Composition of reduced N_2 (N_2H_4/NH_3) for $[(C_5Me_5)_2ZrN_2]_2N_2$ as a function of acid and solvent.

solvent	acid	N_2 evolved/ dimer[a]	N_2 missing/ dimer[a]	H_2 evolved/ dimer	NH_3/ dimer[b]	N_2H_4/ dimer[b]	total N_2 as NH_3 and N_2H_4	% red. equiv. as NH_3 and N_2H_4
Toluene	HCl	2.060	0.840	0.203	0.23(4)	0.75(2)	0.87(4)	0.92(4)
	HBr	2.000	0.900	0.142	0.13(4)	0.80(2)	0.87(4)	0.90(4)
	H_2SO_4	2.353	0.547	0.899	0.20(4)	0.46(2)	0.56(4)	0.61(4)
diethyl ether	HCl	2.618	0.282	1.543	0.09(4)	0.14(2)	0.19(4)	0.21(4)
	HBr	2.205	0.695	0.402	0.12(4)	0.68(2)	0.74(4)	0.77(4)
	H_2SO_4	1.916	0.984	0.112	0.14(4)	0.92(2)	0.99(4)	1.03(4)
Methanol	HCl	2.220	0.680	0.495	0.43(4)	0.43(2)	0.65(4)	0.72(4)
	HBr	2.193	0.707	0.555	0.32(4)	0.50(2)	0.66(4)	0.74(4)
	H_2SO_4	2.135	0.765	0.323	0.41(4)	0.52(2)	0.73(4)	0.83(4)

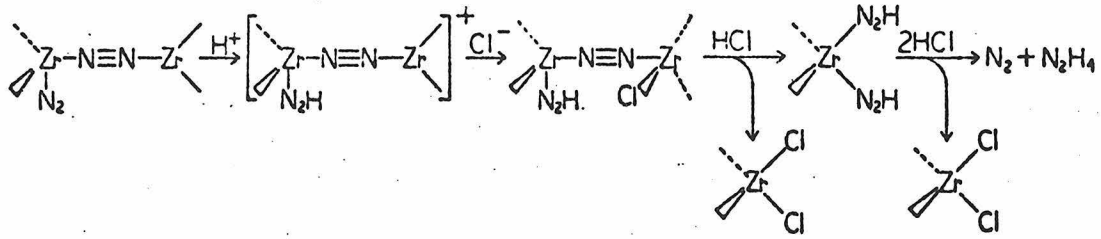
[a] N_2 missing was determined by substracting the N_2 evolved in the reaction with HCl from the real amount of N_2 in the complex, the latter number was determined by decomposition of the complex in toluene under vacuo. A blank gave 2.900 mmol N_2/mmol dimer (~97% pure).

[b] Ammonia determined by indophenol reagent, hydrazine by p-dimethyl aminobenzaldehyde reagent.

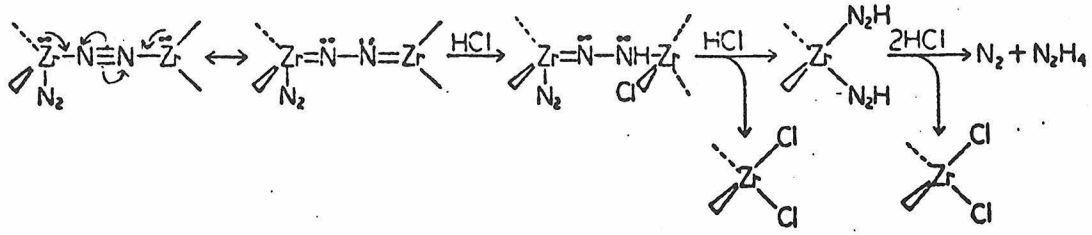
Scheme I.



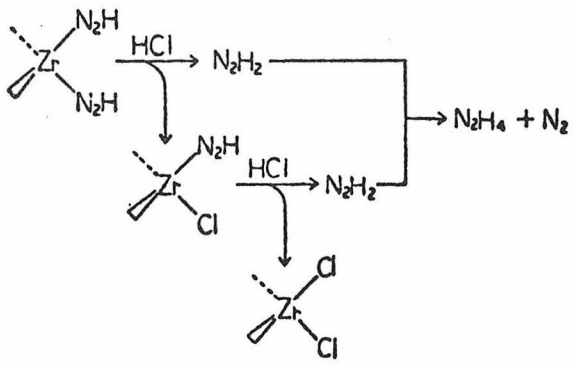
Scheme IIa.



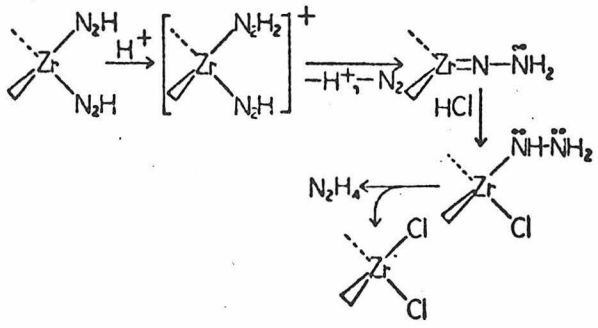
Scheme IIb.



Scheme IIIa.



Scheme IIIb.



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6. The presence of two terminal N-N stretching frequencies and the unexpected moderate intensity of the bridgint N-N stretching mode for 3 has been interpreted on the basis of a coupling of the symmetric combination of terminal N-N stretches with the bridging N-N stretching mode, the later gaining intensity from the former. In agreement with this interpretation the bridging N-N stretching mode for 5 is very weak.

7. A support to the possible existence of $Cp_2Zr{=}N{-}NH_2$, is the recent preparation of $Cp_2V{=}N{-}N(SiMe_3)_2$, and suggested structure for $Cp_2Ti{=}N{-}N(SiMe_3)_2$. N. Wiberg, H.W. Häring, and O. Shieda, Angew. Chem. Internat. Ed., 15, 386 (1976).

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Part E.

Binuclear Dinitrogen Complexes of Bis(pentamethylcyclopentadienyl)-titanium (II) and Bis(pentamethylcyclopentadienyl) zirconium (II). Reaction with $LiAlH_4$.

Abstract

The reactions of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$(1), $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$(2), $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$(3), and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$(4) with $LiAlH_4$ are reported. 2 gives hydrazine (0.5 mol/mol of 2), and ammonia (1 mol/mol of 2) after hydrolysis of the reaction products with HCl. 1 also gives ammonia and hydrazine but in lower yields. Under the same conditions the reactions of 3 and 4 result in the evolution of most of the dinitrogen. A study of the reaction of 2, labeled with $^{15}N_2$ in the bridge position, showed that the hydrazine and ammonia originate from the bridge position.

Experimental

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian T-60 and A-60-A spectrometers. Mass spectra were obtained from a Dupont model 21-492-B Mass Spectrometer.

Materials. All manipulations were performed either on a vacuum line or in a glove box which was evacuated to <0.1 torr and filled just prior to use with either prepurified argon or nitrogen. Nitrogen used in the experiments was prepurified grade rendered rigorously oxygen and water free by passage over MnO on Vermiculite [1] and activated 4A molecular sieves. All hydrocarbon and

ether solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[2] 1,2,3,4,5-Pentamethylcyclopentadiene and $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ were prepared as described earlier.[2,3] $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, $\{(\eta^5\text{-}C_5Me_5)_2Zr^{15}N_2\}_2{}^{15}N_2$, $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$ were prepared as described in part Ic. The $^{15}N\equiv{}^{15}N$ used was rigorously freed of water and oxygen by contact with solid $\{(C_5(CH_3)_5\}\{C_5(CH_3)_4CH_2\}Ti$,[3] see mass spectrum.[4]

Analyses. Ammonia was determinated by indophenol reagent according to the procedure of: J.A. Russel, J. Biol. Chem., 156, 457 (1944), and hydrazine by p-dimethylaminobenzaldehyde reagent according to the procedure of: I.D. Snell and C.T. Snell, 'Colorimetric Methods of Analysis", Vol. IIA, D. Van Nostrand, New York, N.Y., 1959, p. 707.

Procedures

1. Reaction of $[(C_5Me_5)_2Ti]_2N_2$ with $LiAlH_4$. To $[(C_5Me_5)_2Ti]_2N_2$ (109.7 mg, 0.165 mmol) together with $LiALH_4$ (37 mg, 0.975 mmol) were condensed 9 ml of diethyl ether in vacuo at liquid nitrogen temperature. This mixture was warmed slowly to -80°, whereupon a relatively slow reaction took place during a 1 hr period as evidenced by a gradual color change from purple-blue to pink. After warming to room temperature the gases were passed through a series of liquid nitrogen-cooled traps, and the N_2/H_2 mixture collected via a Toepler pump. $N_2 + H_2$ amounted to 0.213 mmol. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O, which was

removed in a liquid nitrogen-cooled trap. N_2 (0.117 mmol, 0.703 mmol/mmol dimer) remained. Thus, H_2 evolved was 0.096 mmol, 0.585 mmol/mmol dimer. To the residue (after evaporation of the diethyl ether) were added 10 ml of $CHCl_3$ and 5 ml of concentrated HCl in order to destroy excess $LiAlH_4$. This mixture was extracted 4 times with 10 ml portions of 0.1 N HCl. The 0.1 N HCl soluble products were diluted to an appropriate volume and colorimetric determinations for ammonia and hydrazine were carried out. Analysis showed that the reduced N_2 consisted of: NH_3, 0.484 mmol/mmol dimer; N_2H_4, 0.006 mmol/mmol dimer. The $CHCl_3$-soluble portion consisted (after evaporation of the $CHCl_3$ and redisolution in $CDCl_3$) of ~80% yield of $[C_5(CH_3)_5]_2TiCl_2$.

2. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with $LiAlH_4$. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (114.1 mg, 0.141 mmol) together with $LiAlH_4$ (48 mg, 1.27 mmol) were condensed 9 ml of diethyl ether in vacuo at liquid nitrogen temperature. This mixture was warmed slowly to room temperature. A reaction took place between -60° and -40° as evidenced by a color change from dark red to orange. The N_2/H_2 mixture was fractionated from the diethyl ether, collected,and analyzed as described in 1. N_2 evolved-0.2787 mmol, 1.971 mmol/mmol dimer; H_2 evolved-0.009 mmol, 0.064 mmol/mmol dimer. The residue (after evaporation of the diethyl ether) was treated as described in 1. The 0.1 N HCl-soluble products after colorimetric determinations for ammonia and hydrazine showed that the reduced N_2 consisted of: NH_3, 1.04 mmol/mmol

dimer; N_2H_4, 0.53 mmol/mmol dimer. The $CHCl_3$-soluble portion (after evaporation of the $CHCl_3$ and redisolution in $CDCl_3$ consisted of 100% $[C_5(CH_3)_5]_2 ZrCl_2$.

3. Reaction of $[(C_5Me_5)_2Zr(CO)]_2N_2$ with $LiAlH_4$. To $[(C_5Me_5)_2Zr(CO)]_2N_2$ (77 mg, 0.095 mmol) together with $LiAlH_4$ (31.9 mg, 0.84 mmol) were condensed 7 ml of diethyl ether under vacuo at liquid nitrogen temperature. This mixture was warmed slowly to room temperature whereupon a slow reaction took place between $\sim -40°$ and $\sim -10°$ giving a reddish solution with some white precipitate. The residual gases were passed through a series of liquid nitrogen cooled traps and collected via Toepler pump. The total gas collected amounted to 0.091 mmol. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O and CO to CO_2, which were removed in a liquid nitrogen cooled trap. N_2 (0.084 mmol, 0.884/mmol dimer) remained. Then, the liquid nitrogen-cooled trap was replaced by a dry-ice-acetone-cooled trap in order to separate CO_2 from water. No CO_2 was collected, thus H_2 evolved was 0.007 mmol, 0.074 mmol/mmol dimer. The residue after reaction with HCl and extraction with $CDCl_3$ consisted of 100% $[C_5(CH_3)_5]_2ZrCl_2$.

4. Reaction of $[(C_5Me_5)_2Zr(PF_3)]_2N_2$ with $LiAlH_4$. This reaction was performed in the apparatus shown in figure 1. 5 ml of a solution of $LiAlH_4$ in diethyl ether (0.13 mmol/ml, 0.65 mmol) were placed via syringe in the bulb A (this operation was carried out in a glove box). After the bulb A was evacuated (by freezing this solution

3 times at liquid N_2 temperature), the stopcock was closed and the apparatus connected to the reaction flask as shown in figure 1. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (112 mg, 0.139 mmol) were added 8 ml of toluene at -80° in vacuo. This mixture was warmed to 0° and stirred over a 10 min period at this temperature in order to dissolve the complex. This solution was then submerged in a cooled liquid nitrogen-CCl_4 slush bath (-23°) and the temperature allowed to equilibrate with stirring for 5 min. PF_3 (0.536 mmol) was introduced and after 15 min under stirring at this temperature the system was cooled to -80°. The N_2 was fractionated from PF_3 by passage through a series of liquid nitrogen cooled-traps and collected via Toepler pump. N_2 collected amounted to 0.257 mmol, 1.849 mmol/mmol dimer. Then the liquid nitrogen cooled-traps were replaced by dry-ice acetone cooled-traps in order to collect the PF_3. PF_3 collected amounted to 0.272 mmol, thus PF_3 consumed was 0.264 mmol, 1.899 mmol/mmol dimer. To the above solution of the complex, $[(C_5Me_5)_2Zr(PF_3)]_2N_2$ at - 80°, the solution of $LiAlH_4$ in diethyl ether was added (previously cooled to ~-20°) through the stopcock of the bulb A and warmed slowly to room temperature. A color change from red to yellow-orange was observed. Then the residual gases were passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. Collected gas amounted to 0.607 mmol. This gas mixture (N_2 + H_2) was analyzed as described in 1. N_2 evolved, 0.121 mmol (0.871 mmol/mmol dimer) H_2 evolved 0.436 mmol (3.496 mmol/

mmol dimer). No PF_3 was evolved in the reaction. The amount of N_2 in the complex as determined by a blank was 2.8 mol/mol dimer.

5. Label Experiment. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (660 torr) at -23° (30 min) and reaction with $LiAlH_4$.

a) Exchange with free natural N_2. This reaction was performed in the apparatus shown in figure 1. 3 ml of a solution of $LiAlH_4$ (0.22 mmol/ml, 0.66 mmol) were introduced in the bulb A and degassed as described in 4. Then the bulb was connected to the reaction flask as shown in figure 1. To $[(C_5Me_5)_2Zr^{15}N_2]^{15}N_2$ (138.3 mg, 0.1701 mmol) were condensed 8 ml of toluene in vacuo at liquid nitrogen temperature. This mixture was warmed to 0° and stirred over a 15 min period at this temperature in order to dissolve the complex. This solution was then submerged in a cooled liquid nitrogen-CCl_4 slush bath (-23°) and allowed to equilibrate at this temperature for 5 min. Natural $^{14}N_2$ was admitted (660 torr), and the system quickly closed off. After 30 min of stirring the exchange was quenched by rapid cooling to liquid nitrogen temperature. The gas phase was passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. N_2 collected amounted to 1.7930 mmol. An appropriate portion of the gas phase was then transferred to a sample bulb and analyzed by mass spectrometry for $^{14}N\equiv{}^{14}N$ (28), $^{15}N\equiv{}^{14}N$ (29) and $^{15}N\equiv{}^{15}N$ (30). A small correction for residual N_2 trapped in the frozen toluene (0.0185 mmol as determined by a blank) was made in calculating

the expected fraction of 28, 29, and 30 in the gas phase. Mass spectrum of the gas phase showed the following composition: $\chi_{28}=0.8610$, $\chi_{29}=0.0069$, $\chi_{30}=0.1321$. The composition of terminal positions after the exchange was calculated by a procedure similar to the one outlined in the Appendix II. (No complete exchange was observed due to the form of the apparatus used, see figure 1.)

b) Reaction with $LiAlH_4$. Following the above exchange, the solution of $LiAlH_4$ in diethyl ether was added (previously cooled to $\sim -20°$). This mixture was warmed slowly to room temperature whereupon a reaction between $-60°$ and $-40°$ took place. The N_2/H_2 mixture was fractionated from the diethyl ether, collected and analyzed as described in 1. N_2 evolved 0.3412 mmol, 2.005 mmol/mmol dimer; H_2 evolved 0.020 mmol, 0.118 mmol dimer. Then, an appropriate portion of the N_2 was transferred to a sample bulb and analyzed by mass spectrometry for 28, 29, and 30 dinitrogens. A small correction for residual N_2 trapped in the frozen toluene, 0.0185 mmol, was made to the observed fraction of 28, 29, and 30 N_2 evolved upon the addition of $LiAlH_4$. Mass spectrum of the N_2 evolved showed the following composition: $\chi_{28}=0.7026$, $\chi_{29}=0.0168$, $\chi_{30}=0.2806$. The expected composition of the N_2 evolved in the addition of $LiAlH_4$ was calculated by a procedure similar to the one outlined in the Appendix II.

c) Recovery of the N_2 in the hydrazine. The oxidation of hydrazine to N_2 and ammonia to N_2 was done by the procedure described by Yamamura and Sikes. Anal. Chem. 35, 1958 (1963).

N_2 collected from hydrazine (Br_2 oxidation) 0.083 mmol, 0.488 mmol/mmol dimer.

N_2 collected from ammonia (hypobromite oxidation) 0.021 mmol, 0.123 mmol/mmol dimer.

Mass spectrum of N_2 collected from hydrazine showed the following composition: $\chi_{28}=0.0044$, $\chi_{29}=0.0036$, $\chi_{30}=0.9921$.

Mass spectrum of N_2 collected from NH_3 showed the following composition: $\chi_{28}=0.0569$, $\chi_{29}=0.1988$, $\chi_{30}=0.7443$.

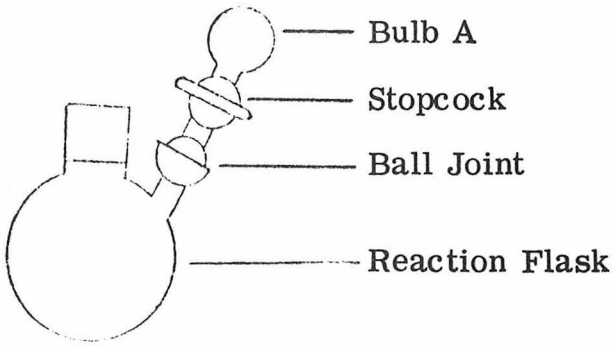

Figure 1.

Results

The results of the reactions of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$(1), $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$(2), $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$(3) and $\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$(4) with $LiAlH_4$ are summarized in table I. From table I we see that the reaction of 2 results in the complete reduction of one of the three dinitrogen ligands, and from the hydrolysis of the product(s) with HCl, hydrazine (0.53 mol/mol dimer) and ammonia (1.04 mol/mol dimer) are obtained. The

amount of $LiAlH_4$ required per mol of $\underset{\sim}{2}$ and the nature of the product(s) are not yet known, thus tentatively we can write this reaction as (equations 1 and 2):

$$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2 + \chi\, LiAlH_4 \rightarrow [\text{products}] + 2N_2 \qquad (1)$$

$$[\text{products}] \xrightarrow{HCl} 2(C_5Me_5)_2ZrCl_2 + 0.5\ N_2H_4 + NH_3 + [H_2,\ LiCl,\ AlCl_3] \qquad (2)$$

The reaction of $\underset{\sim}{1}$ yields mostly ammonia, but about one half that for $\underset{\sim}{2}$; hydrazine is obtained only in trace amounts. However the reactions of $\underset{\sim}{3}$ and $\underset{\sim}{4}$ result in the evolution of most of its dinitrogen, but the ligands CO and PF_3 are apparently quantitatively reduced.

The results of the N_2 labeling experiments for the reaction of $\underset{\sim}{2}$ with $LiAlH_4$ are in Table II. The first column gives the extent of ^{15}N labeling in both terminal and bridge positions for $\underset{\sim}{2}$ after exchange of $\underset{\sim}{2}$-$(^{15}N_2)_3$ with free $^{14}N_2$ in toluene at -23° for 30 min. A determination of which of the three dinitrogens are reduced to hydrazine or ammonia in the reaction with $LiAlH_4$ should thus be possible.

The results (table II) clearly indicate that the dinitrogen which is reduced to hydrazine is exclusively the μ - N_2. The ammonia appears contaminated by a small per cent of terminal N_2; however, the failure to recover the N_2 quantitatively via hypobromite oxidation of the ammonia makes these results suspect (see Experimental

Part). Nevertheless, the excellent agreement for evolved N_2 and N_2H_4 labeling indicates that the overall reaction (to N_2H_4 and NH_3) proceeds through reduction of the μ-N_2 in $\geq$ 90%.

At the present stage of this research, without knowledge of the nature of the products, it is not possible to draw a mechanism. Since (1) the N_2 which is reduced is almost exclusively the μ- N_2 and (2) the N-N stretching mode for this μ-N_2 is very low (1556 cm^{-1}), it is possible that the reaction could bear some similarity to the reduction of azocompounds with diborane.

The failure to reduce the μ- N_2 in $\underset{\sim}{3}$ and $\underset{\sim}{4}$ may be rationalized if we assume that the CO and PF_3 ligands are more reactive than the μ-N_2. However, the failure to reduce quantitatively the μ-N_2 in $\underset{\sim}{1}$ still is not clear since the reaction conditions were different.

Finally, it should be mentioned that we have also carried out the reaction of $\underset{\sim}{2}$ with $[Al(CH_3)_3]_2$ and reduction of one of the three dinitrogen occurs. The nature of the products obtained, particularly the likely formation of amines or substituted hydrazines, has not yet been investigated, however.

Table I. Product Distribution of the Reaction of Binuclear Dinitrogen Complexes of Bis(pentamethyl-cyclopentadienyl) titanium (II) and zirconium (II) with $LiAlH_4$. All the values are mmol/mmol dimer.

COMPLEX	N_2 evolved	N_2 missing	H_2 evolved	CO or PF_3 evolved	CO or PF_3 missing	AFTER Hydrolysis of the reaction products with HCl: N_2H_4	AFTER Hydrolysis of the reaction products with HCl: NH_3
$\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$	0.703	0.297	0.585	---	---	0.006	0.48
$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$	1.971	1.029	0.064	---	---	0.53	1.04
$\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$	0.884	0.116	0.074	0.000	2.000	?	?
$\{(\eta^5\text{-}C_5Me_5)_2Zr(PF_3)\}_2N_2$	0.920[a]	0.080[a]	0.486	0.000	2.000	?	?

[a] N_2 missing was determinated by subtraction of the N_2 evolved in the exchange + N_2 evolved in the reaction from the real amount of N_2 in the complex as determined by a blank.

