SYNTHETIC AND STRUCTURAL INVESTIGATIONS OF DINITROGEN, CARBONYL, OLEFIN, DICHLORIDE, AND HYDRIDE DERIVATIVES OF BIS(PENTAMETHYL-CYCLOPENTADIENYL)TITANIUM AND ZIRCONIUM

Thesis by

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This thesis is dedicated
to the memory of my colleague
and best friend

Robert Alan Stalzer
1949-1976

Through his words and deeds he taught me
the value of elegance. I miss him deeply.

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I found this section extremely painful to write because implied in its writing was the realization that I'll soon be leaving everyone and everything I've learned to love these past four years. However, saving the sentimentality for what is to follow, I'll merely quote Roger McGuinn: "I trust everything will turn out all right."

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ABSTRACT

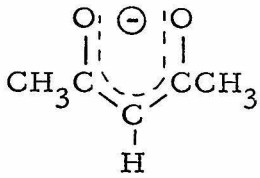
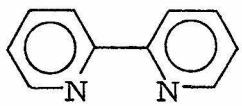
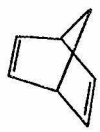
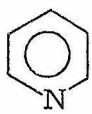
The crystal structures of three compounds containing the $(\eta^5\text{-}C_5Me_5)_2M$ (M = Ti, Zr) moiety have been determined by single crystal X-ray diffraction methods. $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ has a distorted tetrahedral configuration about titanium comprised of the two chlorine atoms and the centroids of the two $\eta^5\text{-}C_5Me_5$ rings. Several ring methyl groups are bent considerably out of the cyclopentadienyl plane away from titanium due to chlorine methyl and inter-ring methyl-methyl crowding. The final R factor was 0.032. The structure of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ consists of two $(\eta^5\text{-}C_5Me_5)_2Ti$ moieties bridged by N_2 in a linear Ti–N≡N–Ti arrangement. The final R index was 0.058. A qualitative molecular orbital treatment of the bonding consistent with the structure is presented. The structure of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ consists of two $(\eta^5\text{-}C_5Me_5)_2ZrN_2$ subunits bridged by a third dinitrogen ligand. Terminal and bridging dinitrogen ligands are bound end-on to zirconium with essentially linear Zr–N≡N and Zr–N≡N–Zr arrangements. The final R factor was 0.035. A qualitative picture of the zirconium-dinitrogen bonding consistent with the structure and other physical properties of the compound is presented.

The synthesis and characterization of the zirconacyclopentanes $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHR)_2CH_2)$, R = H, Me, Et is described. These compounds are prepared from $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (1) and ethylene, propylene, or 1-butene. The stereochemistry at the β,β' positions is found to be trans. The synthesis and characterization of

the fused ring metallocycles $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH(CH_2)_nCHCH_2)$, n = 3 or 4 is also described. These compounds were prepared from 1 and 1,6-heptadiene or 1,7-octadiene. A mixture of cis and trans β,β' isomers was found in both compounds. Reaction of 1 and cis or trans-2-butene gives $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^3\text{-}C_4H_7)$ which may be converted to $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHEt)_2CH_2)$ upon heating with excess olefin and a mechanistic scheme which accounts for this interconversion is presented.

Reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ with H_2 gives $(\eta^5\text{-}C_5Me_5)_2$-$Zr(H)(OCH_3)$. The synthesis and characterization of $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OC=CH(CHR)_2CH_2)$, R = H, Me, Et made from the zirconacyclopentanes and CO is presented. These enolate hydrides may be converted to their respective ketone upon treatment with HCl. The stereochemistry at the β,β' positions in the metallocycle is maintained in the formation of the enolate hydride. The formation of the enolate hydride complexes is shown to be consistent with the existence of an "oxycarbene" intermediate caused by the unusual "side-on" coordination of the acyl or formyl group. This intermediate may insert into Zr–C or Zr–H bonds followed by further rearrangement to products.

Abbreviations Used in This Thesis

Acac	 (Acetylacetonate)
bipy	 (bipyridine)
COD	1,5-cyclooctadiene
Cp	η^5-C_5H_5 (cyclopentadienyl)
diphos	$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$
Et	$-CH_2CH_3$
Me	$-CH_3$
NBD	 (norbornadiene)
Ph	$-C_6H_5$ (phenyl)
py	 (pyridine)

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CHAPTER I*

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(PENTAMETHYLCYCLOPENTADIENYL)-DICHLOROTITANIUM(IV)

Introduction

Reaction systems derived from the electron-deficient sandwich compound dicyclopentadienyltitanium(II), $(\eta\text{-}C_5H_5)_2Ti$ are of current interest, especially in connection with the fixation and reduction of dinitrogen.[1-3] Efforts toward the isolation and characterization of low-valent titanocene derivatives from these systems are often thwarted, however, owing to side reactions involving rearrangement to titanium hydride species via a ring-to-titanium α-hydrogen shift.[1,4-6] In view of these complicating features inherent in $(\eta\text{-}C_5H_5)_2Ti$ based systems, we have more recently investigated the closely related bis(cyclopentadienyl)titanium(II) derivative, $[\eta\text{-}C_5(CH_3)_5]_2Ti$, and its behavior toward N_2.[7,8]

While the chemistry of $[\eta\text{-}C_5(CH_3)_5]_2Ti$ and $(\eta\text{-}C_5H_5)_2Ti$ derivatives are in many respects quite similar, we have noted a definite preference for monomeric $[\eta\text{-}C_5(CH_3)_5]_2Ti$ derivatives,[1,8] apparently as a result of steric crowding of bulky $[\eta\text{-}C_5(CH_3)_5]$ rings in dimeric or polymeric species. Furthermore, a recent structure determination of $[\eta\text{-}C_5(CH_3)_5](\eta\text{-}C_5H_5)TiCl_2$ shows ring

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*This chapter has been published previously. See T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, J. Organometal. Chem., 102, 457 (1975).

methyl groups to be pushed out of the plane of the ring carbons, apparently as a result of intramolecular $(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CH_3)_5]$ crowding.[9] In order to establish the extent of such crowding in a complex containing two $[\eta\text{-}C_5(CH_3)_5]$ rings and to provide a basis for interpreting the structures of $[\{\eta\text{-}C_5(CH_3)_5\}_2M]_2(N_2)_n$ (M = Ti, n = 1; M = Zr, n = 3) presently under investigation, we have undertaken an X-ray structure determination of $[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$.

Experimental

$[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$ was prepared as described previously[8] and obtained as dark purple-brown needles from chloroform. A series of Weissenberg and precession photographs (taken with Cu-K_α and Mo-K_α radiation) indicated an orthorhombic unit cell of space group $P2_12_12_1$ (systematic absences: h00, h odd; 0k0, k odd; 00ℓ, ℓ odd). Unit cell dimensions were obtained by a least-squares fit to the observed $\sin^2\theta/\lambda^2$ values for 29 reflections measured on a diffractometer. The density was measured by flotation in aqueous zinc chloride/HCl solution. Crystal data are given in Table 1.

A crystal (elongated along its b axis) was mounted with its b axis slightly skew to the φ axis of a G.E. XRD-5 quarter-circle diffractometer automated by Datex. Using Mo-K_α radiation monochromated with a graphite crystal, one octant of intensity data was measured between 4° and 45° in 2θ (corresponding to a spacing of 0.93 Å) employing the θ-2θ step scan technique. A scan rate of 1°/min and scan width of 1.75° were selected, and 30-sec background counts were taken before and after each scan. Intensities

of three check reflections measured every 45 reflections showed no crystal decomposition during the data collection. A variance $\sigma^2(I)$ was calculated for each reflection based on counting statistics and a term in $(0.02S)^2$, where S is the scan count. Intensities and their variances were corrected for Lorentz and polarization effects but not for absorption ($\mu = 7.2$ cm^{-1}). The data were then placed on an absolute scale by means of a Wilson plot.[10] Scattering factors for all atoms were calculated by the method of Cromer and Mann.[11] The intensities of 1516 reflections were collected; 20 were deleted as systematic absences, 66 were given zero weight and zero structure factor since for these $F < \sigma(F)$, and one reflection (102) exceeded the counter capacity and was accordingly given a structure factor and weight of zero.

Solution and Refinement

The remaining 1429 reflections were used to generate a three-dimensional sharpened Patterson map from which the titanium and two chlorine atoms were located. Structure factors calculated using these positions yielded an R index ($\Sigma \| F_o | - | F_c \| / \Sigma | F_o |$) of 0.39. Two successive structure factor calculations interspersed with Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Refinement was by least-squares minimization of the quantity $\Sigma \omega | F_o^2 - s^2 F_c^2 |^2$, where $1/s$ is the scale factor for F_o and $w = 1/\sigma^2(F_o)^2$. In the initial least-squares cycles, positions of all nonhydrogen atoms, isotropic temperature factors for the carbon atoms, and anisotropic temperature factors for titanium and

chlorine atoms were refined to an R index of 0.074. At this point a difference Fourier was generated from which all 30 hydrogen atoms were located. The titanium and chlorine atoms were then treated as anomalous scatterers using values from the "International Tables,"[12] and final full matrix least-squares refinement was performed using two matrices, one containing hydrogen coordinates, the scale factor, and anisotropic temperature factors for all nonhydrogen atoms, the other containing nonhydrogen positional parameters. Isotropic thermal parameters for the hydrogen atoms were set approximately 1 $Å^2$ larger than those for their respective carbon atoms, but these hydrogen thermal parameters were not refined.

The final R index was 0.032 and the goodness of fit, $[\Sigma\omega(F_o^2 - s^2F_c^2)/(N - P)]^{\frac{1}{2}}$ was 1.53 for N = 1429 reflections and P = 298 parameters.[13] All crystallographic computations were performed under the CRYM system with an IBM 370/155 computer. Final parameters are shown in Tables 2 and 3.

Results and Discussion

The molecular configuration of $[C_5(CH_3)_5]_2TiCl_2$ is given in Figure 1, a stereoscopic view in Figure 2, and the packing of molecules in the unit cell is shown in Figure 3. The geometry about the titanium atom may be viewed as a distorted tetrahedral configuration with centroid-Ti-centroid and Cl-Ti-Cl angles of 137.4(1)° and 92.94(4)°, respectively. The two π-bonded rings are staggered with centroid-Ti distances of 2.13 Å and an average Ti-C

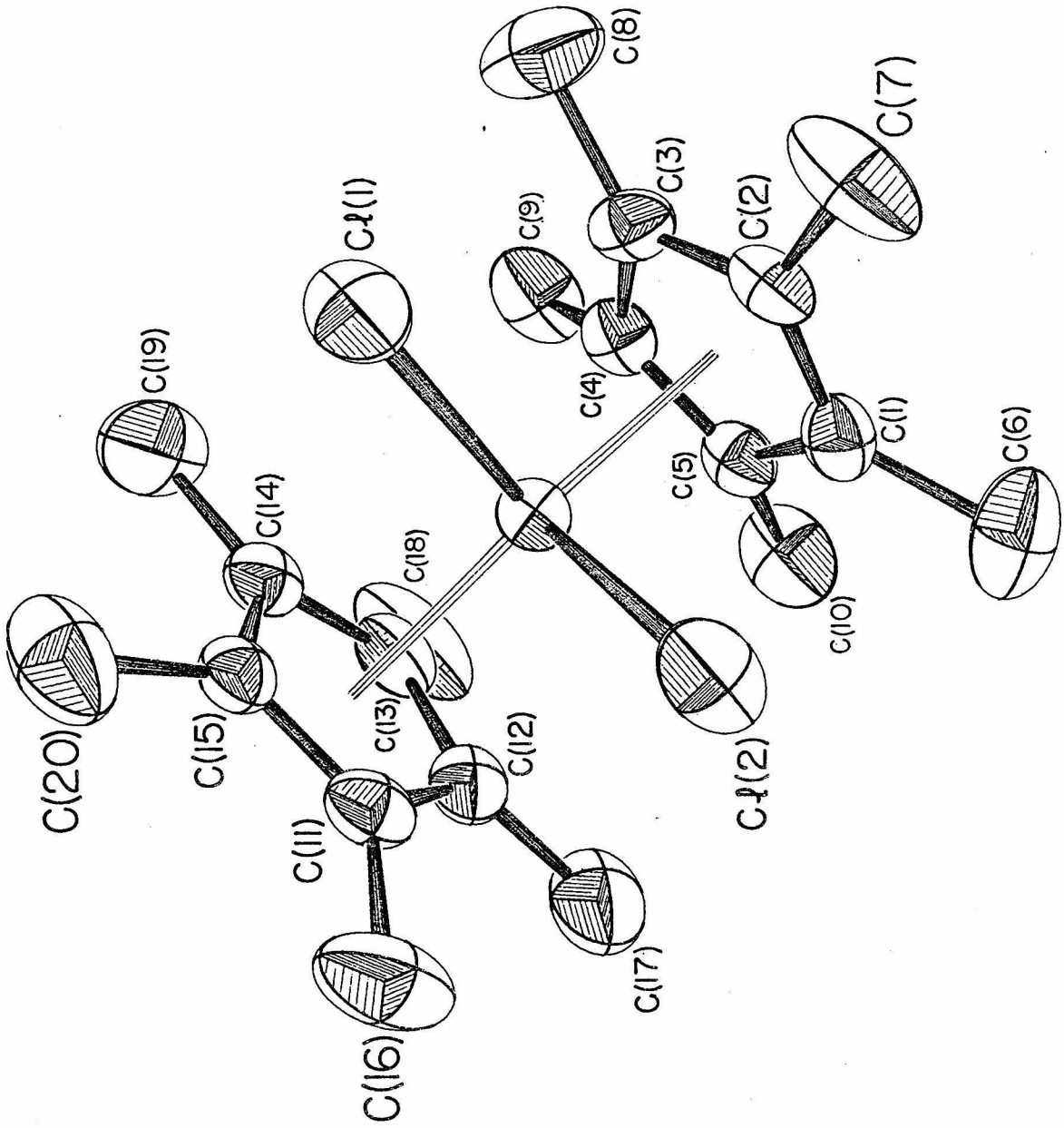

Figure 1. The molecular configuration of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$. In this and subsequent figures, the thermal ellipsoids are drawn at the 50% probability level.[22]

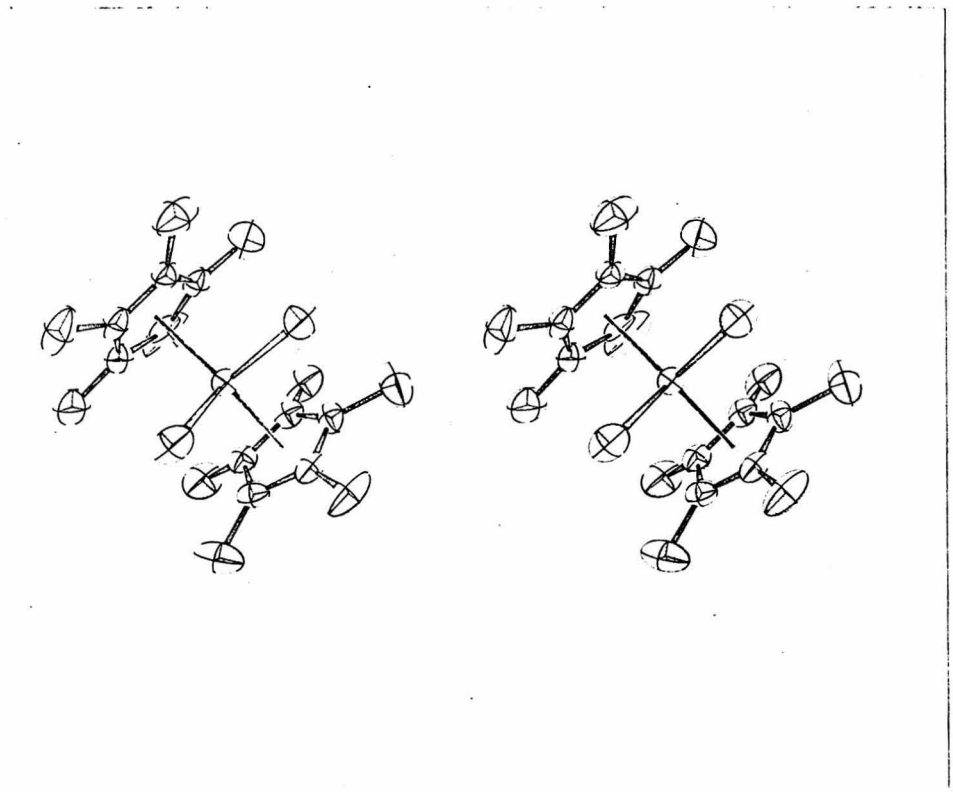

Figure 2. Stereoscopic view of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$. The figure is oriented to match the labeled Figure 1.

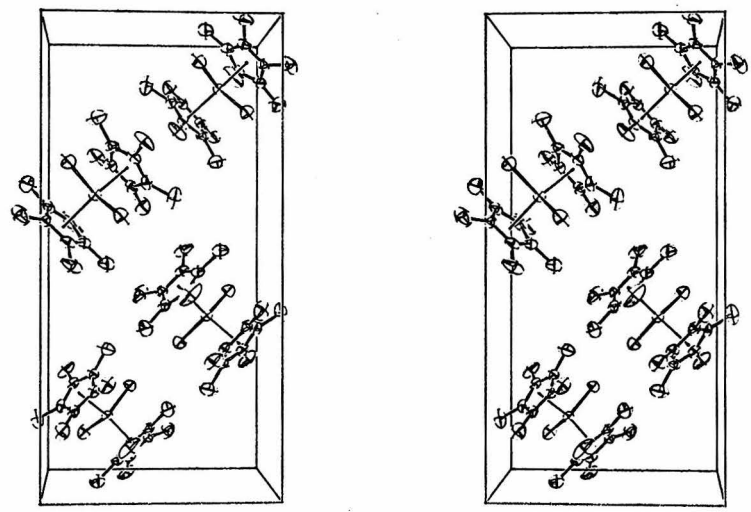

Figure 3. Stereoscopic view of the packing of molecules in the unit cell. Positive x runs from left to right, positive y from back to front, positive z from bottom to top.

distance of 2.44 Å (Table 4), values comparable to those found for derivatives of the type $(\eta\text{-}C_5H_5)_2TiX_2$ (X = Cl, Ph, S, $\eta^1\text{-}C_5H_5$).[14-18] Both rings are very nearly planar (maximum out-of-plane deviations < 0.03 Å) (Table 6), and the $(C\text{-}C\text{-}C)_{ring}$ bond angles range from 107.0(3)° to 109.6(3)° (Table 5) with an average angle of 108° as expected for a planar pentagon. The Ti-Cl distances of 2.352(1) and 2.346(1) Å are not unlike those reported for $[(CH_2)_3(C_5H_4)_2]TiCl_2$, 2.368(4) Å;[15] $(C_5H_5)[C_5(CH_3)_5]TiCl_2$, 2.329(8) Å;[9] and $(C_5H_5)_2TiCl_2$, 2.36 Å.[14]

An interesting feature of this structure is the fact that several of the methyl groups are bent considerably out of the cyclopentadienyl plane and away from the titanium atom (Table 6) by an amount which ranges from only 2° for C(19) to as much as 19° for C(18). The trend for these out-of-plane deviations indicates that this strain results from chlorine-methyl crowding and methyl-methyl contacts between the two rings. Thus the 0.49 Å out-of-plane deviation for C(18) arises from crowding of its hydrogen atoms with those of C(9) and C(10) (Table 7). Smaller out-of-plane deviations of ring methyl groups (0.025-0.191 Å) have been reported for $[\eta\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$.[19,20] The two shortest H-H nonbonded distances for this interaction average 2.07(7) Å, significantly less than twice the Van der Waals contact radius of a hydrogen atom (ca. 2.4 Å). C(9) and C(10) appear to distribute the strain associated with this contact and thus exhibit similar and somewhat smaller out-of-plane deviations of 0.345 and 0.332 Å, respectively. Similarly, several hydrogen-chlorine and

carbon-chlorine distances smaller than Van der Waals contacts of ca. 3.0 and 3.4 Å, respectively, reflect the steric crowding and accompanying deviations from planarity exhibited by C(6), C(8), C(16), and C(20). C(7) is pushed only slightly out of the ring plane despite the fact that two of its hydrogen atoms are pointed toward the two chlorine atoms with H-Cl(1) and H-Cl(2) contacts of only 2.71(5) and 2.84(5) Å, respectively. The relatively long C(7)-Cl distances of 3.44(4) and 3.49(4) Å appear to indicate a reduction in crowding here, however.

Previous structure determinations for $(\eta\text{-}C_5H_5)_2TiX_2$ (X = Cl, Ph, S, $\eta^1\text{-}C_5H_5$) and $(C_5H_5)[C_5(CH_3)_5]TiCl_2$ have shown the cyclopentadienyl rings to be tilted at a Cp-Ti-Cp angle of 130 to 136°.[9,15-18] For $[C_5(CH_3)_5]_2TiCl_2$, this angle is somewhat expanded (137.4°), apparently as a result of methyl-methyl contacts between the two rings. Further expansion is probably opposed largely by increased methyl-chlorine crowding, since the strength of the titanium-ring bonding should depend only slightly on the angle of tilt over this small range.[21] The final ring positions are thus viewed as that balance which minimizes chlorine-methyl and methyl-methyl nonbonding interactions in the molecule.

In view of the extent of intramolecular crowding, it is indeed remarkable to note that the ^1H NMR spectrum of $[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$ remains a sharp singlet at -50°C, thus indicating that "free" rotation of rings and ring methyl groups is maintained even at this temperature.[1] This process must therefore resemble a set of rapidly turning, closely meshed gears.

References

1. J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, J. Am. Chem. Soc., 94, 1219 (1972), and literature cited therein.
2. E. E. van Tamelen, Acc. Chem. Res., 3, 361 (1970), and literature cited therein.
3. Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, E. F. Kvashina, A. K. Shilova and A. E. Shilov, J. Chem. Soc., Chem. Commun., 169 (1973), and literature cited therein.
4. H. H. Brintzinger and J. E. Bercaw, J. Am. Chem. Soc., 92, 6182 (1970).
5. E. E. van Tamelen, W. Cretney, N. Klaentschi and J. S. Miller, J. Chem. Soc., Chem. Commun., 481 (1972).
6. M. E. Vol'pin, A. A. Belyi, V. B. Shur, Y. I. Lyakhovetsky, R. V. Kudryavtsev, and N. N. Bubnov, J. Organomet. Chem., 27, C5 (1971).
7. J. E. Bercaw, E. Rosenberg and J. D. Roberts, J. Am. Chem. Soc., 96, 612 (1974).
8. J. E. Bercaw, J. Am. Chem. Soc., 96, 5087 (1974).
9. T. L. Khotsyanov and S. I. Kuznetsov, J. Organomet. Chem., 57, 155 (1973).
10. A. J. C. Wilson, Nature, 150, 151 (1942).
11. D. T. Cromer and J. B. Mann, Acta Crystallogr., A24, 321 (1968).

12. International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962, pp. 213-215.

13. Structure factors calculated using the atomic coordinates and thermal parameters of the other enantiomer resulted in an increase of the R index to 0.035 and the goodness to fit to 1.73, thus indicating the original enantiomer was in fact the correct choice.

14. V. V. Tkachev and L. O. Atovinyan, J. Struct. Chem. (USSR), 13, 263 (1972).

15. B. R. Davis and I. Bernal, J. Organomet. Chem., 30, 75 (1971).

16. V. Kocman, J. C. Rucklidge, R. J. O'Brian, and W. Santo, Chem. Commun., 1340 (1971).

17. E. F. Epstein and I. Bernal, J. Organomet. Chem., 26, 229 (1971).

18. J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, J. Am. Chem. Soc., 93, 3592 (1971).

19. M. R. Churchill and J. Wormald, Inorg. Chem., 10, 572 (1971).

20. M. R. Churchill and S. W.-Y. Ni, J. Am. Chem. Soc., 95, 2150 (1973).

21. C. J. Ballhausen and J. P. Dahl, Acta Chem. Scand., 15, 1333 (1961).

22. C. K. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Program for Crystal Structure Illustrations," U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE I

CRYSTAL DATA

$C_{20}H_{30}TiCl_2$	Orthorhombic space group $P2_12_12_1$
a = 10.816(1) Å	FW = 389.2
b = 8.132(1) Å	ρ_{obs} = 1.31(1) g·cm^{-3}
c = 22.259(1) Å	ρ_{calc} = 1.32 g·cm^{-3}
V = 1958 Å^3	Z = 4
λ(Mo Kα) = 0.71069 Å	μ = 7.2 cm^{-1}

TABLE II

FINAL NONHYDROGEN ATOM PARAMETERS (Coordinates $\times 10^5$, $U_{IJ} \times 10^4$, Esd's in parentheses)[a, b]

	X	Y	Z	U11	U22	U33	U12	U13	U23
Ti	27847(7)	97604(8)	12722(3)	327(4)	209(4)	315(4)	3(3)	18(4)	-16(3)
Cl1	38795(11)	115982(14)	18910(5)	582(8)	513(8)	567(8)	-210(6)	98(7)	-246(6)
Cl2	17039(11)	118844(13)	7894(6)	591(8)	427(7)	659(9)	204(6)	179(7)	220(6)
C1	6407(37)	91848(49)	15393(20)	318(26)	411(28)	484(29)	-33(21)	60(23)	50(23)
C2	11770(37)	100147(52)	20322(17)	418(26)	419(26)	383(26)	-13(26)	147(23)	-50(23)
C3	20899(40)	89708(47)	22820(17)	463(29)	397(25)	319(25)	-115(25)	-10(23)	66(19)
C4	21373(40)	75299(44)	19371(18)	404(25)	314(24)	432(26)	12(22)	72(26)	104(20)
C5	12283(39)	76567(48)	14788(18)	392(26)	357(25)	422(28)	-123(22)	83(24)	-44(20)
C11	38843(38)	100928(49)	3001(17)	448(26)	398(26)	354(24)	78(25)	113(23)	-7(22)
C12	32617(39)	85531(50)	3087(18)	407(27)	490(30)	371(27)	3(23)	48(23)	-190(22)
C13	38417(42)	75591(46)	7441(19)	455(28)	251(23)	520(30)	53(22)	170(27)	-25(20)
C14	47483(38)	85331(49)	10383(17)	374(27)	415(26)	375(27)	139(22)	70(22)	29(21)
C15	47817(35)	100565(48)	7413(17)	343(24)	390(27)	342(25)	-13(22)	63(21)	-59(21)
C6	-5077(42)	97186(64)	12122(26)	414(32)	761(42)	1047(51)	-46(31)	-135(36)	104(42)
C7	8042(48)	116551(59)	22906(23)	824(50)	461(33)	783(43)	-21(33)	451(41)	-132(30)
C8	27324(56)	92363(64)	28660(21)	948(50)	845(46)	451(33)	-295(40)	-148(35)	74(30)
C9	27568(51)	59885(55)	21519(22)	729(38)	531(34)	720(40)	164(34)	203(38)	288(28)
C10	7343(47)	62762(60)	11093(24)	682(43)	582(40)	869(49)	-292(33)	139(38)	-248(34)
C16	37198(53)	114085(60)	-1647(22)	915(48)	646(39)	552(39)	300(39)	263(37)	235(29)
C17	23197(52)	80654(73)	-1408(23)	607(41)	1166(53)	616(39)	-88(43)	76(36)	-360(40)
C18	37340(62)	57107(56)	7570(29)	1164(65)	346(33)	1183(66)	11(37)	677(59)	-81(34)
C19	56214(49)	80095(72)	15140(24)	591(41)	975(50)	650(43)	363(43)	-6(39)	120(38)
C20	57432(48)	113663(62)	8246(25)	690(44)	659(39)	823(44)	-232(34)	255(37)	-208(37)

[a] The final value of the scale factor is 0.9329(19).