Table II. Results of the N_2 Labeling Experiment for the Reaction:

$$[(C_5Me_5)_2ZrN_2]_2N_2 + \chi LiAlH_4 \xrightarrow{HCl} 2(C_5Me_5)_2ZrCl_2 + 2N_2 + \tfrac{1}{2}N_2H_4 + 1NH_3$$

mole fractions $\chi(^{30}N_2)$ $\chi(^{29}N_2)$ $\chi(^{28}N_2)$ in two positions of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$			$\chi(^{30}N_2)$ in N_2 evolved on addition of $LiAlH_4$		$\chi(^{30}N_2)$ in Hydrazine obtained on $LiAlH_4$/HCl addition		mole fractions $\chi(^{30}N_2)$ $\chi(^{29}N_2)$ $\chi(^{28}N_2)$ in ammonia obtained on $LiAlH_4$/HCl addition		
χi	terminal	bridge	Calcd.[a]	Obsd.	Calcd.[a]	Obsd.[b]	Calcd.[a]	Obsd.	Calcd.[c]
$\chi(^{30}N_2)$	0.285	0.988	0.277	0.281	0.988	0.992	0.977	0.744	0.711
$\chi(^{29}N_2)$	0.0040	0.0012					0.023	0.199	0.264
$\chi(^{28}N_2)$	0.711	0.011					0.0001	0.057	0.025

[a] Calculated for reaction proceeding 100% according to:

$$[(C_5Me_5)_2ZrN_2^t]_2(N_2^b) + \chi LiAlH_4 \xrightarrow{HCl} 2(C_5Me_5)_2ZrCl_2 + 2N_2^t + \tfrac{1}{2}N_2^bH_4 + 1N^bH_3.$$

[b] No $^{15}N\equiv{}^{14}N$ was formed in hydrazine.

[c] Calculated from the observed composition in ammonia (79.32% bridging, N_2, 20.68% terminal N_2). See text for explanation of this number.

References

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2. J.E. Bercaw, R.H. Marvich, L.G. Bell, and H.H. Brentzinger, J. Amer. Chem. Soc., 94, 1219 (1972).

3. J.E. Bercaw, J. Amer. Chem. Soc., 96, 5087(1974).

4. STHOLER ISOTOPE CHEMICALS "$^{15}N \equiv {}^{15}N$: 30, 98.83%; 29, 0.12%; 28, 1.05%.

Chapter II

Hydrogen Reduction of Carbon Monoxide Promoted by Mononuclear Carbonyl and Hydride Complexes of Bis(pentamethylcyclopentadienyl)-zirconium

Abstract

The synthesis and characterization of $(\eta^5 - C_5Me_5)_2 Zr(CO)_2$, $(\eta^5 - C_5Me_5)_2 ZrH_2$ and $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ prepared from $\{(\eta^5 - C_5Me_5)_2 ZrN_2\}_2 N_2$ are described. $(\eta^5 - C_5Me_5)_2 Zr(CO)_2$ and $\{(\eta^5 - C_5Me_5)_2 Zr(CO)\}_2 N_2$ react with H_2 forming $(\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3)$ in high yields. $(\eta^5 - C_5Me_5)_2 ZrH_2$ reacts with CO and PF_3 at -80° to yield $(\eta^5 - C_5Me_5)_2 Zr(H)_2 L$ where L = CO and PF_3. $(\eta^5 - C_5Me_5)_2 Zr(H)_2CO$ dimerizes to $\{(\eta^5 - C_5Me_5)_2 Zr(H)\}_2 (\eta - OCH = CHO)$ above -50°. In the presence of $(\eta^5 - C_5Me_5)_2 ZrH_2$, $(\eta^5 - C_5Me_5)_2 Zr(H_2)CO$ may be reduced to $(\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3)$. These observations are interpreted in terms of a reaction sequence mediated by the formyl hydride complex $(\eta^5 - C_5Me_5)_2 Zr(H)(CHO)$ derived from $(\eta^5 - C_5Me_5)_2 Zr(H)_2(CO)$ via migratory insertion. The possible determining factor in the rearrangement of $(\eta^5 - C_5Me_5)Zr(H)_2(CO)$ to $(\eta^5 - C_5Me_5)_2 Zr(H)(CHO)$ and the plausible mechanisms for the formation of $(\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3)$ and $\{(\eta^5 - C_5Me_5)_2 Zr(H)\}_2 (\eta - OCH = CHO)$ are discussed.

Introduction

Although the synthesis of hydrocarbons from CO and H_2 by the Fisher-Tropsch process has been known for more than 5 decades, until recently no well-established precedent existed in homogeneous catalysis for the formation of a metal-formyl complex from a metal carbonyl hydride via migratory insertion or for the conversion of a metal formyl species to methanol. It has been suggested that metal clusters may be required to achieve the H_2 reduction of CO,[1] and indeed, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were found to catalyze the hydrogen reduction of carbon monoxide to methane at 140° and ~ 2 atm, although rates were rather low.

We observed reduction of CO very early in this research, first in an attempt to prepare $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ from $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and CO and later in the reaction of $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ with HCl. However it was only at the end, together with Donald R. McAlister and Robert D. Sanner from our laboratory, that a systematic study of the reactions of the carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl) zirconium was undertaken. At the end of this chapter the complex $(\eta^5\text{-}C_5Me_5)_2HfH_2$ is mentioned. This compound was mostly due to the work of Bob Gay.

Results

I. Synthesis and characterization of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ and $(\eta^5\text{-}C_5Me_5)_2ZrH_2$.

$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$. Treatment of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (1) with carbon monoxide in toluene at room temperature leads to the absorption of CO (3.94 mol/mol of 1), the evolution of N_2 (2.84 mol/mol of 1) and the complex $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (2) according to reaction 1:

$$\underset{1}{\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2} + 4CO \rightarrow \underset{2}{2(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2} + 3N_2 \quad (1)$$

Reaction 1 is rather slow and proceeds first through the formation of $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ which then reacts slowly with excess CO to yield 2.

Compound 2 is isolated in yields ~65% as brown crystals by cooling petroleum ether solutions of the complex. Elemental analysis (see Experimental Section); infrared, two carbonyl absorptions at 1942 and 1850 cm^{-1}; as well as its nmr spectrum, a singlet at δ 1.77 ppm (toluene-d_8) are consistent with a pseudo-tetrahedral structure analogous to that found in $(C_5H_5)_2Ti(CO)_2$[2] and proposed for $(C_5H_5)_2M(CO)_2$ where M = Zr, Hf[3,4].

Treatment of 2 with HCl leads to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, with the evolution of H_2 (0.72 mol/mol of 2) and CO (1.70 mol/mol of 2) in slightly lower yields than those expected according to

reaction 2:

$$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2 + 2\,HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + H_2 + 2\,CO \quad (2)$$

$\underset{\sim}{2}$

$(\eta^5\text{-}C_5Me_5)_2ZrH_2$. Reaction of $\underset{\sim}{1}$ with H_2 in toluene at room temperature leads to the absorption of H_2 (2.03 mol/mol of $\underset{\sim}{1}$), the evolution of N_2 (2.87 mol/mol of $\underset{\sim}{1}$) and the complex $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ ($\underset{\sim}{3}$) quantitatively according to reaction 3:

$$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2 + 2H_2 \rightarrow 2\,(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 3N_2 \quad (3)$$

$\underset{\sim}{1}$ $\qquad\qquad$ $\underset{\sim}{3}$

$\underset{\sim}{3}$ is isolated as pale yellow crystals by cooling petroleum ether solutions of the complex. Compound $\underset{\sim}{3}$ has been characterized by elemental analysis (see Experimental section), molecular weight, infrared and proton magnetic resonance. On the basis of the physical and chemical properties which follow the complex is assigned a monomeric pseudotetrahedral structure analogous to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$.

The molecular weight determined cryoscopically for a solution containing 65.4 mg of $\underset{\sim}{3}$ per gram of benzene was 318 ± 50 (364 is calculated for $\underset{\sim}{3}$). Thus in contrast to polymeric $\{(\eta^5\text{-}C_5H_5)_2ZrH_2\}_x$[5,6] $\underset{\sim}{3}$ is monomeric and very soluble in hydrocarbons and ethers.

The ^{1}H-nmr spectrum of $\underset{\sim}{3}$ (benzene-$\underline{d}_6$, shows a singlet absorption at δ 2.02 ppm (30H) illustrating the equivalence of all ring methyl groups in addition to a singlet absorption at δ 7.46

ppm (2H) assigned to the ZrH_2 moiety of 3, and confirmed by its absence in the dideuteride derivative $(\eta^5 - C_5Me_5)_2 Zr D_2$.

The infrared spectrum of 3 (nujol mull) exhibits in addition to those bands characteristic of $(\eta^5 - C_5Me_5)$ rings a broad medium strong band at 1555 cm^{-1} which shifts upon substitution with deuterium to 1100 cm^{-1}. Therefore this absorption must be associated with Zr-H stretch.

Reaction of 3 with HCl leads to $(\eta^5 - C_5Me_5)_2ZrCl_2$, and the evolution of H_2 (1.85 mol/mol of 3) in agreement with reaction 4.

$$(\eta^5 - C_5Me_5)_2 ZrH_2 + 2\,HCl \rightarrow (\eta^5 - C_5Me_5)_2 ZrCl_2 + 2\,H_2 \qquad (4)$$

3

II. Hydrogen reduction of Carbon Monoxide promoted by carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl zirconium).

Reaction of 2 with H_2. 2 reacts with H_2 (1.5 atm) in toluene to yield $(\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3)$ (4) when photolyzed (366 nm) at room temperature or when heated to 110°. H_2 (2.10 mol/mol of 2) is absorbed and CO (0.98 mol/mol of 2) is evolved according to reaction 5:

$$(\eta^5 - C_5Me_5)_2 Zr(CO)_2 + 2\,H_2 \xrightarrow[\text{or } 110^\circ]{h\nu} (\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3) + CO \qquad (5)$$

2 4

$\underset{\frown}{4}$ is isolated nearly quantitatively as white crystals upon removal of toluene, but may be further purified by sublimation 130° (10^{-3} torr). Elemental analysis[7], molecular weight, infrared and ^{1}H nmr data for $\underset{\frown}{4}$ as shown below are indicative of a monomeric structure completely analogous to $(\eta^5 - C_5Me_5)_2ZrCl_2$. The molecular weight determined cryoscopically for a solution containing 85.7 mg of $\underset{\frown}{4}$ per gram of benzene was 402 ± 30 (394 is the calculated for $\underset{\frown}{4}$). The infrared spectrum of $\underset{\frown}{4}$(nujol mull) shows bands attributable to ν(C - H, methoxide) at 2800 cm^{-1}(m, sh); ν(Zr - H) at 1590 cm^{-1}(m, br) and ν(C - O) at 1140 cm^{-1}(s); the first two bands shift upon substitution of deuterium to 2040 and 1130 cm^{-1}, respectively. In addition there is a new band at 1080 cm^{-1} (m, sh) attributable to the ν(C-C, bending) of the methoxide. The ^{1}H nmr spectrum in benzene-d_6, shows a singlet at δ 1.96 ppm (30H) due to the $(\eta^5 - C_5Me_5)$ ring hydrogens, a singlet at δ 3.87 ppm (3H) attributable to the hydrogens in the methoxide and a singlet at δ 5.70 ppm (1H) assigned to the Zr - H hydride.

Reaction of $\underset{\frown}{4}$ with HCl leads to $(\eta^5 - C_5Me_5)_2$, $ZrCl_2$, H_2 (0.74 mol/mol of $\underset{\frown}{4}$) and CH_3OH (0.78 mol/mol of $\underset{\frown}{4}$), in slightly lower yields than those expected according to equation 6:

$$\underset{\frown}{4} \quad (\eta^5 - C_5Me_5)_2Zr(H)(OCH_3) + 2\ HCl \rightarrow (\eta^5 - C_5Me_5)_2ZrCl_2 + CH_3OH + H_2 \qquad (6)$$

Reaction of $\{(\eta^5 - C_5Me_5)_2 Zr(CO)\}_2 N_2$ with H_2. Reaction 5 suggested to us that 4 might be prepared by alternate routes. In fact, the first reasonable step in the thermal or photolytic reaction of 2 with H_2 is the generation of the reactive, coordinatively unsaturated species $(\eta^5 - C_5Me_5)_2 Zr(CO)$ (5) as shown in reaction 7:

$$(\eta^5 - C_5Me_5)_2 Zr(CO)_2 \xrightarrow[h\nu \text{ or } \Delta]{?} (\eta^5 - C_5Me_5)_2 Zr(CO) + CO \qquad (7)$$

2 5

A good source for 5 was $\{(\eta^5 - C_5Me_5)_2 Zr(CO)\}_2 N_2$ (6), because compound 6 reacts with CO to give 2 and this reaction undoubtedly proceeds by rupture of the zirconium nitrogen bond. We found that treatment of 6 in toluene with 1 atm of H_2 at room temperature leads predominantly to 4 (~ 76%) with the absorption of H_2 (3.55 mol/mol of 6) and evolution of N_2 (1.01 mol/mol of 6), implicating consequently as a major reaction pathway, reaction 8:

$$\{(\eta^5 - C_5Me_5)_2 Zr(CO)\}_2 N_2 + 4\,H_2 \rightarrow 2\,(\eta^5 - C_5Me_5)_2 Zr(H)(OCH_3) + N_2 \qquad (8)$$

6 4

The reaction also produces 9 (see below) in 24% yield.

Reaction of 3 with CO. It occurred to us that the next plausible step after the generation of 5 would involve oxidative addition of H_2 to 5 generating $(\eta^5 - C_5Me_5)_2 Zr(H)_2CO$ (7) as shown in reaction 9:

$$(\eta^5\text{-}C_5Me_5)_2ZrCO + H_2 \xrightarrow{?} (\eta^5\text{-}C_5Me_5)_2Zr(H)_2CO \qquad (9)$$

$\underset{\sim}{5}$ $\underset{\sim}{7}$

and furthermore that this complex might be prepared from $\underset{\sim}{3}$ and CO. We found that toluene solutions of $\underset{\sim}{3}$ absorb CO (1.01 mol/mmol of $\underset{\sim}{3}$) at -80° to generate the carbonyl hydride $\underset{\sim}{7}$[8] (equation 10).

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + CO \rightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)_2CO \qquad (10)$$

$\underset{\sim}{3}$ $\underset{\sim}{7}$

Although $\underset{\sim}{7}$ is not sufficiently stable for isolation (see below), it has been partially characterized in solution at low temperature. Thus $\underset{\sim}{7}$ reacts with HCl at -80° to yield $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, H_2 (1.77 mol/mol of $\underset{\sim}{7}$), and CO (0.85 mol/mol of $\underset{\sim}{7}$), equation 11.

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2CO + 2\,HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2\,H_2 \qquad (11)$$

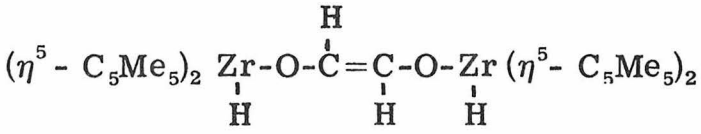
$\underset{\sim}{7}$

Its NMR spectrum at -64° (toluene-$\underline{d}_8$) consists of a singlet at δ 1.84 ppm (30H) due to the methyl hydrogens of the two equivalent $(\eta^5\text{-}C_5Me_5)$ rings and a singlet at δ 1.07 (2H) attributable to the two equivalent hydride ligands. The spectrum of $\underset{\sim}{7}$-(^{13}CO) exhibits the same singlet at δ 1.84 ppm but the hydride resonance is now the expected doublet ($^2\underline{J}_{^1H\text{-}^{13}C}$ = 25.1 Hz). $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(PF_3)$ ($\underset{\sim}{8}$), prepared similarly (also too unstable for isolation at room temperature), exhibits a ^{1}H nmr spectrum at -50° (toluene $\underline{d}_8$) consisting of a singlet at δ 1.77 ppm due to the methyl hydrogens of the $(\eta^5\text{-}C_5Me_5)$ rings and a doublet of quartets centered at δ 0.55 ppm attributable to the two equivalent hydride ligands ($^2\underline{J}_{^1H\text{-}^{31}P}$ = 108 Hz, $^3\underline{J}_{^1H\text{-}^{19}F}$ = 21.5 Hz). Based on these data, the structures

of 7 and 8 appear to be similar to $(\eta^5 - C_5H_5)_2 Ta H_3$ with CO and PF_3 occupying the central equatorial positions mutually cis to both hydride ligands.

When toluene solutions of 7 are warmed above ca. -50°, the appearance of a new set of ^1H nmr signals (toluene-d_8) consisting of a $(\eta^5 - C_5Me_5)$ resonance at δ 1.94 ppm (30H), a singlet at δ 5.73 ppm (1H), and a singlet at δ 6.55 ppm (1H) accompanies the disappearance of the spectrum for 7. Independent experiments, performed in a vacuum line, so that H_2 and/or CO evolution could be monitored, indicate that no H_2 or CO evolution is associated with the conversion of 7 to this new compound 9. Hence both must have the same empirical formula.

Compound 9 is slightly soluble in aromatic solvents, but insoluble in aliphatic Hc and ethers solvents and can be isolated as pale yellow microcrystals at room temperature toluene/pentane solutions. 9 has been characterized by elemental analysis (see Experimental Section), infrared, ^1H and ^{13}C nmr. On the basis of the experimental evidence which follows 9 is assigned a dimeric structure bridged through the ligand, ethylenedioxy, in its trans configuration as is shown below:



9

The infrared spectrum of 9 (nujol mull) exhibits in addition to

those bands characteristic of $(\eta^5 - C_5Me_5)$ rings, bands attributable to ν(Zr - H) at 1580 cm^{-1} (m,br), ν(C - O) at 1205 cm^{-1} (S) and two medium bands at 1275 and 872 cm^{-1} attributable to the ν(C - H, bending) in the trans (OCH=CHO) moiety of $\underset{\frown}{9}$. Upon substitution for deuterium, the first and last two bands shift to 1130, 960, and 643 cm^{-1} respectively. In the infrared spectrum of the ^{13}C derivative of $\underset{\frown}{9}$ the $\nu(^{13}C - O)$ shifts to 1180 cm^{-1}.

The ^1H-nmr spectrum of $\underset{\frown}{9}$ in benzene-$\underline{d}_6$, shows a singlet at δ 1.94 ppm (30H) due to the $(\eta^5 - C_5Me_5)$ ring hydrogens, a singlet at δ 5.73 ppm (1H) and a singlet at δ at 6.55 ppm (1H). The ^1H nmr spectrum for $\{(\eta^5 - C_5Me_5)_2 ZrH\}_2 (O^{13}CH = {}^{13}CHO)$ (also in benzene-$\underline{d}_6$) shows the expected singlet at δ 1.94 ppm (30H), a singlet at δ 5.73 ppm (1H) and an AA′ XX′ pattern centered at δ 6.55 ppm. Thus we can assign the singlet at δ 5.73 ppm to the Zr - H hydride resonance and the AA′ XX′ pattern to the hydrogens of the $(H - {}^{13}C = {}^{13}C - H)$ moiety. The ten line AA′ XX′ pattern shows the following coupling constants: $^1\underline{J}_{^{13}C - H} = 176.5$ Hz, $^1\underline{J}_{^{13}C - {}^{13}C} = 99$ Hz, $^2\underline{J}_{^{13}C - H} = 7.5$ Hz and $^3\underline{J}_{H - H} = 9$ Hz. The $^3\underline{J}_{H - H} = 9$ Hz agrees with the infrared in suggesting a transconfiguration of the bridging ligand. The $\{^1H\}$ ^{13}C nmr shows a singlet at δ 137.4 ppm, supporting the presence of a carbon-carbon double bond and the non-$\{^1H\}$ ^{13}C nmr spectrum shows the same AA′ XX′ pattern.

Reaction of $\underset{\frown}{9}$ with HCl leads to $(\eta^5 - C_5Me_5)_2 ZrCl_2$, H_2 (1.81 mol/mol of $\underset{\frown}{9}$) and an organic product(s) as yet not identified

(reaction 12).

$$\underset{\wedge}{9}\ \{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCH{=}CHO) + HCl \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2H_2 + \text{organic product(s)}. \quad (12)$$

Although no attempt to identify the organic product(s) has been made, one would expect to yield first "1,2 ethylenediol" which rapidly rearranges to hydroxyethanal, since it is well known from organic chemistry that the ketone is substantially more stable than its corresponding enol.

Compound $\underset{\wedge}{9}$ reacts smoothly with methyl iodide to yield methane (1.65 mol/mol of $\underset{\wedge}{9}$) and an orange crystalline complex $\{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(OCH{=}CHO)$ ($\underset{\sim}{10}$) (equation 13), which on the basis of elemental analysis (see experimental section), infrared, and nmr data (see below) is assigned a structure analogous to $\underset{\wedge}{9}$, with the hydride substituted by iodide.

$$\underset{\wedge}{9}\ \{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCH{=}CHO) + 2CH_3I \rightarrow \underset{\sim}{10}\ \{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(OCH{=}CHO) + 2CH_4 \quad (13)$$

$\underset{\sim}{10}$, similar to $\underset{\wedge}{9}$, is only slightly soluble in aromatic solvents and is insoluble in nonaromatic and ether solvents, however in contrast to $\underset{\wedge}{9}$ which reacts with cloroform, $\underset{\sim}{10}$ does not react and is very soluble.

Its infrared spectrum is essentially identical to the infrared

spectrum of 9 with the exception that the band at 1580 cm^{-1} attributable to the Zr-H stretch in 9 is absent in 8, thus it shows bands attributable to ν(C-O) at 1195 cm^{-1} (S) and two medium bands at 1270 and 875 cm^{-1} attributable to the ν(C-H, bending) in the trans (OCH=CHO) moiety of 10. In the ^{13}C derivative the $\nu(^{13}C-O)$ shifts to 1175 cm^{-1}.

Its ^{1}H-nmr spectrum in benzene-d_6, shows a singlet at δ 1.94 ppm (30H) illustrating the equivalence of all ring methyl groups in addition to a singlet absorption at δ 6.83 ppm (1H) attributable to the (OC<u>H</u>=C<u>H</u>O) hydrogens.

The ^{1}H nmr spectrum for $\{(\eta^5-C_5Me_5)_2ZrI\}_2(O^{13}CH=^{13}CHO)$ in chloroform-$\underline{d}_1$, shows a singlet at δ 2.00 ppm and an AA'XX' pattern centered at δ 6.38 ppm with the following coupling constants: $^{1}\underline{J}\,^{13}C-H=180.3$ Hz, $^{1}\underline{J}\,^{13}C-^{13}C=100.3$ Hz, $^{2}\underline{J}\,^{13}C-H=6.7$ Hz and $^{3}\underline{J}_{H-H}=10.4$ Hz. It is clear that the only difference in the ^{1}H nmr data of 10 from that of 9 is the missing singlet at δ 5.73 ppm attributed to the Zr-H hydride resonance.

Compound 9 could not be reduced to 4 with H_2 with or without added 3. If 7 is warmed to room temperature under an H_2 atmosphere, again only 9 is obtained. A mixture of 7 (1 mol) and 3 (1.29 mol) does, however, yield 4 (0.92 mol) along with a trace of 9 (0.08 mol) when warmed from -80° to 25° under H_2. 3 is recovered nearly quantitative implying consequently, equation 14: as almost the exclusive reaction pathway.

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \xrightarrow{H_2} (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \quad (14)$$

$\underset{\sim}{7}$ $\underset{\sim}{3}$ $\underset{\sim}{4}$ $\underset{\sim}{3}$

When CO is allowed to diffuse into an N_2-blanketed solution of $\underset{\sim}{3}$ (1 mol) at 25°, $\underset{\sim}{4}$ (~0.5 mol) is also generated, along with a transient dark red complex (probably a mixture of $\underset{\sim}{1}$ and $\underset{\sim}{6}$) which is eventually converted to $\underset{\sim}{2}$ (~0.5 mol) by excess CO, in agreement with reaction 15:

$$2(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 3CO \rightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + (\eta^5\text{-}C_5Me_5)_2Zr(CO)_2 \quad (15)$$

$\underset{\sim}{3}$ $\underset{\sim}{4}$ $\underset{\sim}{2}$

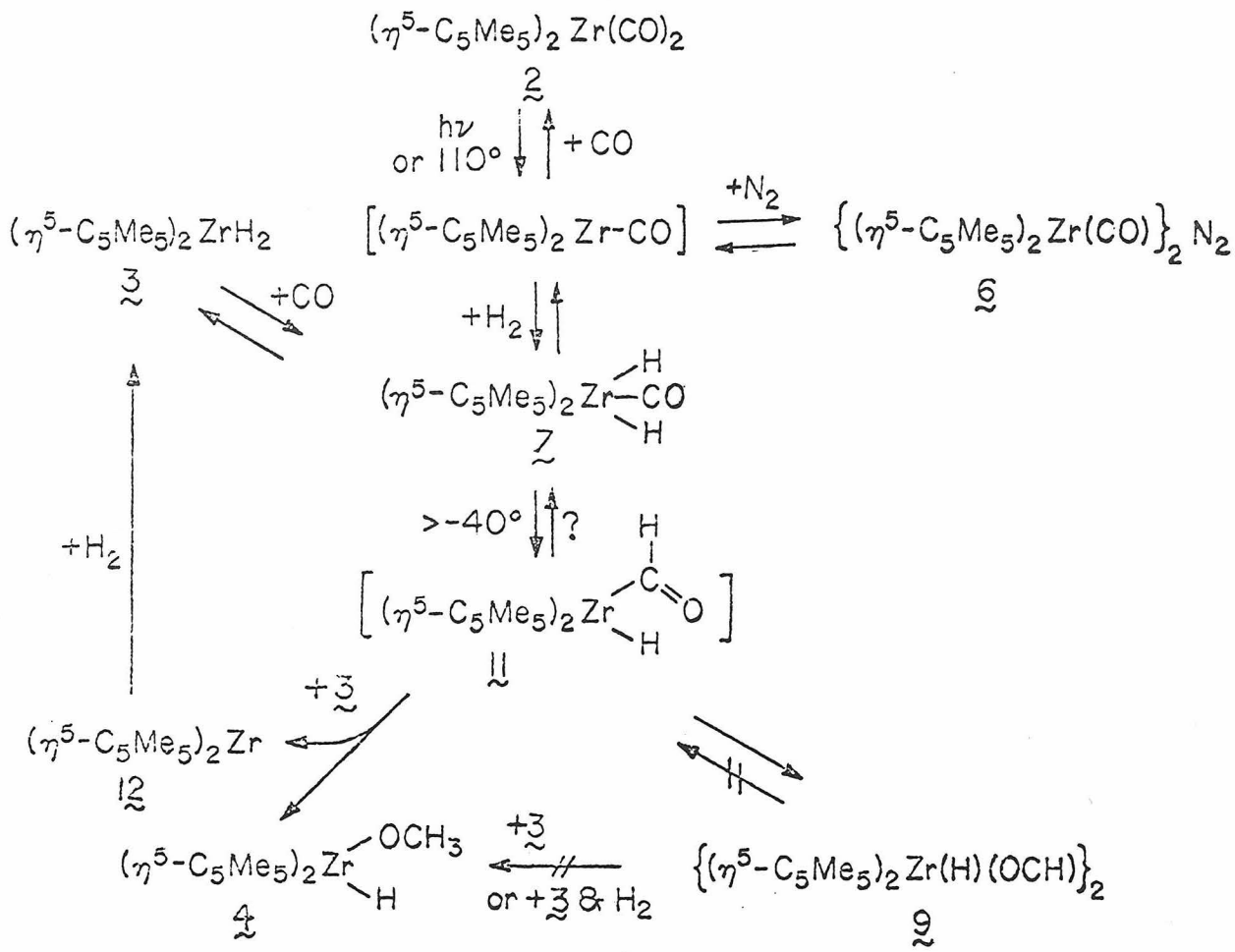
If CO is diffused into an H_2-blanketed solution of $\underset{\sim}{3}$ at 25°, essentially pure $\underset{\sim}{4}$ is obtained, thus offering a new route to $\underset{\sim}{4}$ in accord with reaction 16:

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + CO + H_2 \rightarrow (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) \quad (16)$$

$\underset{\sim}{3}$ $\underset{\sim}{4}$

These observations indicate that $\underset{\sim}{4}$ is formed from $\underset{\sim}{7}$ only in the presence of $\underset{\sim}{3}$ and that dimerization to $\underset{\sim}{9}$ occurs in its absence. We therefore suggest that $\underset{\sim}{7}$ rearranges to the reactive formyl hydride complex $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)$ ($\underset{\sim}{11}$), which is subsequently reduced to $\underset{\sim}{4}$ by $\underset{\sim}{3}$ (releasing $[\eta^5\text{-}C_5Me_5]_2Zr[\underset{\sim}{12}]$) in competition with its dimerization to $\underset{\sim}{9}$ (Scheme I).

Scheme I.

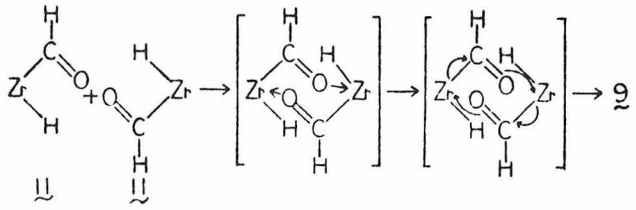

$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$
2
hν or 110°
+CO
$(\eta^5\text{-}C_5Me_5)_2ZrH_2$
3
$[(\eta^5\text{-}C_5Me_5)_2Zr\text{-}CO]$
+N2
$\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$
6
+H2
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(CO)H$
7
>-40° ?
$[(\eta^5\text{-}C_5Me_5)_2Zr(H)(CHO)]$
11
+H2
+3
$(\eta^5\text{-}C_5Me_5)_2Zr$
12
$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$
4
+3 or +3 & H2
$\{(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH)\}_2$
9

That the dimerization is a competitive process with the formation of 4 can be easily seen when reaction 14 is performed with a ratio 7:3 >1.

If a mixture of 7 (4.46 moles) and 3 (1 mol) is warmed from -80° to 25° under H_2, 4 (1.90 moles) along with 9 (2.56 moles) are obtained and again 3 is recovered nearly quantitatively.

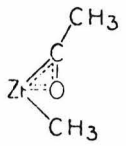
Mechanistic considerations

Two mechanisms can be envisioned for the formation of 9 from 11. The first one can be understood as a tendency of 9 to dimerize in order to achieve an 18 electron configuration through donation of one of the oxygen lone pairs respectively, with further formation of a zirconium oxygen bond and rearrangement to 9 as shown in equation 17 (the η^5-C_5Me_5 rings are not shown):

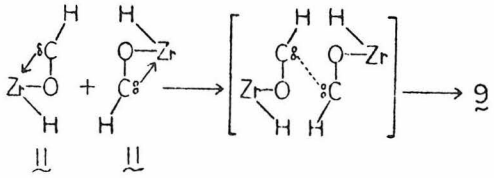


(17)

The idea for the second mechanism comes from the x-ray structure of $(C_5H_5)_2Zr(CH_3)(COCH_3)$ isolated from the reversible carbonylation of the respective dimethyl derivative. This compound shows the acyl group acting as a three electron donor and a short Zr-C bond (acyl) which is interpreted as a metal-carbene-like interaction (9) (see below).



Therefore, assuming a carbene character for the carbon in the formyl species, 11, the formation of 9 can be seen "formally" as the dimerization of two carbenes, although it does not necessarily imply a free carbene (equation 18).

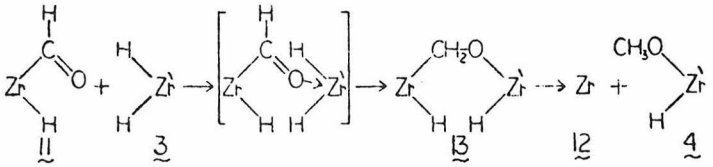


(18)

It might appear that from reaction 18 we could obtain 9 in its trans as well as cis configuration. Hence the fact that 9 is obtained only in its trans form could suggest a preference for the mechanism in equation 17. However, CPK model of 9 indicates a large steric interaction in the cis isomer due to the η^5-C_5Me_5 rings.

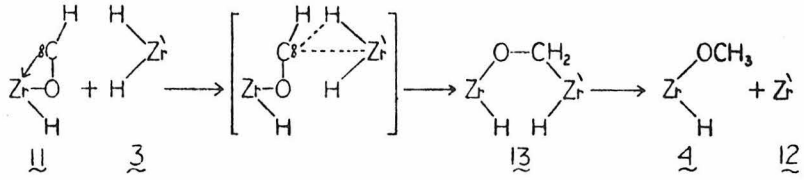
For the formation of 4 there are in principle three plausible mechanisms. The first two make use of essentially the same arguments proposed for the dimerization in equations 17 and 18.

The mechanism analogous to equation 17 above involves donation of an oxygen lone pair to 5 and further insertion of the carbonyl unit into the zirconium hydride bond generating 13. Then reductive elimination of the "alkyl hydride" gives zirconocene and 4 (equation 19).



(19)

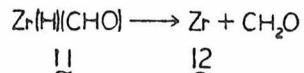
The second mechanism analogous to equation 18, assumes insertion of the "carbene" into the Zr-H bond with generation of the same intermediate as above and further reductive elimination (equation 20)



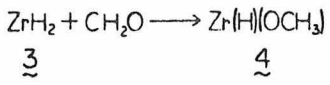
(20)

In the third mechanism formaldehyde is an intermediate in the formation of 4. Formaldehyde can intervene in two ways, as free formaldehyde (reductive elimination) or bound to the zirconium.

In the case of free formaldehyde the mechanism would involve reductive elimination of formaldehyde from the formyl species 11 which in the presence of 3 is further reduced to 4 as shown below (equations 20 and 21).



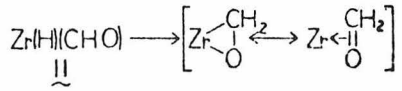
(20)



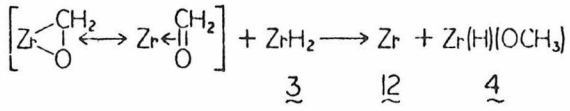
(21)

This mechanism is not likely for the conversion of 7 to 4, since 3 would not be a requirement (since in the presence of H_2 the zirconocene generated in equation 20 should give 3). However in the conversion of 2 and 6 to 4 where there is no direct evidence for the intermediacy of 3, this mechanism is certainly a possibility.

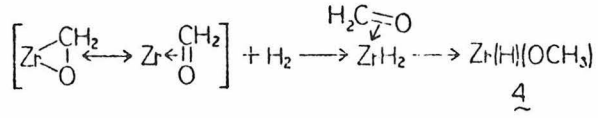
For the second case, where formaldehyde remains attached to the zirconium (equation 22), the mechanism would involve either further reduction of the formaldehyde complex by 3 (equation 23) or oxidative addition of H_2 to the formaldehyde complex with further formation of 4, in which case 3 would not be a requirement and the same arguments as above are applied (equation 24).



(22)



(23)



(24)

This third mechanism (both cases) was investigated and on the basis of the experimental evidence which follows reductive elimination of formaldehyde does not appear to be the pathway by which 4

is formed from either 7, 2, or 6.

When a toluene solution of 3 and paraformaldehyde (as a source of formaldehyde) is heated to 120°, the complex $(\eta^5\text{-}C_5Me_5)_2Zr(OCH_3)_2$ 14 is formed nearly quantitative according to reaction 25:

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 2CH_2O \rightarrow (\eta^5\text{-}C_5Me_5)_2Zr(OCH_3)_2 \qquad (25)$$

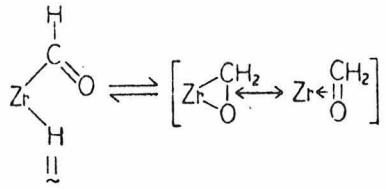
3 14

Complex 14 is isolated as white crystals upon removal of toluene and similarly to 4 may be further purified by sublimation at 130° (10^{-3} torr). 14 has been characterized by infrared and ^{1}H nmr. Its infrared spectrum shows bands attributable to ν(C–H), methoxide) at 2800 cm^{-1} (m, sh) and ν(C–O) at 1125 cm^{-1} (s, br). The ^{1}H nmr spectrum in benzene-d_6 shows a singlet at δ 1.93 ppm (30H) due to the η^5-C_5Me_5 ring hydrogens and a singlet at δ 4.03 ppm (6H) assigned to the hydrogens in the two methoxide groups.

If a mixture of 3 (1 mol) is heated to 120° with paraformaldehyde (1.01 mol of formaldehyde) one obtains 3 (~15%), 14 (~30%) and 4 (~ 55%). A mixture of 14 (1 mol) and 3 (0.83 mol) when heated to 120° in toluene for several days does not yield 4. The above observations indicate that 3 reacts with free formaldehyde to yield 4 but in the presence of more formaldehyde 4 reacts further with formaldehyde to yield 14 in competition with 3. The fact that 14 is not observed in any of the above systems, even in trace amounts,

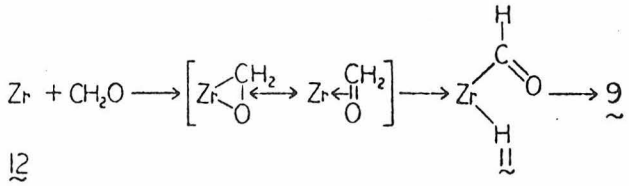
suggests that free formaldehyde is not the pathway by which 4 is generated in these systems. That ligated formaldehyde to the zirconium is not a likely pathway for the conversion of 7 to 4 can be shown as follows:

When toluene solutions of 7 are warmed from -80° to 25° only 9 is produced. However if a mixture of 7 and 3 is warmed from -80° to 25°, essentially pure 4 can be obtained, implying that the following equilibrium must operate (equation 26):



(26)

Hence 9 should be also formed in the reaction between zirconocene and formaldehyde (equation 27):



(27)

12

We found that 1 (used as a source of zirconocene) reacts with formaldehyde gas but did not yield 9. Although the product(s) has not yet been characterized, it appears to be (based on preliminary ir and ^{1}H nmr data) $(\eta^5\text{-}C_5Me_5)_2Zr\begin{matrix}O\text{-}CH_2\\ O\text{-}CH_2\end{matrix}$ and/or $(\eta^5\text{-}C_5Me_5)_2Zr\begin{matrix}CH_2\\ O\end{matrix}$.

The above observations suggest that the formation of 4 from 7 proceeds by either the mechanism shown in equation 19 or

20 (*see footnote). The conversion of $\underset{\sim}{6}$ and $\underset{\sim}{2}$ to $\underset{\sim}{4}$ could proceed by either 19, 20 or by a pathway where formaldehyde ligated to the zirconium is an intermediate.

In principle one could distinguish between 19 and 20 by labelling the zirconium as shown in the equations. This could be done for example, by using $[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}(CH_3)_4(CH_2CH_3)]ZrH_2$ [10] instead $\underset{\sim}{3}$ in which case equation 19 should yield $[\eta^5\text{-}C_5(CH_3)_5][C_5(CH_3)_4(CH_2CH_3)]Zr(H)(OCH_3)$ and $\underset{\sim\sim}{12}$ while equation 20 should give $\underset{\sim}{4}$ and $[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}C_5(CH_3)_4(CH_2CH_3)]Zr$. Unfortunately, these experiments were precluded because we found that when toluene solutions of $\underset{\sim}{7}$ at -80° are exposed to a gas phase of ^{13}CO, exchange is observed (27% in 30 min) implying consequently the following

---

* The observations do not completely rule out the intermediacy of a zirconocene formaldehyde complex $[Zr\langle^{CH_2}_{O} \longleftrightarrow Zr\text{-}\overset{CH_2}{\underset{O}{\|}}]$ in the formation of $\underset{\sim}{4}$, as in equation 23. If the equilibrium of equation 27 lies heavily on the side of $\underset{\sim\sim}{11}$, but reversion of the formaldehyde complex to $\underset{\sim\sim}{11}$ is slow; and, if the further reaction of the formaldehyde complex with excess formaldehyde is very fast then our observation could be rationalized. However, the dimerization of $\underset{\sim\sim}{11}$ to $\underset{\sim}{9}$ appears to be very rapid, even at -40°, so the fact that no dimer ($\underset{\sim}{9}$) could be detected in the reaction of formaldehyde with zirconocene (at R.T.) mitigates against the intermediacy of a zirconocene formaldehyde complex.

equilibrium (equation 28):

$$(\eta^5\text{-}C_5Me_5)_2\,Zr\begin{matrix}H\\-CO\\H\end{matrix} \rightleftharpoons (\eta^5\text{-}C_5Me_5)_2\,ZrH_2 + CO \qquad (28)$$

$$\underset{\sim}{7} \qquad\qquad \underset{\sim}{3}$$

Equation 28 gives an indirect evidence for the presence of $\underset{\sim}{3}$ in the H_2 reduction of $\underset{\sim}{2}$ and $\underset{\sim}{6}$ to $\underset{\sim}{4}$, since even when the equilibrium at -80° favors the formation of $\underset{\sim}{7}$ considering that reactions 5 and 8 are carried at 120° and 25° respectively, the equilibrium constant at this temperatures could change considerably.

Another point to consider in the mechanism of equations 19 and 20 is that both proceed through reductive elimination by the same intermediate, $\underset{\sim}{13}$. That reductive elimination by $\underset{\sim}{13}$ could occur is supported indirectly by the following data about zirconocene. Stirring solutions of $\underset{\sim}{1}$ in toluene at room temperature under vacuum, leads to the quantitative release of the dinitrogen and the complex $[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}C_5(CH_3)_4CH_2]\,ZrH$ ($\underset{\sim}{12'}$) according to equation 29:

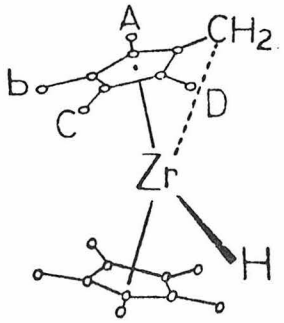
$$\{(\eta^5\text{-}C_5Me_5)_2\,ZrN_2\}_2\,N_2 \rightarrow 2[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}C_5(CH_3)_4CH_2]\,ZrH + 3N_2 \qquad (29)$$

$$\underset{\sim}{1} \qquad\qquad \underset{\sim}{12'}$$

Compound 12′ is isolated as orange-red crystals by cooling petroleum ether solutions of the complex. On the basis of ^1H nmr and infrared (see below) the structure shown below is assigned to this complex. Its ^1H nmr (toluene-$\underline{d}_8$ exhibits a singlet at δ 1.92 ppm (15H) assigned to the $[\eta^5\text{-}C_5(CH_3)_5]$ ring, singlets at δ 2.10,

1.61 and 1.33 ppm (3H), respectively, attributable to the methyls a, b, and c of 12′ (see figure); an unresolved doublet at δ 1.87 ppm (3H) assigned to the methyl d which is possibly through-space coupled to the hydride; two doublets centered at δ 1.30 and 1.07 ppm (1H) respectively for the methylene hydrogens which are non-equivalent and a broad singlet at δ 5.40 ppm due to the Z-H moiety.

The infrared spectrum of 12′ (nujol mull) exhibits a band at 1525 cm^{-1} (m, s) assigned to the Zr-H stretch and a considerably more complex spectrum in the region 1200-400 cm^{-1} in accord with the spectrum expected for a compound with this structure.



12′

An identical structure has been proposed for $[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}C_5(CH_3)_4CH_2]TiH$ formed via a reversible ring methyl hydrogen abstraction by the Ti center from the tautomer $(\eta^5\text{-}C_5Me_5)_2Ti$.[11] But in contrast to the titanium system where there is an equilibrium between both forms, 12′ is the only species observed in the ^1H nmr in a range of temperatures of -50 to 25°.

Treatment of 12′ with H_2 in petroleum ether leads to the absorption of H_2 (0.920 mol/mol of 12′) and 3, quantitatively according to reaction 30:

$$[\eta^5\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH + H_2 \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrH_2 \qquad (30)$$
$$\underset{\sim}{12'} \qquad\qquad \underset{\sim}{3}$$

Reaction of 12′ with HCl gives $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and the evolution of H_2 (0.931 mol/mol of 12′) in agreement with reaction 31:

$$[\eta^5\text{-}C_5(CH_3)_5][\eta^5\text{-}C_5(CH_3)_4CH_2]ZrH + 2HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 1H_2 \qquad (31)$$

Compound 12′ reacts reversibly with N_2 to regenerate 1. This last observation taken together with the reversible ring methyl hydrogen abstraction observed for the Ti systems suggest that the same phenomena occurs in the zirconium system, however the equilibrium constant in the case of the zirconium lies mostly on the side of 12′ as shown in equation 32:

$$[\eta^5\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH \rightleftharpoons [\eta^5\text{-}C_5(CH_3)_5]_2Zr \qquad (32)$$
$$\underset{\sim}{12'} \qquad\qquad \underset{\sim}{12}$$

This difference in the equilibrium constant can be understood as a tendency of the zirconium to increase its oxidation state from +2 to +4 which is in agreement with the observation that as one goes

down in the periodic table for a given group, the highest oxidation states become more stable. The reversibility in equation 32 proceeds formally via reductive elimination of the alkyl hydride 12′ and it is essentially similar to the one proposed in 13.

Both mechanisms-equations 19 and 20-are at present equally satisfactory. From the similarity between the mechanisms proposed for the dimerization and formation of 4 it seems quite likely that if formation of 4 proceeds by equation 19 or 20 then the dimerization occurs by the mechanism in equation 17 or 18 respectively.

Although our experimental evidence can not presently rule out the possibility that the formation of 4 from 2 and/or 6 could operate by a mechanism where ligated formaldehyde is an intermediate, the ^{13}CO exchange experiment and the similarity of the systems suggests that probably all of them go through the same mechanism.

An observation we have made is that when solutions of 7 are rapidly warmed from -80° to 25° under CO, H_2 (0.54 mol/mol of 7) is evolved, CO (0.72 mol/mol of 7) is absorbed and the formation of 9, 2, and 4 is observed indicating that reductive elimination of H_2 also operates (equation 33):

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2CO \rightleftharpoons (\eta^5\text{-}C_5Me_5)_2ZrCO + H_2 \qquad (33)$$

But if it is warmed slowly, 9 is obtained as the primary

product, implying that reductive elimination becomes an important process only at higher temperatures.

Another observation that has been made is that 2 reacts with 3 to yield only 9. Although the result of this experiment require a more detailed study, it seems to indicate, in agreement with the data mentioned before, that the rate of dimerization is much larger than the rate of formation of 4.

III. Bis(η^5-pentamethylcyclopentadienyl) hydrides of Ti, Zr, and Hf. Comparison with other bis(cyclopentadienyl) transition metal hydrides.

In Table I we have the bis(pentamethylcyclopentadienyl) zirconium hydrides with their respective Zr-H stretching frequencies (when possible) and hydride chemical shifts reported in this work. Table II gives a list of some bis(cyclopentadienyl) transition metal hydrides for group IV, V, VI, and VII with their corresponding M-H stretchs and hydride chemical shifts. $(\eta^5\text{-}C_5Me_5)_2HfH_2$, whose synthesis is described in the experimental section, has been included in the last table.