[b] The form of the anistropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2k\ell b^*c^* U_{23})]$.

TABLE III

FINAL HYDROGEN ATOM PARAMETERS (Coordinates $\times 10^4$) [a]

	X	Y	Z	B
H6A	-680(48)	10809(61)	1282(25)	6.50
H6B	-1265(49)	9132(60)	1413(23)	6.50
H6C	-602(48)	8906(63)	896(24)	6.50
H7A	1511(47)	12095(64)	2245(22)	6.00
H7B	120(52)	11598(60)	2611(23)	6.00
H7C	554(46)	12058(66)	1933(23)	6.00
H8A	3015(47)	10439(61)	2940(22)	6.50
H8B	3563(47)	8736(69)	2855(23)	6.50
H8C	2245(47)	8623(61)	3162(22)	6.50
H9A	3613(46)	6139(63)	2191(22)	6.00
H9B	2770(47)	5280(63)	1850(22)	6.00
H9C	2447(47)	5944(57)	2567(22)	6.00
H10A	464(50)	6612(68)	792(24)	6.25
H10B	-69(50)	6009(59)	1236(24)	6.25
H10C	1337(48)	5457(65)	1076(22)	6.25
H16A	3595(51)	12317(65)	54(25)	6.25
H16B	2843(49)	11249(59)	-353(22)	6.25
H16C	4374(46)	11444(61)	-481(22)	6.25
H17A	1517(50)	8444(68)	-45(24)	7.00
H17B	2074(50)	6909(65)	-89(23)	7.00
H17C	2698(53)	8254(66)	-519(22)	7.00
H18A	4002(52)	5373(70)	1125(23)	7.00
H18B	3018(47)	5441(69)	650(25)	7.00
H18C	4406(50)	5682(68)	508(25)	7.00
H19A	5504(55)	8490(73)	1807(26)	7.00
H19B	6382(50)	7814(67)	1420(26)	7.00
H19C	5478(53)	6921(68)	1528(25)	7.00
H20A	5534(48)	12402(61)	894(23)	6.50
H20B	6471(50)	11214(61)	538(23)	6.50
H20C	6150(52)	11303(66)	1182(24)	6.50

[a] Thermal parameters were not refined and are of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

TABLE IV

BOND DISTANCES (Å)

Ti-Cl1	2.352(1)	C1-C2	1.413(5)
Ti-Cl2	2.346(1)	C2-C3	1.416(5)
Ti-R1[a]	2.127(4)	C3-C4	1.402(5)
Ti-R2[a]	2.128(4)	C4-C5	1.420(5)
		C1-C5	1.402(5)
Ti-C1	2.439(4)	C11-C12	1.422(5)
Ti-C2	2.435(4)	C12-C13	1.409(5)
Ti-C3	2.455(4)	C13-C14	1.421(5)
Ti-C4	2.444(4)	C14-C15	1.405(5)
Ti-C5	2.444(4)	C11-C15	1.381(5)
Ti-C11	2.484(4)		
Ti-C12	2.415(4)		
Ti-C13	2.428(4)		
Ti-C14	2.404(4)		
Ti-C15	2.474(3)		
C1-C6	1.504(6)		
C2-C7	1.508(6)		
C3-C8	1.490(6)		
C4-C9	1.500(6)		
C5-C10	1.491(6)		
C11-C16	1.499(6)		
C12-C17	1.482(6)		
C13-C18	1.505(7)		
C14-C19	1.481(6)		
C15-C20	1.500(6)		

[a] R1=C1-C5 ring centroid, R2=C11-C15 ring centroid

TABLE V

BOND ANGLES (deg)

Cℓ1-Ti-Cℓ2	92.94(4)	C12-C11-C16	125.6(4)
R1-Ti-R2	137.4(1)	C15-C11-C16	126.1(4)
R1-Ti-Cℓ1	104.6(1)	C11-C12-C17	123.5(4)
R1-Ti-Cℓ2	104.5(1)	C13-C12-C17	128.0(4)
R2-Ti-Cℓ1	104.4(1)	C12-C13-C18	124.6(4)
R2-Ti-Cℓ2	104.4(1)	C14-C13-C18	125.2(4)
		C13-C14-C19	127.5(4)
C1-C2-C3	107.8(3)	C15-C14-C19	125.0(4)
C2-C3-C4	108.2(3)	C14-C15-C20	125.9(4)
C3-C4-C5	107.9(3)	C11-C15-C20	124.0(4)
C4-C5-C1	108.0(3)		
C5-C1-C2	108.2(3)		
C11-C12-C13	107.7(3)		
C12-C13-C14	107.7(3)		
C13-C14-C15	107.0(3)		
C14-C15-C11	109.6(3)		
C15-C11-C12	107.7(3)		
C2-C1-C6	125.3(4)		
C5-C1-C6	125.7(4)		
C1-C2-C7	127.5(4)		
C3-C2-C7	124.6(4)		
C2-C3-C8	125.5(4)		
C4-C3-C8	125.6(4)		
C3-C4-C9	122.7(4)		
C5-C4-C9	126.8(4)		
C4-C5-C10	126.1(4)		
C1-C5-C10	123.9(4)		

TABLE VI

LEAST-SQUARES PLANES OF CYCLOPENTADIENYL RINGS[a]

Ring 1			Ring 2		
Atom	Deviation (Å)	Angle (deg)[b]	Atom	Deviation (Å)	Angle (deg)[b]
C1	-0.003		C11	-0.007	
C2	0.007		C12	0.023	
C3	-0.008		C13	-0.030	
C4	0.007		C14	0.025	
C5	-0.022		C15	-0.011	
C6	-0.228	8.7	C16	-0.207	7.9
C7	-0.064	2.4	C17	-0.100	3.9
C8	-0.233	9.0	C18	-0.490	19.0
C9	-0.345	13.3	C19	-0.047	1.8
C10	-0.332	12.9	C20	-0.214	8.2

[a] A positive deviation is a deviation toward the titanium atom.

[b] The angle (away from Ti) from the cyclopentadienyl ring plane.

TABLE VII

INTRAMOLECULAR NON-BONDED DISTANCES (Å) LESS THAN OR APPROXIMATING van der WAALS CONTACTS[a]

C4-C13	3.233(3)	Cℓ1-H7A	2.71(5)
C5-C13	3.267(5)	Cℓ1-H8A	2.69(5)
C9-C18	3.305(7)	Cℓ1-H20A	2.92(5)
C10-C18	3.422(7)	Cℓ1-H20C	2.93(5)
		Cℓ2-H6A	2.94(5)
H9A-H18A	2.49(7)	Cℓ2-H7C	2.84(5)
H9B-H18A	2.10(7)	Cℓ2-H16A	2.64(5)
H10C-H18B	2.05(7)	Cℓ2-H16B	2.88(5)
Cℓ1-C3	3.012(4)		
Cℓ1-C2	3.210(4)		
Cℓ1-C15	3.012(3)		
Cℓ2-C1	2.988(4)		
Cℓ2-C2	3.208(4)		
Cℓ2-C11	2.978(4)		
Cℓ1-C8	3.153(5)		
Cℓ1-C7	3.444(5)		
Cℓ1-C20	3.120(5)		
Cℓ2-C7	3.486(5)		
Cℓ2-C16	3.068(5)		
Cℓ2-C6	3.116(5)		
Cℓ1-Cℓ2	3.407(1)		

[a] Listed are all intramolecular nonbonding distances less than 3.50 Å for C-C, 3.50 Å for Cℓ-C, 3.00 Å for Cℓ-H, 2.50 Å for H-H.

CHAPTER II*

STRUCTURE OF μ-DINITROGEN-BIS(BIS-(PENTAMETHYLCYCLOPENTADIENYL)DINITROGEN-ZIRCONIUM(II)), $\{(\eta^5\text{-}C_5(CH_3)_5)_2ZrN_2\}_2N_2$

Introduction

Since their discovery ten years ago, over 100 transition metal compounds which contain molecular nitrogen (dinitrogen) as a ligand have been prepared.[1] However, these complexes have proven to be disappointingly inert with respect to reactions centered at N_2. During the same period several reaction systems involving transition metals have been developed which effectively reduce N_2 at room temperature and atmospheric pressure; however, no dinitrogen intermediates have been isolated from such reducing systems and hence their full structural characterization has not been possible. The nature of these "active" N_2 complex intermediates and their relationship to isolable, "inert" dinitrogen complexes have thus been subjects of considerable interest and speculation.

The relatively high efficiency of titanocene-based N_2 reducing systems has prompted numerous (unsuccessful) attempts to isolate a stable crystalline dinitrogen complex suitable for a structure determination.[2-6] In view of the difficulties associated with cyclopentadienyl-to-metal hydrogen transfer inherent to these systems,

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*This chapter has been published previously. See R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 8351 (1976).

we have more recently investigated the closely related pentamethylcyclopentadienyl derivatives.[4,7-10] We find compounds containing the $(\eta^5\text{-}C_5Me_5)_2M$ (M = Ti, Zr) moiety often more stable and much more amenable to study than their $(\eta^5\text{-}C_5H_5)$ analogues. For example, in contrast to $\{(C_5H_5)_2Ti\}_2N_2$, $\{(C_5Me_5)_2Ti\}_2N_2$ is moderately stable in solution at room temperature and easily obtained as large, well-formed crystals.[9] The title compound $\{(C_5Me_5)_2ZrN_2\}_2N_2$ (1), is of comparable thermal stability and has also been isolated in crystalline form.[10] The unique spectral properties and the chemical reactivity associated with the coordinated N_2 in these complexes prompted us to examine their structures in some detail. This chapter presents the results of an X-ray crystal structure determination for $\{(C_5Me_5)_2ZrN_2\}_2N_2$ and our interpretation of these results in terms of a plausible bonding scheme. An X-ray structure determination for $\{(C_5Me_5)_2Ti\}_2N_2$ has also been conducted.[11]

Experimental

$\{(C_5Me_5)_2ZrN_2\}_2N_2$ was prepared as described previously[10] and obtained as metallic green crystals from diethyl ether. A series of Weissenberg and precession photographs (Cu-K_α and Mo-K_α radiation) showed orthorhombic D_{2h}-mmm Laue symmetry with the systematic absences $h0\ell$, $h+\ell$ odd and 0k0, k odd.

A crystal of dimensions 0.25 × 0.25 × 0.85 mm was mounted in a glass capillary under N_2 with its long axis (c) slightly skew to the φ axis of a G.E. XRD-5 quarter-circle diffractometer

automated by Datex. Unit cell dimensions were obtained by a least-squares fit to the $(\sin^2\theta)/\lambda^2$ values measured on a diffractometer for ten reflections having high 2θ angles. Due to the extreme reactivity of the compound, an experimental density measurement was not attempted, although the calculated value of 1.31 $g \cdot cm^{-3}$ is a reasonable value for an organometallic compound of this type. Crystal data are given in Table I.

Intensities were measured for all $hk\ell$ and $\bar{h}\bar{k}\ell$ reflections between 4 and 153° in 2θ, using a θ-2θ scan technique and a scan of 2°/min; 20-s background counts were taken before and after each scan. The scan width varied linearly from 1.2° at $2\theta = 4°$ to 3.2° at $2\theta = 153°$. A variance $\sigma^2(I)$ was calculated for each reflection based on counting statistics and a term in $(0.02S)^2$, where S is the scan count. Intensities and their variances were corrected for Lorentz and polarization effects, while absorption corrections were made by the method of Wehe, Busing, and Levy using their ORABS program.[12] Intensities of three check reflections measured every 100 reflections indicated no crystal decomposition during data collection.

Intensities of reflections ($hk\ell$ and $\bar{h}\bar{k}\ell$ octants) were collected from which an averaged data set of 4803 intensities was assembled and placed on an absolute scale by means of a Wilson plot,[13] with scattering factors for all atoms calculated by the method of Cromer and Mann.[14] Systematic absences (177), six reflections which exceeded the counter capacity, and eight having an extremely

unsymmetrical background were deleted, leaving 4612 reflections for the working data set.

Solution and Refinement

The systematic absences indicate an n-glide plane perpendicular to the b axis and a 2_1 screw axis parallel to the b axis. There is, however, no orthorhombic space group having this particular combination of symmetry elements, suggesting that one class of absences might be due to a pseudo-symmetry element. A three-dimensional Patterson map was generated, but attempted solution in several orthorhombic space groups containing one or the other of the observed symmetry elements proved futile.

The presence of either a (100) or a (001) twin plane operating on a monoclinic structure with $\beta = 90°$ and space group $P2_1/n$ would give rise to the apparent mmm diffraction symmetry, while the systematic absences characteristic of space group $P2_1/n$ would remain. Such twinning would have to be quite intimate, since there were no significant differences between the two octants of data and the Weissenberg and precession photographs showed no doubling of spots characteristic of twins.

Under these circumstances the intensity of a reflection may be expressed as the sum of the two equal twin contributors:

$$|G(hk\ell)|^2 = |G(\bar{h}k\ell)|^2 = |F(hk\ell)|^2 + |F(\bar{h}k\ell)|^2 \qquad (1)$$

Thus the orthorhombic Patterson map will represent a composite of the monoclinic twins and can be solved accordingly. Provided

(as can be presumed for the centrosymmetric space group $P2_1/n$) that the $F(hk\ell)$'s are real, eq. 1 implies

$$|G(hk\ell)| = |F(hk\ell) + iF(\bar{h}k\ell)| \quad (2)$$

an expression which is analogous to the expression for the structure factor of an acentric crystal. We may define

$$|G(hk\ell)| = |A(hk\ell) + iB(\bar{h}k\ell)| \quad (3)$$

with

$$|A(hk\ell)| = |F(hk\ell)| \quad (4)$$

and

$$|B(\bar{h}k\ell)| = |F(\bar{h}k\ell)| \quad (5)$$

The structure-factor, Fourier, and least-squares programs were easily modified using eq. 1-5. A somewhat similar treatment has been given previously by Wei for the structure determination of $Rh_4(CO)_{12}$.[15]

Zirconium positions obtained from the reinterpreted Patterson map led to an R index ($\Sigma \| G_o| - |G_c \| / \Sigma |G_o|$) of 0.307. Two successive structure-factor calculations interspersed with Fourier syntheses revealed the location of all remaining nonhydrogen atoms, yielding an R index of 0.165.

Refinement was by least-squares minimization of the quantity $\Sigma w |G_o^2 - s^2 G_c^2|^2$, where $1/s$ is the scale factor for G_o and $w = 1/\sigma^2(G_o^2)$. In the initial least-squares cycles, positions and isotropic temperature factors for all nonhydrogen atoms, the scale factor, and a secondary extinction factor[16] were refined to an R index of

0.069. At this point, difference Fourier maps were generated in the planes of the methyl H atoms from which all 60 hydrogen atoms were located. Further full-matrix least-squares refinement was performed using two matrices, one containing coordinates for all nonhydrogen atoms and the other containing scale factor, secondary extinction factor, and anisotropic temperature factors for all nonhydrogen atoms. Isotropic thermal parameters for the hydrogen atoms were set approximately 1 $Å^2$ larger than those for their respective carbon atoms, but neither the thermal parameters nor coordinates of the hydrogen atoms were adjusted. Several least-squares cycles lowered the R index to 0.037, at which time the hydrogen atoms were repositioned on the basis of another set of difference Fourier maps. Two final least-squares cycles led to an R index of 0.035 and a goodness of fit, $\{\Sigma w(G_o^2 - s^2G_c^2)/(N - P)\}^{\frac{1}{2}}$, of 3.42 for N = 4612 reflections and P = 434 parameters. All crystallographic computations were performed under the CRYM system[17] on an IBM 370/158 computer. Final parameters are given in Tables II and III.

Results and Discussion

The molecular structure is shown in Figure 1, a stereoscopic view in Figure 2, and the packing of the molecules in the unit cell is illustrated in Figure 3. The binuclear structure may be viewed as two $(\eta^5\text{-}C_5Me_5)_2ZrN{\equiv}N$ moieties bridged by a third dinitrogen ligand. Of special significance is the fact that the terminal and bridging dinitrogen ligands are bound <u>end-on</u> (η^1-) to zirconium with essentially linear $ZrN{\equiv}N$ and $ZrN{\equiv}NZr$ arrangements.

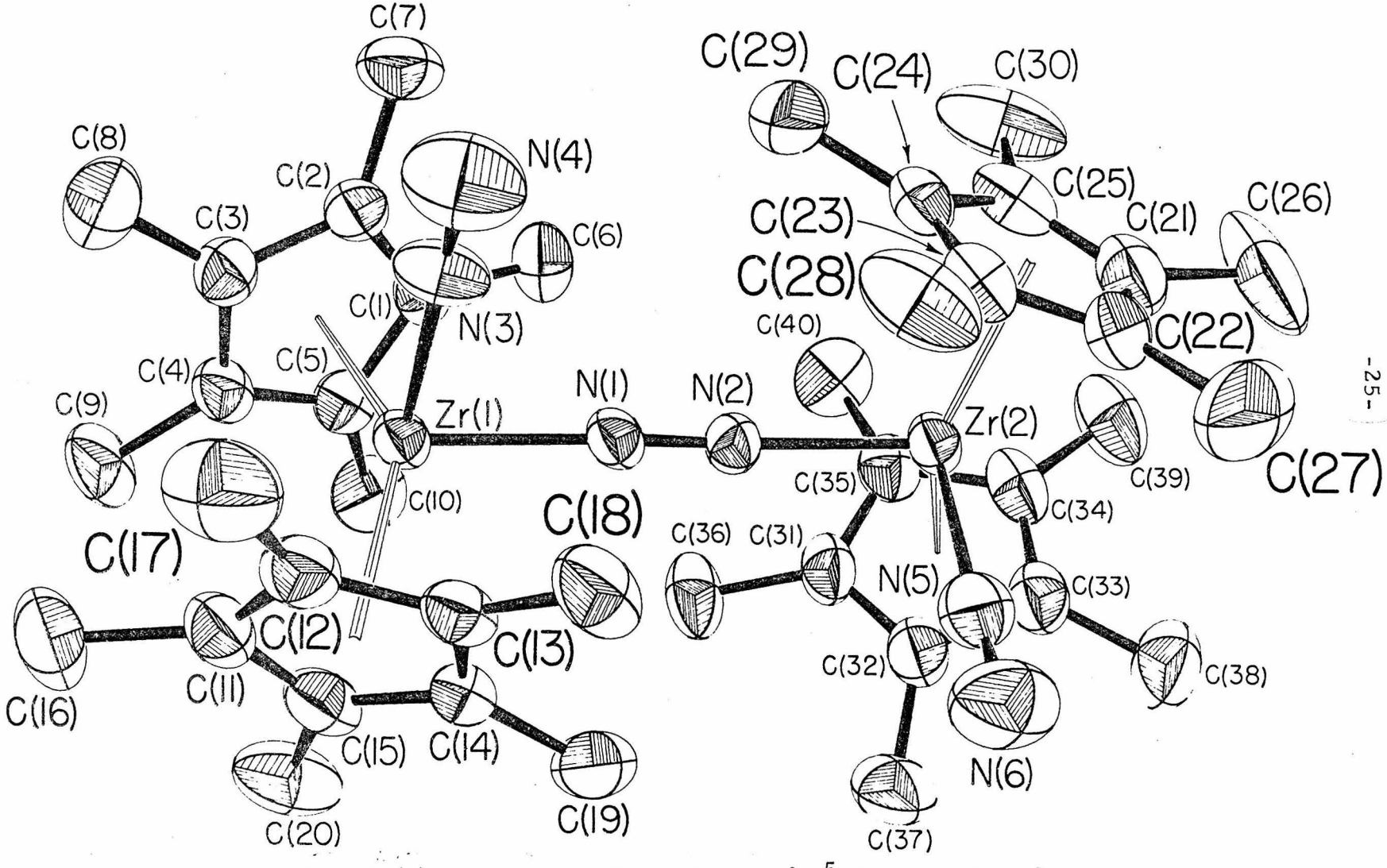


Figure 1. The molecular configuration of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$. In this and subsequent figures, thermal ellipsoids are drawn at the 50% probability level.

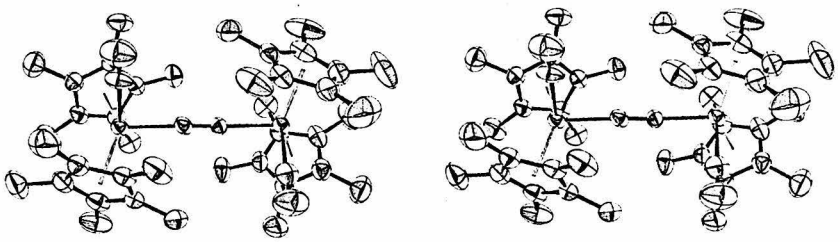


Figure 2. Stereoscopic view of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$. This figure is oriented to match the labeled Figure 1.

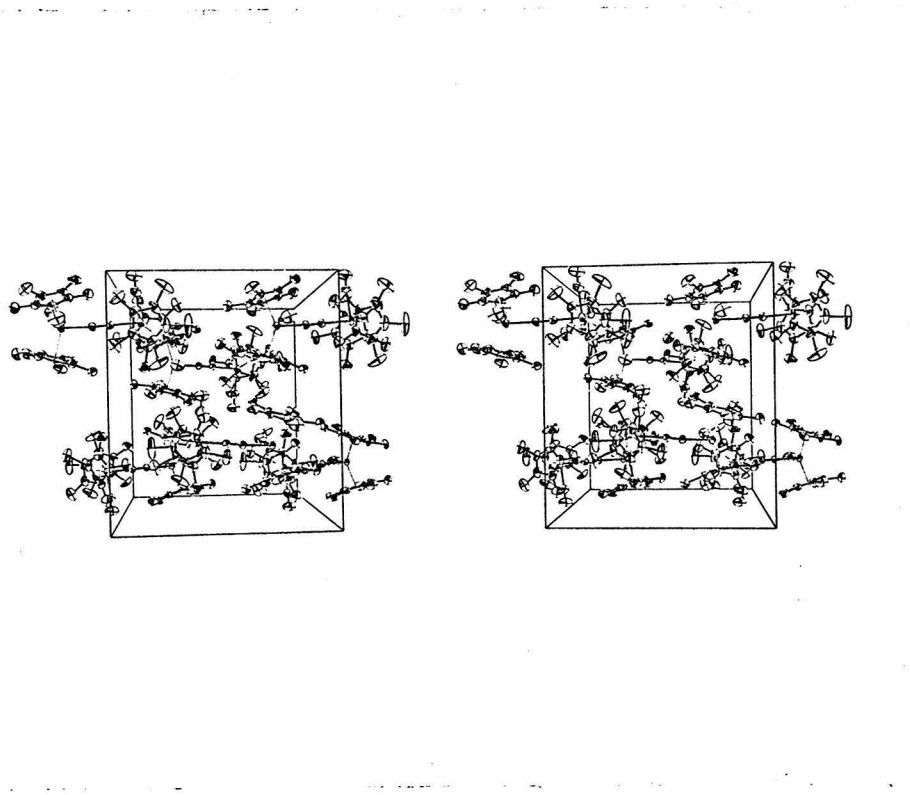


Figure 3. Stereoscopic view of the packing of molecules in the unit cell. Positive x runs from left to right, positive y from bottom to top, positive z from back to front.

The skeletal view shown in Figure 4 illustrates the roughly tetrahedral disposition of (η^5-C_5Me_5) and dinitrogen ligands about Zr, although substantial distortions do exist. Thus the centroid-Zr-centroid angles (R-Zr-R; Table V) average 141.3(3)°, while the N-Zr-N angles average 87.1(8)°.[18] The R-Zr-R angle is larger and the N-Zr-N angle somewhat smaller than found for similar molecules containing unsubstituted C_5H_5 rings, where the corresponding angles are 128 and 96° for $(\eta^5\text{-}C_5H_5)_2ZrF_2$,[19] 126 and 96° for $(\eta^5\text{-}C_5H_5)_2ZrI_2$,[19] and 130 and 94° for $(\eta^5\text{-}C_5H_5)_2ZrCl\{Si(C_6H_5)_3\}$;[20] 134 and 95° for $(\eta^5\text{-}C_5H_5)_2TiS_5$,[21] 130 and 86° for $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$,[22] and 130 and 95° for $(\eta^5\text{-}C_5H_5)_2TiCl_2$.[23] It appears that steric crowding of the methyl groups between rings is responsible for the expansion of the R-Zr-R angles for 1, so that the arrangement of ligands more closely resembles that for $\{\eta^5\text{-}C_5(CH_3)_5\}_2TiCl_2$, where the R-Ti-R and Cl-Ti-Cl angles are 137 and 93°, respectively.[24] The R-Zr-terminal nitrogen and R-Zr-bridging nitrogen angles are more nearly equal, averaging 101.4(8) and 106.0(4)°, respectively.

Metal-Ring Bonding. The cyclopentadienyl rings are nearly planar (Table VI). Zr-R [2.232(3) Å] and Zr-ring C distances [2.54(3) Å] are not unlike those found for $(\eta^5\text{-}C_5H_5)_nZrX_{4-n}$ (n = 1, 2) derivatives.[19,20,25-27] The symmetrical metal-to-ring bonding is most evident from the Zr-C distances, which fall in the narrow range 2.495-2.595 Å; small tilts of all four rings with respect to the Zr-ring centroid vector (Table VI) account for the

variations in these bond lengths. The average $(C-C)_{ring}$ bond length of 1.413(14) Å is nearly identical with that found for $\{\eta^5-C_5(CH_3)_5\}_2TiCl_2$ [1.409(13) Å][24] and within the range found for $(\eta^5-C_5H_5)_nZrX_{4-n}$ (n = 1, 2) derivatives. Although these $(C-C)_{ring}$ distances vary from 1.384 to 1.441 Å with individual esd's of 0.009 Å, this variation is probably not significant, so that all four $\{C_5(CH_3)_5\}$ rings may be considered bonded to the zirconium atoms in a true pentahapto fashion.

As shown in Table VI, all methyl groups are bent out of their respective cyclopentadienyl planes away from zirconium. Methyl-methyl contacts between rings, as observed previously for the structure of $(\eta^5-C_5Me_5)_2TiCl_2$,[24] may be cited to explain the variations of these deviations. Thus the two shortest inter-ring C···C nonbonded distances are observed for C9-C16 [3.371(9) Å] and C26-C39 [3.325(9) Å], and accordingly these four carbon atoms exhibit the greatest deviations from their ring planes. All other inter-ring C···C contacts exceed 3.7 Å. Close contacts between the methyl and terminal N_2 groups prevent two rings bonded to a single zirconium atom from being strictly staggered. Appreciable CH_3-N crowding appears to remain, however, resulting in deviations from planarity for several other methyl groups in the molecule. Thus C7-N3, C17-N3, C37-N5, and C27-N5 contacts of 3.068(8), 3.082(9), 3.104(8), and 3.106(8) Å, respectively, lead to substantial deviations of these methyl groups from ring planarity.