Infrared. From table II we can see that an increase in the M-H stretch is observed as one proceeds from group IV to group VII. There is one exception for the group IV. For $(\eta^5\text{-}C_5H_5)_2Zr(H)(BH_4)$, the only known monomeric zirconium hydride, a Zr-H stretch at 1945 cm^{-1} and a chemical shift for the hydride at δ 5.47 ppm have been reported.[12] Although the chemical shift agrees very

well with ours, the Zr-H stretch seems to be highly exaggerated and it has not been included in table II because the assignment is probably wrong. The low frequency for the M-H stretch, implying a decreased bond strength for the group IV hydrides is not only in contrast with other bis(cyclopentadienyl) transition metal hydrides, but in fact there are at present no transition metal hydrides with the exception of group IV with an M-H stretch below 1600 cm^{-1}. For $(\eta^5\text{-}C_5Me_5)_2TiH_2$, this decreased bond strength has been related to the ease that this complex releases its coordinated H_2.[13] However, the zirconium compound under similar circumstances does not lose its coordinated H_2. These apparently contradictory observations could be reconciled by adding a second factor which makes use of the analogy between metal alkyls and hydrides. Chatt and coworkers have suggested[14] that the stability to dissociation of metal carbon σ bonds depends inter alia on the energy separation, ΔE, between the highest occupied electronic level in the molecule and the lowest unoccupied level. The larger the energy difference, the more likely is the complex to be stable. In agreement with the above theory is the fact that thermal stability increases with increasing atomic number of the metal.

^{1}H nmr. From table II it is also clear that group IV shows the hydride resonance at very low field. As with the M-H stretch it can be said that at present there are no known transition metal hydrides, either bis(cyclopentadienyl) derivatives or others, which exhibit a hydride resonance at lower field than δ - 1.63 ppm (this

is the hydride resonance for the unique proton in $(\eta^5\text{-}C_5H_5)_2TaH_3$). Transition metal hydrides in general exhibit resonances shifted upfield between δ -2 to -20 ppm, and may come as high as -50 ppm. The most accepted theory which accounts for the magnitude of these high field shifts is that proposed by Buckingham and Stevens.[15] The high field shifts are derived from two effects, a paramagnetic shielding term (σ^p) arising from the mixing into the ground state of excited electronic states and from diamagnetic shielding (σ^d). The total shielding ($\sigma = \sigma^p + \sigma^d$) of the proton due to the nonbonding electrons is found to be very sensitive to anisotropy in the metal atom. In agreement with the second effect we found that metal hydrides which contain empty or completely filled d orbitals show considerably lower chemical shifts. For example, $(\eta^5\text{-}C_5H_5)_2NbH_3$ and $(\eta^5\text{-}C_5H_5)_2TaH_3$ (both "formally" d^0) have hydride resonances between δ -1.63 and -3.72 ppm. $(\eta^5\text{-}C_5Me_5)_2MH_2$ where M = Ti, Zr, and Hf (also "formally" d^0) exhibit the hydride resonances between δ +0.25 and +15.54 ppm. Tin and germanium hydrides (both d^{10}) show their hydride resonances between δ +2 and +5 ppm.[16,17] An agreement with the first effect could be the difference in chemical shift observed for example for $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with a hydride resonance at δ +7.46 ppm and $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$ which shows the hydride resonance at δ +1.07 ppm. (Note that based on simple arguments of shielding one would expect the hydride resonance for $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$ to be at even lower

field than that for $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, since CO as good π acceptor could deshield the hydride even more. However the contrary is observed.) A study of the electronic spectrum of both complexes might prove an interesting test of the above theory. Unfortunately at present there is no way to quantify both effects and therefore it is impossible to judge the relative polarity of the M-H bond by comparing the chemical shifts.

Chemistry. The hydride in $(\eta^5\text{-}C_5Me_5)_2TiH_2$ and all the related derivatives of zirconium are extremely reactive toward H_2O and acids. The evolution of H_2 is always observed in these reactions. This reactivity to water and acids suggests a more hydridic character not only compared with the simple carbonyl hydrides like $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$ which behave in water as acids ionizing to give the carbonylate ions, but also with the other transition metal hydrides, which in general are stable to water and acids. One of the few exceptions is the complex, $(\eta^5\text{-}C_5H_5)_2TaH_3$, which is decomposed by acids.[18]

Table I.

Infrared frequencies and ^{1}H nmr chemical shifts of bis(pentamethylcyclopentadienyl)Zr hydrides.

Complex	frequency cm^{-1} hydride	frequency cm^{-1} deuteride	δ, ppm ^{1}H nmr	solvent
$(\eta^5\text{-}C_5Me_5)_2ZrH_2$	1555	1100	+7.46	benzene $\underline{d}_6$
$(\eta^5\text{-}C_5Me_5)_2ZrHOCH_3$	1590	1130	+5.70	benzene $\underline{d}_6$
$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$	--	--	+1.07	toluene $\underline{d}_8$
$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(PF_3)$	--	--	+0.55	toluene $\underline{d}_8$
$[(\eta^5\text{-}C_5Me_5)_2ZrH]_2(OCH{=}CHO)$	1580	1130	+5.73	benzene $\underline{d}_6$
$[(\eta^5\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$	1525	--	+5.30	toluene $\underline{d}_8$

Table II.

Infrared frequencies and ^1H nmr of some bis(cyclopentadienyl) hydrides.

	complex	frequency cm^{-1} hydride	^1H nmr (M-H) δ ppm	reference
IV	$(\eta^5\text{-}C_5Me_5)_2TiH_2$	1560	+0.28	a
	$(\eta^5\text{-}C_5Me_5)_2ZrH_2$	1555	+7.46	-
	$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$	--	+1.07	-
	$(\eta^5\text{-}C_5Me_5)_2HfH_2$	1600	+15.54	-
V	$(\eta^5\text{-}C_5H_5)_2NbH_3$	1710	-2.73 (B), -3.72 (A_2)	b
	$(\eta^5\text{-}C_5H_5)_2Nb(H)(PPhMe_2)$	1630	-7.53	c
	$[(\eta^5\text{-}C_5H_5)_2Nb(H)_2(PPhMe_2)]^+$	1740	-3.96	c
	$(\eta^5\text{-}C_5H_5)_2Nb(H)(CO)$	1695	-6.39	b
	$(\eta^5\text{-}C_5H_5)_2TaH_3$	1735	-1.63 (B), -3.02 (A_2)	d
	$(\eta^5\text{-}C_5H_5)_2Ta(H)(CO)$	1750	-6.80	b
VI	$(\eta^5\text{-}C_5H_5)_2MoH_2$	1847	-8.76	d
	$[(\eta^5\text{-}C_5H_5)_2MoH_3]^+$	--	-6.08	d
	$(\eta^5\text{-}C_5H_5)_2WH_2$	1896	-12.28	d
	$[(\eta^5\text{-}C_5H_5)_2WH_3]^+$	--	-6.08 (B), -6.44 (A_2)	d
VII	$(\eta^5\text{-}C_5H_5)_2TcH$	1923	-7.80	e
	$[(\eta^5\text{-}C_5H_5)_2TcH_2]^+$	1984	-7.70	e
	$(\eta^5\text{-}C_5H_5)_2ReH$	2030	-12.80	f
	$[(\eta^5\text{-}C_5H_5)_2ReH_2]^+$	2025	---	f

a) J.E. Bercaw, R.H. Marvich, L.G. Bell, and H.H. Brintzinger, J. Amer. Chem. Soc., 94, 1219 (1972).

b) F.N. Tebbe and G.W. Parshall, J. Amer. Chem. Soc., 93, 3793 (1971).

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d) M.L.H. Green, J.A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4854 (1961).

e) E.O. Fisher and M.W. Schmidt, Angew. Chem. Internat. Ed., 6, 93 (1961).

f) M.L.H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc., 3916 (1958).

Discussion

In section II, we have seen that mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl) zirconium are capable of promoting the stoichiometric hydrogen reduction of carbon monoxide under very mild conditions. Our observations have been interpreted in terms of a reaction sequence mediated by the reactive formyl hydride complex 11 (not observed) derived from 7 via migratory insertion. Since previous to this work no well established precedent existed either for the formation of a metal-formyl complex from a metal carbonyl hydride via migratory insertion or for the conversion of a metal formyl species to CH_3OH, the main question to be settled is which are the determining factor(s) in the rearrangement of 7 to 11 and in the subsequent reduction of 11 to 3. One could wonder at this point, because of the similarity between the inorganic and organometallic chemistry of Ti, Zr, and Hf, if this ability of the zirconium to promote the H_2 reduction of CO is also present in the derivatives of Ti and Hf. Preliminary results (given in the experimental section) show that $(\eta^5\text{-}C_5Me_5)_2TiH_2$ also promotes the H_2 reduction of CO, thus it seems very likely that the hafnium derivative will behave in much the same way as the zirconium.

From the comparison in section III between the hydrides of group IV with others transition metal complexes two differences can be suggested; a decreased bond strength and a greater hydridic character.

The first could only explain why the rearrangement of 7 to 11 and/or the subsequent reduction of 11 to 4 occurs at very low temperatures ($\sim -50^{\circ}$), but could hardly be the determining factor for the migratory insertion. The second is that the hydridic character of the hydride seems more significant. That the hydridic character of the hydrogens could be one of the determining factors is supported in the reduction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(PPh_3)]^+$ to $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CH_3$ with borohydride,[19] and the recent report of the preparation of a series of metal formyl complexes from the reactions of metal carbonyl compounds with trialboxyborohydrides.[20] It is not worthy of mention at this point that we have noted that quantitative reduction of the CO occurs in the complex $[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]_2N_2$ when it is treated with $LiALH_4$. However, the product(s) of this reaction have not been identified. From the above results it is clearly seen that whenever reduction of CO has been achieved, a substantially hydridic compound has been present. Interestingly, recently it has been found that the complex $(\eta^5\text{-}C_5H_5)_2NbH(CO)$ where we can expect a similar hydridic character when compared with $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$, also affords methanol,[21] thus supporting the idea that the hydridic character of the hydride may play a key role in the hydrogen reduction of CO.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded on Varian HR-220, T60 and an A-60-A spectrometers. ^{13}C spectra was recorded on a Varian T-60 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer. Mass spectra were obtained from a Dupont-21-492-B mass spectrometer. Molecular weights were obtained cryoscopically in benzene using an air-tight cell as described in (11).

Materials. All manipulations were performed either on a vacuum line or in a glove box which was evacuated to < 0.1 torr and filled just prior to use with either prepurified argon or nitrogen. Argon and nitrogen used in the experiments were prepurified grade and were rendered rigorously oxygen and water-free as described in (11).

All hydrocarbon and ether solvents were purified by distillation first from $LiAlH_4$ and then from "titanocene".[13] 1, 2, 3, 4, 5-Pentamethylcyclopentadiene and $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ were prepared according to (11, 13). $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ and $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ were prepared as described in part Ic of this work.

Methanol Analysis. Was determinated colorimetrically with chromotropic acid as described by F.D. Snell and C.T. Snell, "Colorimetric Methods of Analysis", Vol. III, D. Van Nostrand Company, Inc. (1953), p. 45.

Procedures

1. $(C_5Me_5)_2Zr(CO)_2$. To $[(C_5Me_5)_2ZrN_2]_2$ (276.0 mg, 0.342 mmol) were condensed 25 ml of toluene at -80°. CO (4.069 mmols) was introduced and the reaction mixture was allowed to warm to room temperature. After stirring for 12 hrs at room temperature, the color changed from dark red to brown red and the N_2 (CO mixture was passed through a series of liquid nitrogen-cooled traps and collected via a Toepler pump. $N_2 + CO$ amounted 3.690 mmols. This gas mixture was cycled over CuO at 320° to convert CO to CO_2, which was removed in a liquid nitrogen-cooled trap. N_2 (0.970 mmol, 2.836 mmol/mmol dimer) remained. Thus CO unreacted was 2.720 mmols and CO consumed 1.349 mmols, 1.972 mmols/mmol Zr. Then the toluene was removed in vacuo and the remaining brown microcrystalline residue was dissolved in 10 ml of petroleum ether and filtered. The filtrate was cooled slowly to -80° and brown crystalline $(C_5Me_5)_2Zr(CO)_2$ was precipitated. The crystalline slurry was then filtered and the filtrate and crystals were dried under vacuo (yield 186 mg, 65%).

Anal. calculated for $C_{22}H_{30}O_2Zr$: C, 63.30; H, 7.19. Found: C, 63.44; H, 7.30. Ir data (nujol mull on KBr) ν(CO) 1942 (vs), 1850 (vs).

NMR (toluene-d_8) $[\eta^5\text{-}C_5(CH_3)_5]$ s, δ 1.77.

2. Reaction of $(C_5Me_5)_2Zr(CO)_2$ with HCl. To $(C_5Me_5)_2Zr(CO)_2$ (58.8 mg, 0.141 mmol) were condensed 8 ml of toluene at -80°. HCl (0.67 mmol) was introduced whereupon an instantaneous

reaction took place as evidenced by a color change from brown-red to pale yellow with gas evolution. After the mixture was warmed to room temperature, the gases were passed through a series of liquid nitrogen-cooled traps and the CO/H_2 mixture collected via a Toepler pump. $CO + H_2$ amounted 0.341 mmol. This gas mixture was cycled over CuO at 320° to convert CO to CO_2 and H_2 to H_2O, the latter was removed in a dry ice-acetone cooled trap. CO_2 collected 0.239 mmol, 1.695 mmols/mmol Zr. Thus H_2 evolved was 0.102 mmol, 0.723 mmol/mmol Zr. The $CDCl_3$-soluble portion of the residue (nmr) consisted of 100% $(C_5Me_5)_2ZrCl_2$.

3. $(C_5Me_5)_2ZrH_2$. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (205.7 mg, 0.255 mmol) were condensed 10 ml of toluene at -80°. H_2 (4.156 mmols) was introduced and the reaction mixture was allowed to warm to room temperature. After stirring for 2 hrs at room temperature the color changed from dark red to blue pale. Then the N_2/H_2 mixture was passed through a series of liquid nitrogen-cooled traps and collected via Toepler pump. $N_2 + H_2$ amounted to 4.371 mmols. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O which was removed in a liquid nitrogen-cooled trap. N_2 0.732 mmol, 2.871 mmols/mmol dimer remained. Thus H_2 unreacted was 3.639 mmols and H_2 consumed 0.517 mmol, 1.014 mmols/mmol Zr. Then the toluene was removed under vacuo, and the remaining microcrystalline residue was dissolved in 10 ml of petroleum ether and filtered. The filtrate was cooled slowly to -80° and pale-blue crystalline $(C_5Me_5)_2ZrH_2$ was precipitated.

The crystalline slurry was then filtered and the filtrate and crystals were dried under vacuo, (yield 133 mg, 72%). $(C_5Me_5)_2ZrH_2$ must be stored under Ar, it reacts with N_2. Note: The blue color comes apparently from an impurity, white-yellow $(C_5Me_5)_2ZrH_2$ can be obtained by heating the toluene solution under H_2 to 90° for 30 min, but there is no difference in chemical and physical properties between the two.

Anal. Calculated for $C_{20}H_{32}Zr$: C, 66.10; H, 8.80. Found: C, 66.29; H, 8.54.

Molecular weight for 65.4 mg $(C_5Me_5)_2ZrH_2$ per g C_6H_6; 318 ± 50 (calc. 363.67).

Ir data (nujol mull on KBr, cm^{-1}) ν(Zr-H) 1555 (ms, br).

NMR (benzene-$\underline{d}_6$) [η^5-$C_5(\underline{C}H_3)_5$]s, δ 2.02 (30H); Zr$\underline{H}_2$ s, δ 7.46 (2H).

4. $(C_5Me_5)_2ZrD_2$. It was prepared in a similar way to $(C_5Me_5)_2ZrH_2$, with the difference that H_2 was substituted by D_2 and the reaction was performed at 0°.

Ir data (nujol mull on KBr, cm^{-1}) ν(Zr-D) 1100 (ms, br).

5. Reaction of $(C_5Me_5)_2ZrH_2$ with HCl. To $(C_5Me_5)_2ZH_2$ (71.7 mg, 0.197 mmol) were condensed 8 ml of toluene at -80°. HCl (0.88 mmol) was introduced whereupon an immediate reaction took place with gas evolution. After warming to room temperature the evolved H_2 was passed through a series of liquid nitrogen-cooled traps and collected via Toepler pump. H_2 evolved 0.365 mmol, 1.853 mmols/mmol Zr. The $CDCl_3$-soluble portion of the residue (nmr) consisted of 100% $(C_5Me_5)_2ZrCl_2$.

6. $(C_5Me_5)_2ZrH_2CO$. Characterization in solution. To $(C_5Me_5)_2ZrH_2$ (156.9 mg, 0.431 mmol) were condensed 8 ml of toluene at -80°. CO (2.102 mmols) was introduced and the mixture was stirred for 30 min at this temperature. Then the residual gas passed through a series of liquid nitrogen cooled traps and collected via Toepler pump. CO collected 1.667 mmols, thus CO consumed was 0.435 mmol, 1.009 mmol/mmol Zr. The identity of this gas was confirmed by cycling it over CuO at 320°C. and removing any trace of water (H_2) in a dry ice-acetone cooled trap. CO_2 collected 0.435 mmol.

NMR (toluene-$\underline{d}_8$), -64°, [η^5-$C_5(\underline{C}H_3)_5$] s, δ 1.84 (30H); $Zr\underline{H}_2$ s, δ 1.07 (2H).

In a separate experiment c.a, 0.20 mmol of $(C_5Me_5)_2ZrH_2CO$ were prepared by treating $(C_5Me_5)_2ZrH_2$ with CO in butane and then removing the butane at -60°. A white crystalline material was obtained which upon warming above -40° decomposed giving a brown amorphous material.

7. $(C_5Me_5)_2ZrH_2{}^{13}CO$. This was made in an identical fashion as $(C_5Me_5)_2ZrH_2CO$ with the exception that ^{13}CO (90% isotopic purity, obtained from Stholer Isotope Chemicals) was used instead of normal CO.

NMR (toluene-$\underline{d}_8$), -50°, [η^5-$C_5(\underline{C}H_3)_5$] s, δ 1.84 (30H); $\underline{Zr}H_2$ doublet, $^2J\,{}^1H$-^{13}C = 25.1 Hz.

8. Exchange of $(C_5Me_5)_2ZrH_2CO$ with ^{13}CO in toluene at -80° (30 min). The exchange was performed in the apparatus showed in figure 1. ^{13}CO (~ 1.75 mmols) of composition χ 28=0.0908,

χ 29=0.8423, χ 30=0.0082, χ 31=0.0587, was introduced into the gas storage bulb and connected to the reaction flask as shown in figure 1. To $(C_5Me_5)_2ZrH_2$ (83.9 mg, 0.2307 mmol) were condensed 8 ml of toluene at -80°. Normal CO (0.7776 mmol) was introduced and the mixture stirred for 30 min at this temperature. Afterwards the residual CO was passed through a series of liquid nitrogen cooled traps and collected via Toepler pump. CO collected 0.5627 mmol. Thus CO consumed was 0.2149 mmol, 0.9315 mmol/mmol Zr. Then ^{13}CO was admitted (~ 0.5 atm) by opening the stop cock of the gas storage bulb and the system was quickly closed off. After 30 min of stirring the gas phase was passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. CO collected 1.2238 mmols. Mass spectrum of the gas phase showed the following composition: χ 28=0.1271, χ 29=0.8079, χ 30=0.0089, χ 31=0.0560. The procedure used in the calculations of the expected composition of the gas phase and the percent of the CO in the complex which exchanged is outlined in the appendix.

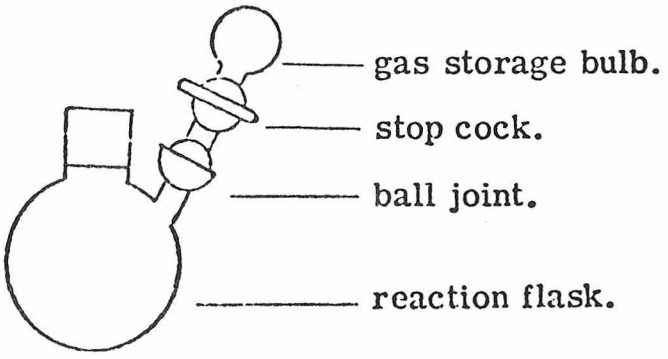

Figure 1.

9. Reaction of $(C_5Me_5)_2ZrH_2CO$ with HCl. To $(C_5Me_5)_2ZrH_2$ (58.8 mg, 0.162 mmol) were condensed 6 ml of toluene at -80°. CO (0.714 mmol) was introduced and the reaction mixture was stirred for 30 min at this temperature. Then the residual CO was removed from the yellowish solution, passed through a series of liquid nitrogen cooled-traps and collected via a Toepler pump. CO collected amounted to 0.563 mmol. Thus CO consumed amounted 0.151 mmol, 0.932 mmol/mmol Zr. Then HCl (0.48 mmol) was introduced. The reaction began immediately (-80°) with gas evolution and formation of a white-yellow ppt. After 15 min the mixture was warmed to room temperature, the CO/H_2 mixture was passed through a series of liquid nitrogen-cooled traps, collected and analyzed as described in 2. CO evolved 0.137 mmol, 0.846 mmol/mmol Zr; H_2 evolved 0.287 mmol, 1.772 mmols/mmol Zr. Composition of $CDCl_3$-soluble portion of the residue (nmr): 100% $(C_5Me_5)_2ZrCl_2$.

10. $(C_5Me_5)_2ZrH_2PF_3$. Characterization in solution. To $(C_5Me_5)_2ZrH_2$ (68.1 mg, 0.187 mmol) were condensed 8 ml of toluene at -80°. PF_3 (0.395 mmol) was introduced and the reaction mixture was stirred for 30 min at this temperature, a color change from yellow to reddish was observed during this period of time. Then the residual gas was passed through a series of liquid nitrogen cooled-traps in order to fraction PF_3 from possible H_2 evolved during the reaction. No gas was collected, thus there was no H_2 evolution. After the liquid nitrogen cooled-traps were

replaced by dry ice-aceton cooled-traps, the PF_3 was collected. PF_3 collected 0.229 mmol, thus PF_3 consumed was 0.166 mmol, 0.888 mmol/mmol Zr. Upon warming solutions of $(C_5Me_5)_2ZrH_2PF_3$ above -20° decomposition is observed.

NMR (toluene-$\underline{d}_8$), -50°, [η^5-$C_5(\underline{C}H_3)_5$] s, δ 1.77 (30H); doublet of quartets centered at 0.55 δ, $^2\underline{J}^1H$-^{31}P = 108 Hz; $^3\underline{J}^1H$-^{19}F = 21.5 Hz.

11. $\underline{[(C_5Me_5)_2ZrH]_2(OCH{=}CHO)}$. The toluene solution of $(C_5Me_5)_2ZrH_2CO$ in 6 was allowed to warm slowly to room temperature in a closed system. A color change from yellow to brown-yellow was observed between -40° and -20°. Once at room temperature the system was checked for CO or H_2 evolution. No gas was collected. Then the toluene solution was concentrated to a final volume of 2 ml by removing the toluene under vacuo, 10 ml of petroleum ether were condensed into the flask and yellow microcrystalline $[(C_5Me_5)_2ZrH]_2$ (OCH=CHO) was precipitated. The crystalline slurry was then filtered and the filtrate and crystals dried under vacuo. (yield c.a. 70%).

Anal. Calculated for $C_{21}H_{32}OZr$: C, 64.39; H, 8.24; Zr, 23.29. Found: C, 64.09; H, 8.40; Zr, 23.30.

Ir data (nujol mull on hBr, cm^{-1}) ν(Zr-H) 1580 (m,br); ν(C-O) 1205 (s); ν(C-H, bending) 1275, 872 (m).