Metal Dinitrogen Bonding. 1 appears to represent the only structurally characterized compound of zirconium(II), so that a strict comparison of Zr-N bond lengths of 1 to other Zr(II) complexes cannot be made. Three X-ray crystal structures for Zr(IV) complexes which contain N-bound ligands have been reported however. An unusually long Zr-N distance of 2.539(8) Å was observed for the eight-coordinate complex tetrakis(N-ethylsalicylaldimato)-zirconium(IV).[28] A similar, but somewhat shorter value of 2.439(9) Å has been reported for the dodecahedral $Zr[N(CH_2COO)_3]_2^{2-}$ ion.[29] The two Zr-N distances of 2.110(5) and 2.124(5) Å observed for $(\eta^5\text{-}C_5H_5)_2Zr(NCO)_2$[30] compare more favorably to those for 1 [2.188(4), 2.188(4), 2.087(3), and 2.075(3) Å].

The conventional end-on bonding mode established herein for both terminal and bridging dinitrogen ligands is of special significance in light of several earlier suggestions that either an edge-on[4,8,9] or doubly bent (azo)[3] coordination should be favored for complexes of this type. The two terminal N-N bond lengths [1.116(8) and 1.114(7) Å] are the same as those found previously for other mononuclear dinitrogen complexes (1.11 ± 0.01 Å),[1] only slightly expanded from that for free N_2 (1.0976 Å). The bridging dinitrogen ligand, however, exhibits a significantly longer N-N distance [1.182(5) Å], indicative of a substantial reduction in bond order.

A qualitative description of the $Zr\text{-}N_2$ bonding may be formulated by suitable combinations of dinitrogen lone pair, π, and π^* orbitals with those of the bent bis(η^5-cyclopentadienyl)zirconium(II)

fragments. With respect to the latter, several theoretical and experimental papers have examined the shapes and energies of the frontier orbitals of a bent $(\eta^5\text{-}C_5H_5)_2M$ unit.[31-35] Figure 5 shows these orbitals as recently reported by Lauher and Hoffmann for an eclipsed-ring geometry (C_{2v} symmetry). If it is assumed that eclipsed and staggered configurations are of similar energies and also that substitution of methyl groups for the ten cyclopentadienyl hydrogens exerts no major effects, then for $\theta = 141°$ the energies of these five frontier orbitals are approximately as shown.[36] The three low-lying orbitals have significant extent in the yz plane; the b_2 orbital is chiefly d_{yz} in character; the two a_1 orbitals each contain some contribution from s and p_z orbitals in addition to $d_{x^2-y^2}$ and d_{z^2}.

As can be seen orbitals b_2 and $2a_1$ are of proper symmetry for interaction with both terminal and bridging dinitrogen lone-pair orbitals. π bonding is also possible utilizing N_2 π^* acceptor orbitals and the filled $1a_1$ orbital of zirconium. As shown in Figure 6, the N3-Zr···Zr-N5 torsion angle of 87.3(2)° (Table VII) approximates that expected for interaction of one of the bridging N_2 π^* acceptor orbitals with the filled $1a_1$ orbital of Zr(1), the other with the corresponding electron pair on Zr(2). This favorable bonding situation undoubtedly contributes to the greater overall stability of the gauche configuration of the dimer relative to the cis or trans forms and results in additional weakening of the N≡N bond of the N_2 bridge.

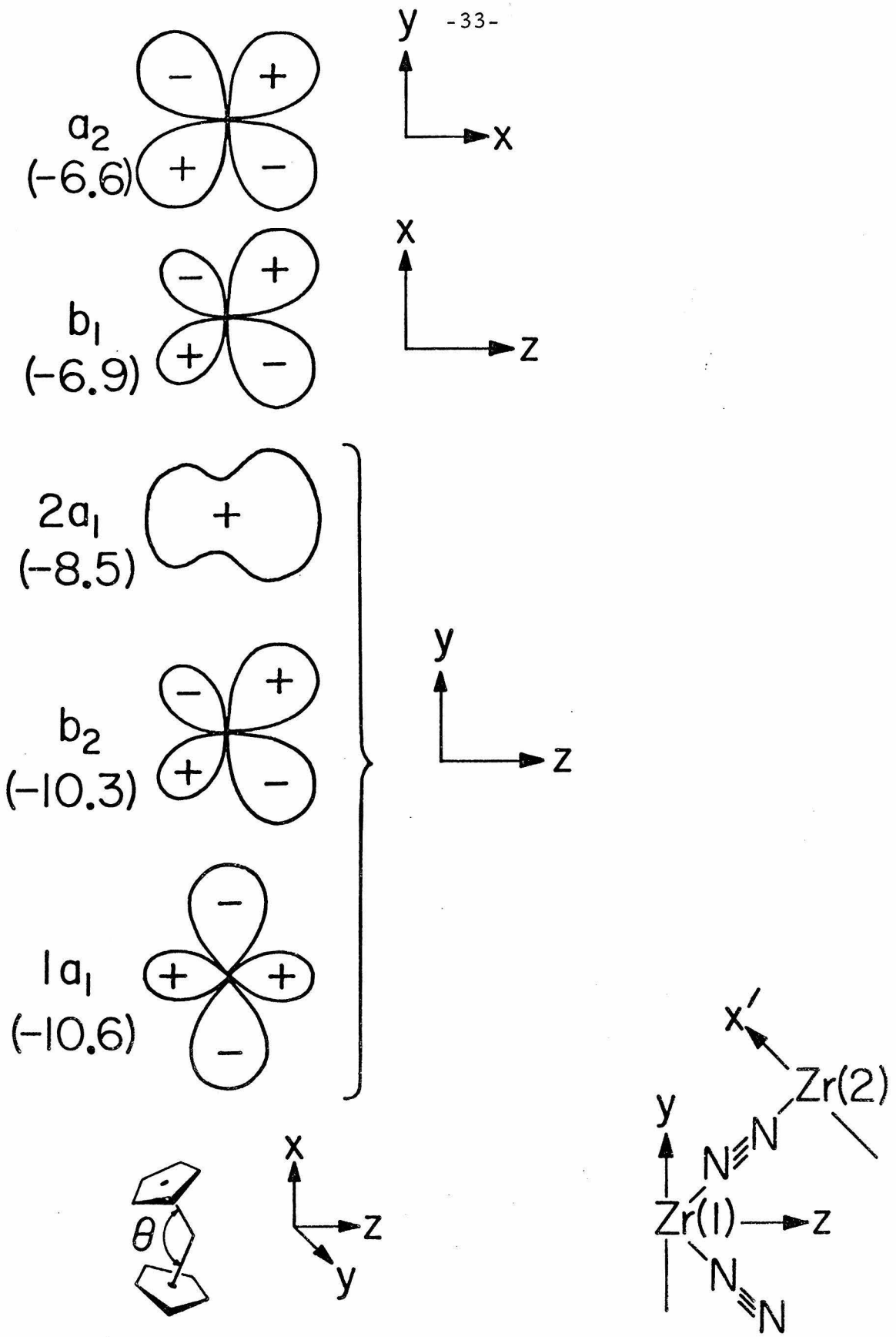


Figure 5. Contours of the five frontier orbitals of a bent, eclipsed $(\eta^5\text{-}C_5H_5)_2M$ fragment. Approximate energies (eV) from ref. 36 for $\theta = 141°$ are given in parentheses.

three bands [2040 (s), 2003 (vs), and 1578 cm^{-1} (m)] attributable to N-N stretching modes.[10,38] Apart from the exceptionally low frequency for one of the bands, two features of the spectrum were rather unexpected: (i) in view of the nearly orthogonal spatial relationship of the two terminal N_2's, the observation of <u>two</u> terminal N-N stretching frequencies requires substantial electronic (rather than through-space dipolar) coupling of these vibrations; and (ii) the intensity of the bridging N-N stretching mode is much higher than would be expected considering the symmetry of the dimer. Both features are reconciled, however, if the spectrum is interpreted on the basis of a coupling of the symmetric combination of terminal N-N stretches (2040 cm^{-1}) with the bridging N-N mode (1578 cm^{-1}), the latter gaining intensity from the former. The strongest band (2003 cm^{-1}) may then be attributed to the antisymmetric combination of terminal N-N stretching modes. Such coupling of bridge and terminal N_2 stretching modes is indeed expected, since both terminal and bridging dinitrogens compete for the same zirconium la_1 electron pair density, which, according to the arguments presented above, should be delocalized over the entire ZrN≡NZr subunit.

Both terminal and bridging dinitrogen ligands coordinated to the same metal appear to be a feature unique to $\{(\eta^5\text{-}C_5Me_5)_2\text{-}ZrN_2\}_2N_2$. There do exist, however, a number of examples where a comparison can be made between a monomeric complex containing a terminal N_2 and the analogous binuclear complex in which N_2 bridges two metal centers, at least one of which is identical with

the monomeric metal fragment (Table VIII). A comparison of $[(NH_3)_5RuN{\equiv}N]^{2+}$ to $[(NH_3)_5RuN{\equiv}NRu(NH_3)_5]^{4+}$ reveals that coordination of a second $[(NH_3)_5Ru]^{2+}$ fragment to the terminal N_2 of the monomer results in only a minor reduction in N-N bond order. Similarly, coordination of a second Mo(0) or Fe(II) d^6 metal center to the terminal N_2 of (η^6-arene)$(PPh_3)_2MoN{\equiv}N$ leads to a relatively small reduction of the N-N stretching frequency. The large shift to lower energy of the ν (NN) band and a large increase in N-N bond length observed upon complexation of $MoCl_4(OCH_3)$ to <u>trans</u>-$[(PMe_2Ph)_4ClReN{\equiv}N]$ stands in sharp contrast, however.

As first suggested by Chatt[46, 48] and co-workers and later restated by Sellman,[1] the relationship between the d-electron configuration of the acceptor metal atom bound to the free end of the dinitrogen ligand and the extent of N≡N bond reduction may be understood qualitatively in terms of four center π-molecular orbitals spanning both metals via the μ-N_2 π system (Figure 8). A major factor governing the strengths of the M-N and N-N bonds are the occupancies of the 2e and 3e levels. Population of the 2e level (π^* N_2 in character) will result in a marked reduction in N-N bond order, whereas population of 3e (π N_2 in character) will increase the N-N bond strength. Thus in the cases for which <u>both</u> M and M′ possess formal d^6 configurations (e.g., $[(NH_3)_5RuN{\equiv}NRu(NH_3)_5]^{4+}$), both 2e and 3e levels are occupied and little net reduction in N-N bond order beyond that for the monomer is achieved. On the other hand, when M′ possesses two d electrons (which may be placed in the d_{xy} δ-type orbital) or less, only the 2e level is occupied, and a

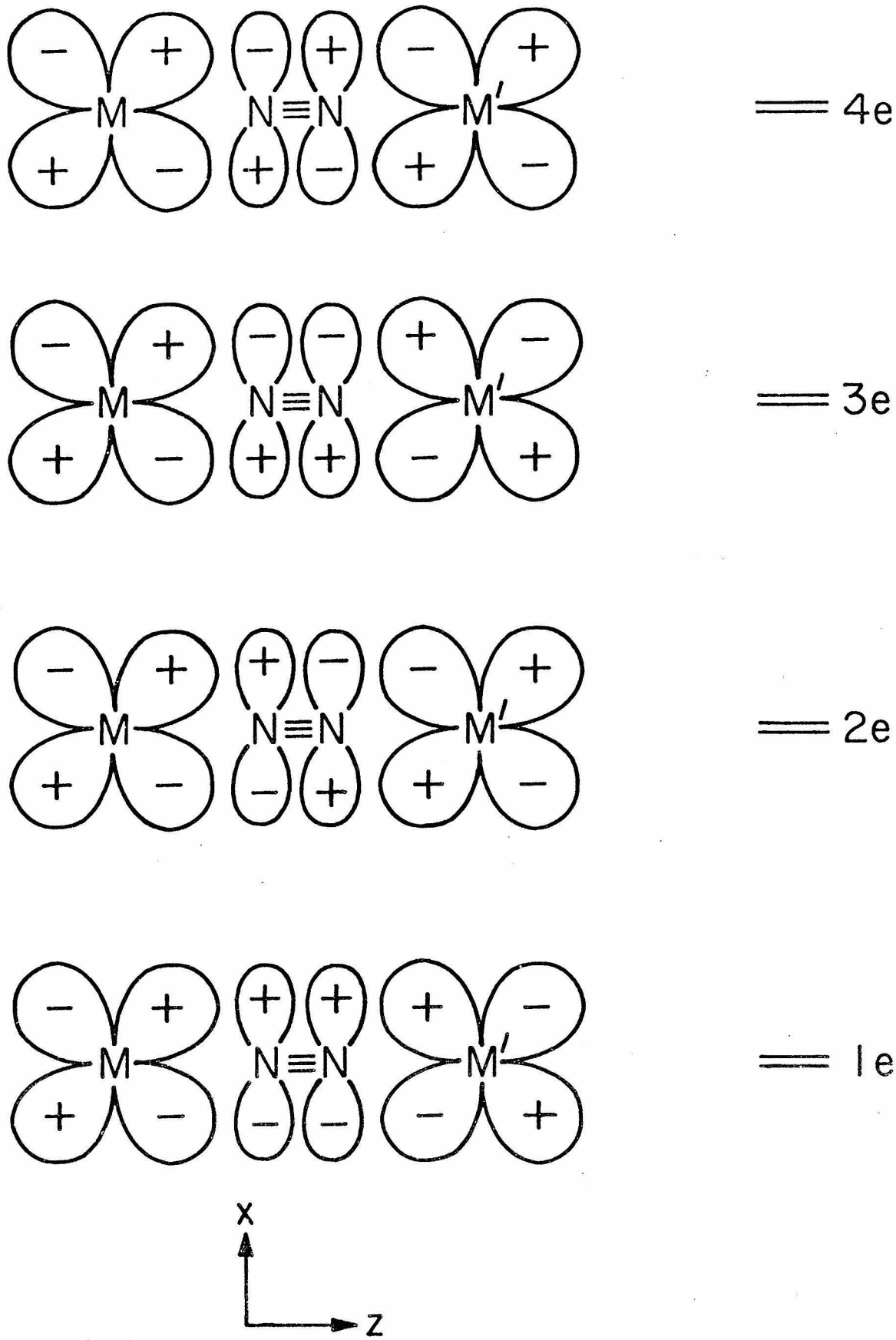


Figure 8. Qualitative four-center molecular orbital scheme for binuclear dinitrogen complexes in idealized C_{4v} symmetry. Shown is one of the two equivalent π-type orbitals only. Ordering of levels is that proposed in ref. 43.

marked reduction in N-N bond order results (e.g., trans-$[(PMe_2Ph)_4ClReN{\equiv}NMoCl_4(OCH_3)]$). Alternatively, we note that the presence of empty acceptor metal (M′) d orbitals of proper symmetry for interaction with the μ-N_2 π orbitals enhances the donor metal (M)-to-N_2 π interaction, thereby increasing the M-N_2 and M′-N_2 bonding and decreasing the μ-N≡N bond order. The resulting situation may be viewed as a type of "push-pull" π bonding with substantial polarization of the MN≡NM′ unit.

$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ falls into this general class of binuclear complexes for which N_2 bridges a π-donor to a π-acceptor metal; however, it offers the added feature that the effect works in both directions. It is interesting to note that the intense visible absorptions observed for binuclear adducts of trans-$[(PMe_2Ph)_4ClReN_2]$ have been tentatively assigned to Re-to-M′ charge transfer.[49] We are presently investigating the possibility that at least one of the three intense bands (392, 544, 771 nm) exhibited by 1 are associated with Zr-to-Zr charge transfer.[51] Such facile charge transfer across the ZrN≡NZr unit may well play a deciding role in the HCl-promoted reduction of one N_2 to hydrazine.[10,52]

References

1. For recent reviews, see A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, Chem. Rev., 73, 11 (1973); D. Sellman, Angew. Chem., Int. Ed. Engl., 13, 639 (1974).
2. E. E. van Tamelen, Acc. Chem. Res., 3, 361 (1970), and literature cited therein.
3. (a) A. E. Shilov, A. K. Shilova, and E. F. Kvashina, Kinet. Katal., 10, 1402 (1969); (b) A. E. Shilov, E. F. Kvashina, and T. A. Vorontsolva, Chem. Commun., 1590 (1971); (c) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, J. Chem. Soc., Chem. Commun., 1178 (1972); (d) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, E. F. Kvashina, A. K. Shilova, and A. E. Shilov, ibid., 169 (1973).
4. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Am. Chem. Soc., 94, 1219 (1972).
5. C. Ungurenasu and E. Streba, J. Inorg. Nucl. Chem., 34, 3753 (1972).
6. E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, J. Chem. Soc., Chem. Commun., 481 (1972).
7. J. E. Bercaw and H. H. Brintzinger, J. Am. Chem. Soc., 93, 2046 (1971).
8. J. E. Bercaw, E. Rosenberg, and J. D. Roberts, J. Am. Chem. Soc., 96, 612 (1974).

9. J. E. Bercaw, J. Am. Chem. Soc., 96, 5087 (1974).

10. J. M. Manriquez and J. E. Bercaw, J. Am. Chem. Soc., 96, 6229 (1974).

11. See Chapter 3 of this thesis.

12. D. J. Wehe, W. R. Busing, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962, Report ORNL-TM-229.

13. A. J. C. Wilson, Nature (London), 150, 151 (1942).

14. D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 24, 321 (1968).

15. C. H. Wei, Inorg. Chem., 8, 2384 (1969).

16. A. C. Larson, Acta Crystallogr., 23, 664 (1967).

17. D. J. Duchamp, American Crystallographic Association, Bozeman, Montana, 1964, Paper B-14.

18. The standard deviation given in parentheses following an average bond distance or angle, $\bar{x}$, is defined as:

$$\sigma = \left[\sum_i (x_i - \bar{x})^2 / (N - 1) \right]^{\frac{1}{2}}$$

where N is the number of observations, x_i.

19. M. A. Busch and G. A. Sim, J. Chem. Soc. A, 2225 (1971).

20. K. W. Muir, J. Chem. Soc. A, 2663 (1971).

21. E. F. Epstein, I. Bernal, and H. Köpf, J. Organomet. Chem., 26, 229 (1971).

22. J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, J. Am. Chem. Soc., 93, 3592 (1971).

23. V. V. Tkachev and L. O. Atovinyan, J. Struct. Chem. USSR, 13, 262 (1972); A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, Can. J. Chem., 53, 1622 (1975).

24. T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, J. Organomet. Chem., 102, 457 (1975).

25. I. A. Ronova, N. V. Alekseev, N. V. Gapotchenko, and Y. T. Struchkov, J. Organomet. Chem., 25, 149 (1971).

26. J. J. Stezowski and H. A. Rick, J. Am. Chem. Soc., 91, 2890 (1969).

27. M. Elder, Inorg. Chem., 8, 2103 (1969).

28. D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, Chem. Commun., 368 (1970).

29. J. L. Hoard, E. W. Silverton, and J. V. Silverton, J. Am. Chem. Soc., 90, 2300 (1968).

30. A. A. Kossiakoff, R. H. Wood, and J. L. Burmeister, private communication.

31. C. Ballhausen and J. P. Dahl, Acta Chem. Scand., 15, 133 (1961).

32. N. W. Alcock, J. Chem. Soc. A, 2001 (1967).

33. J. C. Green, M.L.H. Green, and C. K. Prout, J. Chem. Soc., Chem. Commun., 30, 373 (1972).

34. H. H. Brintzinger and L. S. Bartell, J. Am. Chem. Soc., 92, 1105 (1970).

35. A. J. Petersen and L. F. Dahl, J. Am. Chem. Soc., 96, 2248 (1974).

36. J. W. Lauher and R. Hoffmann, J. Am. Chem. Soc., 98, 1729 (1976).

37. It is possible that if Zr-ring bonding is not weakened significantly, then the b_1 and a_2 orbitals may rehybridize such that one points more directly at the μ-N_2 π^* orbital.

38. D. M. Duggan, J. M. Manriquez, and J. E. Bercaw, unpublished results.

39. A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Saroff, J. Am. Chem. Soc., 89, 5595 (1967).

40. F. Bottomley and S. C. Myburg, Acta Crystallogr., Sect. B, 24, 1289 (1968).

41. D. E. Harrison, H. Taube, and E. Weissberger, Science, 159, 320 (1968).

42. J. Chatt, A. B. Nikolsky, R. L. Richards, and J. R. Sanders, Chem. Commun., 154 (1969).

43. I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, J. Am. Chem. Soc., 91, 6512 (1969).

44. M.L.H. Green and W. E. Silverthorn, J. Chem. Soc., Dalton Trans., 301 (1973).

45. M. L. Green and W. E. Silverthorn, Chem. Commun., 577, (1971).

46. J. Chatt, J. R. Dilworth, and G. J. Leigh, Chem. Commun., 687 (1969).

47. B. R. Davis and J. A. Ibers, Inorg. Chem., 10, 578 (1971).

48. J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, Chem. Commun., 955 (1970).

49. J. Chatt, R. C. Fay, and R. L. Richards, J. Chem. Soc. A., 702 (1971).

50. M. Mercer, R. H. Crabtree, and R. L. Richards, J. Chem. Soc., Chem. Commun., 808 (1973).

51. D. M. Duggan, M. Burke, T. G. Spiro, and J. E. Bercaw, unpublished results.

52. J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 3042 (1976).

Table I. Crystal Data.

$C_{40}H_{60}N_6Zr_2$	Monoclinic space group $P2_1/n$
a = 14.831 (1) Å	FW = 807.4
b = 16.992 (1) Å	ρ_{calc} = 1.31 g·cm^{-3}
c = 16.260 (3) Å	Z = 4
β = 90.00°	μ = 47.0 cm^{-1}
V = 4098 Å	$\lambda(CuK_\alpha)$ = 1.54178 Å

Table II. Final Nonhydrogen Atom Parameters (Coordinates $\times 10^5$, $U_{IJ} \times 10^4$)[a, b, c]

ATOM	X	Y	Z
Zr1	123828 (2)	18592 (2)	22868 (3)
Zr2	87925 (3)	16516 (2)	24155 (3)
N1	109789 (24)	18157 (18)	23566 (28)
N2	101869 (23)	17512 (18)	23986 (28)
N3	122166 (36)	17908 (24)	9520 (27)
N4	121397 (54)	17327 (33)	2720 (41)
N5	89709 (31)	3736 (25)	24109 (30)
N6	90327 (46)	-2796 (29)	24050 (44)
C1	120012 (29)	33250 (23)	25265 (38)
C2	124926 (36)	32832 (24)	17901 (34)
C3	133857 (35)	30095 (27)	19886 (37)
C4	134217 (32)	28972 (27)	28451 (35)
C5	125625 (35)	30644 (25)	31877 (32)
C6	110681 (33)	36443 (27)	26061 (44)
C7	121782 (43)	35957 (32)	9830 (39)
C8	141556 (44)	29794 (37)	13889 (52)
C9	142758 (40)	28146 (36)	33459 (48)
C10	123536 (50)	30872 (34)	40906 (40)
C11	136289 (31)	8481 (25)	26027 (37)
C12	131856 (36)	6052 (29)	18842 (35)
C13	122805 (33)	4062 (25)	20839 (30)
C14	121750 (31)	5229 (27)	29341 (33)
C15	130004 (37)	8084 (30)	32603 (36)
C16	146271 (35)	9584 (35)	26872 (57)
C17	136395 (53)	4742 (39)	10735 (47)
C18	115916 (43)	289 (30)	15368 (46)
C19	113474 (44)	2992 (36)	34062 (46)
C20	131951 (58)	9466 (40)	41513 (43)
C21	75734 (41)	18972 (44)	13385 (38)
C22	80270 (43)	12200 (38)	11101 (40)
C23	89359 (35)	14357 (32)	8953 (34)
C24	89991 (36)	22511 (31)	10111 (33)
C25	81655 (44)	25432 (37)	12836 (37)
C26	65596 (54)	19459 (78)	14105 (60)
C27	76025 (70)	4212 (49)	9653 (53)
C28	96030 (55)	9087 (43)	5020 (42)
C29	98068 (50)	27443 (45)	7665 (45)
C30	79028 (79)	33897 (47)	14009 (53)
C31	91366 (35)	19916 (36)	39393 (38)
C32	86962 (37)	12597 (33)	39309 (34)
C33	78074 (37)	13680 (38)	36253 (36)
C34	77056 (36)	21755 (37)	34652 (35)
C35	85410 (38)	25591 (33)	36286 (34)
C36	100689 (39)	21453 (44)	42677 (39)
C37	90516 (49)	5104 (45)	43132 (44)
C38	70704 (49)	7594 (50)	36247 (49)
C39	68134 (44)	25759 (52)	33325 (47)
C40	86993 (58)	34308 (38)	36296 (47)

Table II - extension

Atom	U11	U22	U33	U12	U13	U23
Zr1	326(2)	324(2)	358(2)	-2(1)	-75(2)	7(1)
Zr2	321(2)	462(2)	383(2)	-11(1)	-67(2)	0(2)
N1	367(19)	357(16)	464(24)	-15(13)	-123(18)	3(16)
N2	330(18)	354(16)	448(24)	13(12)	-8(18)	26(17)
N3	769(34)	535(24)	295(23)	101(22)	-77(22)	16(17)
N4	1257(60)	825(40)	536(40)	161(37)	-27(39)	-3(29)
N5	646(27)	570(23)	464(26)	-65(20)	-107(23)	-24(22)
N6	1277(51)	545(28)	880(45)	-40(30)	-215(43)	-35(31)
C1	404(22)	314(18)	587(33)	-40(16)	-64(23)	-35(20)
C2	473(27)	365(22)	512(31)	-60(19)	-47(25)	46(18)
C3	438(26)	398(24)	605(35)	-52(19)	-32(24)	15(22)
C4	422(25)	429(22)	560(33)	-72(19)	-147(23)	4(22)
C5	495(27)	375(22)	489(29)	-84(20)	-93(25)	-55(19)
C6	465(25)	425(22)	667(43)	-35(19)	-50(30)	-13(28)
C7	736(38)	485(27)	599(38)	-68(26)	-115(31)	154(26)
C8	553(36)	641(37)	539(56)	-70(28)	160(36)	6(36)
C9	556(25)	600(33)	952(52)	-89(26)	-405(35)	-16(34)
C10	804(42)	647(34)	571(36)	-111(32)	-102(36)	-134(28)
C11	414(22)	414(22)	656(37)	42(17)	-120(25)	27(24)
C12	494(26)	462(26)	517(32)	77(21)	-13(24)	35(23)
C13	500(25)	333(19)	457(28)	21(19)	-138(22)	14(18)
C14	386(23)	408(23)	524(30)	44(18)	-17(21)	109(21)
C15	584(30)	434(25)	514(33)	43(22)	-202(26)	4(23)
C16	388(25)	641(32)	1389(70)	55(22)	-143(40)	15(44)
C17	884(50)	716(38)	734(48)	264(37)	125(42)	24(35)
C18	715(39)	426(27)	920(51)	-36(26)	-397(37)	-63(30)
C19	611(36)	640(35)	674(45)	96(30)	118(36)	332(34)
C20	1244(64)	693(39)	557(41)	70(41)	-419(44)	3(33)
C21	413(29)	1153(52)	470(33)	-2(33)	-40(27)	95(33)
C22	652(37)	756(39)	547(38)	-230(31)	-265(31)	131(31)
C23	467(29)	602(29)	454(30)	76(24)	-109(24)	-16(24)
C24	486(28)	571(29)	426(30)	-30(23)	-162(24)	38(23)
C25	710(39)	700(37)	450(33)	230(30)	-159(30)	-10(28)
C26	483(41)	3269(165)	669(59)	207(64)	-251(40)	49(75)
C27	1532(86)	1055(56)	811(57)	-713(61)	-523(60)	88(46)
C28	1001(55)	910(46)	562(40)	412(43)	-159(40)	-103(35)
C29	820(46)	1066(48)	585(42)	-333(40)	-193(37)	281(38)
C30	1791(99)	868(50)	645(50)	696(58)	-81(57)	65(39)
C31	356(24)	780(38)	483(34)	-19(24)	-6(23)	-19(28)
C32	454(28)	686(33)	455(31)	-10(25)	-28(25)	41(25)
C33	467(29)	809(38)	433(31)	-90(27)	-32(24)	13(28)
C34	358(27)	808(36)	484(32)	100(26)	-40(24)	-65(27)
C35	557(32)	611(31)	410(30)	0(25)	-2(24)	-82(24)
C36	447(29)	1188(51)	412(33)	-111(33)	-67(26)	-141(34)
C37	778(44)	1001(51)	602(42)	35(39)	2(36)	311(39)
C38	661(41)	1159(61)	724(50)	-334(40)	33(37)	52(46)
C39	511(33)	1307(65)	679(47)	260(33)	-59(34)	-135(47)
C40	965(53)	662(51)	719(46)	-3(37)	97(45)	-125(33)

[a]The final value of the scale factor is 0.7537 (16) .

[b]The final value of the secondary extinction factor is $1.13\ (6) \times 10^{-6}$.

[c]The form of the anisotropic temperature factor is $\exp\left[-2\pi^2(h^2a^{*2}u_{11}+\ldots+2klb^*c^*u_{23})\right]$.

Table III. FINAL HYDROGEN ATOM PARAMETERS (Coordinates x 10^4)[a]

ATOM	X	Y	Z	B
H6A	10907	3664	3175	5.13
H6B	11040	4166	2380	5.13
H6C	10652	3310	2318	5.13
H7A	12165	4151	1002	5.50
H7B	12566	3427	574	5.50
H7C	11582	3391	869	5.50
H8A	14607	2616	1592	5.89
H8B	13950	2737	880	5.89
H8C	14422	3485	1332	5.89
H9A	14134	2544	3855	5.88
H9B	14711	2532	3051	5.88
H9C	14501	3336	3486	5.88
H10A	12567	3562	4328	6.13
H10B	11721	3054	4182	6.13
H10C	12641	2652	4370	6.13
H16A	14902	476	2812	6.71
H16B	14866	1156	2181	6.71
H16C	14748	1326	3116	6.71
H17A	13966	-7	1090	6.80
H17B	13201	446	651	6.80
H17C	14025	898	948	6.80
H18A	11051	331	1562	5.71
H18B	11811	18	1001	5.71
H18C	11478	-481	1727	5.71
H19A	11413	446	3957	6.01
H19B	10852	530	3159	6.01
H19C	11272	-270	3361	6.01
H20A	12638	992	4449	6.54
H20B	13540	520	4364	6.54
H20C	13514	1417	4221	6.54
H26A	6346	1539	1770	8.94
H26B	6375	2436	1581	8.94
H26C	6284	1834	868	8.94
H27A	7258	285	1442	8.00
H27B	7206	464	511	8.00
H27C	8050	40	875	8.00
H28A	9513	383	674	7.07
H28B	9557	954	-88	7.07
H28C	10201	1081	637	7.07
H29A	10326	2547	1014	6.65
H29B	9855	2743	188	6.65
H29C	9699	3278	927	6.65
H30A	7649	3469	1926	7.39
H30B	8407	3715	1331	7.39
H30C	7458	3536	995	7.39

H36A	10076	2616	4573	6.04
H36B	10243	1714	4618	6.04
H36C	10501	2120	3832	6.04
H37A	8855	481	4855	6.51
H37B	8813	73	4011	6.51
H37C	9688	506	4281	6.51
H38A	6693	828	4081	6.27
H38B	6731	794	3138	6.27
H38C	7351	233	3659	6.27
H39A	6586	2752	3845	7.04
H39B	6910	3021	2978	7.04
H39C	6414	2231	3067	7.04
H40A	8705	3620	4179	6.19
H40B	9257	3541	3376	6.19
H40C	8226	3688	3322	6.19

[a]Thermal parameters are of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

Table IV. BOND DISTANCES (Å)

ZR1 - N1	2.087 (3)		
ZR1 - N3	2.188 (4)	ZR2 - C21	2.551 (6)
ZR2 - N2	2.075 (3)	ZR2 - C22	2.516 (6)
ZR2 - N5	2.188 (4)	ZR2 - C23	2.508 (5)
N1 - N2	1.182 (5)	ZR2 - C24	2.519 (5)
N3 - N4	1.116 (8)	ZR2 - C25	2.559 (6)
N5 - N6	1.114 (7)	ZR2 - C31	2.595 (5)
		ZR2 - C32	2.556 (5)
ZR1 - R1[a]	2.232 (4)	ZR2 - C33	2.497 (5)
ZR1 - R2[a]	2.232 (5)	ZR2 - C34	2.511 (5)
ZR2 - R3[a]	2.229 (5)	ZR2 - C35	2.531 (5)
ZR2 - R4[a]	2.237 (5)		
		C1 - C2	1.404 (6)
ZR1 - C1	2.584 (4)	C2 - C3	1.441 (7)
ZR1 - C2	2.556 (4)	C3 - C4	1.407 (7)
ZR1 - C3	2.504 (5)	C4 - C5	1.420 (6)
ZR1 - C4	2.512 (5)	C5 - C1	1.430 (6)
ZR1 - C5	2.532 (4)	C1 - C6	1.492 (7)
ZR1 - C11	2.575 (4)	C2 - C7	1.490 (7)
ZR1 - C12	2.527 (5)	C3 - C8	1.502 (8)
ZR1 - C13	2.495 (4)	C4 - C9	1.512 (8)
ZR1 - C14	2.522 (4)	C5 - C10	1.501 (8)
ZR1 - C15	2.556 (5)		

C11 - C12	1.403 (7)	C21 - C26	1.510 (12)
C12 - C13	1.422 (7)	C22 - C27	1.515 (11)
C13 - C14	1.405 (6)	C23 - C28	1.480 (9)
C14 - C15	1.420 (7)	C24 - C29	1.515 (9)
C15 - C11	1.420 (7)	C25 - C30	1.502 (11)
C11 - C16	1.499 (8)		
C12 - C17	1.497 (9)	C31 - C32	1.405 (8)
C13 - C18	1.499 (7)	C32 - C33	1.421 (8)
C14 - C19	1.497 (8)	C33 - C34	1.405 (8)
C15 - C20	1.496 (9)	C34 - C35	1.425 (8)
		C35 - C31	1.402 (8)
C21 - C22	1.384 (9)	C31 - C36	1.505 (8)
C22 - C23	1.440 (8)	C32 - C37	1.512 (9)
C23 - C24	1.401 (7)	C33 - C38	1.505 (9)
C24 - C25	1.404 (8)	C34 - C39	1.504 (9)
C25 - C21	1.409 (9)	C35 - C40	1.500 (9)

[a]R1 = C1-C5 ring centroid, R2 = C11-C15 ring centroid, R3 = C21-C25 ring centroid, R4 = C31-C35 ring centroid.

Table V. BOND ANGLES (DEG)

ZR1 - N1 - N2	176.7 (3)	C2 - C1 - C6	125.0 (4)
ZR1 - N3 - N4	177.9 (5)	C5 - C1 - C6	126.0 (4)
ZR2 - N2 - N1	177.4 (3)	C1 - C2 - C7	124.8 (5)
ZR2 - N5 - N6	177.8 (5)	C3 - C2 - C7	126.9 (5)
		C2 - C3 - C8	124.4 (5)
N1 - ZR1 - N3	86.5 (2)	C4 - C3 - C8	127.5 (5)
R1 - ZR1 - R2	141.5 (2)	C3 - C4 - C9	125.3 (5)
R1 - ZR1 - N1	106.6 (2)	C5 - C4 - C9	124.0 (5)
R1 - ZR1 - N3	102.2 (2)	C1 - C5 - C10	127.4 (5)
R2 - ZR1 - N1	105.6 (2)	C4 - C5 - C10	125.1 (5)
R2 - ZR1 - N3	100.3 (2)		
N2 - ZR2 - N5	87.7 (2)	C11 - C12 - C13	108.8 (4)
R3 - ZR2 - R4	141.1 (2)	C12 - C13 - C14	107.2 (4)
R3 - ZR2 - N2	105.9 (2)	C13 - C14 - C15	108.6 (4)
R3 - ZR2 - N5	101.4 (2)	C14 - C15 - C11	107.5 (4)
R4 - ZR2 - N2	105.9 (2)	C15 - C11 - C12	107.8 (4)
R4 - ZR2 - N5	101.6 (2)	C12 - C11 - C16	125.2 (5)
		C15 - C11 - C16	125.8 (5)
C1 - C2 - C3	107.6 (4)	C11 - C12 - C17	124.5 (5)
C2 - C3 - C4	107.5 (4)	C13 - C12 - C17	126.2 (5)
C3 - C4 - C5	109.1 (4)	C12 - C13 - C18	127.6 (5)
C4 - C5 - C1	106.8 (4)	C14 - C13 - C18	124.6 (4)
C5 - C1 - C2	108.9 (4)	C13 - C14 - C19	124.0 (5)

C15 - C14 - C19	127.0 (5)	C24 - C25 - C30	127.4 (6)
C11 - C15 - C20	126.5 (5)		
C14 - C15 - C20	125.6 (5)	C31 - C32 - C33	108.7 (5)
		C32 - C33 - C34	106.9 (5)
C21 - C22 - C23	108.0 (5)	C33 - C34 - C35	108.6 (5)
C22 - C23 - C24	106.4 (5)	C34 - C35 - C31	107.5 (5)
C23 - C24 - C25	109.5 (5)	C35 - C31 - C32	108.2 (5)
C24 - C25 - C21	107.1 (5)	C32 - C31 - C36	125.8 (5)
C25 - C21 - C22	109.1 (6)	C35 - C31 - C36	126.0 (5)
C22 - C21 - C26	123.4 (7)	C31 - C32 - C37	125.4 (5)
C25 - C21 - C26	125.6 (6)	C33 - C32 - C37	125.2 (5)
C21 - C22 - C27	125.8 (6)	C32 - C33 - C38	125.8 (6)
C23 - C22 - C27	125.4 (6)	C34 - C33 - C38	126.4 (6)
C22 - C23 - C28	125.2 (5)	C33 - C34 - C39	124.3 (6)
C24 - C23 - C28	127.7 (5)	C35 - C34 - C39	125.8 (5)
C23 - C24 - C29	124.4 (5)	C31 - C35 - C40	125.5 (5)
C25 - C24 - C29	125.7 (5)	C34 - C35 - C40	126.0 (5)
C21 - C25 - C30	125.2 (6)		

Table VI. Least-Squares Planes of Cyclopentadienyl Rings

Ring 1 (α = 2.2°)[a]		Ring 2 (α = 2.0°)[a]	
Atom	Deviation (Å)[b]	Atom	Deviation (Å)[b]
C1	0.012	C11	0.004
C2	-0.002	C12	0.000
C3	-0.008	C13	-0.005
C4	0.015	C14	0.008
C5	-0.016	C15	-0.008
C6	0.134	C16	0.273
C7	0.185	C17	0.168
C8	0.149	C18	0.152
C9	0.366	C19	0.153
C10	0.127	C20	0.109

Ring 3 (α = 1.6°)[a]		Ring 4 (α = 2.7°)[a]	
C21	0.002	C31	0.011
C22	-0.003	C32	0.001
C23	0.002	C33	-0.013
C24	-0.001	C34	0.020
C25	-0.001	C35	-0.019
C26	0.327	C36	0.113
C27	0.200	C37	0.202
C28	0.200	C38	0.164
C29	0.161	C39	0.352
C30	0.138	C40	0.153

[a]Tilt angle α = angle defined by the intersection of the Zr-ring centroid vector with the normal to the cyclopentadienyl ring plane.

[b]A positive deviation is a deviation away from Zr.

Table VII. Torsion Angles.

Atom 1	Atom 2	Atom 3	Atom 4	Angle (deg)[a]
N3	Zr1	Zr2	N5	87.3(2)
N3	Zr1	Zr2	R3	-13.7(2)
N3	Zr1	Zr2	R4	-171.5(2)
R1	Zr1	Zr2	N5	-171.3(2)
R1	Zr1	Zr2	R3	87.7(2)
R1	Zr1	Zr2	R4	-70.1(2)
R2	Zr1	Zr2	N5	-12.2(2)
R2	Zr1	Zr2	R3	-113.2(2)
R2	Zr1	Zr2	R4	89.0(2)

[a]Looking from atom 2 to atom 3, the angle of clockwise rotation for bond 3-4 with reference to bond 1-2.

Table VIII. Comparison of NN Bond Lengths and Stretching Frequencies for Monomeric and Analogous Binuclear Dinitrogen Complexes.

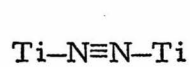
Complex	Electronic Configuration	ν(NN), cm^{-1}	d(NN), Å	ref
$[(NH_3)_5Ru\text{-}N{\equiv}N]^{2+}$	d^6	2130	1.12(8)	39, 40
$[(NH_3)_5Ru\text{-}N{\equiv}N\text{-}Ru(NH_3)_5]^{4+}$	d^6, d^6	2100 (Raman)	1.124(15)	41-43
$(\eta^6\text{-}C_6H_5CH_3)(PPh_3)_2Mo\text{-}N{\equiv}N$	d^6	1988	...	44
$(\eta^6\text{-}C_6H_6)(PPh_3)_2Mo\text{-}N{\equiv}N\text{-}Mo(PPh_3)_2(\eta^6\text{-}C_6H_6)$	d^6, d^6	1910 (Raman)	...	44, 45
$\{(\eta^6\text{-}C_6H_5CH_3)(PPh_3)_2Mo\text{-}N{\equiv}N\text{-}Fe(Me_2PCH_2CH_2PMe_2)(\eta^5\text{-}C_5H_5)\}^+$	d^6, d^6	1930	...	44
trans-$[(PMe_2Ph)_4ClRe\text{-}N{\equiv}N]$	d^6	1925	1.055(30)	46, 47
trans-$[(PMe_2Ph)_4ClRe\text{-}N{\equiv}N\text{-}CrCl_3(THF)_2]$	d^6, d^3	1890	...	48, 49
trans-$[(PMe_2Ph)_4ClRe\text{-}N{\equiv}N\text{-}MoCl_4(OMe)]$	d^6, d^1	1660	1.21	48, 50
trans-$[(PMe_2Ph)_4ClRe\text{-}N{\equiv}N\text{-}ZrCl_4]$	d^6, d^0	1790	...	48
trans-$[(PMe_2Ph)_4ClRe\text{-}N{\equiv}N\text{-}AlEt_3]$	d^6	1890	...	48

CHAPTER III*

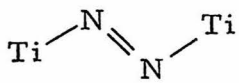
CRYSTAL STRUCTURE OF μ-DINITROGEN-BIS(BIS(PENTAMETHYLCYCLOPENTADIENYL)-TITANIUM(II)), $\{(\eta^5\text{-}C_5(CH_3)_5)_2Ti\}_2N_2$

Introduction

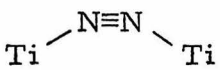
Titanocene-based N_2-fixing systems have been extensively investigated since the original report by Vol'pin and Shur that mixtures of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and ethylmagnesium bromide efficiently reduce N_2 at room temperature.[1-10] One of the species identified in such reaction mixtures, the binuclear dinitrogen complex $\{(C_5H_5)_2Ti\}_2N_2$, has been widely discussed in the literature, and at least four TiN_2Ti arrangements (a-d) have been suggested. As



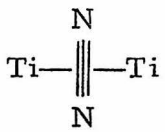
a



b



c



d

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*This chapter has been published previously. See R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 8358 (1976). A paragraph describing the magnetism of this complex has been deleted from the original publication in the writing of this chapter.

discussed previously,[11] the instability of $(C_5H_5)_2Ti$ derivatives has precluded the X-ray crystal structure determination needed to settle the issue.

The title compound $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (1) proved sufficiently stable for crystallization, and we have solved its structure, albeit with difficulty, by single-crystal X-ray methods.

Experimental

$\{(C_5Me_5)_2Ti\}_2N_2$ was obtained as blue-black needles by slow diffusion of N_2 into an argon blanketed pentane solution of $(\eta^5\text{-}C_5Me_5)_2Ti$ at 0°C. A series of Weissenberg and precession photographs (Cu-K_α and Mo-K_α radiation) indicated a trinclinic unit cell, which was assigned space group $P\bar{1}$. Unit cell dimensions were obtained by a least-squares fit to the observed $(\sin^2\theta)/\lambda^2$ values for 32 reflections measured on a diffractometer. Due to the extreme instability of the compound, an experimental density determination was not attempted. The calculated value of 1.19 $g\cdot cm^{-3}$ is, however, a reasonable value for an organometallic compound of this type. Crystal data are given in Table I.

A crystal of dimensions 0.3 × 0.8 × 0.3 mm was mounted in a glass capillary under N_2 with its needle axis (b) slightly skew to the φ axis of a G.E. XRD-5 quarter circle diffractometer automated by Datex. Using Mo-K_α radiation monochromated with a graphite crystal, one hemisphere of data was measured between 1.5 and 45° in 2θ, using a θ-2θ scan technique at a scan rate of 1°/min; 30-s background counts were taken before and after each scan. The

scan width varied linearly from 2° at 2θ = 4° to 2.5° at 2θ = 45°. Intensities of three check reflections measured every 45 reflections showed no crystal decomposition during data collection.

Independent reflections (9711) were measured, 1001 of which were measured twice and averaged. A variance $\sigma^2(F_o^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$, where S is the scan count. Intensities and their weights were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 4.77$ cm^{-1}). The data were then placed on an absolute scale by means of a Wilson plot,[12] with scattering factors for all atoms calculated by the method of Cromer and Mann.[13] Reflections having $F_o^2 < 1.5\sigma(F_o^2)$ were deleted, leaving 7187 reflections for the working data set.

Solution and Refinement

Reflections other than those having h, k, and ℓ all even or all odd are systematically very weak as shown in Table II. It seemed probable, then, that the four molecules in the unit call form an approximate face-centered array with their Ti-N-N-Ti axes closely parallel and that the contributions to the systematically weak reflections are due primarily to different orientations of the various C_5Me_5 groups; indeed, a three-dimensional Patterson map clearly indicated a single orientation for all of the Ti-N vectors. Two such arrangements were considered: (1) four independent, centrosymmetric molecules in the cell, each lying on a different center of symmetry at, e.g., 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$; (2) two pairs

of independent, acentric molecules with their midpoints at, e.g., $\pm(\frac{1}{4}0\frac{1}{4};\ \frac{1}{4}\frac{1}{2}\frac{3}{4})$. Arrangement 1 seemed unlikely, since it would require that the C_5Me_5 groups on the two ends of each molecule be eclipsed; accordingly, attention was concentrated on arrangement 2.

This preliminary model contained no information for phasing the weak reflections with mixed index parities, and electron density maps reflected a composite of the orientations of all eight independent C_5Me_5 groupings. Eventually an arrangement of atoms in one pair of C_5Me_5 groups was derived and used for preliminary phasing of the weak reflections. After many subsequent cycles of structure factor and electron density calculations, tentative parameters had been assigned to all the carbon atoms; however, least-squares convergence was very slow and the R index ($\Sigma \| F_o | - | F_c \| / \Sigma | F_o |$) remained at about 0.44.

At this time, the program MULTAN 74[14] became available to us, and quickly led to the correct structure. The most crucial aspect of this program was undoubtedly the routine "NORMAL," which permitted the normalization of E values for each separate group of index parities (Table II) and thus led to successful phasing of the weak reflections which describe the different orientations of the C_5Me_5 groups. The resulting E map indicated the positions of the Ti and N atoms and 65 of the C atoms; the remaining 15 C atoms were positioned from geometrical considerations, yielding an R factor of 0.39.

In hindsight, the earlier model developed by electron density maps was essentially correct; six of the eight C_5 rings had been positioned within 0.1 Å of their correct locations and the atoms of the remaining two rings were misplaced by an average of about 0.3 Å. However, misplacements of a few of the methyl groups were more serious, ranging up to 2.0 Å -- a value too large to be recovered by standard least-squares refinement. It is apparent that further Fourier refinement would have been needed, and that this refinement would have been expedited by emphasizing the influence of the weak reflections that serve to differentiate between the various C_5Me_5 groups.

Initial refinement was by full-matrix least-squares adjustment of the coordinates of the Ti, N, and C atoms with isotropic temperature parameters and scale factor held constant. The quantity $\Sigma w \left| F_o^2 - s^2 F_c^2 \right|^2$ was minimized, where $1/s$ is the scale factor for F_o and $w = 1/\sigma^2(F_o^2)$. A single cycle reduced the R index to 0.19 for the inner 3027 reflections. Five more cycles of least squares were run, with additional thermal parameters introduced in alternate cycles. In the fifth cycle atomic coordinates were placed in one matrix and the anisotropic thermal parameters placed in two matrices, one for each dimer. An R index of 0.087 based on 5748 reflections was obtained at this point.

Difference Fourier maps then were calculated in the 40 general planes in which the hydrogen atoms of the methyl groups were expected to lie; these maps clearly indicated the positions of all 120 hydrogen atoms. Their coordinates were not further adjusted,

and their isotropic temperature factors were set at values 1.0 $Å^2$ larger than the isotropic values of the carbon atoms to which they are bonded.

During the course of the refinement, it became apparent that ten reflections had overrun the counter capacity and that an additional 40 reflections with large k values -- hence large χ values -- had systematically low values of F_o, presumably due to misalignment or slippage of the crystal. These 50 reflections were assigned weights of zero.

Final refinement was by block diagonal least squares, a 3 × 3 matrix of coordinates and a 6 × 6 matrix of anisotropic temperature parameters being collected for each of the 88 Ti, N, and C atoms. Eight cycles in this configuration gave a final R index of 0.058 and a goodness of fit, $[\Sigma w(F_o^2 - s^2F_c^2)/(N-P)]^{\frac{1}{2}}$, of 2.51 for N = 7137 reflections of nonzero weight and P = 792 parameters. In the final cycle 40 parameters shifted by more than 0.5σ, five by more than 1.0σ. All crystallographic computations were performed under the CRYM system[15] on an IBM 370-158 computer. Final parameters are given in Tables III and IV.

The standard deviations listed in Table III were obtained directly from the inverse matrices, and are undoubtedly underestimated for two reasons. First, the refinement was stopped somewhat short of complete convergence. More important, the block-diagonal configuration of the matrices ignored the correlations between different atoms; some of these correlations, particularly those relating the Ti and N atoms of different N-Ti groupings,

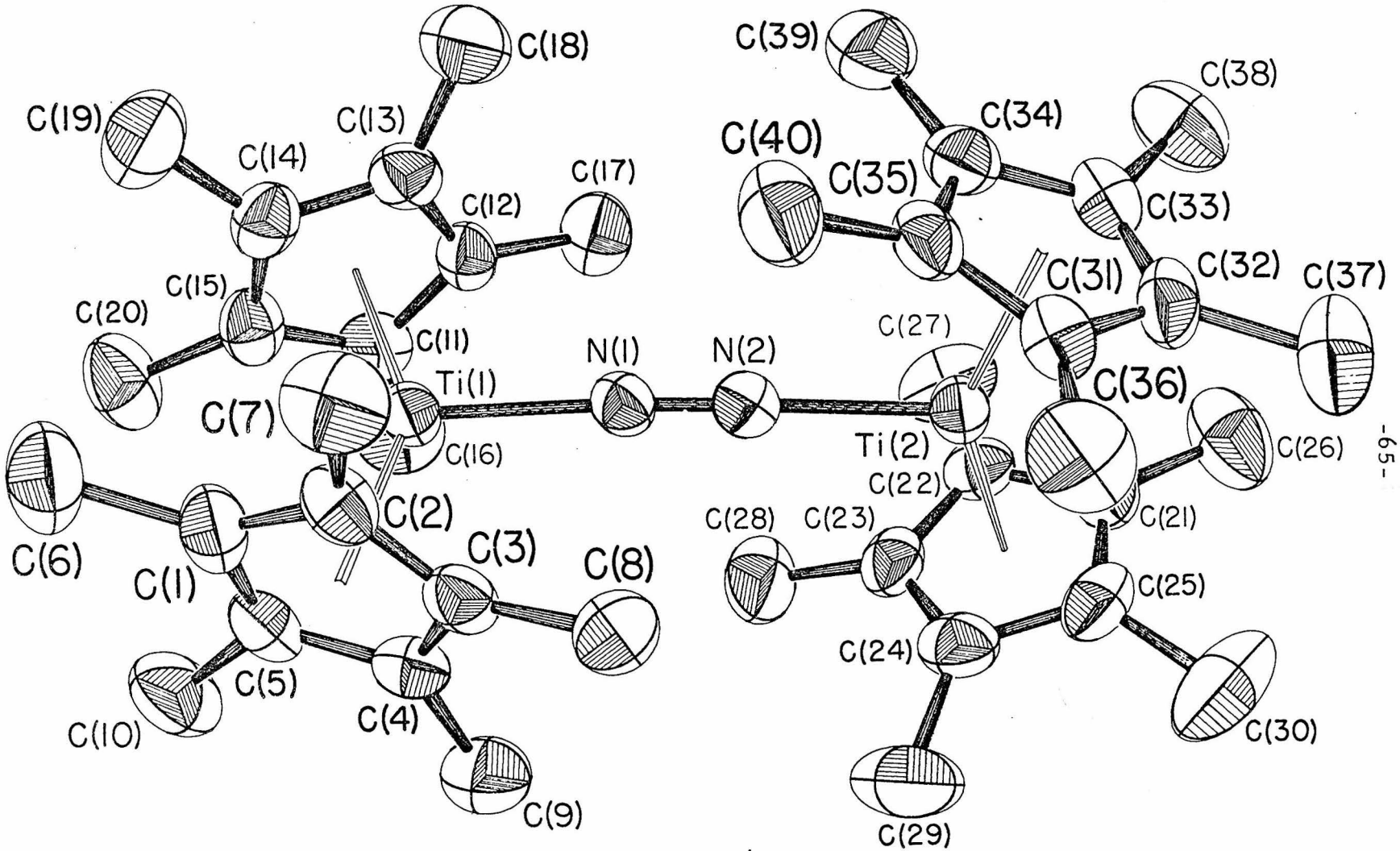


Figure 1. The molecular configuration of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (Ti(1) - Ti(2) dimer). In this and subsequent figures, thermal ellipsoids are drawn at the 50% probability level.