NMR (benzene-$\underline{d}_6$) [η^5-$C_5(\underline{C}H_3)_5$] s, δ 1.94 (30H); (Zr-$\underline{H}$) s, δ 5.73 (1H); (M-O-$\underline{C}H{=}\underline{C}H$-O) s, δ 6.55 (1H).

12. $[(C_5Me_5)_2ZrD]_2(OCD{=}CDO)$. Was made in an identical way as $[(C_5Me_5)_2ZrH]_2$ (OCH=CHO) with the difference that $(C_5Me_5)_2ZrD_2$ was used instead of $(C_5Me_5)_2ZrH_2$.

Ir data (nujol mull on KBr, cm^{-1}) ν(Zr-D) 1130 (m,br); ν(C-D, bending) 960, 643 (w).

13. $[(C_5Me_5)_2ZrH]_2(O^{13}CH{=}{}^{13}CHO)$. Was made in an identical way as $[(C_5Me_5)_2ZrH]_2$ (OCH=CHO) with the difference that ^{13}CO (90% isotopic purity) was used instead of normal CO.

Ir data (nujol mull on KBr, cm^{-1}) $\nu(^{13}C\text{-}O)$ 1180.

^1H NMR (benzene-$\underline{d}_6$) [η^5-$C_5(CH_3)_5$] s, δ 1.94 (30H), (Zr-$\underline{H}$) s, δ 5.73 (1H), (η-O-$^{13}CH{=}{}^{13}CH$) a ten line pattern centered at δ 6.55. The ten line AA′XX′ pattern was analyzed as described by Emsley, Feeney, and Sutcliffe, "High Resolution Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Oxford (1965), p. 396. $^1\underline{J}\,^{13}C\text{-}H$=176.5 Hz, $^1\underline{J}\,^{13}C\text{-}^{13}C$=99 Hz, $^2\underline{J}\,^{13}C\text{-}H$=7.5 Hz, $^3\underline{J}H\text{-}H$=9 Hz. $\{^1H\}$ ^{13}C nmr, s, δ 137.4 (TMS). Non-$\{^1H\}$ ^{13}C nmr spectrum shows the same AA′XX′ pattern.

14. Reaction of $[(C_5Me_5)_2ZrH]_2(OCH{=}CHO)$ with HCl. To $[(C_5Me_5)_2ZrH]_2$ (OCH=CHO) (53.4 mg, 0.068 mmol) were condensed 6 ml of toluene at -80°. HCl (0.55 mmol) was introduced at this temperature whereupon an immediate reaction with gas evolution took place. After 15 min the mixture was warmed to room temperature and the gases passed through a series of liquid nitrogen cooled-traps and collected via a Toepler pump. Collected gas amounted to 0.123 mmol, which was identified as H_2 by its quantitative conversion to H_2O (trapped in a dry ice-acetone cooled trap, after cycling

the gas over CuO at 320°C.) Thus H_2 evolved 0.123 mmol, 0.904 mmol/mmol Zr. Composition of $CDCl_3$-soluble portion of the residue (nmr): 100% $(C_5Me_5)_2ZrCl_2$.

15. $[(C_5Me_5)_2ZrI]_2(OCH{=}CHO)$. To $(C_5Me_5)_2ZrH_2$ (758.3 mg, 2.085 mmols) were condensed 20 ml of toluene at -80°. An atmosphere of CO was introduced and the reaction mixture was stirred for 30 min at this temperature. Then the excess CO was removed in vacuo and the flask was closed off. The resulting solution of $(C_5Me_5)_2ZrH_2CO$ was allowed to warm slowly to room temperature in order to form $[(C_5Me_5)_2ZrH]_2(OCH{=}CHO)$. The solution was then cooled to -80° and CH_3I (6 mmols) was introduced (previously degassed and dried over molecular sieves). After warming to room temperature a color change from yellow to orange was observed. Then the gases evolved were passed through a series of liquid nitrogen cooled-traps and collected via a Toepler pump. Collected gas amounted to 1.717 mmols, this gas was identified as CH_4 by its quantitative recovery after cycling it over CuO at 320° and removing any trace of H_2O or CO_2 in a liquid nitrogen-cooled trap. Thus CH_4 evolved was 1.717 mmols, 0.824 mmol/mmol Zr. The toluene and CH_3I unreacted were removed in vacuo and the orange microcrystalline residue was redissolved in 15 ml of toluene, filtered and concentrated to a final volume of 5 ml by removing the toluene under vacuo, 20 ml of petroleum ether were condensed in and orange microcrystalline $[(C_5Me_5)_2ZrI]_2$ (OCH=CHO) was precipitated. The crystalline slurry was then filtered

and the filtrate and crystals dried under vacuo (yield 620 mg, 57% yield).

Anal. Calculated for $C_{21}H_{31}OIZr$: C, 48.73; H, 6.04; I, 24.52; Zr, 17.62. Found: C, 49.03; H, 6.09; I, 24.20; Zr, 17.61.

Ir data (nujol mull on KBr, cm^{-1}) ν(C-O) 1195 (vs), ν(C-H, bending) 1270, 875 (m).

NMR (benzene-$\underline{d}_6$) [η^5-$C_5(\underline{C}H_3)_5$] s, δ 1.94 (30H); (O$\underline{H}$C=C$\underline{H}$O) s, δ 6.83 (1H).

16. $[(C_5Me_5)_2ZrI]_2(O^{13}CH=^{13}CHO)$. Was prepared in an identical way to $[(C_5Me_5)_2ZI]_2$(OCH=CHO) with the difference that ^{13}CO (90% isotopic purity) was used instead of normal CO.

Ir data (nujol mull on KBr, cm^{-1}) $\nu(^{13}C$-O) 1175 (vs).

NMR (^1H) (chloroform-$\underline{d}_1$) [η^5-$C_5(CH_3)_5$] s, δ 2.00; (O$\underline{H}$ ^{13}C=^{13}C$\underline{H}$O) a ten line pattern centered at δ 6.83 with $^1\underline{J}\,^{13}C$-H=180.3 Hz, $^1\underline{J}\,^{13}C$-^{13}C=100.3 Hz, $^2\underline{J}\,^{13}C$-H=6.7 Hz, $^3\underline{J}$ H-H=10.4 Hz.

17. $(C_5Me_5)_2Zr(H)(OCH_3)$.

a) From $[(C_5Me_5)_2ZrCO]_2N_2$. To $[(C_5Me_5)_2ZrCO]_2N_2$ (84.0 mg, 0.104 mmol) were condensed 5 ml of toluene -80°. H_2 (1.459 mmols) was introduced and the mixture was warmed to 35°. After stirring this mixture for 2 hrs at this temperature a color change from red to pale yellow was observed. The residual gases were passed through a series of liquid nitrogen cooled-traps and collected. Total gas collected amounted to 1.195 mmol. This gas was cycled over CuO at 320° in order to

convert H_2 to H_2O and possible CO to CO_2 which were trapped in a liquid nitrogen cooled-trap. N_2 0.105 mmol, 1.010 mmol/mmol dimer remained. Then the liquid nitrogen cooled-trap was replaced by a dry ice-acetone-cooled trap in order to collect the CO_2. No gas was collected, thus H_2 unreacted was 1.090 mmols and H_2 consumed 0.369 mmol, 3.548 mmols/mmol dimer. Composition of the residue (nmr, benzene-$\underline{d}_6$) showed ~76% $(C_5Me_5)_2Zr(H)(OCH_3)$ and ~24% $[(C_5Me_5)_2ZrH]$ (OCH=CHO). White microcrystalline $(C_5Me_5)_2Zr(H)(OCH_3)$ was obtained after sublimation of the residue at 130°, 10^{-3} torr.

b) From $(C_5Me_5)_2ZrH_2$. This reaction was performed in the apparatus showed in figure 2. To $(C_5Me_5)_2ZrH_2$ (78.6 mg, 0.216 mmol) were condensed 5 ml of toluene at -80° under vacuo. H_2 (0.662 mmol) was introduced into the 50 ml reaction flask and the stopcock 1 was closed. This mixture was allowed to warm to room temperature. CO (0.342 mmol) was admitted into the 25.6 ml gas storage bulb, thus the pressure in both parts of the apparatus (reaction flask and gas storage bulb) was approximately the same. Then the stopcock 1 was open and the CO allowed to diffuse into the reaction flask. After stirring this mixture for 12 hrs at room temperature the residual CO/H_2 mixture was collected and analyzed as described above. CO collected 0.160 mmol, thus CO consumed was 0.182 mmol 0.843 mmol/mmol dimer and H_2 collected 0.495 mmol, thus H_2 consumed was 0.167 mmol, 0.773 mmol/mmol dimer. Composition of the residue (nmr,

benzene $\underline{d}_6$) showed ~ 77% $(C_5Me_5)_2Zr(H)(OCH_3)$ and ~16% starting material $(C_5Me_5)_2ZrH_2$. A trace of $\{(C_5Me_5)_2ZrH\}_2$ (OCH-CHO) was identified by infrared.

18. $(C_5Me_5)_2Zr(O)(OCD_3)$. Was prepared in an identical way to $(C_5Me_5)_2Zr(H)(OCH_3)$ as in 17a, with the difference that H_2 was substituted by D_2.

Ir data (nujol mull on KBr, cm^{-1}) ν(C-O) 1140 (νs), ν(Zr-D) ~1130 (ms,br), ν(C-D, methoxide) 1080 (ν, sh), 2040 (ν, sh).

19. Reaction of $(C_5Me_5)_2Zr(H)(OCH_3)$ with HCl. To $(C_5Me_5)_2Zr(H)(OCH_3)$ (88.0 mg, 0.224 mmol) were condensed 5 ml of methylcyclohexane at -80°. HCl (0.89 mmol, 4M excess) was introduced at this temperature where upon an immediate reaction with the formation of the white-yellow precipitate and gas evolution took place. The mixture was warmed to room temperature and the gas collected. Collected gas amounted to 0.166 mmol, which was identified as H_2 by its quantitative conversion to H_2O as described in 14. Thus H_2 evolved was 0.166 mmol, 0.741 mmol/mmol Zr. The residue after evaporation of the methylcyclohexane under vacuo consisted (nmr, $C\underline{D}Cl_3$) 100% $(C_5Me_5)_2ZrCl_2$. Colorimetric determination for methanol after four extractions from the methylcyclohexane with 10 ml portions of water gave 0.78 mmol methanol/mmol Zr.

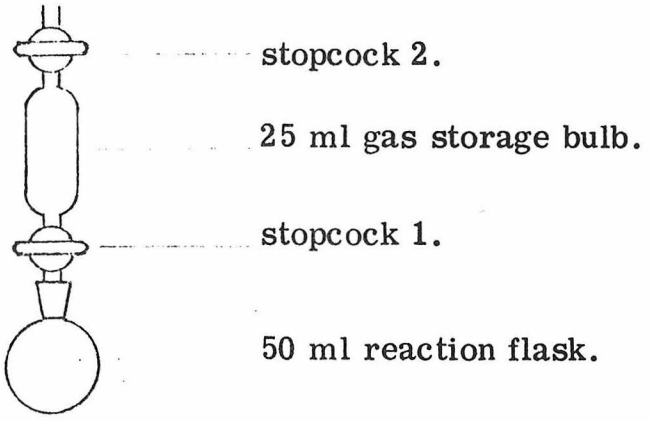

Figure 2

20. Reaction of $(C_5Me_5)_2ZrH_2$ with CO diffused through N_2. To $(C_5Me_5)_2ZrH_2$ (65.6 mg, 0.180 mmol) placed in the apparatus shown in figure 2 were condensed 7 ml of petroleum ether. N_2 (1 atm) was introduced in the reaction flask, then the stopcock 1 was closed and CO (1 atm) was admitted into the gas storage bulb previous evacuation of the N_2. The stopcock 2 was closed and 1 opened in order to diffuse the CO into the reaction flask. The mixture was stirred for 12 hrs at room temperature. A color change from yellow to dark red and finally to brown red was observed during this period of time. The residue after removal of the petroleum ether consisted (nmr, benzene-$\underline{d}_6$) ~50% $(C_5Me_5)_2Zr(H)(OCH_3)$ and ~50% $(C_5Me_5)_2Zr(CO)_2$.

21. Reaction of $(C_5Me_5)_2Zr(H_2)(CO)$ with $(C_5Me_5)_2Zr(H_2)$ under H_2. To $(C_5Me_5)_2Zr(H_2)$ (62.5 mg, 0.172 mmol) were condensed 8 ml of toluene under vacuo at -80°. CO (0.075 mmol) was introduced

and stirred this mixture for 30 min at this temperature in order to convert part of the $(C_5Me_5)_2Zr(H_2)$ (~44%) to $(C_5Me_5)_2Zr(H_2)(CO)$. The H_2 (0.471 mmol) was admitted and the mixture was warmed slowly to room temperature. The residual gas was passed through a series of liquid nitrogen cooled-traps and collected. Gas collected amounted to 0.402 mmol which was identified as H_2 by its quantitative conversion to H_2O as described in 14. Thus, H_2 consumed was 0.069 mmol, 0.92 mmol/mmol $(C_5Me_5)_2Zr(H_2)(CO)$. The residue after removal of the toluene consisted (nmr, benzene-$\underline{d}_6$) ~50% $(C_5Me_5)_2Zr(H)(OCH_3)$ and 50% $(C_5Me_5)_2Zr(H_2)$.

In another experiment, to $(C_5Me_5)_2Zr(H_2)$ (81.5 mg, 0.224 mmol) were condensed 8 ml of toluene at -80°. CO (0.183 mmol) was introduced and the mixture was stirred at this temperature to convert part of the $(C_5Me_5)_2Zr(H_2)$ (~82%) to $(C_5Me_5)_2Zr(H_2)(CO)$. Then H_2 (0.409 mmol) was admitted and the mixture was warmed slowly to room temperature. Afterwards the residual gas was collected and identified as H_2 as described above. H_2 amounted to 0.331 mmol, thus H_2 consumed was 0.078 mmol, 0.426 mmol/mmol $(C_5Me_5)_2Zr(H_2)(CO)$. The residue after removal of the toluene consisted (nmr, benzene-$\underline{d}_6$) of $(C_5Me_5)_2Zr(H)(OCH_3)$, $[(C_5Me_5)_2Zr(H)]_2(OCH{=}CHO)$ and $(C_5Me_5)_2Zr(H_2)$.

22. $\underline{(C_5Me_5)_2Zr(OCH_3)_2}$. This reaction was performed in the apparatus shown in figure 3. To $(C_5Me_5)_2Zr(H_2)$ (61.5 mg, 0.169 mmol) and paraformaldehyde (13.6 mg, 0.453 mmol of formaldehyde) were condensed 3 ml of toluene. H_2 (200 torr) was introduced and the system closed off. Then the apparatus was submerged

in an oil bath previously heated to 120° and stirred at this temperature for 12 hrs. A color change from yellow to white was observed during this period of time. After the H_2 was removed the toluene solution was transferred via a syringe to a flask in a glovebox under prepurified Ar, the flask was attached to the vacuum line and the toluene removed under vacuo. Composition of the white residue (soluble portion in benzene-$\underline{d}_6$) showed only $(C_5Me_5)_2Zr(OCH_3)_2$. White microcrystalline $(C_5Me_5)_2Zr(OCH_3)_2$ was obtained after sublimation of the residue at 130°, 10^{-3} torr. (H_2 is recovered quantitatively, however it is necessary in the reaction.)

Ir data (nujol mull on KBr, cm^{-1}) ν(C-O) 1125 (s, br), ν(C-H, methoxide) 2800 (νsh).

NMR (benzene-$\underline{d}_6$) [η^5-$C_5(CH_3)_5$] s, δ 1.93 (30H), (O-$\underline{CH}_3$) s, δ 4.03 (6H).

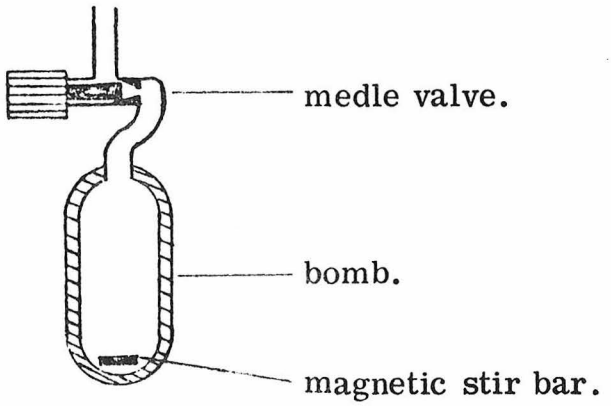

Figure 3

23. Reaction of $(C_5Me_5)_2Zr(H_2)$ with Formaldehyde mol to mol. To $(C_5Me_5)_2Zr(H_2)$ (323.2 mg, 0.889 mmol) and paraformaldehyde (27 mg, 0.900 mmol) placed in the apparatus shown in figure 3 were condensed 5 ml of toluene. H_2 (200 torr) was introduced and the system was closed off. After stirring the mixture for 12 hrs at 120° and performing all the operations described above, the nmr (benzene-d_6) of the residue showed the following composition: ~ 55% $(C_5Me_5)_2Zr(H)(OCH_3)$, ~30% $(C_5Me_5)_2Zr(OCH_3)_2$ and ~ 15% $(C_5Me_5)_2Zr(H_2)$.

24. Reaction of $\{(C_5Me_5)_2ZrN_2\}_2N_2$ with formaldehyde gas. This reaction was performed in the apparatus shown in figure 4. Paraformaldehyde (30 mg, 1 mmol) were placed in the bulb A which was then evacuated and connected to the apparatus as shown in figure 4. To $\{(C_5Me_5)_2ZrN_2\}_2N_2$ (59 mg, 0.073 mmol) placed in the reaction flask of figure 4 were condensed 6 ml of toluene at -80°. This mixture was warmed to room temperature, and allowed to react with gaseous formaldehyde generated by heating the bulb A with a heat-gun. After ~30 min the color changed from dark-red to yellow. The gases were passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. Collected gas amounted to 0.201 mmol. This gas was identified as N_2 by its quantitative recovery after cycling it over CuO at 320° and removing any trace of H_2O or CO_2 in a liquid nitrogen cooled-trap. Thus N_2 evolved was 2.75 mols/mol of dimer. The toluene was removed in vacuo and an nmr and a ir to the white

yellow residue were taken. Ir of the residue showed only a strong band at 1137 cm^{-1} (besides those bands characteristic of (η^5- C_5Me_5) rings). NMR showed mostly a singlet at δ ~1.6 ppm and two other singlets at δ ~3.7 and δ 4.35 ppm respectively. No further characterization was made.

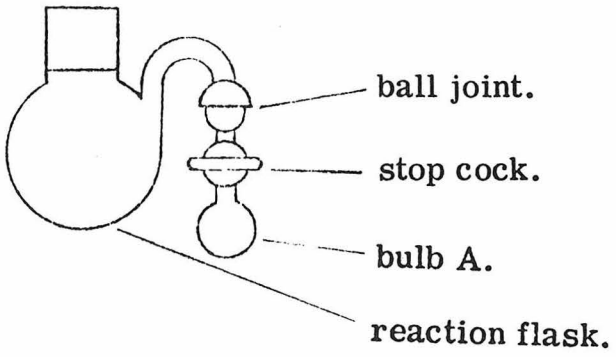

Figure 4

25. $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$. To $\{(C_5Me_5)_2ZrN_2\}_2N_2$ (800 mg, 0.991 mmol) were added 20 ml of toluene at -80°. The slurry was warmed to 10°. After vigorous stirring for 4 hrs in vacuo at this temperature a color change from dark-red to orange-red was observed. Then the toluene was removed in vacuo and the remaining red microcrystalline residue was redissolved in 10 ml of petroleum ether and filtered. The filtrate was cooled slowly to -80° and red crystalline $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ was precipitated. The crystalline slurry was then filtered and the

filtrate and crystals were dried under vacuo (yield 60 mg, 84% yield).

Ir data (nujol mull on KBr, cm^{-1}) ν(Zr-H) 1525, complex spectrum in the region 1200-400.

NMR (toluene-$\underline{d}_8$) [η^5-$C_5(\underline{CH}_3)_5$] s, δ 1.92 (15H), [$C_5(\underline{CH}_3)_4CH_2$] s, δ 210, 1.61, 1.33 (3H), an unresolved doublet J-2 Hz centered at δ 1.87 (3H), [$C_5(CH_3)_5\underline{CH}_2$] two doublets ($^2J_{^1H-^1H}$=6Hz) centered at δ 1.30 and 1.07 (1H each), [Zr-H] s, δ 5.40 (1H) broad.

26. Reaction of $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ with H_2. To $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ (433.8 mg, 1.199 mmols) were condensed 20 ml of petroleum ether at -80°. H_2 (2.950 mmols) was introduced and the reaction mixture was allowed to warm to room temperature. A color change from orange-red to pale-blue was observed. Then the residual gas was passed through a series of liquid nitrogen-cooled traps and collected via Toepler pump. Collected gas amounted to 1.847 mmol which was identified as H_2 by its quantitative conversion to H_2O after cycling it over CuO at 320° and removing the H_2O in a dry-ice acetone-cooled trap. Thus H_2 consumed was 1.103 mmols, 0.920 mmol H_2/mmol Zr. NMR of the residue consisted of 100% $(C_5Me_5)_2ZrH_2$.

27. Reaction of $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ with HCl. To $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$ (57.8 mg, 0.160 mmol) were condensed 10 ml of toluene at -80°. HCl (2.378 mmols) was introduced whereupon an instantaneous reaction took place as

evidenced by a color change from orange-red to pale yellow. After warming to room temperature the evolved H_2 was passed through a series of liquid nitrogen-cooled traps and collected. H_2 collected amounted to 0.149 mmol (the identity of this gas was confirmed as in 26). Thus H_2 evolved was 0.931 mmol/mmol Zr. NMR of the product ($CDCl_3$) consisted of 100% $(C_5Me_5)_2ZrCl_2$.

28. Decomposition of $(C_5Me_5)_2ZrH_2CO$ under CO.

a) Fast warming. To $(C_5Me_5)_2ZrH_2$ (82.2 mg, 0.226 mmol) were condensed 15 ml of petroleum ether at -80°. CO (1.871 mmols) was introduced and the mixture was stirred for 30 min at this temperature in order to form $(C_5Me_5)_2ZrH_2CO$. Then this mixture was warmed to room temperature and after stirring for a period of two hours at this temperature the residual gases were passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. Total gas collected amounted to 1.605 mmols. This gas mixture was cycled over CuO at 320° to convert CO to CO_2 and H_2 to H_2O which was removed (the H_2O) in a dry ice acetone cooled-trap. CO_2 1.482 mmols remained, thus CO consumed was 0.721 mmol/mmol of $(C_5Me_5)_2ZrH_2CO$ and H_2 evolved 0.123 mmol, 0.544 mmol/mmol of $(C_5Me_5)_2ZrH_2CO$. Infrared of the residue showed the presence of $(C_5Me_5)_2Zr(CO)_2$, $[(C_5Me_5)_2ZrH]_2(OCH{=}CHO)$ and $(C_5Me_5)_2Zr(H)(OCH_3)$.

b) Slow warming. This experiment was done in an identical way as above with the exception that the reaction mixture was left to warm slowly to room temperature.

CO consumed was: 0.29 mmol/mmol of $(C_5Me_5)_2ZrH_2CO$ and H_2 evolved was 0.090 mmol/mmol of $(C_5Me_5)_2ZrH_2CO$.

Infrared of the residue showed the presence of $[(C_5Me_5)_2ZrH]_2$ (OCH=CHO), $(C_5Me_5)_2Zr(CO)_2$ and a trace $(C_5Me_5)_2Zr(H)(OCH_3)$.

29. $(C_5Me_5)_2HfH_2$. This complex was prepared by the reduction of $(C_5Me_5)_2HfCl_2$ (see below) in toluene with Na/Hg amalgam (1%) under H_2 for 3 days. Then the toluene was removed under vacuo, petroleum ether was condensed into the residue and the resulting solution was filtered. Cooling the petroleum ether solution yielded white crystals which were identified as $(C_5Me_5)_2HfH_2$ by ir and ^1H nmr.

Ir data (nujol mull on hBr, cm^{-1}) ν(Hf-H) 1600 (ms, br)

NMR (toluene-$\underline{d}_8$) [η^5-C_5Me_5] s, δ 2.02 (30H); ZrH_2 s, δ 15.54.

$(C_5Me_5)_2HfCl_2$ was made in an identical way as $(C_5Me_5)_2ZrCl_2$, unfortunately the yield for the hafnium is extremely low (c.a. ~10-5%). Attempts to increase the yield in this reaction by changing the solvent (THf, diglime), temperature and time conditions have been for the moment, unsuccessful.

NMR ($COCl_3$) for $(C_5Me_5)_2HfCl_2$: [$C_5(CH_3)_5$] s, δ 2.04.

30. Preliminary results of the reaction of $(C_5Me_5)_2TiH_2$ with CO. To $[(C_5Me_5)_2Ti]_2N_2$ (114.9 mg, 0.173 mmol) were condensed 8 ml of toluene at -80°. The slurry was allowed to warm slowly to room temperature. Quantitative collection of the gas evolved after vigorous stirring at room temperature in vacuo yielded 0.172

mmol N_2 (0.993 mmol/mmol of dimer). Then 1 atm of H_2 was introduced in order to convert $(C_5Me_5)_2Ti$ to $(C_5Me_5)_2TiH_2$. After stirring for 30 min under 1 atm of H_2 at room temperature the system was cooled to -80° and evacuated. CO (0.777 mmol) was introduced at -80° and stirred at this temperature for 30 min. A color change from orange to brown was observed. Then the residual gas passed through a series of liquid nitrogen cooled-traps and collected via Toepler pump. CO collected 0.489 mmol, thus CO consumed was 0.288 mmol, 0.834 mmol/mmol of Ti. The identity of this gas was confirmed as in experiment 6. Then to the above solution H_2 (0.529 mmol) was introduced and the reaction mixture was allowed to warm slowly to room temperature. Once at room temperature it was cooled again to -80° and the residual gases passed through a series of liquid nitrogen cooled-traps and collected. Total gas collected amounted to 0.396 mmol. This gas was analyzed for CO and H_2 as in experiment 2. H_2 absorbed amounted to 0.167 mmol, 0.483 mmol/mmol Ti and CO evolved 0.035 mmol, 0.101 mmol/mmol Ti.

NMR of the product (toluene-$\underline{d}_8$) consisted of 3 broad singlets at δ 1.9 (~30H) 3.6 (~1H) and 4.1 (~3H).

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Appendix I.

Experimental Section (Procedures) to Part IB. Reaction of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ with Hydrazine and Labelling Experiments.

Procedures

1. Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with hydrazine. To $[(C_5Me_5)_2ZrN_2]_2N_2$ (180 mg; 0.223 mmol) were condensed 9 ml of toluene under vacuo at liquid nitrogen temperature. 1.1 mmol of anhydrous N_2H_4 (5 M excess) were condensed onto the frozen toluene solution. This mixture was warmed slowly to room temperature whereupon an immediate reaction took place, and the dark-red color faded to orange with gas evolution within a period of ~10 min. The gases were passed through a series of liquid nitrogen cooled-traps, and the N_2/H_2 mixture collected via a Toepler pump and analyzed as described in 1. The N_2 evolved was 0.645 mmol, 2.892 mmol/mmol dimer; the H_2 evolved was 0.019 mmol, 0.085 mmol/mmol dimer. Then, the series of liquid nitrogen cooled-traps were replaced by dry ice acetone cooled-traps and the non-condensable gas was collected via Toepler pump (0.4791 mmol of gas, 2.148 mmol/mmol dimer). This gas was transferred to a gas cell i.r. and identified as ammonia.

2. Preparation of $[(C_5Me_5)_2Zr\ ^{15}N_2]_2\ ^{15}N_2$. This compound was made in the same way as described in Part C of this work. ~1.5 gm of $[(C_5Me_5)_2ZrN_2]_2N_2$ were decomposed in toluene under vacuo.

The resulting orange crystalline material $[(C_5Me_5)(C_5Me_4)CH_2ZrH]$ was dissolved in 10 ml of pet-ether, filtered off, and exposed to 1 atm of $^{15}N_2$ (99.36% $^{15}N\equiv{}^{15}N$, 0.59% $^{15}N\equiv{}^{14}N$, obtained from STHOLER ISOTOPE CHEMICALS, previous purification as described before). After ~20 hrs the crystals were filtered, washed three times with pet-ether, dried in vacuo and transferred to a storage ampoule in a glove box under Ar; the yield was ~ 1 g.

3. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (1 atm) in toluene at -23° (15 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (102.1 mg; 0.1255 mmol) were condensed 8 ml of toluene under vacuo at liquid nitrogen temperature. This mixture was warmed to 0°C and stirred over a 15 min. period at this temperature in order to dissolve the complex. This solution was then submerged in a cooled nitrogen-CCl_4 slush bath (-23°) and allowed to thermally equilibrate under stirring for 5 min. Natural $^{14}N_2$ was admitted (1 atm), and the system was quickly closed off. After 15 min of stirring the exchange was quenched by rapid cooling to liquid nitrogen temperature. The gas phase was passed through a series of liquid nitrogen cooled-traps and collected via a Toepler pump. The N_2 collected was 2.0879 mmols. Then, an appropriate portion of the gas phase was transferred to a sample bulb and analyzed by mass spectrometry for $^{14}N\equiv{}^{14}N(28)$, $^{15}N\equiv{}^{14}N(29)$, and $^{15}N\equiv{}^{15}N(30)$. A small correction for residual N_2 trapped in the frozen toluene (0.0185 mmol as determined by a blank) was

made in calculating the expected fraction of 28, 29, and 30 in the gas phase. Mass spectrum of gas phase showed the following composition: $\chi_{28}=0.8858$, $\chi_{29}=0.0077$, and $\chi_{30}=0.1066$. The expected composition of the gas phase for complete exchange of one, two, or the three dinitrogen ligands was calculated by the procedure outline in the appendix II.

b) Reaction with HCl. Following the above exchange, 2.51 mmols HCl (20M excess) were condensed onto the frozen toluene solution. This mixture was warmed slowly to -80° whereupon an immediate reaction accompanied melting (<10 seconds to completion) took place as evidenced by a color change from intense red to pale yellow. After warming to room temperature the N_2/H_2 mixture was fractionated from HCl, collected, and analyzed as described in 1. N_2 evolved was 0.2730 mmol; H_2 evolved was 0.0162 mmol. After, an appropriate portion of the N_2 was then transferred to a sample bulb and analyzed by mass spectrometry for 28, 29, and 30. A small correction for residual N_2 trapped in the frozen toluene, 0.0185 mmol, was made to the observed fraction of 28, 29, and 30 evolved in the addition of HCl. Mass spectrum of the N_2 showed the following composition: $\chi_{28}=0.6240$, $\chi_{29}=0.0073$, $\chi_{30}=0.3687$. The expected compositions of the N_2 evolved in the addition of HCl was calculated by the procedure outlined in the appendix II.

c) Recovery of the N_2 in hydrazine. Following the HCl reaction, 10 ml of $CHCl_3$ were added to the residue after

evaporation of the toluene and the solution was extracted 2 times with 10 ml portions of 0.1 N HCl. Then 10 ml of 0.1 N KIO_3 were transferred via syringe into a bulb A (see apparatus shown in figure 1) degassed and connected to the reaction flask. The 0.1 N HCl-soluble products together with 4 ml concentrated HCl were transferred to the reaction flask, degassed (by freezing the mixture 3 times at -80° and evacuating residual gas) and the KIO_3 added to the solution. After a period of 15 min under stirring at room temperature, the N_2 was passed through a series of liquid nitrogen cooled-traps, and the N_2 collected via a Toepler pump. The N_2 collected was 0.1000 mmols. Mass spectrum of the N_2 showed the following composition: $\chi_{28}=0.4649$, $\chi_{29}=0.0070$, $\chi_{30}=0.5282$. The expected compositions of the N_2 in hydrazine was calculated by the procedure outlined in the appendix II.

4. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (1 atm) in toluene at -23° (30 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (155.0 mg; 0.1906 mmol) were condensed 8 ml of toluene under vacuo, and all the operations described in 3a were performed with the only difference that the exchange was quenched by rapid cooling to liquid nitrogen temperature after 15 min. The N_2 collected was 2.1456 mmols. The mass spectrum of the N_2 collected showed: $\chi_{28}=0.8408$, $\chi_{29}=0.0074$, $\chi_{30}=0.1518$.

b) Reaction with HCl. Following the above exchange, 3.81 mmols HCl (20 M excess) were condensed onto the frozen

toluene solution and the same operations described in 3b were performed. The N_2 evolved was 0.3960 mmol, the H_2 evolved was 0.0212 mmol. Composition of the N_2 evolved was $\chi_{28}=0.6152$, $\chi_{29}=0.0075$, $\chi_{30}=0.3773$.

c) Recovery of the N_2 in hydrazine. The same procedure described in 3c was performed. The N_2 collected was 0.1514 mmol. Mass spectrum of the N_2 showed the following composition: $\chi_{28}=0.4457$, $\chi_{29}=0.0069$, $\chi_{30}=0.5474$.

5. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (1 atm) in toluene at -23° (60 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (88.7 mg; 0.1091 mmol) were condensed 8 ml of toluene under vacuo and all the operations described in 3a were performed, with the only difference that the exchange was quenched by rapid cooling to liquid nitrogen temperature after 60 min. The N_2 collected was 2.3190 mmols. Mass spectrum of the N_2 collected showed: $\chi_{28}=0.9063$, $\chi_{29}=0.0074$, $\chi_{30}=0.0863$.

b) Reaction with HCl. Following the above exchange, 2.2 mmols HCl (20 M excess) were condensed onto the frozen toluene solution and the same operations described in 3b were performed. The N_2 evolved was 0.2216 mmols, the H_2 evolved was 0.0176 mmol. Composition of the N_2 evolved showed: $\chi_{28}=0.6844$, $\chi_{29}=0.0072$, $\chi_{30}=0.3084$.

c) Recovery of the N_2 in hydrazine. After performing

the same procedure described in 3c, the N_2 collected was 0.0838 mmol. Mass spectrum of the N_2 showed the following composition: $\chi_{28} = 0.5057$, $\chi_{29} = 0.0068$, $\chi_{30} = 0.4875$.

6. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (1 atm) in toluene at -23° (15 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (99 mg; 0.1217 mmol) were condensed 8 ml of toluene under vacuo and the operations described in 3a were performed, with the only difference that the exchange was quenched by rapid cooling to liquid nitrogen temperature after 5 min. The N_2 collected was 2.1360 mmols. Mass spectrum of the N_2 collected showed: $\chi_{28} = 0.9211$, $\chi_{29} = 0.0061$, $\chi_{30} = 0.0728$.

b) Reaction with HCl. Following the above exchange, 2.4 mmols HCl (20 M excess) were condensed onto the frozen toluene solution and the same operations described in 3b were performed. The N_2 evolved was 0.2527 mmol, the H_2 evolved was 0.0162 mmol. Composition of the N_2 evolved showed: $\chi_{28} = 0.4508$, $\chi_{29} = 0.0067$, $\chi_{30} = 0.5424$.

c) Recovery of the N_2 in hydrazine. After performing the same procedure described in 3c, the N_2 collected was 0.1000 mmol. Mass spectrum of the N_2 showed the following composition: $\chi_{28} = 0.3293$, $\chi_{29} = 0.0059$, $\chi_{30} = 0.6648$.

7. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (0.5 atm) in toluene at -23° (15 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (92.8 mg, 0.1141 mmol) were condensed 8 ml of toluene under vacuo and all the operations described in 3a were performed, with the only difference that natural $^{14}N_2$ (0.5 atm) was admitted. The N_2 collected was 1.1209 mmols. Mass spectrum of the N_2 collected showed: $\chi_{28}=0.8456$, $\chi_{29}=0.0071$, $\chi_{30}=0.1473$.

b) Reaction with HCl. Following the above exchange, 2.3 mmols HCl (20 M excess) were condensed onto the frozen toluene solution and the same operations described in 3b were performed. The N_2 evolved was 0.2332 mmol, the H_2 evolved was 0.0200 mmol. Composition of the N_2 evolved showed: $\chi_{28}=0.4815$, $\chi_{29}=0.0076$, $\chi_{30}=0.5109$.

c) Recovery of the N_2 in hydrazine. After performing the same procedure described in 3c, the N_2 collected was 0.0892 mmol. Mass spectrum of the N_2 collected showed: $\chi_{28}=0.3593$, $\chi_{29}=0.0066$, $\chi_{30}=0.6341$.

8. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (0.5 atm) in toluene at -23° (10 min) and reaction with HCl.

a) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (84.3 mg, 0.1036 mmol) were condensed 8 ml of toluene under vacuo and all the operations described in 3a were performed, except that natural $^{14}N_2$ (0.5 atm) was admitted and the exchange was quenched by rapid cooling to liquid nitrogen temperature after 5 min. The N_2 collected was 1.1065 mmols. Mass spectrum of the N_2 collected showed: $\chi_{28}=0.8803$, $\chi_{29}=0.0071$, $\chi_{30}=0.1126$.

b) Reaction with HCl. Following the above exchange, 2.1 mmols HCl (20 M excess) were condensed onto the frozen toluene solution and the same operations as described in 3b were performed. The N_2 evolved was 0.2122 mmol, the H_2 evolved was 0.0189 mmol. Composition of the N_2 evolved: $\chi_{28}=0.3965$, $\chi_{29}=0.0065$, $\chi_{30}=0.5970$.

c) Recovery of the N_2 in hydrazine. After performing the same procedure described in 3c, the N_2 collected was 0.0824 mmol. Mass spectrum of the N_2 collected: $\chi_{28}=0.3112$, $\chi_{29}=0.0064$, $\chi_{30}=0.6824$.

9. Exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ with free natural N_2 (1 atm) in toluene at -23° (15 min) and reaction with DCl.

a) Preparation of DCl. Prior to the preparation, all exposed glass in the vacuum line was wetted several times with D_2O (99.5% isotopic purity). To 10 ml of $POCl_3$ (degassed) were condensed 3 ml of D_2O (99.5% isotopic purity) under vacuo and allowed to react with the $POCl_3$. The evolved DCl was passed through a series of dry ice acetone cooled-traps and condensed into a storage bulb. Isotopic purity was determined as by reaction with a sodium mirror and mass spectroscopy of the evolved D_2, HD, and H_2.

b) Exchange with free natural N_2. To $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (72.2 mg, 0.0888 mmol) were condensed 8 ml of toluene under vacuo and all the operations described in 3a were performed. The N_2 collected was 2.20335 mmols. Mass spectrum of the N_2

collected: $\chi_{28}=0.9137$, $\chi_{29}=0.0075$, $\chi_{30}=0.0788$.

c) Reaction with DCl. Following the above exchange 1.8 mmols DCl (20 M excess) were condensed onto the frozen toluene solution and the same operations described in 3b were performed. The N_2 evolved was 0.1892 mmol, the H_2 evolved was 0.0122 mmol. Composition of the N_2 evolved: $\chi_{28}=0.6815$, $\chi_{29}=0.0082$, $\chi_{30}=0.3104$.

d) Recovery of the N_2 in hydrazine. After performing the same procedure as described in 3c, the N_2 collected was 0.0743 mmol. Mass spectrum of the N_2 collected: $\chi_{28}=0.4711$, $\chi_{29}=0.0068$, $\chi_{30}=0.5221$.

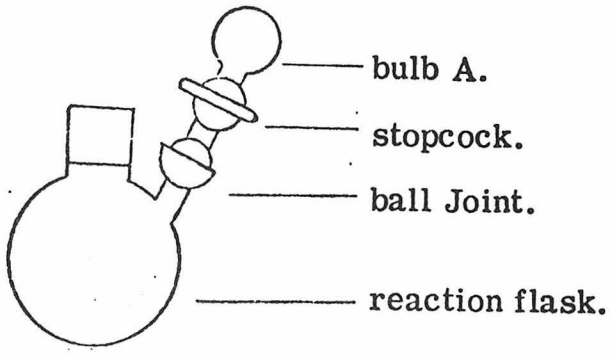


Figure 1.

Appendix II.

Calculations for the Exchange and Labelling Experiments Corresponding to Part IB.

Here and on the following five pages is given an example of the procedure used for the calculations in the exchange and labeling studies. The values used correspond to the experiment #4.

I. Calculation of the expected composition of the gas phase for the complete exchange of 1, 2, or 3 N_2 ligands of $[(C_5Me_5)_2Zr\,^{15}N_2]_2\,^{15}N_2$ with free natural $^{14}N_2$.

Amount of complex: 0.1906 mmol.

Composition of $^{15}N_2$ in the complex: $\chi_{30}=0.9936$, $\chi_{29}=0.0059$, $\chi_{28}=0.0005$.

Composition of natural $^{14}N_2$ used for the exchange: $\chi_{28}=0.9926$, $\chi_{29}=0.0074$, (The 30 cannot be detected under our experimental conditions).

Amount of $^{14}N_2$ used for the exchange: 2.1456 mmols + 0.0185 mmols (N_2 trapped in the frozen toluene solution) =2.1641 mmols.

Composition of the gas phase after the exchange: $\chi_{28}=0.8408$, $\chi_{29}=0.0074$, $\chi_{30}=0.1518$.

a) Complete exchange of 1 N_2 ligand only (bridging).

Total N_2 for exchange=2.1641 mmols + 0.1906 mmol = 2.3547 mmols.

mmols 28 in total N_2=mmols 28 in natural $^{14}N_2$ added + mmols 28 in bridge position

=2.1641 mmols $\times$ 0.9926 + 0.1906 mmols $\times$ 0.005

=2.1482 mmols

mmols 29 in total N_2 = mmols 29 in natural $^{14}N_2$ added + mmols 29 in bridge position

= 2.1641 mmols × 0.0074 + 0.1906 mmol × 0.0059

= 0.0171 mmol

mmols 30 in total N_2 = mmols 30 in bridge position

= 0.1906 mmol × 0.9936

= 0.1894 mmol

therefore the expected composition of the gas phase for exchange 1 N_2 ligand only (bridging) is:

$$\chi_{28} = \frac{2.1482}{2.3547} = 0.9123 , \quad \chi_{29} = \frac{0.0171}{2.3547} = 0.0073 ,$$

$$\chi_{30} = \frac{0.1894}{2.3547} = 0.0804 .$$

b) Complete exchange of 2 N_2 ligands only (terminals).

Total N_2 for exchange = 2.1641 mmols + 2 × 0.1906 mmol = 2.5453 mmols.

mmols 28 in total N_2 = mmols 28 in natural $^{14}N_2$ added + mmols 28 in terminal positions.

= 2.1641 mmols × 0.9926 + 2 × 0.1906 mmol × 0.0005

= 2.1483 mmols

mmols 29 in total N_2 = mmols 29 in natural $^{14}N_2$ added + mmols 29 in terminal positions.

= 2.1641 mmols × 0.0074 + 2 × 0.1906 mmol × 0.0059

= 0.0182 mmol

mmols 30 in total N_2 = mmols 30 in terminal positions.

$$= 2 \times 0.1906 \text{ mmol} \times 0.9936$$

$$= 0.3788 \text{ mmol}$$

therefore the expected composition of the gas phase for exchange of 2 N_2 ligands only (terminals) is:

$$\chi_{28} = \frac{2.1483}{2.5453} = 0.8440 , \quad \chi_{29} = \frac{0.0182}{2.5453} = 0.0072 ,$$

$$\chi_{30} = \frac{0.3788}{2.5453} = 0.1488 .$$

c) Complete exchange of 3 N_2 ligands (terminals and bridging).

Total N_2 for exchange = 2.1641 mmols + 3×0.1906 mmol = 2.7359 mmols.

mmols 28 in total N_2 = mmols 28 in natural $^{14}N_2$ added + mmols 28 in complex.

$$= 2.1641 \text{ mmols} \times 0.9926 + 3 \times 0.1906 \text{ mmol} \times 0.005$$

$$= 2.1484 \text{ mmols}$$

mmols 29 in total N_2 = mmols 29 in natural $^{14}N_2$ added + mmols 29 in complex.

$$= 2.1641 \text{ mmols} \times 0.0074 + 3 \times 0.1906 \text{ mmol} \times 0.0059$$

$$= 0.0194 \text{ mmol}$$

mmols 30 in total N_2 = mmols 30 in complex

$$= 3 \times 0.1906 \text{ mmol} \times 0.9936$$

$$= 0.5681 \text{ mmol}$$

therefore the expected composition of the gas phase for the exchange of 3 N_2 ligands (terminal and bridging) is:

$$\chi_{28} = \frac{2.1484}{2.7359} = 0.7853 , \quad \chi_{29} = \frac{0.0194}{2.7359} = 0.0071 ,$$

$$\chi_{30} = \frac{0.5681}{2.7359} = 0.2076 .$$

II. Calculation of net mmols of N_2 exchanged per mmol of dimer.

This is calculated from the expression:

$$\text{mmols } N_2 \text{ exchanged/mmol dimer} = \frac{2 \times \chi_{30} \text{ (observed)}}{\chi_{30} \text{ (calculated)}}$$

where χ_{30} (calculated) is the obtained in Ib, χ_{30} (observed) = 0.1518.

$$\text{therefore mmols exchanged/mmol dimer} = \frac{2 \times 0.1518}{0.1488} = 2.040$$

III. Calculation of the expected composition of the gas evolved for the reaction: $[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$.

a) Expected composition of the N_2 evolved for a mechanism where the bridging N_2 is reduced.

As the terminal nitrogens have the same composition as the gas phase after the exchange, the evolved N_2 after the HCl should have the same composition as in I. Therefore, χ_{28} = 0.8408, χ_{29} = 0.0074, χ_{30} = 0.1518.

b) Expected composition for a mechanism where 1 terminal N_2 is reduced.

In this case χi is given by the expression:

$$\chi_i = \frac{\chi i \text{ (terminal)} + \chi i \text{ (bridging)}}{2}$$

$$\chi_{28} = \frac{0.8408 + 0.0005}{2} = 0.4207$$

$$\chi_{29} = \frac{0.0074 + 0.0059}{2} = 0.0067$$

$$\chi_{30} = \frac{0.1518 + 0.9936}{2} = 0.5727$$

c) Expected composition for a mechanism where $\frac{1}{2}$ N_2 bridging is reduced.

In this case χi is given by the expression:

$$\chi_i = \frac{\chi i \text{ (terminal)} + \frac{1}{2}[\chi i \text{ (terminal)} + \chi i \text{ (bridging)}]}{2}$$

$$\chi_{28} = \frac{0.8408 + \frac{1}{2}[0.8408 + 0.0005]}{2} = 0.6307$$

$$\chi_{29} = \frac{0.0074 + \frac{1}{2}[0.0074 + 0.0059]}{2} = 0.0070$$

$$\chi_{30} = \frac{0.1518 + \frac{1}{2}[0.1518 + 0.9936]}{2} = 0.3623$$

d) Expected composition for a mechanism where there is no preference for either terminal or bridging N_2.