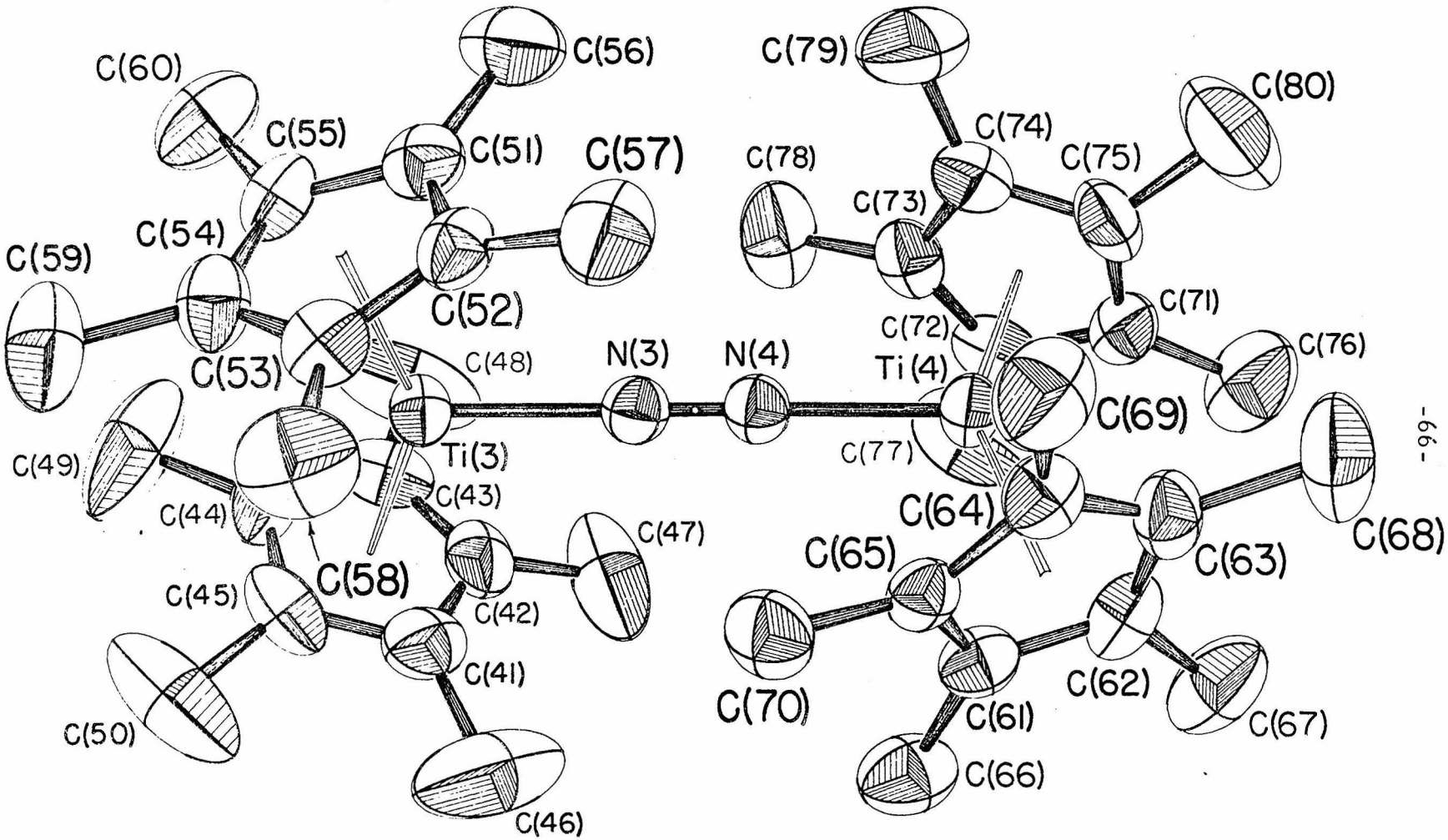


Figure 2. The molecular configuration of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (Ti(3) - Ti(4) dimer).

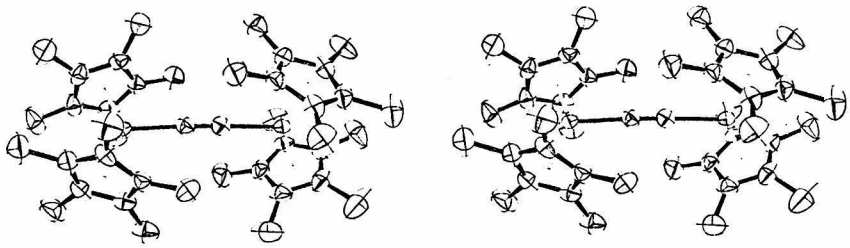


Figure 3. Stereoscopic view of $\{(C_5Me_5)_2Ti\}_2N_2$ (Ti(1) - Ti(2) dimer). This figure is oriented to match the labeled Figure 1.

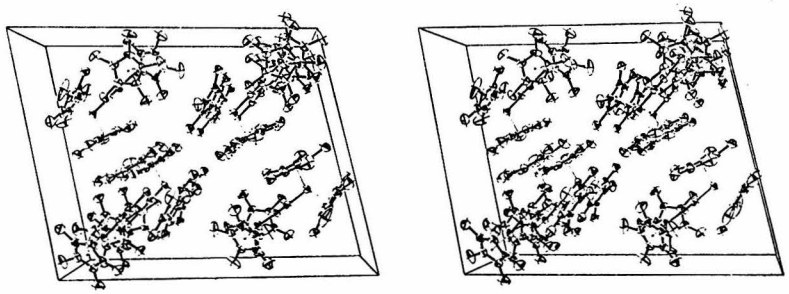


Figure 4. Stereoscopic view of the packing of molecules in the unit cell. Positive a runs from bottom to top, positive b from back to front, positive c from left to right.

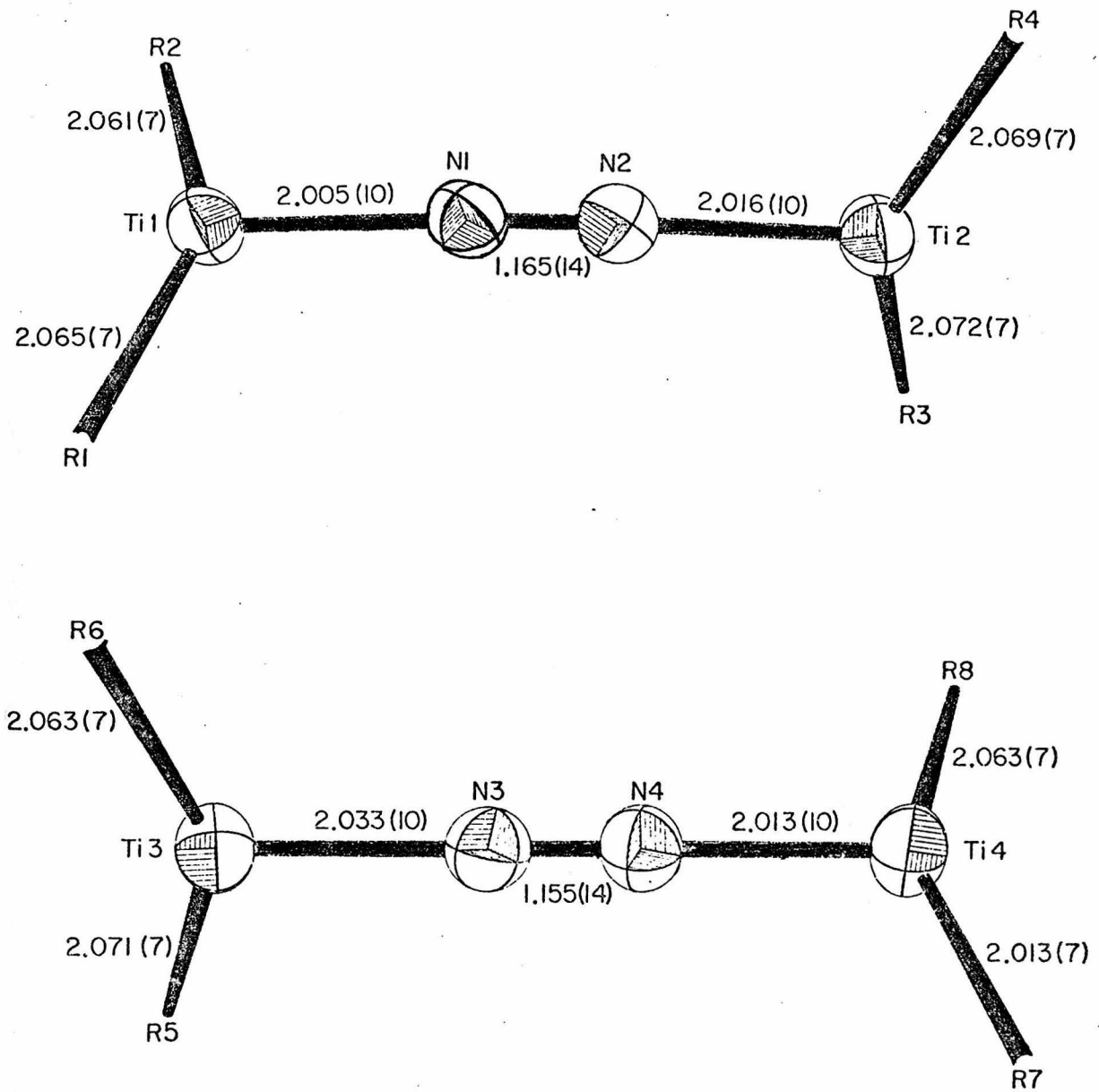


Figure 5. Skeletal view of the two independent molecules of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$.

$(\eta^5\text{-}C_5Me_5)_2TiCl_2$, 137°.[24] The R-Ti-R expansion for 1 may be attributed to reduced ligand crowding in the trigonal, rather than tetrahedral geometry about Ti. The R-Ti-N angles average 107.2(4)°.

The cyclopentadienyl rings are closely planar (Table VII), and although $(C\text{-}C)_{ring}$ bond lengths vary from 1.378 to 1.443 Å (av = 1.404(14) Å) (Table VI), this variation is probably not significant. Ti-ring C distances fall in the narrow range 2.363-2.416 Å, averaging 2.387(11) Å, so that all $C_5(CH_3)_5$ rings may be considered bonded to Ti in a true pentahapto fashion. It should be noted that the average Ti-ring C distance for 1 (2.387(11) Å) is significantly shorter than that for $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ (2.442(25) Å). This reduction in Ti-C bond distances is consistent with the suggestion by Atwood[23] that the two additional electrons in bis(cyclopentadienyl)titanium(II) derivatives occupy a molecular orbital with some metal-ring bonding character; however, it may simply reflect the reduced ligand crowding in the trigonal geometry about Ti for 1 as compared to the pseudotetrahedral $(\eta^5\text{-}C_5Me_5)_2TiCl_2$.

As shown in Table VII, all methyl groups are bent out of their respective cyclopentadienyl planes away from titanium. Again, as observed previously for $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ and $\{(\eta^5\text{-}C_5Me_5)_2Zr\text{-}N_2\}_2N_2$, methyl-methyl contacts between rings may be cited to explain the variations of these deviations. Thus short inter-ring C···C nonbonded distances are observed for C6-C19 (3.39 Å), C10-C20 (3.36 Å), C26-C37 (3.65 Å), C26-C38 (3.42 Å), C30-C37 (3.41 Å), C49-C59 (3.51 Å), C49-C60 (3.54 Å), C50-C59 (3.52 Å),

C67-C76 (3.33 Å), and C68-C80 (3.43 Å), and accordingly these methyl carbons exhibit the greatest deviations from their ring planes. All other inter-ring methyl C···C contacts exceed 3.7 Å. No two rings bonded to a single Ti are strictly staggered, as indicated by the inequality of the contacts [e.g., C6-C19 (3.39 Å), C6-C20 (3.73 Å), C10-C20 (3.36 Å)].

Metal Dinitrogen Bonding. The only other authentic bis(cyclopentadienyl)titanium(II) compound which has been structurally characterized appears to be $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$.[23] The Ti-C(carbonyl) bond lengths for this complex (2.030(11) Å) compare favorably with the Ti-N bond lengths for 1 (av = 2.017(12) Å), as do the two Ti-N distances (2.035(17) Å) for $(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$.[25] The conventional end-on N_2 bonding mode for 1, as for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, is of special significance. It is therefore reasonable to assume the same linear TiN≡NTi arrangement for the parent compound $\{(\eta^5\text{-}C_5H_5)_2\text{-}Ti\}_2N_2$, rather than the doubly bent or edge-on TiN_2Ti arrangements suggested earlier.[4,5,9,10]

The binuclear structures for 1 and $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ cast considerable doubt on the claim that a monomeric bis(pentamethylcyclopentadienyl)titanium(II) dinitrogen complex $(\eta^5\text{-}C_5Me_5)_2\text{-}TiN_2$, forms when solutions of 1 or $(\eta^5\text{-}C_5Me_5)_2Ti$ are cooled below -20°C under N_2. On the basis of NMR and IR data $(\eta^5\text{-}C_5Me_5)_2\text{-}TiN_2$ 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. However, ^1H and ^{15}N NMR and IR spectra subsequently obtained for

$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$[26,27] were noted to be conspicuously similar to those for this unstable dinitrogen complex of $(\eta^5\text{-}C_5Me_5)_2Ti$. We therefore began to suspect that the stoichiometry $\{(\eta^5\text{-}C_5Me_5)_2Ti\text{-}N_2\}_n$ originally assigned this complex was, in fact, incorrect, and that this dinitrogen complex is rather the titanium analogue of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$. In order to reconcile these apparent contradictions, it should be noted that the stoichiometry of this complex was previously measured at residual N_2 pressures (ca. 0.005 Torr) substantially different from those maintained while obtaining NMR and IR spectra (ca. 1 atm). We have therefore examined the stoichiometry of this dinitrogen complex under the same conditions as those for the NMR and IR experiments. We indeed find that $(\eta^5\text{-}C_5Me_5)_2Ti$ absorbs 1.41 mol N_2/mol Ti in toluene at -80°C under 0.85 atm N_2, close to that ratio required for $\{(\eta^5\text{-}C_5Me_5)_2\text{-}TiN_2\}_2N_2$.[28] The apparent 1:1 stoichiometry obtained previously arose because under reduced pressure at -80°C the solution undoubtedly contains a mixture of $\underset{\sim}{1}$ and $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$. No evidence appears to remain, therefore, in support of any dinitrogen complex of titanocene (or zirconocene) containing N_2 bonded edge-on to the metal.

A qualitative description of the Ti-N_2 bonding for $\underset{\sim}{1}$ may be formulated (as for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$) by suitable combinations of dinitrogen lone pair, π, and π^* orbitals with those of the bent bis(η^5-cyclopentadienyl)titanium(II) fragments (Figure 6). As is seen (Figure 7), all RTi···TiR torsion angles are nearly 90° (average 90.0(4.8)°). If each $(C_5Me_5)_2Ti$ approximates an eclipsed $(C_5H_5)_2Ti$

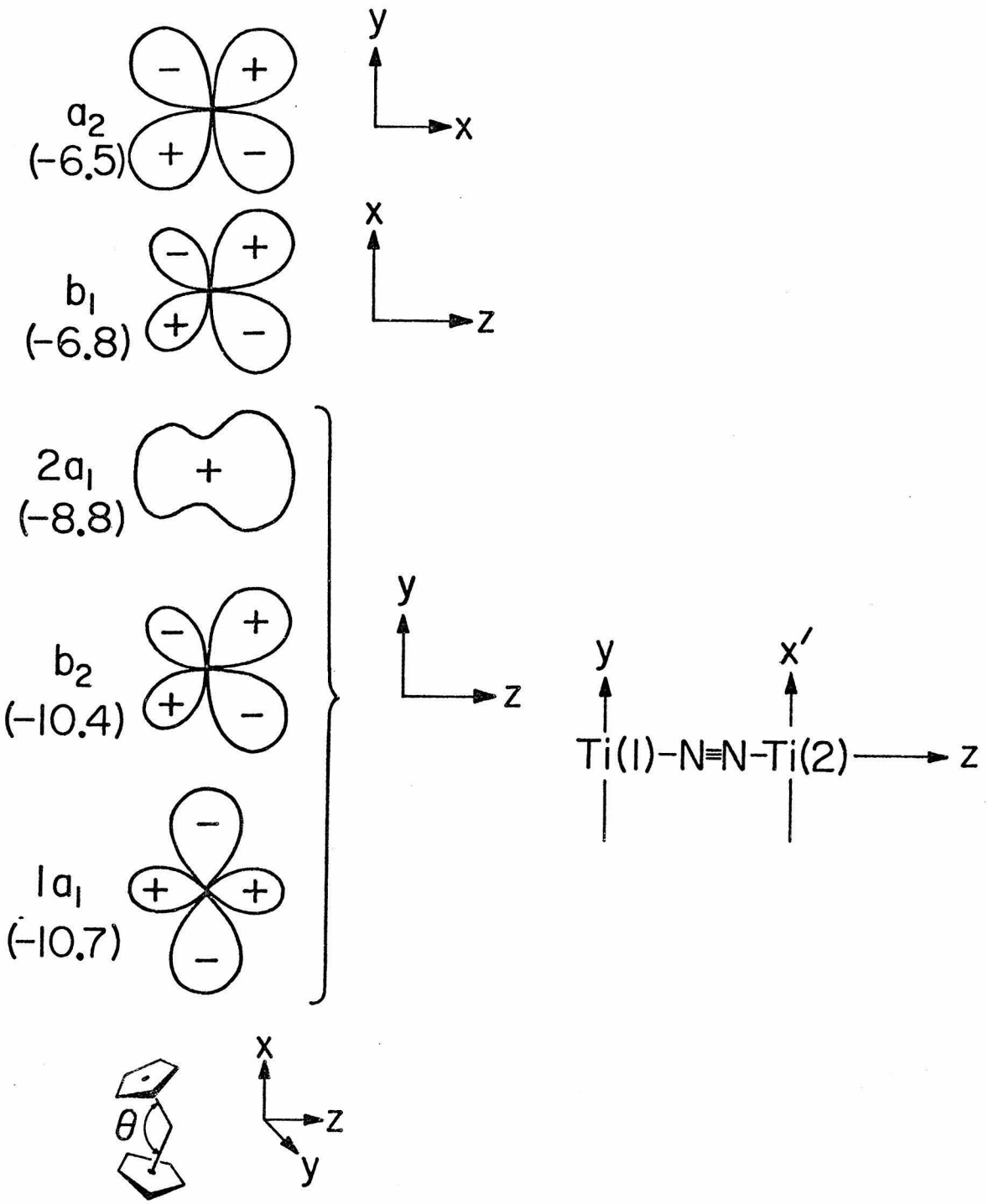


Figure 6. Contours of the five frontier orbitals of a bent, eclipsed $(\eta^5\text{-}C_5H_5)_2Ti$ fragment. Approximate energies (eV) from ref. 29 for $\theta = 146°$ are given in parentheses.

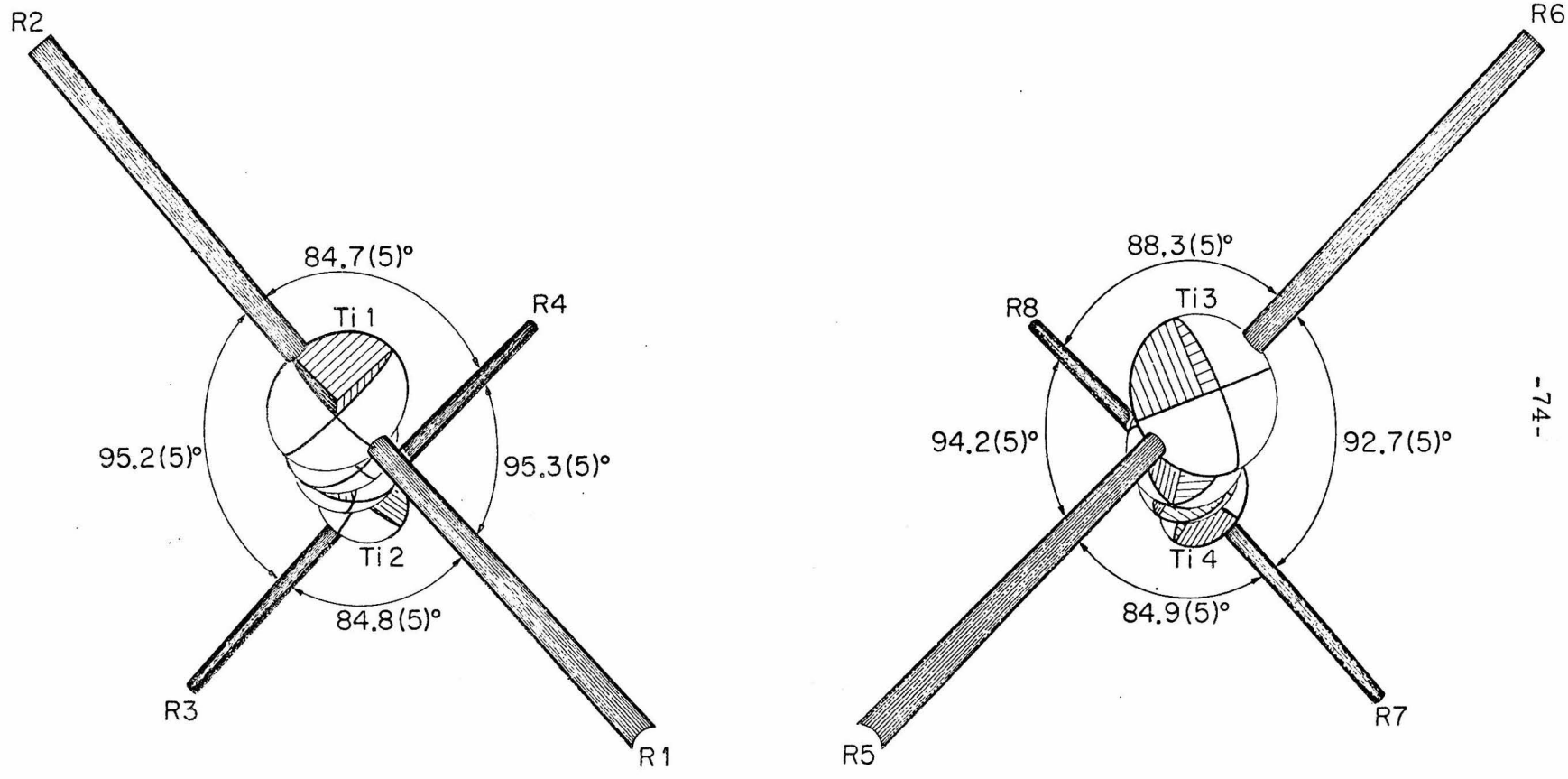


Figure 7. Skeletal view down the Ti-Ti axes revealing torsion angles.

unit (C_{2v} symmetry) and RTi···TiR torsion angles assume exactly 90°, then the dimer possesses perfect D_{2d} symmetry.

The two $(C_5H_5)_2Ti$ orbitals of interest in considering the bonding in the dimer are $1a_1$ and b_2 (Figure 6).[29] In the D_{2d} dimer the two fragment $1a_1$ orbitals transform as $a_1 + b_2$ and the two fragment b_2 orbitals form a degenerate e combination. The dimer a_1 orbital may be expected to interact with the N_2 σ_g and thus be somewhat destabilized; the b_2 will mix with the lower lying N_2 σ_u, and should be destabilized less. Whether the e set should go up or down is difficult to anticipate, since it should interact with both π and π^* N_2 orbitals, the former pushing e up, the latter down. A calculation by Hoffmann and Thorn[30] indicates that the interaction with N_2 π^* dominates, and hence e is stabilized. The calculated level ordering is shown below:

$$a_1 - -10.61$$
$$b_2 - -10.67$$
$$e = -11.17 \text{ eV}$$

Four electrons, two from each $(\eta^5\text{-}C_5Me_5)_2Ti$ unit, are to go into this scheme. The calculated level ordering would dictate a high-spin $e^2b_2^1a_1^1$ configuration, since the gap of only 0.5 eV is well below a reasonable electron pairing energy (ca. 2 eV) for a d^2 Ti(II) ion. The dominant component of the TiN≡NTi bonding is thus π interaction of the two Ti b_2 orbitals with N_2 π^* orbitals. Interaction of the empty π-acceptor orbital on each Ti(b_1) with filled N_2 π orbitals further enhances the N_2 π^* interaction with the Ti b_2

orbitals. Thus 1 falls into the general class of binuclear complexes, discussed in the preceding chapter, where N_2 bridges a π-donor to a π-acceptor metal. As for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, the MN≡NM bonding for 1 may be viewed as a "push-pull" interaction in the two orthogonal planes along the TiN≡NTi axis. A reduction in bond order for the $\mu\text{-}N_2$ of 1 comparable to that for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ is thus achieved.

The effect exerted on the MN≡NM bonding by the empty b_1 π-acceptor orbitals on each Ti in 1 is illustrated by comparison to $\{(C_6H_{11})_3P\}_2NiN{\equiv}NNi\{P(C_6H_{11})_3\}_2$,[31] which also possesses nearly perfect D_{2d} symmetry. Even though Ti(II) formally possesses eight fewer d electrons than Ni(0), the presence of low-lying empty π-type orbitals for Ti effects a reduction in $\mu\text{-}N_2$ bond order (av N-N distance 1.160(7) Å) greater than that for the Ni dimer (N-N distance 1.12 Å). A sizeable reduction in N-N bond order does not appear to guarantee N_2 activation, however. The observations that 1 liberates only minor amounts of reduced N_2 (5-20%)[32] when treated with HCl, while $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ and $\{(\eta^5\text{-}C_5Me_5)_2\text{-}TiN_2\}_2N_2$[28] give nearly quantitative yields of hydrazine under identical conditions, are indicative of more stringent requirements. Indeed, the results of a labeling study of the reaction of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ with HCl suggest that here the terminal dinitrogen ligands play the deciding role.[27]

References

1. M. E. Vol'pin and V. B. Shur, Nature (London), 209, 1236 (1966); Dokl. Akad. Nauk SSSR, 1102 (1964).
2. G. Henrici-Olive and S. Olive, Angew. Chem., 80, 398 (1968).
3. E. E. van Tamelen, Acc. Chem. Res., 3, 361 (1970), and literature cited therein.
4. (a) A. E. Shilov, A. K. Shilova, and E. F. Kvashina, Kinet. Katal., 10, 1402 (1969); (b) A. E. Shilov, E. F. Kvashina, and T. A. Vorontsolva, Chem. Commun., 1590 (1971); (c) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, J. Chem. Soc., Chem. Commun., 1178 (1972); (d) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, E. F. Kvashina, A. K. Shilova, and A. E. Shilov, ibid., 169 (1973).
5. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Am. Chem. Soc., 94, 1219 (1972).
6. C. Ungurenasu and E. Streba, J. Inorg. Nucl. Chem., 34, 3753 (1972).
7. E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, J. Chem. Soc., Chem. Commun., 481 (1972).
8. J. E. Bercaw and H. H. Brintzinger, J. Am. Chem. Soc., 93, 2046 (1971).
9. J. E. Bercaw, E. Rosenberg, and J. D. Roberts, J. Am. Chem. Soc., 96, 612 (1974).
10. J. E. Bercaw, J. Am. Chem. Soc., 96, 5087 (1974).