In this case χi is given by the expression:

$$\chi i = \frac{2\,\chi i\,(\text{terminal}) + \chi i\,(\text{bridging})}{3}$$

$$\chi_{28} = \frac{2 \times 0.8408 + 0.0005}{3} = 0.5607$$

$$\chi_{29} = \frac{2 \times 0.0074 + 0.0059}{3} = 0.0069$$

$$\chi_{30} = \frac{2 \times 0.1518 + 0.9936}{3} = 0.4324$$

e) Correction of observed mol fraction due to trapped N_2 in toluene.

Amount of N_2 collected after the HCl addition: 0.3960 mmol.

Composition of the N_2 collected: $\chi_{28}=0.6152$, $\chi_{29}=0.0075$, $\chi_{30}=0.3773$.

real mmols gas evolved in the reaction=0.3960 - 0.0185 = 0.3775 mmol.

real mmols 28 evolved=0.3960 mmol × 0.6152 - 0.0185 mmol × 0.8408 = 0.2281 mmol

real mmols 29 evolved=0.3960 mmol × 0.0075 - 0.0185 mmol × 0.0074 = 0.0028 mmol

real mmols 30 evolved=0.3960 mmol × 0.3773 - 0.0185 mmol × 0.1518 = 0.1466 mmol

therefore, the corrected observed composition is:

$$\chi_{28} = \frac{0.2281}{0.3775} = 0.6042$$

$$\chi_{29} = \frac{0.0028}{0.3775} = 0.0074$$

$$\chi_{30} = \frac{0.1466}{0.3775} = 0.3884$$

III. Calculation of the expected composition of the N_2 in hydrazine for the reaction: $[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$.

a) Bridging N_2 is reduced.

As the bridging N_2 does not exchange, the composition of the N_2 in hydrazine should be the same as in the starting complex. $\chi_{28} = 0.0005$, $\chi_{29} = 0.0059$, $\chi_{30} = 0.9936$.

b) 1 terminal N_2 is reduced.

In this case the composition of the N_2 in hydrazine should have the same composition of the gas phase after the exchange (for complete exchange only).
$\chi_{28} = 0.8408$, $\chi_{29} = 0.0074$, $\chi_{30} = 0.1518$.

c) $\frac{1}{2}$ terminal N_2 and $\frac{1}{2}$ bridging N_2 is reduced.

In this case the composition of the N_2 in hydrazine is given by the expression:

$$\chi i = \frac{\chi i \text{ (terminal)} + \chi i \text{ (bridging)}}{2}$$

$$\chi_{28} = \frac{0.8408 + 0.0005}{2} = 0.4207$$

$$\chi_{29} = \frac{0.0074 + 0.0059}{2} = 0.0067$$

$$\chi_{30} = \frac{0.1518 + 0.9936}{2} = 0.5727$$

d) No preference for either terminals or bridging N_2.

In this case the composition of the N_2 in hydrazine should be the same as in IIId.

$\chi_{28} = 0.5607$, $\chi_{29} = 0.0069$, $\chi_{30} = 0.4324$.

The calculations for the other experiments were made in an identical form. The results are summarized in the next four pages.

Table I. Results of N_2 exchange of $[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (99.36% $^{15}N\equiv{}^{15}N$) with free natural N_2 (99.26% $^{14}N\equiv{}^{14}N$) in toluene at -23°C (estimated standard deviations).

$[(C_5Me_5)_2Zr^{15}N_2]_2{}^{15}N_2$ (mmol)	$^{14}N_2$ added (mmol)	$\tilde{P}_{N_2}$ (atm)	exposure time (min)	$\chi_{(^{14}N_2)}{}^{calcd}{}^{a}$ $\chi_{(^{15}N_2)}$	$\chi_{(^{14}N_2)}{}^{calcd}{}^{b}$ $\chi_{(^{15}N_2)}$	$\chi_{(^{14}N_2)}{}^{calcd}{}^{c}$ $\chi_{(^{15}N_2)}$	$\chi_{(^{14}N_2)}{}^{obsd}$ $\chi_{(^{15}N_2)}$	mmol N_2 exchd[d] per mmol/dimer
0.1255(2)	2.106(1)	1.0	15	0.937 0.0559	0.887 0.106	0.842 0.151	0.886(1) 0.107(1)	2.02(2)
0.1906(2)	2.164(1)	1.0	30	0.912 0.0804	0.844 0.149	0.785 0.208	0.841(1) 0.152(1)	2.04(2)
0.1091(2)	2.338(1)	1.0	60	0.948 0.0443	0.908 0.0848	0.871 0.122	0.906(1) 0.0863(10)	2.04(2)
0.1217(2)	2.154(1)	1.0	5	0.940 0.0531	0.892 0.101	0.849 0.144	0.921(1) 0.0728(10)	1.44(2)
0.1036(2)	1.116(1)	0.5	10	0.908 0.0844	0.837 0.156	0.776 0.217	0.830(1) 0.113(1)	1.45(2)
0.1141(2)	1.130(1)	0.5	15	0.902 0.0911	0.826 0.167	0.762 0.231	0.846(1) 0.147(1)	1.77(2)

[a] Mol fractions $^{14}N\equiv{}^{14}N$ and $^{15}N\equiv{}^{15}N$ expected in the gas phase for complete exchange of 1 N_2 ligand only (bridging).

[b] Mol fractions $^{14}N\equiv{}^{14}N$ and $^{15}N\equiv{}^{15}N$ expected in the gas phase for complete exchange of 2 N_2 ligands only (terminals).

[c] Mol fractions $^{14}N\equiv{}^{14}N$ and $^{15}N\equiv{}^{15}N$ expected in the gas phase for complete exchange of 3 N_2 ligands (bridging and terminals).

[d] Observed mmols N_2 exchanged per mmol of dimer assuming exchange of terminal N_2 ligands only.

Table II. Results of N_2 evolved in the labeling experiments for the reaction:

$[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$ (estimated standard deviations).

$\chi(^{15}N_2)$ in two positions of $[(C_5Me_5)_2ZrN_2]_2N_2$		calcd. case 1[a]	calcd. case 2[b]	calcd. case 3[c]	calcd. case 4[d]	observed
terminal	bridge	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$
0.107(5)	0.9936(1)	0.107(4)	0.550(4)	0.328(4)	0.402(4)	0.388(1)
0.152(5)	0.9936(1)	0.152(4)	0.573(4)	0.362(4)	0.432(4)	0.388(1)
0.086(5)	0.9936(1)	0.086(4)	0.540(4)	0.313(4)	0.389(4)	0.329(1)
0.349(5)	0.9936(1)	0.349(4)	0.671(4)	0.510(4)	0.564(4)	0.580(1)
0.264(5)	0.9936(1)	0.264(4)	0.629(4)	0.446(4)	0.507(4)	0.526(1)
0.388(5)	0.9936(1)	0.388(4)	0.691(4)	0.539(4)	0.590(4)	0.619(1)
0.079(5)[e]	0.9936(1)[e]	0.079(4)[e]	0.536(4)[e]	0.308(4)[e]	0.384(4)[e]	0.335(1)[e]

[a] Case 1. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + 2N_2^t + N_2^bH_4$

[b] Case 2. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + N_2^t + N_2^b + N_2^tH_4$

[c] Case 3. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + \frac{3}{2}N_2^t + \frac{1}{2}N_2^b + \frac{1}{2}N_2^tH_4 + \frac{1}{2}N_2^bH_4$

[d] Case 4. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + \frac{4}{3}N_2^t + \frac{2}{3}N_2^b + \frac{2}{3}N_2^tH_4 + \frac{1}{3}N_2^bH_4$

[e] DCl substituted for HCl.

Table III. Results of N_2 in hydrazine in the labeling experiments for the reaction: $[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$ (estimated standard deviations).

$\chi(^{15}N_2)$ in two positions of $[(C_5Me_5)_2ZrN_2]_2N_2$		calcd. case 1[a]	calcd. case 2[b]	calcd. case 3[c]	calcd. case 4[d]	observed[f]
terminal	bridge	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$	$\chi(^{15}N_2)$
0.107(5)	0.9936(1)	0.9936(3)	0.107(3)	0.550(3)	0.402(3)	0.528(1)
0.152(5)	0.9936(1)	0.9936(3)	0.152(3)	0.573(3)	0.432(3)	0.547(1)
0.086(5)	0.9936(1)	0.9936(3)	0.086(3)	0.540(3)	0.389(3)	0.488(1)
0.349(5)	0.9936(1)	0.9936(3)	0.349(3)	0.671(3)	0.564(3)	0.665(1)
0.264(5)	0.9936(1)	0.9936(3)	0.264(3)	0.629(3)	0.507(3)	0.634(1)
0.388(5)	0.9936(1)	0.9936(3)	0.388(3)	0.691(3)	0.590(3)	0.682(1)
0.079(5)[e]	0.9936(1)[e]	0.9936(3)[e]	0.079(3)[e]	0.536(3)[e]	0.384(3)[e]	0.522(1)[e]

[a] Case 1. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + 2N_2^t + N_2^bH_4$

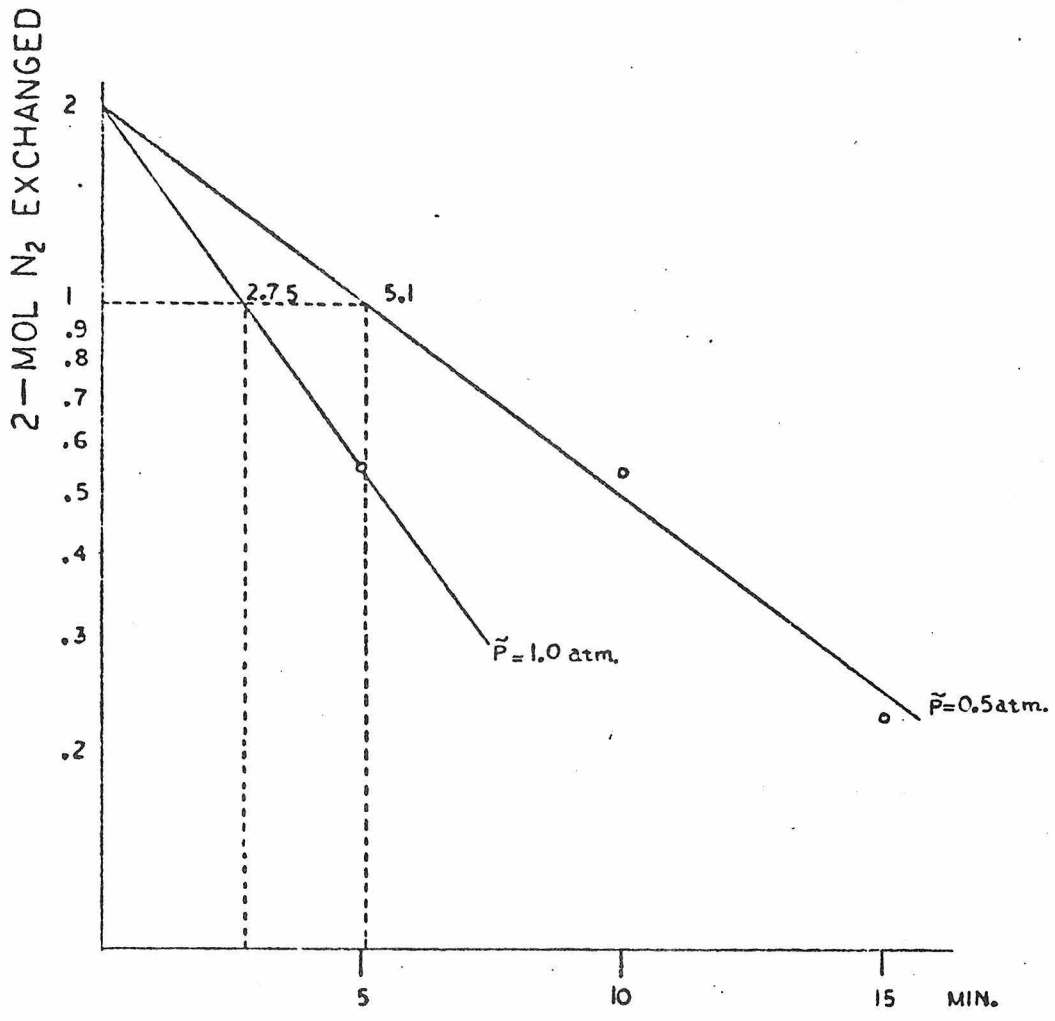
[b] Case 2. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + N_2^t + N_2^b + N_2^tH_4$

[c] Case 3. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + \frac{3}{2}N_2^t + \frac{1}{2}N_2^b + \frac{1}{2}N_2^tH_4 + \frac{1}{2}N_2^bH_4$

[d] Case 4. $[(C_5Me_5)_2Zr(N_2^t)]_2(N_2^b) + 4HCl \xrightarrow{100\%} 2(C_5Me_5)_2ZrCl_2 + \frac{4}{3}N_2^t + \frac{2}{3}N_2^b + \frac{2}{3}N_2^tH_4 + \frac{1}{3}N_2^bH_4$

[e] DCl substituted for HCl.

[f] No $^{15}N\equiv{}^{14}N$ was formed in reaction.



terminal N_2 exchange half-life for $\tilde{p}_{N_2}$ = 1 and 0.5 atm.

Appendix III.

The compound bis(pentamethylcyclopentadienyl) dimethyl zirconium (IV), $[C_5(CH_3)_5]_2Zr(CH_3)_2$ was prepared during this work, however as I have not done any chemistry with it, it does not fit in any place, and therefore its preparation and characterization is described here.

Preparation of $[C_5(CH_3)_5]_2Zr(CH_3)_2$. Pale yellow crystalline bis(pentamethylcyclopentadienyl) dichloro zirconium (IV) (1 gm, 2.31 mmol) was slurried in ~30 ml of diethyl ether at -80°. 2.3 M methyl lithium (2.5 ml, 5.75 mmol) in ether was syringed into the mixture, allowed to warm slowly to room temperature, and stirred for 3 hr. The mixture was then cooled to -80° and 1 ml of CH_3OH was added to destroy any excess methyl lithium. The ether and C CH_3OH were removed in vacuo and the white $[C_5(CH_3)_5]_2Zr(CH_3)_2$ was dissolved from the residue with ~60 ml petroleum ether and filtered off. The filtrate was cooled to -80°, and the white needles filtered off, dried in vacuo and stored under argon (yield c.a. 70-80%).

Anal. Calcd. for $C_{22}H_{36}Zr$: C, 67.50; H, 9.20; Zr, 23.30. Found: C, 67.33; H, 9.08; Zr, 23.52.

NMR (benzene-d_6) $[\eta^5-C_5(\underline{C}H_3)_5]$ s, δ 1.79 (30H); $Zr(\underline{C}H_3)_2$, s, δ -0.6 (6H).

Appendix IV.

Calculation for the Exchange of $(\eta^5\text{-}C_5Me_5)_2Z(H)_2CO$ with ^{13}CO Corresponding to Part II.

Composition of the ^{13}CO used for the exchange: $\chi_{28}=0.0908$, $\chi_{29}=0.8423$, $\chi_{30}=0.0082$, $\chi_{31}=0.0587$.

mmols of ^{13}CO used for the exchange: 1.2238 mmols

mmols $(C_5Me_5)_2Z(H_2)(CO)$ =0.2149

natural abundance ^{12}CO and ^{13}CO: $\chi_{28}=0.9889$, $\chi_{29}=0.0111$

Total CO for the exchange=mmols CO in carbonyl + CO added

=1.2238 mmols + 0.2149 mmol

=1.4387

mmols 28 in total CO = 1.2238 mmols×0.0908 + 0.2149 mmol× 0.9889 = 0.3236

mmols 29 in total CO = 1.2238 mmols×0.8423 + 0.2149 mmol× 0.0111 = 1.0332

mmols 30 in total CO = 1.2238 mmols×0.0082 = 0.0100

mmols 31 in total CO = 1.2238 mmols×0.0587 = 0.0718

Therefore the predicted composition for complete exchange is:

28 = 0.3236/1.4387 = 0.2249

29 = 1.0332/1.4387 = 0.7181

30 = 0.0100/1.4387 = 0.0070

31 = 0.0718/1.4387 = 0.0499

The observed composition was: $\chi_{28} = 0.1271$, $\chi_{29} = 0.8079$, $\chi_{30} = 0.0089$, $\chi_{31} = 0.0560$.

Thus the amount of CO exchanged was:

CO exchanged/mmol $(C_5Me_5)_2Z(H_2)(CO)$ =

$$\frac{0.1271 - 0.0908}{0.2249 - 0.0908} = \frac{0.0363}{0.1341} = 0.2707$$

Proposition I.

Synthesis and Chemistry of Organometallic Compounds of the Actinides in Low Oxidation States

The actinide elements comprising elements actinium (Z = 89) through Lawrencium (Z = 103), derive their unique properties, like the lanthanides, from the filling of an inner electronic level, in this case the 5f shell.

Although the actinide elements have been the subject of considerable research by metallurgists and coordination chemists over the past 20 years, the organometallic chemistry of the actinides has been largely ignored.

Interest in organoactinide chemistry and in the elucidation of the role of the 5f orbitals in the bonding of these compounds did not fully awaken until the report by Streitwiesser and Müller-Westerhoff of the bis(cyclooctatetraenyl) uranium (IV), "uranocene",[1,2] an authentic sandwich complex of the 5f series.

While these elements show general trends analogous to those observed in the lanthanides series, their chemistry is more complicated as a result of the fact that the 5f orbitals have a greater spatial extension relative to the 6s and 6p orbitals than the 4f orbitals have relative to the 5s and the 5p orbitals. Another difference is that for elements in the first half of the period, less energy is required for the promotion of the 5f → 6d than for 5f → 5d promotion in the lanthanides. Thus we have a situation in which the energies of the 5f, 6d, 7s, and 7p orbitals are

comparable, and since the orbitals also overlap spatially, bonding can involve any or all of them. Experimentally this situation is indicated by the fact that the actinides have an enhanced tendency for covalent bonding when compared to the lanthanides, where the bonding is almost exclusively ionic.

At present the majority of organoactinides which have been reported contain the cyclopentadienyl group. Organoactinides which contain the cyclopentadienyl group are of three types, $(\pi - C_5H_5)_3MR$ where R = OC_4H_9, OCH_3, Cl, Br, I, alkyl, allyl, aryl, BH_4, acetylenes and M = U,Th; $(\pi - C_5H_5)_4M$ where M = U,Th,Pa, Np; and $(\pi - C_5H_5)_3M$ where M = Pu, Am, Cm, Bk, and Cf.[3,4,5]

The corresponding $(\pi - C_5H_5)_2MCl_2$, which form the basis of much Ti, Zr, and Hf organometallic chemistry have not been prepared. It has been found recently that $(\pi - C_5H_5)_2UCl_2$ in solution is actually a mixture involving $(\pi - C_5H_5)_3UCl$ and solvated $(\pi - C_5H_5)UCl_3$.[6] One approach to avoid this ligand redistribution which has been attempted recently, is joining the cyclopentadienyl rings.[7]

Here it is proposed to avoid the above ligand redistribution by the use of bulky substituents on the cyclopentadienyl ligand, (for example $C_5(CH_3)_5$ and $C_5(C_6H_5)_5$), since for steric reasons the corresponding $(\pi - C_5R_5)_3MCl$ where M = U, Th or other actinide and R = CH_3, C_6H_5 could not be formed.

If is proves possible to prepare $(C_5R_5)_2MCl_2$ (where R =

CH_3, C_6H_5 and M = actinide), we could potentially develop a whole new organometallic chemistry since these complexes could be the starting materials to complexes of the type $(C_5R_5)_2M$ and $(C_5R_5)_2MLn$ (where L = alkene, alkyne, NO, CO, H, N_2, Phosphines, etc.), and the bonding characteristics, reactivity patterns and the influence of the 5f orbitals on these properties could be studied.

The above complexes could be synthesized either by the standard procedures, that is, treatment of the respective tetrachloride with the Li or Na salt of the ligands (see footnote)* or by metal atom deposition, in which case the respective $(\eta^5\text{-}C_5R_5)_2MH_2$ could be obtained directly as in equation 1.

$$2\ C_5R_5H + M \rightarrow (\pi\text{-}C_5R_5)_2MH_2 \qquad (1)$$

Metal atom deposition has been used successfully in the preparation of other sandwich-hydrides compounds, thus for example $(C_5H_5)_2MH_2$ (M = Mo, W) is formed in the reaction of cyclopentadiene with molibdenum and tungsten atoms.[9]

The dichloride could be obtained from the dihydride by reaction with HCl.

Reduction of the dichlorides could afford $(\pi\text{-}C_5R_5)_2M$ (M = actinide), which in the presence of the respective L could

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* Although $C_5(C_6H_5)_5H$ has been reported before[8] the Li or Na salt has not been prepared, but it seems quite likely that treatment of the ligand with Na or $Na(NH_2)$ should give the sodium salt and treatment with n-butyl lithium the lithium salt.

form $(\pi - C_5R_5)_2MLn$.

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Proposition II.

Reductions at low temperatures

Inorganic or organometallic compounds in higher oxidation states are in general the most frequently used starting materials to obtain organometallic compounds in low oxidation states. The usual way to accomplish that is by the use of a reducing agent like Na, Na/Hg, Zn, Zn/Hg, Al, Mg, etc., at 0° or higher temperature. Although this method in general works very well for the synthesis of a large number of organometallics, there are several examples where either the yield is low or the reduction do not work.

One of the most frequent reasons for the failure of the above method results from the fact that at the temperature at which the reduction is carried out there are one or more accessible secondary reaction pathways to more stable forms for the reduced species.

As a typical, familiar example, which is valid for other transition metal organometallic compounds, consider the reduction of the bis (pentamethylcyclopentadienyl) metal dichlorides of the group IV (M=Ti, Zr, and Hf).

The synthesis of the complex $[(C_5Me_5)_2Ti]_2N_2$ can not be carried out in a similar way to $[(C_5Me_5)_2ZrN_2]_2N_2$ (reduction of the dichloride with Na/Hg under N_2) since for titanium the major species isolated is the thermal decomposition product, $[(C_5(CH_3)_5][C_5(CH_3)_4CH_2]Ti$, and an indirect route must be used.[1]

Although the metallocene $(C_5Me_5)_2Ti$ can be isolated, the analogous $(C_5Me_5)_2Zr$ can not due to the rearrangement to a more stable form $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]ZrH$.

Reduction of $(C_5Me_5)_2HfCl_2$ under identical conditions to the Zr analog does not yield a dinitrogen complex, and the probable reason is rearrangement to $[(C_5(CH_3)_5][C_5(CH_3)_4CH_2]HfH$, which does not reverse to $(C_5Me_5)_2Hf$ as with Zr. We have observed that reduction at low temperature $\sim -40^\circ$ with Na/Naphthalene yields a dinitrogen complex.

In order to avoid these "thermal side reactions" it is proposed to develop a method to carry out reductions at low temperatures. Low temperature reductions could be useful not only in the preparation of organometallics which are not accessible by normal routes, but also could be used as a way to increase the yield in the preparation of many other compounds.

At present low temperature reductions make use of the solubility of the alkaline metals in crown ethers or in the presence of naphthalene in solvents like THF, $(CH_3)_2O$, and glyme.

Several disadvantages can be seen with the above methods. There are severe limits on solvents to be used (some organometallics reacts with oxygen-solvents or coordinate) and in the case of the sodium naphthalene there can be, besides reaction of the reduced species with the naphthalene, a problem in the separation of the product.

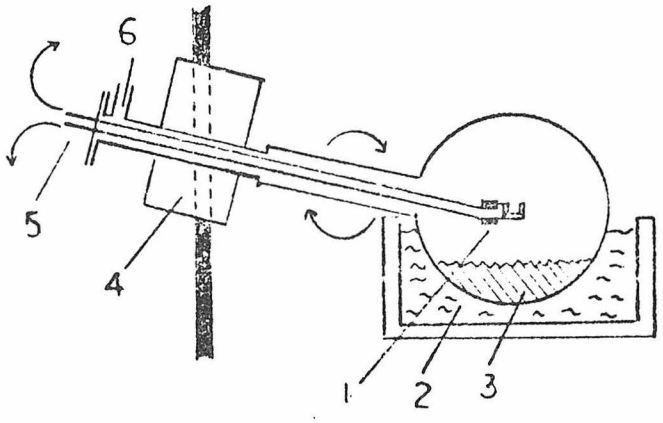
Here, it is proposed to perform reductions in solution at

low temperatures by atomic species such as Li, Na, K, Mg, or Zn by metal atom deposition.

On the one hand, reductions by atomic species could be extremely fast even at low temperatures since an atomic species has minimal steric requirements, readily available electrons or orbitals, and the atomic species is of higher energy than the normal state of the element.

On the other hand, a large number of inert solvents could be chosen, the product could be isolated easily from the salt by choosing a solvent where one species is insoluble. Finally there are no practical difficulties in vaporizing the metals mentioned, all of them vaporize at a temperature $<1000°$.

The reductions at low temperature could be easily done in an apparatus such as the one described by P. L. Timms[2] and shown in the figure.



1, evaporating metal; 2, cooling bath; 3, substrate solution; 4, rotary drive mechanism; 5, water and electrical power; 6, high vacuum.

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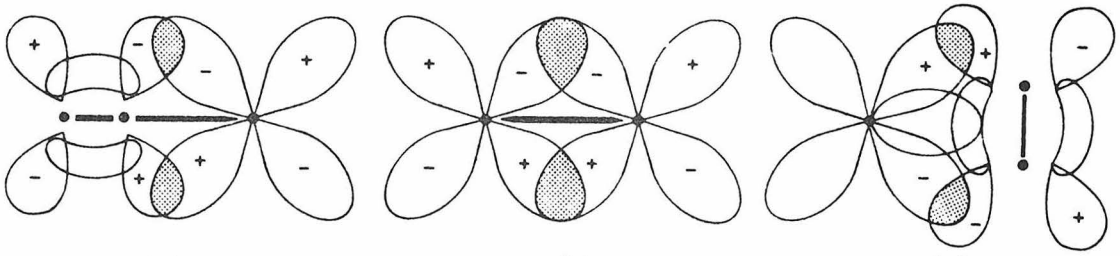
Proposition III.

P_2 as a Potential π-acid and/or σ donor Ligand

One of the main characteristics of the d-group transition metals is their ability to form complexes with a variety of neutral molecules such as N_2, CO, isocyanides, phosphines, arsines, etc. It is a characteristic of these ligands that they can stabilize low oxidation states, this property being associated with the fact that these ligands possess vacant π orbitals in addition to lone pairs.

These vacant π orbitals accept electron density from filled metal orbitals to form a type of π-bonding that complements the σ-bonding arising from the lone pair donation.

Of the various orbitals which can overlap to form a π-bond, the $d\pi$-$d\pi$ overlap (a), the $d\pi$-π_π^* (b), and the $d\pi$-$\pi_{\pi_u}^*$ (c), are generally considered.



(a) (b) (c)

(CO, N_2) (phosphines, arsines) (alkenes, alkynes)

Among the most common ligands in compounds of metals in low oxidation states, the phosphines (arsines) and CO occupy an important place.

The above picture has stimulated considerable research to

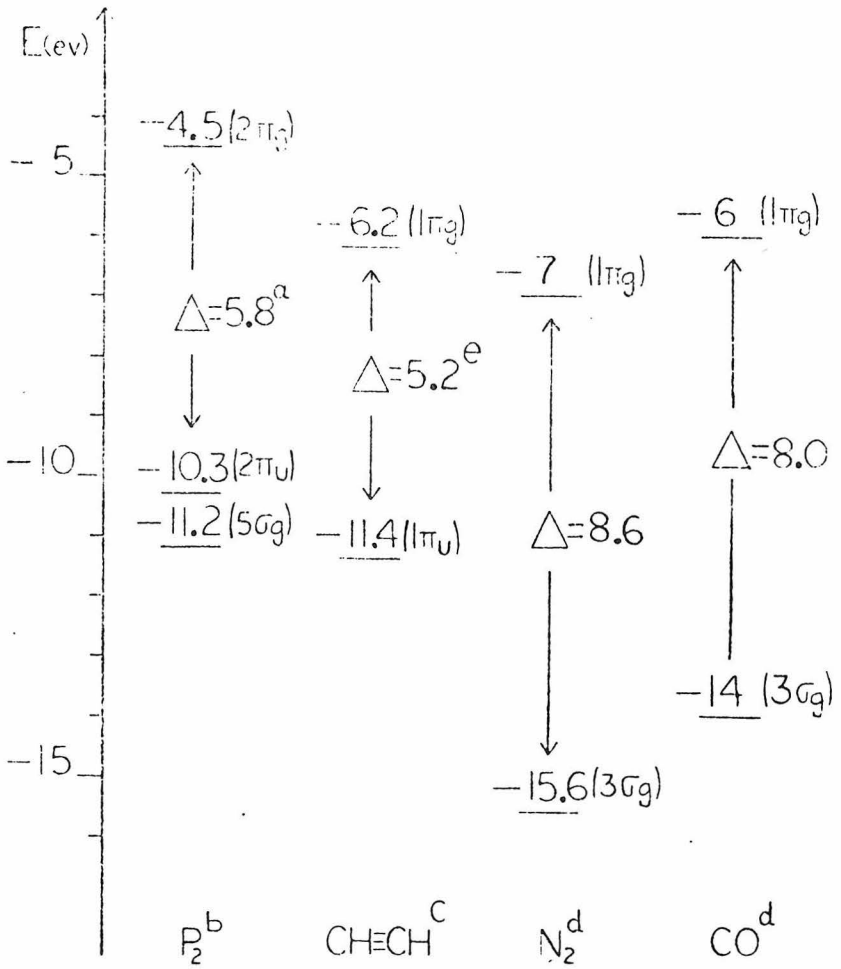
find an experimental proof of back donation, and although the existence of π- back donation in specific cases like CO, N_2, and PF_3 is generally accepted, direct proof for the π- back donation has not been achieved.

Where much discussion has surged the existence of π- back bonding as in the case of the phosphines (arsines), alkenes, and alkynes. What is proposed here is to attempt, on the one hand, to increase the number of examples of π-acid ligands from which (by comparison with the known examples) some additional information could be gained, and, on the other hand, to possibly obtain some interesting chemistry.

The P_2 molecule is formed by heating the vapor of phosphorous. This consists of P_4 molecules up to about 800°, and above that temperature begins to dissociate into P_2 molecules. At 1700° the vapor consists of a mixture of about equal amounts of P_4 and P_2 molecules. Its dissociation energy is 117 kcal/mole, that is about $\frac{1}{2}$ that of N_2 (225).

The ground state configuration, together with the energy level diagram of the two highest occupied and the lowest unoccupied orbitals is given on the next page. The π - acid ligands HC≡CH, N_2, and CO have also been included for comparison.

From the energy levels we can see a large similarity between P_2 and the alkynes. The two highest occupied orbitals for the P_2 molecule ($5\sigma g$, -11.2 eV and $2\pi u$, - 10.3 eV) poses energies comparable with those of the d orbitals of metal complexes and on



Energy level of the highest occupied and lowest unoccupied orbitals for P_2, $CH{\equiv}CH$, N_2, and CO.

The ground state configuration for these molecules is:

$P_2=(1\sigma g)^2(1\sigma u)^2(2\sigma g)^2(2\sigma u)^2(3\sigma g)^2(1\pi u)^4(1\pi g)^4(3\sigma u)^2(4\sigma u)^2(5\sigma g)^2(2\pi u)^4$

$CH{\equiv}CH=(1\sigma g)^2(1\sigma u)^2(2\sigma g)^2(2\sigma u)^2(3\sigma g)^2(1\pi u)^4$

$N_2=(1\sigma g)^2(1\sigma u)^2(2\sigma g)^2(2\sigma u)^2(1\pi u)^4(3\sigma g)^2$

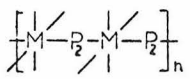
$CO=(1\sigma g)^2(1\sigma u)^2(2\sigma g)^2(2\sigma u)^2(1\pi u)^4(3\sigma g)^2$

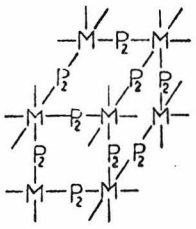
---

[a] obtained from the experimental observed transition in reference 2. [b] from reference 3. [c] from reference 4. [d] taken from reference 5. [e] taken from reference 6.

this basis we can predict that edge-on and end-on complexes could be formed. Another interesting property of the P_2 molecule is that, in the same way as N_2 or C_2H_2 it could serve as a bridging ligand.

If stable complexes could be obtained of P_2, as a bridging ligand could form an interesting class of "clusters" or inorganic polymers as shown below.





A weak point of the P_2 molecule is the fact that its dissociation energy is low, this could present problems if a technique like cocondensation of the metal atom with the P_2 molecule is used, since formation of a phosphide might take place, however this could be avoided for example by the use of a ligand displacement reaction like:

$$MLn + P_2 \xrightarrow{(h\nu)?} MLn\text{-}1\ P_2 + L$$

where MLn represents a transition metal complex in low oxidation state.

In case of success this would open the possibility of investigating other diatomic molecules of the nitrogen family which have

a reasonable dissociation energy like AsN, As_2, and PAs.

Although it has been mentioned indirectly, by the nature of the P_2 molecule, it is obvious that a technique similar to the metal atom deposition or in case that unstable compounds are obtained matrix isolation must be used.

It should be mentioned at this point, that during the search of the literature for this proposition, which at the beginning was going to include the PN molecule, it was found that P. L. Timms[1] in a recent publication mentions the reaction of Ni and Ag atoms with PN molecules and AgPN and nickel-PN complexes are formed.

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Proposition IV.

Chemistry of transition metal oxides, molecular species

Oxides range from essentially ionic compounds of the more electropositive elements to the molecular oxides of the non-metals. For a given element which forms several oxides, the oxide with the element in the lowest formal oxidation state is in general more ionic.

The formation of an ionic oxide requires the expenditure of considerable energy. On the one hand, we have the energy expended in vaporizing and ionizing the metal atoms and on the other hand, the energy expended in the formation of the oxide ion.

$$\tfrac{1}{2} O_2 (g) \rightarrow O (g) \quad \Delta H = 248 \text{ k J mol}^{-1}$$

$$O (g) + 2e \rightarrow O^{2-} (g) \quad \Delta H = 752 \text{ k J mol}^{-1}$$

Nevertheless, many essentially ionic oxides exist and are very stable because the energies of lattices containing the double charged oxide ion are quite high.[1]

Metal oxides are used in a number of heterogeneous catalytic processes, for example: Fisher-Tropsch, cyclization and aromatization of hydrocarbons, hydrogenation of aromatic compounds etc.; however, the mechanism of the catalysis is not known. Modern trends favor models in which catalytic activity is attributed to the surface coordinative insaturation rather than to the collective properties of the solid.[2] In this sense molecular species of metal

oxides offer the maximum possible coordinative unsaturation and the study of the chemistry of these molecular species could be useful to our understanding of the mechanism and improvement of the present catalysts.

As a consequence of the lack of stabilizing lattice energy of the oxide ion and a generation of a coordinatively unsaturated molecule, molecular species of transition metal oxides can be expected to show quite different properties from that in the crystal.

Here it is proposed to study the reactivity of different transition metal oxides as molecular species with substrates such as π-acid ligands and H_2.

There are several articles in the literature where the techniques used for the generation and low temperature condensation of high temperature species is described.[3,4,5] A short summary of those appropriate to this proposition are given here.

Generation: Metal oxides, as molecular species, are generated in the so called "containerless methods". The essential feature of these methods is the introduction of energy in such a way that the material to be evaporated is in contact only with the cooler portions of itself or with a water cooled-metal surface with which it will not react. The most widely used containerless method for high vacuum evaporation is electron bombardment heating using a focused electron beam. An intense

beam of electrons striking any solid surface will cause local heating and then evaporation. A scheme of a typical apparatus is given on the next page.

Condensation: There are three main ways in which atomic or molecular species can be brought into contact with another compound on a cold surface.

a) The species and a compound with which it may react are cocondensed, i.e., condensed simultaneously on the cold surface.

b) The species and at least a hundred fold excess of an inert gas are cocondensed on the cold surface, to isolate the species in an inert matrix. A compound which it may react with the species is then condensed in the matrix and is allowed to diffuse into the matrix on warming.

c) The species is condensed onto a cold sample of a potentially reactive compound in a solid, liquid,or solution form.

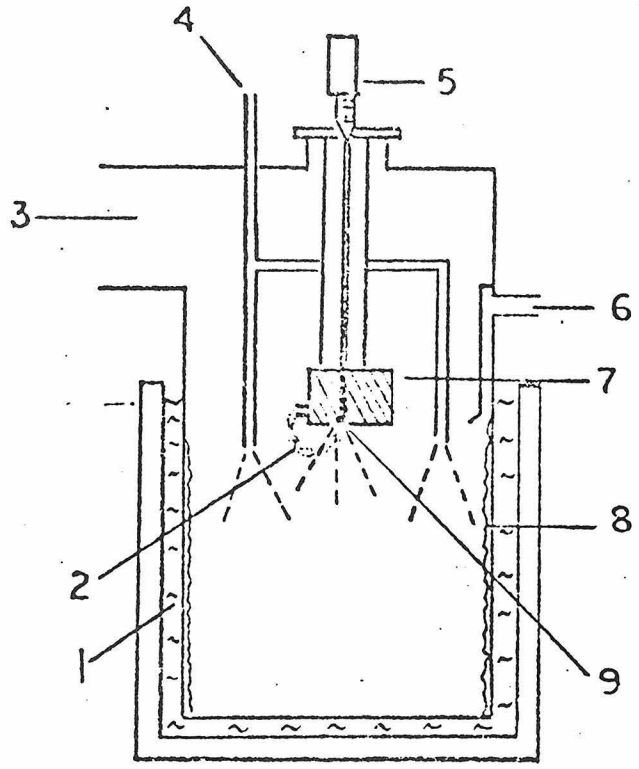
If the matrix is connected with a spectrometer, information about bonding, molecular geometry, and reaction pathway can be obtained.

As an example of a possible reaction which could be studied let' s take for example ZrO_2, one of the ingredients in some of the Fisher-Tropsch catalysts.

$$ZrO_2 + CO \overset{?}{\rightarrow} ZrO_2(CO)_n \xrightarrow{+H_2} ?$$

or

$$ZrO_2 + H_2 \overset{?}{\rightarrow} H_2Zr\begin{matrix}O\\|\\O\end{matrix} \overset{?}{\rightarrow} Zr\begin{matrix}OH\\\\OH\end{matrix}$$



Electron bombardment vaporization apparatus.

1. liquid nitrogen. 2. electron beam. 3. pumping line. 4. cocondensation gas. 5. sample feed mechanism. 6. product pump-out. 7. electron gun. 8. cocondensate. 9. sample.

It could be interesting if these oxides species after reaction with phosphines, alkines, etc., remained stable to polymerization on warming and could be isolated as stable species.

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Proposition V.

Electronegativity of "Organometallic Groups"

Electronegativity was first defined by Pauling as: The power of an atom in a molecule to attract electrons to itself. He based his electronegativity scale on thermochemical data. It had been observed that bonds between dissimilar atoms were almost always stronger than might have been expected from the strength of bonds of the same elements when bonded in homonuclear bonds.

Pauling suggested that molecules formed from atoms of different electronegativity would be stabilized by ionic resonance energy resulting from resonance of the sort:

$$\psi_{AB} = \psi_{A-B} + \psi_{A^+-B^-} + \psi_{A^--B^+}$$

Although electronegativity as defined by Pauling is an invariant property of the atoms, it actually depends upon the valence state of the atom in the molecule. Two factors determine the attraction of atoms for electrons, the charge on the atom and the hybridization of the atom. An atom which has achieved a positive charge will tend to attract electrons to it more readily than will a neutral atom. In turn a negatively charged atom will attract electrons less than a neutral atom. Hybridization affects electronegativity because of the lower energy and hence greater electron attracting power of s orbitals. The experimental evidence for the importance of hybridization and partial charge is ample and many workers have attempted to improve electronegativity theory to include these factors.

Of the various systems, which we can call "theoretical" since they are based only on the fundamental energies of isolated atoms, the Mulliken-Jaffe' system is the more satisfying. In this system the electronegativity is expressed as a function not only of hybridization, but also of charge. For a given hybridization the electronegativity (or orbital electronegativity) is given as a linear function of the partial charge on an atom, $\chi = a + b\delta$ where χ = orbital electronegativity and δ = partial charge. The parameter a is the inherent or neutral atom electronegativity. This is the electronegativity as estimated by the Mulliken method (based on ionization energy and electron affinity) or other similar estimates. The parameter b is termed the charge coefficient and measures the rate of change of electronegativity with charge.

An extension of the "orbital electronegativity" was the introduction of the concept of "group orbital electronegativity". This was introduced as a necessity to obtain electronegativities not only, for example, of a tetrahedral carbon atom, but of the group X_3C with respect to an atom Y with which it forms a bond in the compound X_3CY. A simple way to calculate "group electronegativity" is by making use of the "electronegativity equalization".[1]

The electronegativity equalization concept suggested by Anderson[2] states that when a bond forms between two atoms, electron density will shift from one to the other until the electronegativities have become equalized.

In terms of Mulliken-Jaffe electronegativity values, the

electronegativity equalization is written as:

$$\chi_A = a_A + b_A\delta_A = \chi_B = a_B - b_B\delta_B$$

For the illustration of the calculation of the group electronegativity, the methyl group will be used as an example. The theoretical justification for the equations is given in reference 3. The electronegativity of this group is not that of unbonded tetrahedral carbon (χCte) per se, but the adjusted electronegativity of a carbon atom in the environment of three hydrogen substituents. The calculation involves the following steps.

a) Calculation of the charge distribution and resultant adjusted electronegativity of a neutral methyl group (radical).

$$\chi\text{Cte} = a_C + b_C\delta_C = \chi_H = a_H + b_H\delta_H$$
$$\delta_C + 3\delta_H = 0$$

taking the values of a_C, b_C, a_H, and b_H from tables gives:

$$\chi\text{Cte} = 7.97 + 13.27\delta_C = \chi_H = 7.17 + 12.85\delta_H$$
$$\delta_C + 3\delta_H = 0$$
$$7.97 - 3(13.27)\delta_H = 7.17 + 12.85\delta_H$$
$$\delta_H = \frac{0.80}{52.66} = 0.015$$
$$\chi_{CH_3} = 7.97 - 3\times13.27\times0.015 = 7.37 = a_{CH_3}$$

b) Calculation of the charge distribution of either the methyl cation or the methanide anion. For the methyl cation, the same equations hold except that

$$\delta_C + 3\delta_H = 1$$

Solving, we get $\delta_H = +0.27$

$$\chi_{CH_3^+} = 10.63$$

Similarly for the methanide ion we get

$$\delta_H = -0.24$$

$$\chi_{CH_3^-} = 4.05$$

straight line when plotted vs charge, and we can get the slope of that line to give

$$\chi_{CH_3} = 7.37 + 3.24\delta_{CH_3}$$

The above calculation can be trivially extended to more general cases, thus for example for the group $W\text{-}\overset{X}{\underset{Z}{Y}}$ using the equations

$$a_W + b_W\delta_W = a_X + b_X\delta_X = a_Y + b_Y\delta_Y = a_Z + b_Z\delta_Z$$

$$\delta_W + \delta_X + \delta_Y + \delta_Z = 0 \text{ (neutral)}$$

$$\delta_W + \delta_X + \delta_Y + \delta_Z = +1 \text{ (cation)}$$

$$\delta_W + \delta_X + \delta_Y + \delta_Z = -1 \text{ (anion)}$$

we obtain

$$\chi_{WXYZ} = \frac{a_W b_X b_Y b_Z + a_X b_W b_Y b_Z + a_Y b_W b_X b_Z + a_Z b_W b_X b_Y + b_W b_X b_Y b_Z \delta_{WXYZ}}{b_X b_Y b_W + b_X b_Z b_W + b_X b_Y b_Z + b_Y b_Z b_W}$$

and so on.

Because of the variation of electronegativity with charge, single electronegativity values have little inherent value. This is especially true for groups. The Pauling unit values (the "inherent" electronegativity) are useful in the following context. If two groups or atoms have the same inherent electronegativity, they will form a covalent bond. If they do not have identical values, the relative

values of a determine the direction of bond polarity, but it is necessary to utilize both a and b to determine how polar a particular bond will be. One big disadvantage of the Mulliken-Jaffé system stems from its specificity: one must know the proper hybridization. Although for non-transition metals the hybridization can be generally inferred from bond angles for transition metals, there is no unambiguous method of choosing the proper hybridization (for example both sp^3 and sd^3 give tetrahedral hybrids, but differ greatly in electronegativity).

The empirical methods have an advantage here resulting from their indirect derivation, since variables such as hybridization are often "built-in" as long as the atom under consideration is in a fairly typical environment.

The terms electropositive and electronegative (or electron density) is widely used in Organometallic chemistry to explain a variety of phenomena. However there is no form to predict, for example, if the hydride in Cp_2WH_2 is more hydridic than in $Cp_2Ti(H)(Cl)$. The bis(cyclopentadienyl) transition metal moiety has a very extensive organometallic chemistry, and for a given bis(cyclopentadienyl) transition metal, a large variety of derivatives of the type Cp_2MXnYn (where X, Y = H, R, Cl, etc.) have been prepared. It would be extremely useful to be able to predict the rank order (not quantitatively) of group polarities for different Cp_2M transition metal derivatives. I propose to consider the Cp_2M unit as a group and to calculate the "group orbital electronegativity"

of the Cp_2M unit. As mentioned before the Cp_2M unit forms part of a large number of organometallic derivatives and for similar compounds such as Cp_2MH_2, $Cp_2M(CH_3)_2$ etc., it seems reasonable that the hybridization will not be too different.

The "group orbital electronegativity" of the Cp_2M unit could be obtained as follows:

$$\chi_{Cp_2M} = a_{Cp_2M} + b_{Cp_2M}\delta_{Cp_2M}$$

Suppose we have two derivatives of the Cp_2M, such as Cp_2MF_2 and Cp_2MCl_2. The following equations are obtained from electronegativity equalization:

$$\chi_{Cp_2M} = a_{Cp_2M} + b_{Cp_2M}\delta_{Cp_2M} = \chi_F = a_F + b_F\delta_F$$

$$\delta_{Cp_2M} + 2\,\delta_F = 0$$

The same is valid for Cp_2MCl_2.

If we calculate δ_F and δ_{Cl} from ESCA, this will give us 2 equations with two unknowns, a_{Cp_2M} and b_{Cp_2M}, and the value of these two parameters can be determinated.

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