11. See Chapter II of this thesis.

12. A.J.C. Wilson, Nature (London), 150, 151 (1942).

13. D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 24, 321 (1968).

14. P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and J.-P. Declercq, "MULTAN 74, A System of Computer Programmes for Automatic Crystal Structure Solution." See also G. Germain, P. Main, and M.M. Woolfson, Acta Crystallogr., Sect. A, 27, 368 (1971).

15. D. J. Duchamp, American Crystallographic Association, Bozeman, Montana, 1964, Paper B-14.

16. P. C. Wailes, R. S. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium," Academic Press, New York, N.Y., 1974.

17. The standard deviation given in parentheses following an average bond distance or angle, $\bar{x}$, is defined as:

$$\sigma = \left[\sum_i (x_i - \bar{x})^2/(N-1) \right]^{\frac{1}{2}}$$

where N is the number of observations, x_i.

18. V. V. Tkachev and L. O. Atovinyan, J. Struct. Chem. (USSR), 13, 262 (1972).

19. A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, Can. J. Chem., 53, 1622 (1975).

20. V. Kocman, J. C. Rucklidge, R. J. O'Brian, and W. Santo, Chem. Commun., 1340 (1971).

21. E. F. Epstein, I. Bernal, and H. Köpf, J. Organomet. Chem., 26, 229 (1971).

22. J. L. Calderon, F. A. Cotton, B. G. De Boer, and J. Takats, J. Am. Chem. Soc., 93, 3592 (1971).

23. J. L. Atwood, K. E. Stone, H. G. Alt, D. C. Hrncir, and M. D. Rausch, J. Organomet. Chem., 96, C4 (1975).

24. T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, J. Organomet. Chem., 102, 457 (1975).

25. A. A. Kossaiakoff, R. H. Wood, and J. L. Burmeister, private communication.

26. J. M. Manriquez and J. E. Bercaw, J. Am. Chem. Soc., 96, 6229 (1974).

27. J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 3042 (1976).

28. J. M. Manriquez and J. E. Bercaw, unpublished results.

29. J. W. Lauher and R. Hoffmann, J. Am. Chem. Soc., 98, 1729 (1976).

30. D. Thorn and R. Hoffmann, private communication.

31. P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, J. Organomet. Chem., 33, 109 (1971).

32. It may well be that the ammonia and hydrazine formed in this reaction result from $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$, which is generated from 1 and liberated N_2 during the reaction with HCl.

Table I. Crystal Data

$C_{40}H_{60}Ti_2N_2$	Triclinic space group $P\bar{1}$
$\underline{a}$ = 18.867(1) Å	V = 3713 Å^3
$\underline{b}$ = 8.968(2) Å	$\lambda(MoK_\alpha)$ = 0.71069 Å
$\underline{c}$ = 22.767(1) Å	FW = 664.73
α = 98.22(1)°	ρ_{calc} = 1.19 g·cm^{-3}
β = 101.83(1)°	Z = 4
γ = 93.86(1)°	μ = 4.77 cm^{-1}

Table II. Mean Values of E^2 According to ($hk\ell$) Parity Group

($hk\ell$) Parity Group	EEE	OEE	EOE	OOE	EEO	OEO	EOO	OOO
Mean E^2 (before normalization)	2.20	0.61	0.54	0.29	0.28	0.57	0.62	2.12
Number in Group	1104	893	895	761	779	901	898	1127
Normalization Factor	0.674	1.280	1.361	1.857	1.890	1.324	1.270	0.687

Table III. Final Nonhydrogen Atom Parameters (Coordinates $\times 10^5$, $U_{IJ} \times 10^4$)[a,b,c]

ATOM	X	Y	Z
TI1	15393 (4)	86362 (9)	15287 (3)
TI2	34256 (4)	115462 (9)	33908 (3)
TI3	33269 (4)	64639 (9)	84493 (3)
TI4	16398 (4)	35278 (9)	64669 (3)
N1	22497 (17)	98516 (37)	22405 (14)
N2	26792 (17)	104962 (39)	26575 (14)
N3	26318 (17)	53812 (39)	76793 (14)
N4	22618 (17)	47300 (39)	72360 (14)
C1	10591 (24)	60291 (51)	12968 (19)
C2	12947 (23)	64084 (48)	19353 (18)
C3	20528 (23)	67121 (47)	20676 (18)
C4	22932 (23)	66063 (49)	15166 (19)
C5	16760 (24)	61764 (49)	10425 (19)
C6	3165 (27)	52945 (60)	9733 (23)
C7	8271 (26)	62871 (59)	23881 (22)
C8	25379 (25)	69229 (55)	26898 (20)
C9	30551 (26)	66695 (60)	14402 (22)
C10	17129 (30)	56404 (62)	3950 (21)
C11	14414 (24)	102414 (52)	7782 (19)
C12	14072 (22)	111704 (47)	13239 (18)
C13	7796 (23)	106570 (50)	15060 (19)
C14	4126 (22)	94295 (52)	10648 (19)
C15	8218 (23)	91956 (52)	6106 (18)
C16	20122 (29)	104633 (67)	4234 (23)
C17	19046 (26)	125649 (54)	16250 (22)
C18	4790 (28)	113894 (63)	20236 (22)
C19	-3403 (26)	87307 (65)	10393 (25)
C20	5647 (30)	82186 (63)	62 (20)
C21	45972 (22)	128834 (55)	35117 (20)
C22	42178 (22)	128764 (52)	29111 (20)
C23	41239 (21)	113706 (56)	26161 (18)
C24	44085 (23)	104379 (54)	30259 (21)
C25	47092 (22)	113788 (58)	35835 (20)
C26	49574 (29)	142420 (70)	39524 (25)
C27	40293 (26)	142096 (65)	26090 (26)
C28	38382 (27)	109134 (71)	19404 (21)
C29	45178 (29)	87847 (64)	28992 (29)
C30	51887 (29)	108611 (84)	41194 (26)
C31	30183 (23)	107374 (51)	42433 (18)
C32	34474 (23)	121760 (55)	44568 (17)
C33	31122 (24)	133100 (52)	41616 (18)
C34	24526 (24)	126231 (52)	37657 (18)
C35	23949 (22)	110890 (53)	38260 (18)
C36	31639 (29)	93269 (60)	44597 (22)
C37	40807 (27)	124455 (66)	49934 (20)

C38	33217 (30)	149831 (59)	42997 (23)
C39	18892 (28)	134220 (67)	34103 (22)
C40	17282 (25)	100000 (65)	35672 (21)
C41	25972 (28)	54064 (58)	90584 (20)
C42	21947 (24)	64139 (63)	87672 (19)
C43	25472 (26)	78520 (57)	89655 (21)
C44	31782 (24)	77477 (58)	94051 (20)
C45	32095 (26)	61901 (60)	94524 (19)
C46	23794 (50)	37660 (76)	90355 (32)
C47	14448 (29)	60217 (5)	83684 (25)
C48	22609 (44)	92699 (84)	87838 (32)
C49	36379 (34)	90492 (87)	98181 (31)
C50	37235 (37)	55164 (95)	99048 (26)
C51	40559 (22)	74015 (53)	78154 (20)
C52	41573 (22)	58698 (52)	78090 (19)
C53	44878 (22)	56328 (52)	83922 (20)
C54	46196 (22)	70634 (56)	87701 (20)
C55	43462 (23)	81388 (51)	84208 (21)
C56	38097 (27)	81749 (70)	72869 (25)
C57	40077 (26)	47086 (64)	72402 (22)
C58	47498 (29)	41816 (62)	85767 (25)
C59	51212 (27)	73784 (72)	93831 (24)
C60	44321 (29)	98232 (61)	86025 (27)
C61	14296 (22)	14690 (49)	69830 (19)
C62	10470 (23)	10492 (52)	63748 (21)
C63	15683 (24)	9436 (50)	60091 (19)
C64	22641 (23)	12846 (50)	63832 (19)
C65	21811 (22)	15868 (47)	69921 (18)
C66	10938 (28)	15088 (61)	75203 (24)
C67	2553 (28)	4948 (63)	61982 (27)
C68	14179 (31)	2155 (63)	53427 (23)
C69	29580 (27)	11602 (62)	61779 (23)
C70	27814 (25)	17658 (55)	75476 (20)
C71	6924 (22)	41059 (52)	56894 (19)
C72	7187 (24)	51788 (59)	62319 (21)
C73	13850 (25)	60580 (52)	63472 (19)
C74	17766 (27)	55577 (61)	59215 (21)
C75	13484 (26)	43859 (59)	55206 (18)
C76	354 (31)	31685 (71)	53177 (27)
C77	1284 (33)	54082 (87)	65630 (29)
C78	16110 (32)	74649 (65)	68165 (25)
C79	24961 (34)	62782 (90)	58542 (29)
C80	15355 (38)	37285 (83)	49234 (24)

[a]The final value of the scale factor is 0.8828.

[b]The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}u_{11} + \cdots + 2klb^*c^*u_{23})]$.

[c]The esd's quoted for C atoms should be doubled while those for Ti and N atoms should be tripled. See text for explanation.

Table III - extension

Atom	U11	U22	U33	U12	U13	U23
T11	438(5)	338(5)	348(4)	46(4)	29(4)	35(4)
T12	382(5)	457(6)	369(4)	5(4)	60(4)	-3(4)
T13	386(5)	479(6)	386(4)	41(4)	51(4)	26(4)
T14	465(5)	361(5)	411(5)	59(4)	-10(4)	22(4)
N1	448(22)	349(23)	425(20)	41(18)	84(17)	36(18)
N2	444(23)	421(24)	462(21)	52(18)	96(18)	39(18)
N3	450(23)	434(24)	443(21)	42(19)	100(18)	66(18)
N4	448(22)	408(24)	426(20)	62(19)	54(17)	64(18)
C1	593(31)	429(31)	506(28)	-39(25)	-20(24)	17(24)
C2	568(30)	343(28)	479(26)	0(23)	140(23)	44(23)
C3	580(30)	310(27)	456(26)	97(23)	81(23)	58(22)
C4	519(29)	368(28)	546(28)	120(24)	157(23)	72(23)
C5	582(33)	303(29)	467(27)	71(25)	125(24)	-29(23)
C6	753(38)	578(38)	825(38)	-141(31)	-85(31)	34(32)
C7	723(37)	647(38)	766(36)	28(30)	311(30)	186(31)
C8	646(33)	575(35)	543(29)	156(28)	15(25)	150(27)
C9	670(35)	690(39)	764(36)	159(30)	247(29)	96(31)
C10	1090(46)	708(41)	539(32)	242(36)	131(31)	-83(30)
C11	621(31)	523(32)	479(27)	116(26)	147(24)	229(25)
C12	521(29)	338(28)	490(26)	28(23)	-4(22)	30(23)
C13	528(29)	422(30)	506(27)	137(24)	84(23)	118(24)
C14	461(28)	531(33)	509(27)	48(25)	6(23)	137(25)
C15	585(31)	511(32)	407(26)	19(26)	-7(23)	97(24)
C16	924(43)	564(48)	706(36)	122(37)	353(33)	298(35)
C17	758(37)	410(33)	821(37)	10(28)	-33(30)	180(29)
C18	778(39)	800(43)	697(35)	266(34)	154(30)	22(32)
C19	543(34)	824(45)	535(41)	-7(31)	12(30)	150(36)
C20	1105(46)	705(41)	437(29)	81(35)	-102(29)	30(29)
C21	415(28)	625(35)	575(29)	-56(25)	137(23)	-21(27)
C22	393(27)	516(32)	629(30)	57(24)	140(23)	115(26)
C23	352(26)	742(37)	462(26)	54(25)	85(22)	56(26)
C24	425(29)	529(33)	762(33)	78(25)	192(25)	58(28)
C25	371(28)	759(40)	580(30)	70(27)	34(23)	176(29)
C26	759(41)	1020(52)	901(42)	-320(37)	295(34)	-258(38)
C27	674(37)	827(46)	1155(47)	137(34)	339(35)	484(39)
C28	609(35)	1227(54)	553(31)	30(35)	179(27)	-93(35)
C29	719(40)	625(42)	1532(59)	220(34)	322(40)	43(41)
C30	649(39)	1729(72)	931(44)	342(43)	36(34)	582(48)
C31	545(30)	478(31)	409(25)	-5(25)	115(22)	27(23)
C32	527(29)	724(37)	390(23)	-22(27)	42(21)	13(24)
C33	623(32)	492(32)	422(26)	-19(26)	131(23)	-39(24)
C34	564(31)	547(33)	431(26)	185(26)	137(23)	62(24)
C35	458(28)	595(33)	411(25)	-43(25)	162(22)	-76(24)
C36	1034(45)	634(39)	672(34)	98(34)	190(32)	226(31)
C37	786(39)	1007(48)	458(29)	-151(35)	28(27)	67(31)
C38	1013(44)	530(37)	807(38)	-27(33)	360(34)	-37(31)
C39	709(39)	1008(48)	604(33)	298(36)	215(29)	55(33)
C40	580(33)	944(46)	624(32)	-164(32)	219(27)	-137(32)

Table III - extension (continued)

C41	998(42)	608(27)	500(29)	-55(32)	349(29)	15(28)
C42	526(31)	1028(47)	429(27)	-41(31)	173(24)	66(30)
C43	741(35)	709(39)	716(33)	364(31)	411(29)	308(30)
C44	532(31)	689(38)	585(30)	-17(28)	193(25)	-159(28)
C45	767(36)	952(42)	358(27)	360(33)	133(25)	112(28)
C46	3232(111)	731(51)	1321(61)	-420(63)	1557(72)	-198(45)
C47	538(39)	3013(110)	648(35)	-80(53)	173(32)	7(55)
C48	2272(84)	1377(68)	1489(64)	1251(65)	1283(64)	836(56)
C49	1020(52)	1533(71)	1460(61)	527(49)	592(47)	1013(55)
C50	1432(61)	2165(88)	716(41)	965(62)	392(42)	654(51)
C51	391(27)	591(35)	651(31)	70(25)	120(24)	186(27)
C52	414(27)	518(32)	537(28)	-15(24)	163(22)	-31(25)
C53	435(28)	500(32)	630(30)	124(24)	159(24)	63(26)
C54	376(27)	657(36)	588(30)	104(26)	25(23)	13(27)
C55	421(28)	422(30)	725(32)	-3(24)	91(24)	-43(26)
C56	630(36)	1156(53)	528(41)	114(36)	200(32)	556(50)
C57	609(34)	867(44)	753(36)	49(32)	294(29)	126(33)
C58	813(40)	652(40)	1045(44)	280(33)	246(35)	235(35)
C59	552(35)	1174(55)	790(38)	59(36)	-80(30)	-115(38)
C60	782(40)	521(38)	1272(50)	-54(32)	320(37)	-40(36)
C61	501(29)	294(29)	595(29)	59(24)	170(24)	94(24)
C62	462(29)	422(31)	742(33)	-11(25)	34(25)	-10(27)
C63	676(33)	359(30)	457(27)	93(26)	29(24)	22(23)
C64	515(29)	403(30)	559(28)	102(24)	145(24)	35(24)
C65	478(27)	314(27)	500(26)	52(22)	81(22)	56(22)
C66	811(39)	675(40)	911(40)	50(32)	431(33)	149(33)
C67	636(37)	641(41)	1262(51)	83(31)	97(35)	196(38)
C68	1161(49)	704(43)	618(34)	154(38)	-71(33)	-198(32)
C69	729(37)	705(41)	667(35)	17(32)	348(32)	-122(33)
C70	643(33)	584(36)	579(30)	144(28)	39(25)	174(27)
C71	448(28)	518(32)	547(28)	3(24)	-90(23)	168(25)
C72	525(30)	821(40)	647(31)	324(29)	229(25)	337(30)
C73	742(35)	471(32)	478(27)	209(28)	18(25)	112(25)
C74	800(38)	752(41)	541(30)	-37(32)	111(28)	243(29)
C75	781(36)	747(39)	333(25)	82(31)	41(24)	66(26)
C76	909(44)	904(51)	1107(49)	-120(38)	-393(36)	312(42)
C77	993(50)	1715(76)	1192(53)	655(52)	521(44)	525(54)
C78	1550(59)	463(38)	827(41)	230(39)	-166(41)	44(33)
C79	1024(52)	1667(80)	1072(52)	577(52)	251(43)	498(54)
C80	1686(67)	1390(67)	524(35)	205(55)	341(40)	87(41)

Table IV. FINAL HYDROGEN ATOM PARAMETERS (Coordinates x 10^4) [a]

ATOM	X	Y	Z	B
H6A	300	4154	964	6.36
H6B	190	5467	586	6.36
H6C	-52	5593	1201	6.36
H7A	1018	6999	2760	6.30
H7B	788	5308	2490	6.30
H7C	347	6548	2254	6.30
H8A	2814	6065	2744	5.54
H8B	2262	7062	3000	5.54
H8C	2881	7798	2750	5.54
H9A	3135	7211	1133	6.24
H9B	3210	5675	1345	6.24
H9C	3385	7153	1817	6.24
H10A	1965	6466	244	6.39
H10B	1259	5373	134	6.39
H10C	2012	4823	366	6.39
H16A	2487	10829	676	7.33
H16B	1896	11163	142	7.33
H16C	2076	9522	175	7.33
H17A	2045	12592	2038	6.84
H17B	1687	13447	1536	6.84
H17C	2345	12542	1454	6.84
H18A	478	10724	2322	6.78
H18B	7	11651	1902	6.78
H18C	782	12311	2238	6.78
H19A	-502	7960	701	7.29
H19B	-687	9488	1026	7.29
H19C	-362	8310	1409	7.29
H20A	948	7917	-169	6.61
H20B	243	8729	-264	6.61
H20C	284	7300	48	6.61
H26A	5417	14555	3920	8.16
H26B	4902	14212	4347	8.16
H26C	4670	15167	3841	8.16
H27A	4363	14460	2367	7.41
H27B	4010	15085	2893	7.41
H27C	3551	14019	2330	7.41
H28A	4191	11069	1716	6.98
H28B	3417	11440	1801	6.98
H28C	3654	9840	1847	6.98
H29A	4984	8658	2844	7.95
H29B	4167	8309	2526	7.95
H29C	4415	8298	3221	7.95
H30A	5598	10430	4027	8.65
H30B	4916	10074	4277	8.65
H30C	5348	11671	4461	8.65

H36A	3664	9302	4634	7.32
H36B	3021	8482	4129	7.32
H36C	2885	9133	4760	7.32
H37A	4478	13108	4920	6.56
H37B	4285	11519	5068	6.56
H37C	3957	12907	5351	6.56
H38A	3754	15245	4617	7.23
H38B	2948	15553	4409	7.23
H38C	3444	15359	3944	7.23
H39A	1807	14337	3650	6.90
H39B	1440	12810	3258	6.90
H39C	2048	13711	3052	6.90
H40A	1832	8990	3644	6.00
H40B	1573	9978	3150	6.00
H40C	1338	10257	3765	6.00
H46A	2785	3162	9056	11.10
H46B	2037	3313	8645	11.10
H46C	2139	3524	9348	11.10
H47A	1290	6891	8181	9.44
H47B	1097	5710	8576	9.44
H47C	1452	5202	8034	9.44
H48A	2597	10152	8956	10.38
H48B	1809	9476	8909	10.38
H48C	2157	9255	8347	10.38
H49A	4043	8732	10064	10.82
H49B	3356	9566	10074	10.82
H49C	3796	9763	9578	10.82
H50A	3894	4627	9722	10.08
H50B	3493	5215	10220	10.08
H50C	4146	6221	10102	10.08
H56A	4170	8830	7212	7.23
H56B	3385	8695	7324	7.23
H56C	3640	7405	6910	7.23
H57A	4315	4968	6969	6.29
H57B	3518	4614	7038	6.29
H57C	4133	3730	7339	6.29
H58A	5233	4076	8546	7.40
H58B	4440	3301	8312	7.40
H58C	4700	4109	8980	7.40
H59A	5597	7158	9375	7.45
H59B	4945	6691	9658	7.45
H59C	5118	8367	9591	7.45
H60A	4766	10125	8999	7.16
H60B	3980	10220	8654	7.16
H60C	4622	10356	8320	7.16
H66A	1376	2266	7858	6.28
H66B	1086	569	7659	6.28
H66C	610	1787	7442	6.28
H67A	68	440	5773	7.29
H67B	-34	1143	6408	7.29
H67C	170	-508	6297	7.29
H68A	1776	638	5159	7.55

H68B	950	395	5146	7.55
H68C	1443	-847	5318	7.55
H69A	3373	1459	6508	6.92
H69B	2999	1890	5892	6.92
H69C	3003	191	5980	6.92
H70A	3241	1740	7435	6.14
H70B	2726	990	7781	6.14
H70C	2769	2747	7796	6.14
H76A	170	2310	5058	8.29
H76B	-252	3744	5042	8.29
H76C	-267	2773	5549	8.29
H77A	320	5646	6997	9.27
H77B	-200	4488	6486	9.27
H77C	-142	6199	6445	9.27
H78A	2049	7403	7072	8.91
H78B	1230	7538	7069	8.91
H78C	1606	8325	6632	8.91
H79A	2828	6702	6227	9.44
H79B	2481	6917	5571	9.44
H79C	2800	5418	5690	9.44
H80A	2044	3404	5000	9.69
H80B	1539	4414	4649	9.69
H80C	1244	2803	4719	9.69

[a]Thermal parameters are of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

Table V. BOND DISTANCES (Å)[a]

TI1 - N1	2.005	TI1 - C13	2.385
TI2 - N2	2.016	TI1 - C14	2.374
TI3 - N3	2.033	TI1 - C15	2.384
TI4 - N4	2.013		
N1 - N2	1.165	TI2 - C21	2.387
N3 - N4	1.155	TI2 - C22	2.377
		TI2 - C23	2.403
TI1 - R1[b]	2.065	TI2 - C24	2.400
TI1 - R2[b]	2.061	TI2 - C25	2.390
TI2 - R3[b]	2.072	TI2 - C31	2.396
TI2 - R4[b]	2.069	TI2 - C32	2.403
TI3 - R5[b]	2.071	TI2 - C33	2.385
TI3 - R6[b]	2.063	TI2 - C34	2.382
TI4 - R7[b]	2.070	TI2 - C35	2.394
TI4 - R8[b]	2.063		
		TI3 - C41	2.388
TI1 - C1	2.394	TI3 - C42	2.391
TI1 - C2	2.375	TI3 - C43	2.373
TI1 - C3	2.401	TI3 - C44	2.391
TI1 - C4	2.385	TI3 - C45	2.384
TI1 - C5	2.378	TI3 - C51	2.385
TI1 - C11	2.374	TI3 - C52	2.385
TI1 - C12	2.403	TI3 - C53	2.383

TI3 - C54	2.398	C12 - C13	1.403
TI3 - C55	2.377	C13 - C14	1.413
		C14 - C15	1.413
TI4 - C61	2.379	C15 - C11	1.400
TI4 - C62	2.381	C11 - C16	1.492
TI4 - C63	2.384	C12 - C17	1.499
TI4 - C64	2.403	C13 - C18	1.498
TI4 - C65	2.416	C14 - C19	1.500
TI4 - C71	2.385	C15 - C20	1.490
TI4 - C72	2.385		
TI4 - C73	2.392	C21 - C22	1.406
TI4 - C74	2.374	C22 - C23	1.402
TI4 - C75	2.363	C23 - C24	1.392
		C24 - C25	1.407
C1 - C2	1.414	C25 - C21	1.407
C2 - C3	1.399	C21 - C26	1.488
C3 - C4	1.412	C22 - C27	1.490
C4 - C5	1.405	C23 - C28	1.509
C5 - C1	1.409	C24 - C29	1.506
C1 - C6	1.501	C25 - C30	1.513
C2 - C7	1.498		
C3 - C8	1.500	C31 - C32	1.404
C4 - C9	1.481	C32 - C33	1.412
C5 - C10	1.501	C33 - C34	1.421
		C34 - C35	1.401
C11 - C12	1.409	C35 - C31	1.420

C31 - C36	1.487	C54 - C59	1.494
C32 - C37	1.502	C55 - C60	1.497
C33 - C38	1.497		
C34 - C39	1.488	C61 - C62	1.409
C35 - C40	1.500	C62 - C63	1.412
		C63 - C64	1.398
C41 - C42	1.375	C64 - C65	1.417
C42 - C43	1.380	C65 - C61	1.410
C43 - C44	1.407	C61 - C66	1.486
C44 - C45	1.420	C62 - C67	1.496
C45 - C41	1.385	C63 - C68	1.525
C41 - C46	1.491	C64 - C69	1.483
C42 - C47	1.505	C65 - C70	1.496
C43 - C48	1.494		
C44 - C49	1.488	C71 - C72	1.443
C45 - C50	1.488	C72 - C73	1.394
		C73 - C74	1.379
C51 - C52	1.398	C74 - C75	1.378
C52 - C53	1.399	C75 - C71	1.387
C53 - C54	1.415	C71 - C76	1.478
C54 - C55	1.395	C72 - C77	1.477
C55 - C51	1.421	C73 - C78	1.507
C51 - C56	1.482	C74 - C79	1.510
C52 - C57	1.505	C75 - C80	1.522
C53 - C58	1.507		

[a]The estimated standard deviations are:

Ti–N	0.010 Å	C–C	0.014 Å
Ti–C	0.010 Å	N–N	0.014 Å
Ti–R	0.007 Å		

Table V. Footnotes continued

[b]R1 = C1 - C5	ring centroid
R2 = C11 - C15	ring centroid
R3 = C21 - C25	ring centroid
R4 = C31 - C35	ring centroid
R5 = C41 - C45	ring centroid
R6 = C51 - C55	ring centroid
R7 = C61 - C65	ring centroid
R8 = C71 - C75	ring centroid

Table VI. BOND ANGLES (DEG)[a]

TI1 - N1 - N2	176.8	C2 - C1 - C6	124.7
TI2 - N2 - N1	178.1	C5 - C1 - C6	126.5
TI3 - N3 - N4	176.9	C1 - C2 - C7	125.6
TI4 - N4 - N3	177.8	C3 - C2 - C7	126.2
		C2 - C3 - C8	125.4
N1 - TI1 - R1	106.8	C4 - C3 - C8	125.3
N1 - TI1 - R2	107.5	C3 - C4 - C9	127.3
R1 - TI1 - R2	145.8	C5 - C4 - C9	124.9
N2 - TI2 - R3	107.5	C1 - C5 - C10	126.4
N2 - TI2 - R4	106.9	C4 - C5 - C10	123.6
R3 - TI2 - R4	145.6		
N3 - TI3 - R5	107.4	C11 - C12 - C13	108.0
N3 - TI3 - R6	107.3	C12 - C13 - C14	108.1
R5 - TI3 - R6	145.3	C13 - C14 - C15	107.5
N4 - TI4 - R7	106.5	C14 - C15 - C11	108.2
N4 - TI4 - R8	107.3	C15 - C11 - C12	108.1
R7 - TI4 - R8	146.1	C12 - C11 - C16	124.5
		C15 - C11 - C16	127.1
C1 - C2 - C3	107.7	C11 - C12 - C17	126.3
C2 - C3 - C4	108.9	C13 - C12 - C17	125.3
C3 - C4 - C5	107.1	C12 - C13 - C18	127.0
C4 - C5 - C1	108.6	C14 - C13 - C18	124.4
C5 - C1 - C2	107.6	C13 - C14 - C19	124.4

C15 - C14 - C19	127.1	C35 - C31 - C36	127.3
C11 - C15 - C20	125.6	C31 - C32 - C37	124.4
C14 - C15 - C20	125.2	C33 - C32 - C37	125.6
		C32 - C33 - C38	127.8
C21 - C22 - C23	107.0	C34 - C33 - C38	123.8
C22 - C23 - C24	109.6	C33 - C34 - C39	126.1
C23 - C24 - C25	107.1	C35 - C34 - C39	126.3
C24 - C25 - C21	108.3	C31 - C35 - C40	125.1
C25 - C21 - C22	108.0	C34 - C35 - C40	124.9
C22 - C21 - C26	126.0		
C25 - C21 - C26	124.8	C41 - C42 - C43	108.8
C21 - C22 - C27	127.5	C42 - C43 - C44	108.0
C23 - C22 - C27	125.0	C43 - C44 - C45	107.0
C22 - C23 - C28	123.3	C44 - C45 - C41	107.1
C24 - C23 - C28	126.7	C45 - C41 - C42	109.1
C23 - C24 - C29	128.4	C42 - C41 - C46	126.8
C25 - C24 - C29	123.6	C45 - C41 - C46	123.5
C21 - C25 - C30	126.6	C41 - C42 - C47	124.7
C24 - C25 - C30	124.2	C43 - C42 - C47	126.0
		C42 - C43 - C48	125.1
C31 - C32 - C33	109.1	C44 - C43 - C48	126.7
C32 - C33 - C34	107.7	C43 - C44 - C49	125.4
C33 - C34 - C35	107.2	C45 - C44 - C49	126.6
C34 - C35 - C31	109.4	C41 - C45 - C50	124.7
C35 - C31 - C32	106.5	C44 - C45 - C50	127.5
C32 - C31 - C36	126.0		

C51 - C52 - C53	109.8	C63 - C62 - C67	128.1
C52 - C53 - C54	107.0	C62 - C63 - C68	125.4
C53 - C54 - C55	108.1	C64 - C63 - C68	124.2
C54 - C55 - C51	108.6	C63 - C64 - C69	125.4
C55 - C51 - C52	106.4	C65 - C64 - C69	126.7
C52 - C51 - C56	127.6	C61 - C65 - C70	125.8
C55 - C51 - C56	125.3	C64 - C65 - C70	125.7
C51 - C52 - C57	124.0		
C53 - C52 - C57	125.9	C71 - C72 - C73	106.3
C52 - C53 - C58	127.2	C72 - C73 - C74	109.9
C54 - C53 - C58	125.3	C73 - C74 - C75	107.2
C53 - C54 - C59	124.0	C74 - C75 - C71	110.5
C55 - C54 - C59	126.3	C75 - C71 - C72	106.1
C51 - C55 - C60	123.3	C72 - C71 - C76	125.7
C54 - C55 - C60	127.5	C75 - C71 - C76	126.8
		C71 - C72 - C77	126.9
C61 - C62 - C63	107.3	C73 - C72 - C77	126.5
C62 - C63 - C64	108.9	C72 - C73 - C78	125.4
C63 - C64 - C65	107.6	C74 - C73 - C78	124.3
C64 - C65 - C61	107.9	C73 - C74 - C79	126.7
C65 - C61 - C62	108.3	C75 - C74 - C79	125.7
C62 - C61 - C66	124.7	C71 - C75 - C80	126.1
C65 - C61 - C66	126.3	C74 - C75 - C80	122.5
C61 - C62 - C67	123.3		

[a]The estimated standard deviations are:

Ti–N–N	0.4°
N–Ti–R	0.3°
R–Ti–R	0.3°
C–C–C	0.5°

Table VII. Least-Squares Planes of the Cyclopentadienyl Rings[a]

Atom	Deviation (Å)	Atom	Deviation (Å)
	Ring 1		Ring 3
C1	-0.012	C21	-0.003
C2	0.017	C22	0.013
C3	-0.015	C23	-0.013
C4	0.008	C24	0.008
C5	0.003	C25	0.000
C6	-0.300	C26	-0.287
C7	-0.096	C27	-0.097
C8	-0.214	C28	-0.204
C9	-0.165	C29	-0.184
C10	-0.254	C30	-0.225
	Ring 2		Ring 4
C11	0.013	C31	0.013
C12	-0.011	C32	-0.010
C13	0.004	C33	0.003
C14	0.004	C34	0.005
C15	-0.011	C35	-0.011
C16	-0.055	C36	-0.053
C17	-0.174	C37	-0.267
C18	-0.151	C38	-0.184
C19	-0.206	C39	-0.117
C20	-0.276	C40	-0.235
	Ring 5		Ring 7
C41	0.000	C61	0.009
C42	-0.006	C62	-0.005
C43	0.010	C63	-0.002
C44	-0.010	C64	0.007
C45	0.006	C65	-0.010

Table VII. (continued)

C46	-0.169	C66	-0.167
C47	-0.198	C67	-0.287
C48	-0.073	C68	-0.299
C49	-0.260	C69	-0.113
C50	-0.166	C70	-0.220
	Ring 6		Ring 8
C51	0.003	C71	-0.004
C52	-0.009	C72	0.009
C53	0.012	C73	-0.011
C54	-0.010	C74	0.009
C55	0.005	C75	-0.003
C56	-0.177	C76	-0.286
C57	-0.179	C77	-0.081
C58	-0.106	C78	-0.199
C59	-0.332	C79	-0.116
C60	-0.162	C80	-0.239

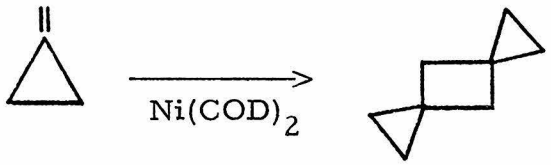
[a]A positive deviation is a deviation toward the titanium atom.

CHAPTER IV

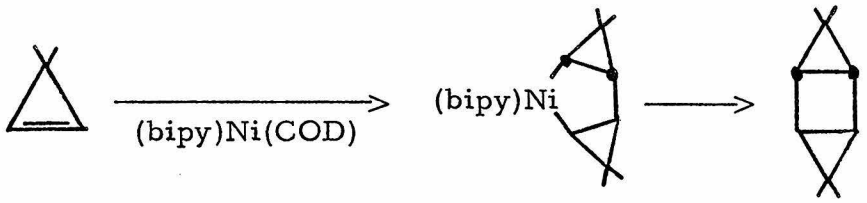
SYNTHESIS AND CHARACTERIZATION OF BIS(PENTAMETHYLCYCLOPENTADIENYL) ZIRCONACYCLOPENTANES

Introduction

Transition metal metallocycles have been suggested as intermediates in a number of metal-catalyzed reactions.[1] Saturated metallocyclopentanes are thought to be involved in the metal-catalyzed cyclodimerization of olefins (eq. 1)[2-5] and the metallocyclic intermediates in several nickel catalyzed reactions have actually been isolated and characterized (eq. 2).[5-6] Numerous



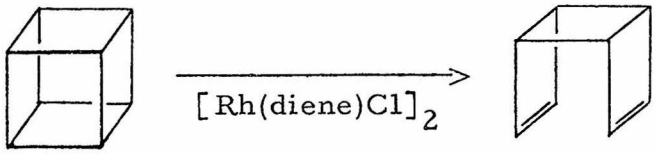
(1)



(2)

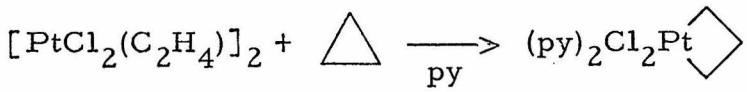
examples of stochiometric reactions of metal complexes with olefins leading to metallocyclopentanes are known,[7-10] confirming the generality of this type of reaction. It should be noted that this type of reaction had, until recently, only been observed with "activated" olefins such as norbornadiene or cyclopropene. A recent paper by Schrock[10] reports the formation of metallocyclopentanes from the "normal" olefin ethylene.

Metallocycles have also been postulated as intermediates in the metal-catalyzed isomerization of strained rings (eq. 3).[11-12]



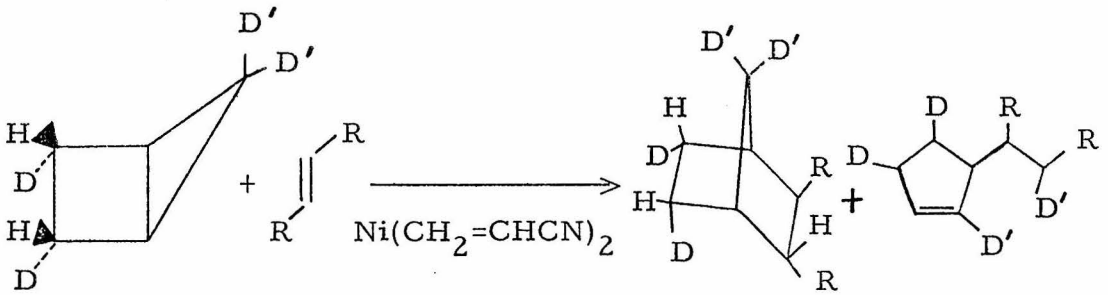
(3)

Although no metallocyclic intermediates have been trapped in these reactions, the synthesis of stable metallocycles from the reaction of a metal complex and a strained ring (eq. 4)[13-18] lends support to the proposed mechanism.

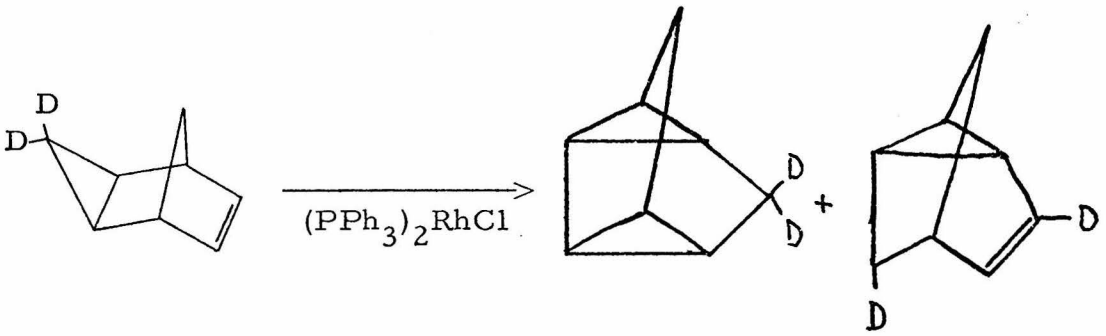


(4)

Another metal-catalyzed reaction in which metallocycles are thought to be involved is the addition of olefins to cyclopropane in either an intermolecular (eq. 5)[19] or intramolecular (eq. 6)[20-22] manner, but no metallocyclic intermediates have been isolated.

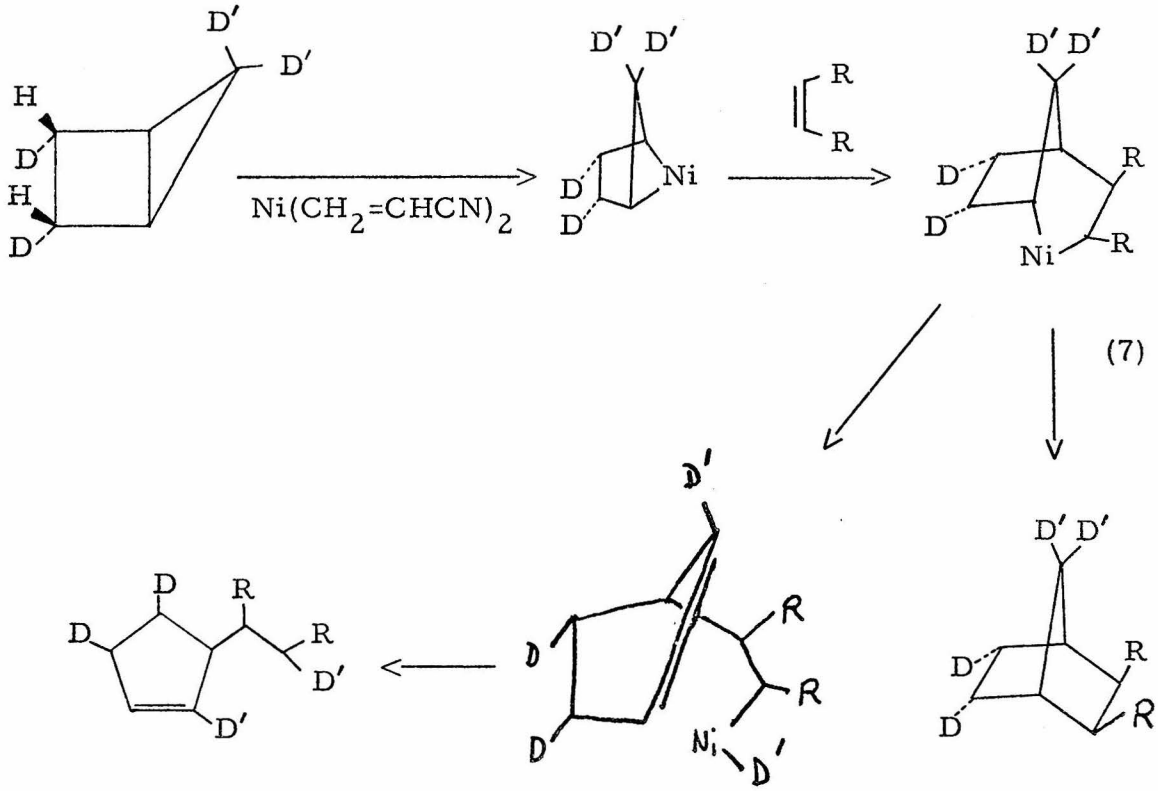


(5)



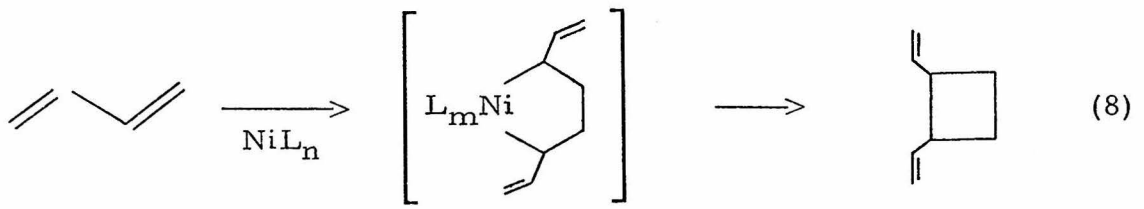
(6)

However, labeling studies[19-21] of this reaction are consistent with such a mechanistic pathway (eq. 7).



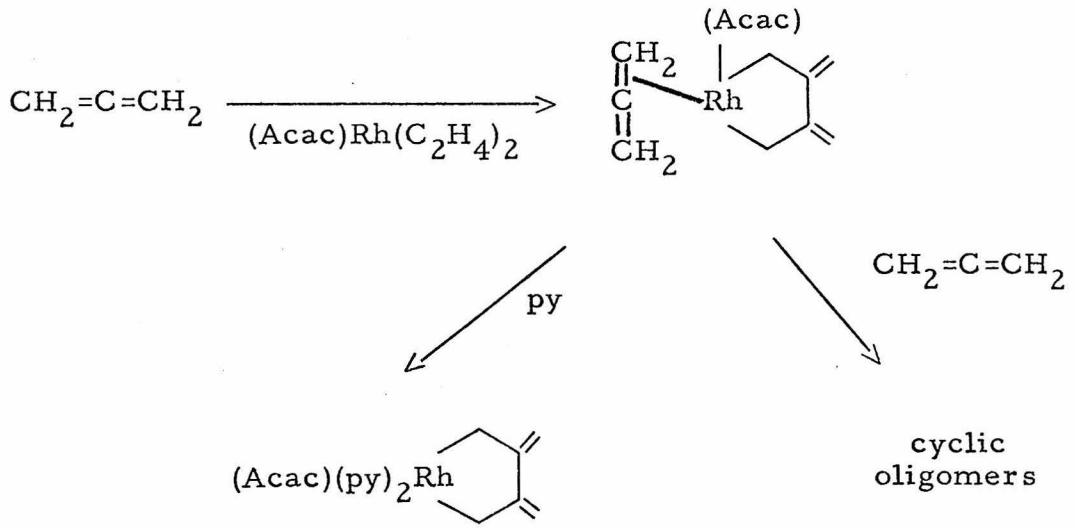
(7)

Metallocyclopentanes have also been mentioned in mechanisms for the catalytic cyclodimerization of 1,3-dienes (eq. 8)[23] and a recent paper reports the synthesis of a stable divinyl metallocyclopentane from $Pt(COD)_2$ and butadiene.[24] The catalytic



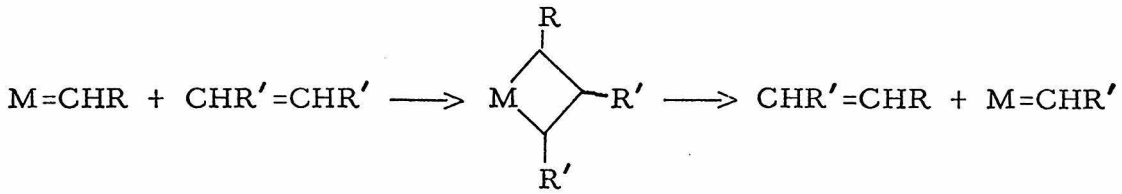
(8)

oligomerization of allenes is thought to involve metallocyclopentanes;[25-28] Ingrosso et al. were able to trap this intermediate at low temperature and determine the crystal structure of the pyridine derivative (eq. 9).[29]



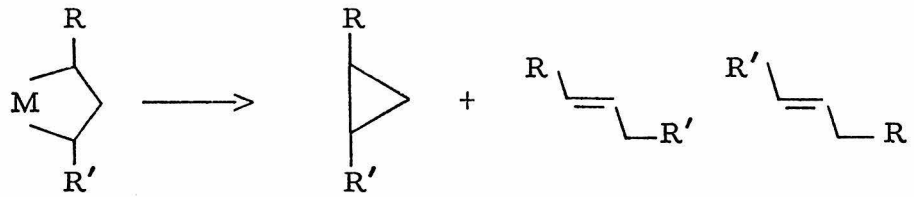
(9)

Finally, metallocycles have been suggested as intermediates in the olefin metathesis reaction.[30] These compounds are proposed to form from a metal carbene complex and free olefin (eq. 10).[31-33]



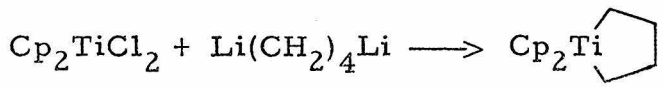
(10)

Reactions such as (10) have been carried out by Casey[32] with observation of the expected products. Recent studies under metathesis conditions by Katz[34] and Grubbs[35] are in complete agreement with the carbene-metallocycle scheme. It should be noted that the metallocyclobutane complex may also form other products (eq. 11). In agreement with this, Casey[32,36] and Schrock[10] have observed such products in the reaction of olefins with carbene complexes.



(11)

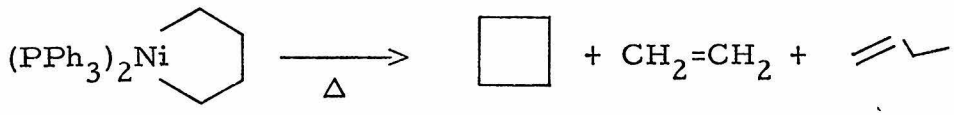
Metallocycles have also been synthesized from lithium or Grignard reagents and transition metal halides (eq. 12).[37-41]



(12)

Although this method does not claim to model a catalytic process, it does allow the synthesis of five, six, and seven membered metallocycles. Whitesides[38,40] and Grubbs[39] have studied the thermal decomposition of metallocycles synthesized from lithium reagents and compared their decomposition pathways with those of

acyclic analogs. In general, it is found that the cyclic compounds are much more stable than acyclic analogs and show decomposition products characteristic of C-C bond formation and cleavage in addition to the β-elimination characteristic of thermal decomposition of transition metal alkyls (eq. 13). As Whitesides has pointed out,



(13)

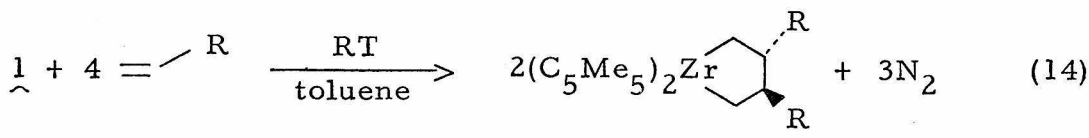
β-elimination should be suppressed in these metallocyclic systems since the M-C-C-H dihedral angle is constrained to values far from the optimal angle of 0°; this should impart additional stability to these compounds and allow one to observe alternate reactivity pathways.

This chapter reports the synthesis and characterization of several zirconacyclopentanes made from the reaction of "normal" olefins with a functional equivalent of "zirconacene." The following chapter describes the reactions of these compounds with carbon monoxide.

Results and Discussion

Reactions with terminal olefins.

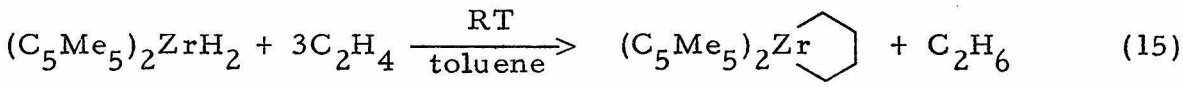
$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (1)[42,43] reacts with ethylene, propylene, or 1-butene at atmospheric pressure in toluene at room temperature to give bis(pentamethylcyclopentadienyl)zirconacyclopentanes in quantitative yield (eq. 14). All products were isolated as yellow crystals; Toepler pump analysis of the reactions indicates



$$\underset{\wedge}{1} + 4 = \diagup^{R} \xrightarrow[\text{toluene}]{\text{RT}} 2(C_5Me_5)_2Zr\langle\text{C}_4\text{H}_2(R)_2\rangle + 3N_2 \qquad (14)$$

$\underset{\wedge}{2}$ R = H
$\underset{\wedge}{3}$ R = CH_3
$\underset{\wedge}{4}$ R = CH_2CH_3

that 2.02 ± 0.05 mol olefin/mol Zr is consumed and molecular weight measurements on $\underset{\wedge}{4}$ indicate the products are monomeric in benzene. $\underset{\wedge}{2}$ has also been prepared from $(\eta^5\text{-}C_5Me_5)_2ZrH_2$[44] and ethylene (eq. 15). Examination of the gaseous products by

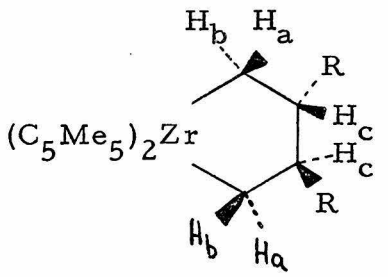


$$(C_5Me_5)_2ZrH_2 + 3C_2H_4 \xrightarrow[\text{toluene}]{\text{RT}} (C_5Me_5)_2Zr\langle\text{C}_4\text{H}_8\rangle + C_2H_6 \qquad (15)$$

infrared spectroscopy indicates that ethane is evolved. The ^{1}H NMR of $\underset{\wedge}{2}$ in benzene-$\underline{d}_6$ shows a singlet at 1.82 δ due to the pentamethylcyclopentadienyl protons and two broad multiplets of equal area are seen at 1.95 δ and 0.50 δ. The upfield resonance is probably due to the zirconium-bound methylene since such protons are usually shifted substantially upfield, as in $(C_5Me_5)_2Zr(CH_3)_2$ and $(C_5Me_5)_2Zr(H)(CH_2CHMe_2)$.[44] Further support of the metallocyclopentane structure is provided by the reaction of $\underset{\wedge}{2}$ with anhydrous HCl which produces exclusively butane; $\underset{\wedge}{2}$ also reacts with H_2 to yield predominantly butane.

The ^{1}H NMR of $\underset{\wedge}{3}$ in benzene-$\underline{d}_6$ shows signals at 1.83 δ (s, 30H) due to the permethyl rings, 1.09 δ (d, 6H, $^3J_{H\text{-}H}$ = 5 Hz)

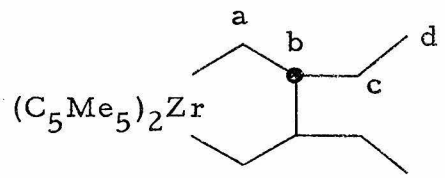
due to the methyls bound to the metallocyclic ring, -0.04 δ (double doublet, 2H), 0.89 δ (t, 2H), and 1.38 δ (m, 2H). If one assumes the triplet at 0.89 δ is actually an overlapping doublet of doublets then the spectrum may be easily assigned. The double doublet at -0.04 δ is due to one of the methylene protons, with $^{2}J_{H-H}$ = 12 Hz and $^{3}J_{H-H}$ = 4 Hz; the triplet (overlapping double doublet) at 0.89 δ is the other methylene proton with $^{2}J_{H-H}$ = 12 Hz and $^{3}J_{H-H}$ ~ 11 Hz. $^{2}J_{H-H}$ falls in the range expected for a geminal coupling constant and the difference between the two $^{3}J_{H-H}$ values is in agreement with the observation that trans vicinal coupling constants are generally larger than cis couplings.[45] Lastly, the multiplet at 1.38 δ is due to the methine proton. This spectrum is consistent with the trans-β,β′-dialkyl structure suggested for 3 in (14) with the resonances at -0.04 δ, 0.89 δ, and 1.38 δ due to H_a, H_b, and H_c respectively:



The ^{1}H NMR spectrum of 4 in benzene-d_6 is quite similar to 3 and exhibits signals at 1.84 δ (s, 30H), -0.10 δ (double doublet, 2H; $^{2}J_{H-H}$ = 12 Hz, $^{3}J_{H-H}$ = 4 Hz), 0.79 δ (t, 2H; $^{2}J_{H-H}$ = 12 Hz, $^{3}J_{H-H}$ ~ 11 Hz), 1.08 δ (m, 10H), 1.54 δ (m, 2H). If we again assume the triplet at 0.79 δ is an overlapping doublet of

doublets, we can make a similar assignment to that made for 3 above. Thus, the peaks at -0.10 δ, 0.79 δ, and 1.54 δ are due to H_a, H_b, and H_c, respectively. Unfortunately, the resonances for the methyl and methylene groups of the alkyl chain seem to overlap, giving a broad multiplet which doesn't reveal any characteristic splitting pattern.

The ^{13}C spectra of 4 in benzene-d_6 shown in Figures 1 and 2 are more informative, however. The ^{1}H-decoupled spectrum (Figure 1) shows a singlet at 117.87 δ, which is where an aromatic ring carbon should lie (C_6D_6 is at 128 δ) and hence is assigned to the C_5 ring. The observation of only <u>one</u> ring resonance suggests the <u>trans</u> structure shown in (14). There are two slightly overlapping singlets at 11.45 δ and 11.72 δ with the downfield peak having the greater intensity (Figure 1); these signals appear as overlapping quartets ($^{1}J_{^{13}C-H}$ = 125 Hz) in the gated decoupled spectrum (Figure 2) and thus may be assigned as the signals due to the pentamethyl grouping (11.72 δ) and the alkyl chain methyl, C_d (11.45 δ):



Further examination of Figure 1 shows a signal at 47.88 δ which splits into a doublet in the gated decoupled spectrum

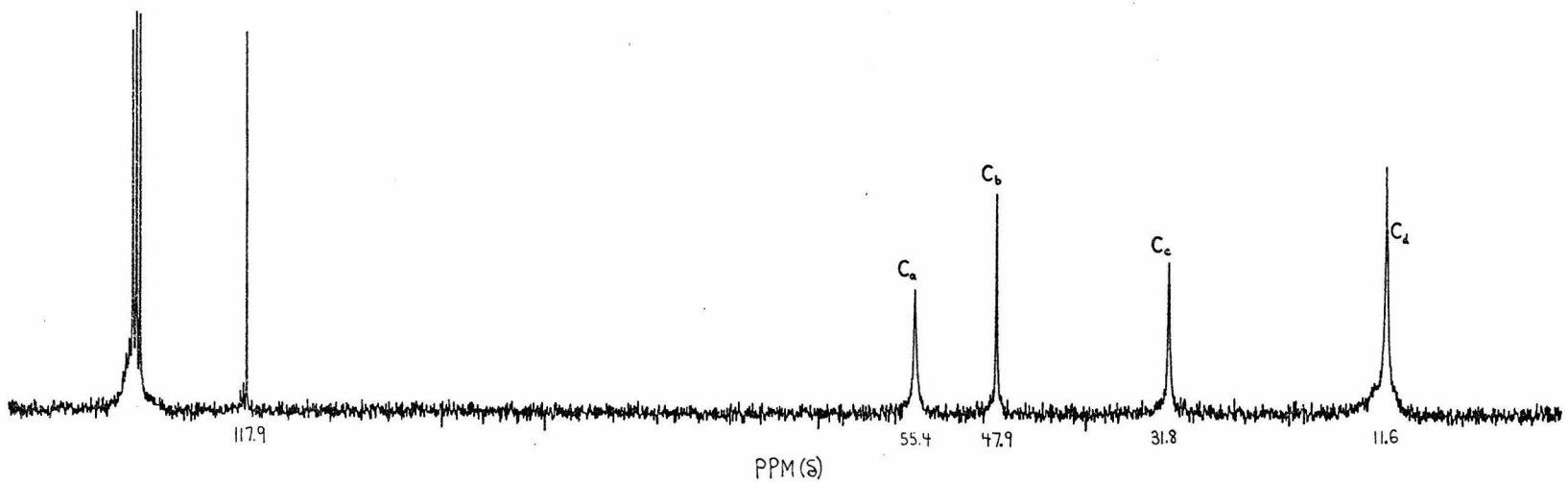


Figure 1. The 67.89-MHz normal decoupled ^{13}C spectrum of $\underset{\sim}{4}$ in C_6D_6 at 25°C.

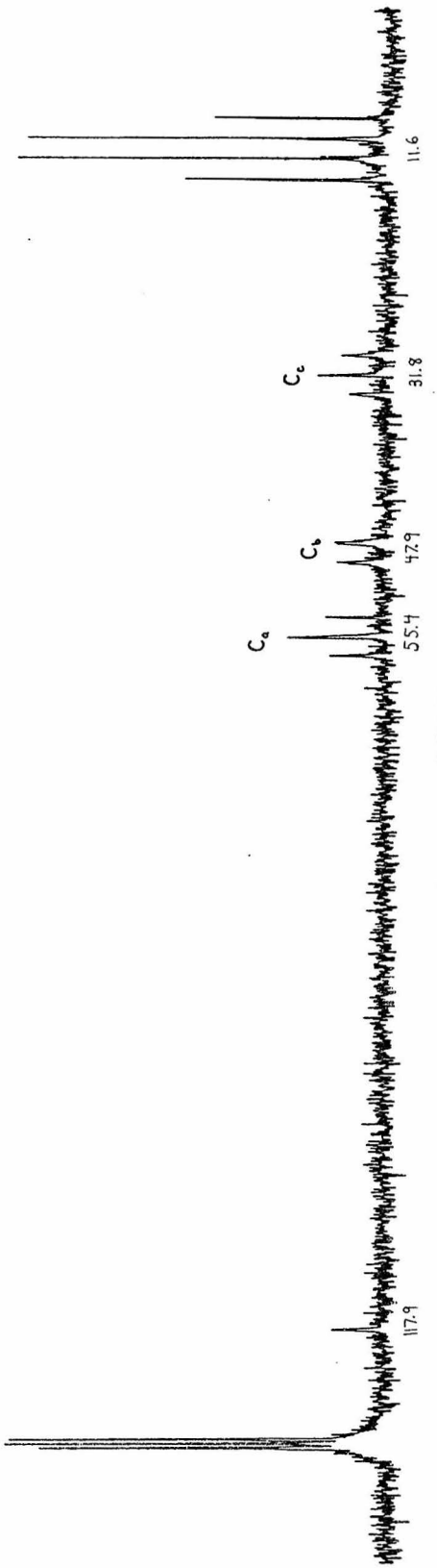


Figure 2. The 67.89-MHz gated decoupled ^{13}C spectrum of $\underset{\sim}{4}$ in C_6D_6 at 25°C.

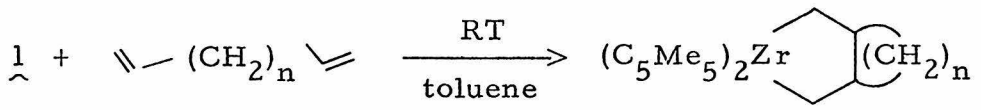
($^1J_{^{13}C-H}$ = 118 Hz) and is assigned to the methine carbon, C_b. Finally, resonances at 31.85 δ and 55.40 δ split into triplets in Figure 2 ($^1J_{^{13}C-H}$ = 120 Hz and 118 Hz for upfield and downfield resonances, respectively) leading to their assignment as methylene carbons. The assignment of the downfield peak as C_a is made on the basis of the observation that it does not shift appreciably in another metallocyclic derivative (vide infra). Indeed, this should be the least sensitive metallocyclic carbon to changes at the β or β′ positions.

A crystal structure in progress at the time of this writing (see Chapter VI) is in agreement with the trans-β,β′-diethyl conformation suggested by the NMR results for 4.

Attempts to prepare a metallocycle from isobutylene were unsuccessful. The reaction mixture was heated to 60° but the only reaction observed was decomposition of 1 as evidenced by a color change from purple to red. Examination of the products by NMR showed that while a small amount of metallocycle may have been formed, it was only one of many products of this reaction. Possibly the steric requirements of the β,β,β′,β′-tetramethyl moiety cannot be met in this system.

Reactions with terminal dienes.

1 is also observed to react with long-chain terminal dienes (16), affording the yellow metallocycles in quantitative yield. Attempts to prepare the metallocycle with n = 2 led to a complex mixture of products, possibly resulting from the formation of



(16)

5 n = 3

6 n = 4

dimers or polymers due to the expected ring strain in the monomeric metallocycle. Molecular weight measurements on 5 verify that it is a monomer in benzene.

The ^{1}H NMR spectrum of 5 in benzene-d_6 shows two closely spaced permethylcyclopentadienyl resonances at 1.80 δ and 1.82 δ, indicating the presence of both cis and trans isomers. Apparently the splitting of the cis isomer into the expected two permethyl resonances is too small to be detected. The only other information to be gleaned from the ^{1}H NMR is the presence of the characteristic upfield methylene resonance at -0.39 δ.

The ^{13}C NMR spectra of 5 in benzene-d_6 are shown in Figures 3 and 4. Examination of the ^{1}H decoupled spectrum (Figure 3) in the aromatic carbon region clearly shows the presence of both the trans (117.10 δ) and cis (117.6 δ and 117.81 δ) isomers in approximately a 1:1 ratio. The two permethylcyclopentadienyl rings are inequivalent in the cis isomer, as expected. The ring methyls appear as a poorly resolved resonance at 11.49 δ in the normal decoupled spectrum but the gated decoupled spectrum (Figure 4) clearly shows three slightly overlapping quartets ($^{1}J_{^{13}C-H}$ = 126 Hz). Although the intensities are off due to poor

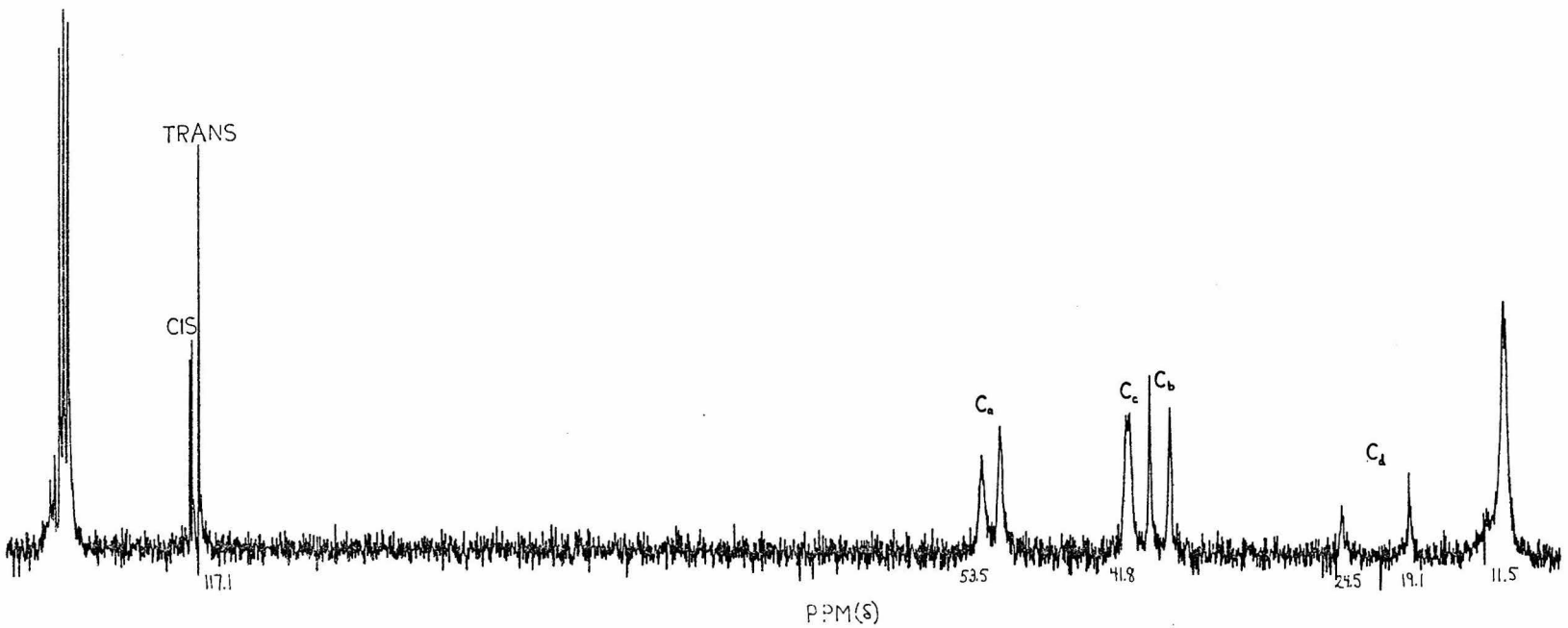


Figure 3. The 67.89-MHz normal decoupled ^{13}C spectrum of 5 in C_6D_6 at 25°C.

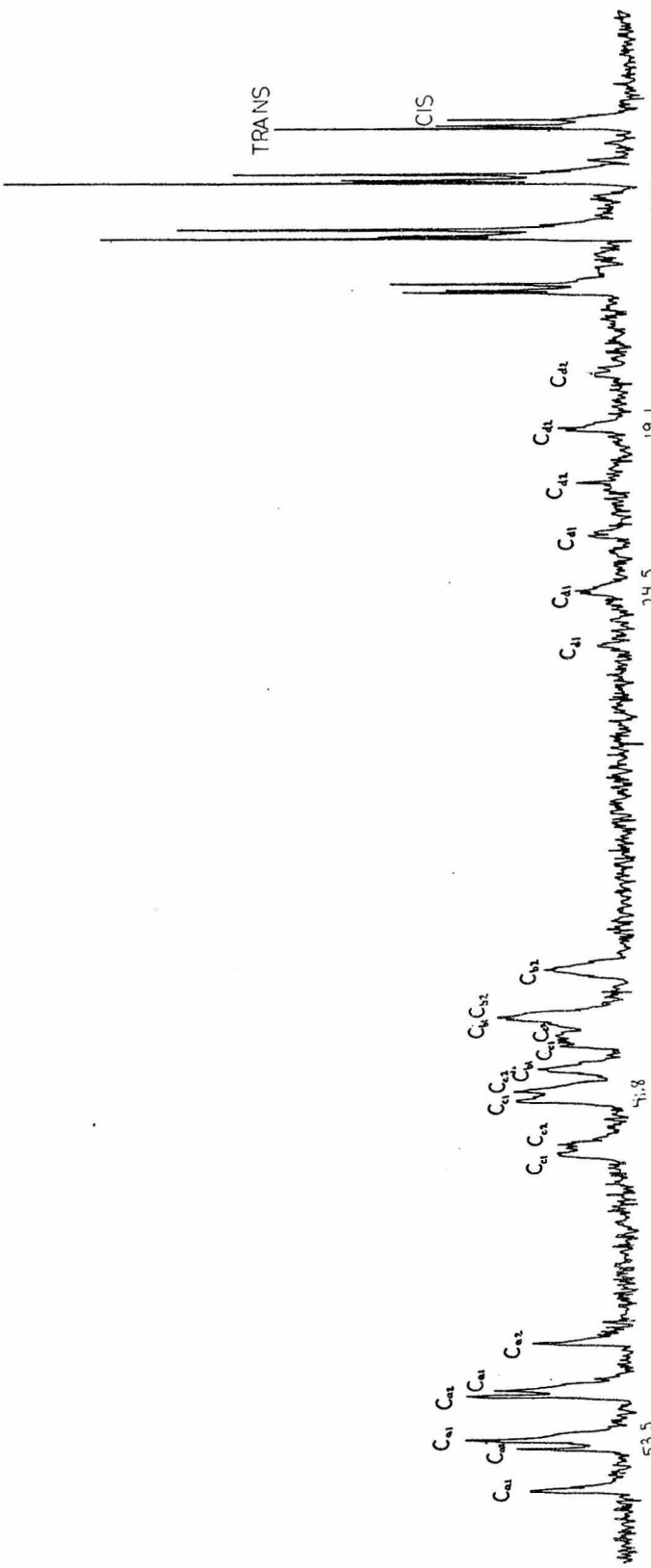
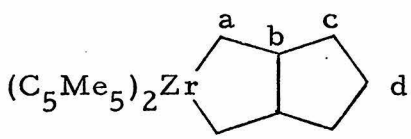


Figure 4. The 67.89-MHz gated decoupled ^{13}C spectrum of 5 in C_6D_6 at 25°C.

phasing, the left-hand set of peaks is probably due to the trans isomer since it seems to form the largest (intensity) set of peaks. Assignment of the metallocyclic ring resonances is a bit more difficult due to several overlapping peaks, but close examination reveals the resonances at 53.52 δ and 52.07 δ in the normal decoupled spectrum split into triplets in the gated decoupled spectrum ($^1J_{^{13}C-H}$ = 116 Hz and 120 Hz, respectively) requiring these to be methylene carbon resonances. The close agreement of chemical shifts between this set of peaks and a peak of $\hat{4}$ (55.40 δ) suggests all these signals may be assigned to C_a since the chemical environment of C_a, compared to that of C_c, is relatively unchanged going from $\hat{4}$ to $\hat{5}$. Other methylene resonances appear at 41.96 δ,



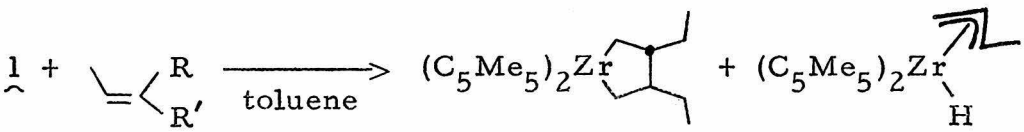
41.68 δ ($^1J_{^{13}C-H}$ = 126 Hz for both) assigned to C_c and 24.53 δ, 19.08 δ ($^1J_{^{13}C-H}$ = 127 Hz and 128 Hz, respectively) assigned to C_d. The only methine resonances are at 40.08 δ and 38.48 δ ($^1J_{^{13}C-H}$ = 115 Hz and 109 Hz, respectively); these are assigned to C_b. All the aforementioned results are in agreement with a mixture of cis and trans isomers in the fused ring metallocycle $\hat{5}$.

The ^{1}H NMR of $\hat{6}$ shows two singlets at 1.82 δ and 1.87 δ probably due to the cis and trans isomers of this compound. The isomer ratio here is considerably different than the 1:1 mixture

exhibited by 5 and is more in the range of a 3:1 ratio. Since linear alkyl substituted metallocycles have been shown to be exclusively trans, one would expect the trans:cis ratio to increase as the size of the fused ring increased due to lessened rigidity in this ring. We may tentatively identify this as a 3:1 trans:cis mixture of isomers although a final proof will have to await the results of a ^{13}C NMR study currently in progress. The ^{1}H NMR also shows the upfield resonance (-0.09 δ) characteristic of these substituted zirconacyclopentanes although the remainder of the spectrum is uninformative, consisting only of broad multiplets.

Reactions with internal olefins.

Reaction of 1 with cis or trans-2-butene leads to two products (eq. 17), with the ratio of products dependent upon starting olefin



(17)

R = CH_3, R′ = H
R = H, R′ = CH_3

4 7

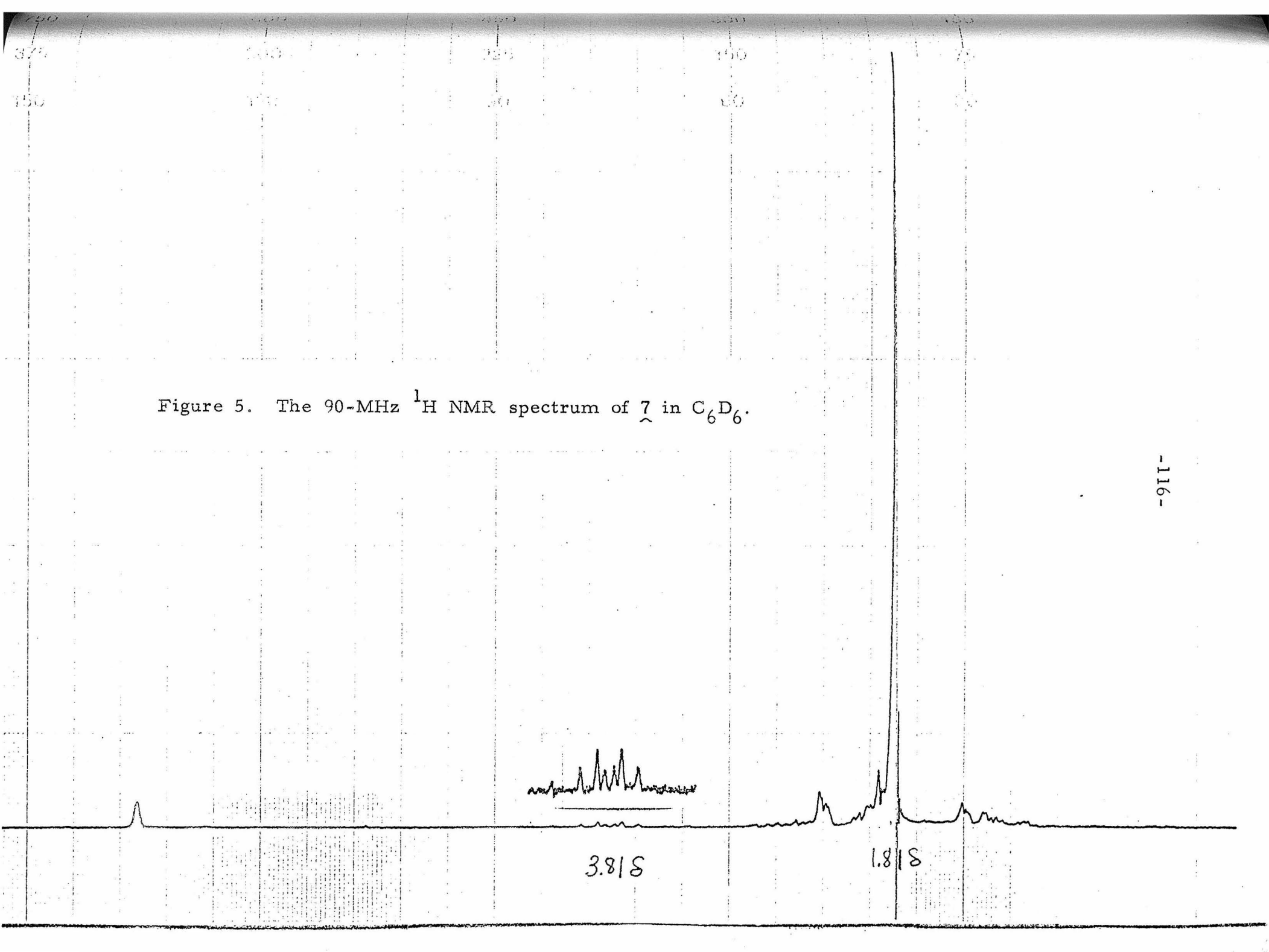
and reaction conditions. Cis-2-butene may be converted completely to 4 by heating overnight at 40° but using trans-2-butene as the olefin under similar conditions leads to formation of both 4 and what we propose as a π-allyl hydride complex 7. It is possible to convert trans-2-butene and 1 completely to 4 only after five days at room temperature. 7 may be prepared in quantitative yield as

orange-brown crystals by heating trans-2-butene and 1 at 40° for several minutes; Toepler pump analysis of this reaction shows that 0.94 mol trans-2-butene/mol Zr is consumed. Attempted synthesis of 7 from cis-2-butene and 1 always gives some 4 as a side product. In summary, then, cis-2-butene and 1 may be converted completely to 4 but not completely to 7. In contrast, trans-2-butene and 1 may be converted completely to 7 but attempts to make 4 quantitatively require a lengthy reaction.

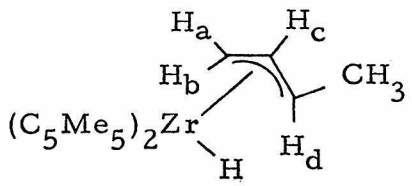
The formulation of 7 as a hydride is based on the facts that it shows a band at 1575 cm^{-1} in the infrared and liberates methane (60% of expected) on treatment with MeI. Unfortunately, this latter reaction does not seem to be a straightforward replacement of hydride by iodide since the NMR shows a fairly complex mixture of products, although there is one product which clearly predominates. The appearance of a singlet substantially upfield of all other resonances at -0.49 δ indicates that one of the products may have a $Zr-CH_3$ grouping, possibly resulting from oxidative addition of CH_3I with displacement of olefin. However, the observation of substantial methane evolution and the disappearance of the band at 1575 cm^{-1} upon addition of MeI does support the formulation of the compound as a hydride.

The ^1H NMR spectrum of 7 in benzene-d_6 is shown in Figure 5. The most interesting feature of this spectrum is the six line pattern at 3.81 δ which seems to be composed of two overlapping triplets. The position of this resonance is in excellent agreement with the only other isolated η^3-allyl hydride complex,[46]

Figure 5. The 90-MHz ^{1}H NMR spectrum of $\underset{\sim}{7}$ in C_6D_6.

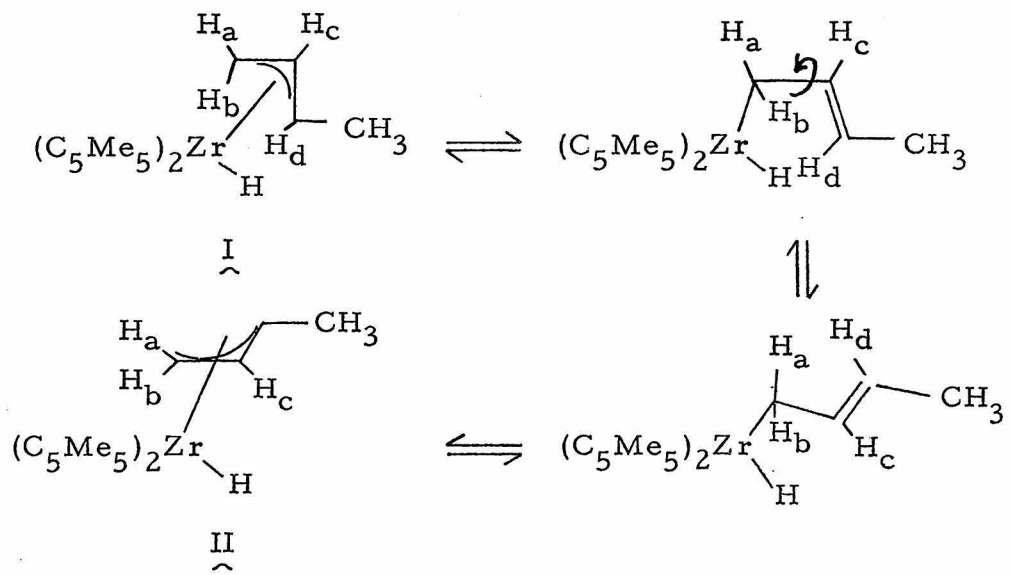


$(diphos)_2Mo(H)(\eta^3\text{-}C_3H_5)$, which has a peak due to the central allyl proton at 3.72 δ. If we postulate the structure shown in (18) and if H_a and H_b become equivalent by some mechanism, then we would



(18)

expect to see a triplet due to splitting of H_c by the H_a-H_b pair which would be split into a doublet of triplets by H_d. The coupling constants obtained from Figure 5 are in excellent agreement with such a proposal; $^3J_{H_{a,b}\text{-}H_c}$ = 10 Hz and $^3J_{H_d\text{-}H_c}$ = 15 Hz. We would expect $^3J_{H_d\text{-}H_c}$ to be larger since it is purely a <u>trans</u> vicinal coupling whereas $^3J_{H_{a,b}\text{-}H_c}$ is an average of a <u>cis</u> and <u>trans</u> vicinal coupling and thus should be smaller. Protons H_a and H_b could become equivalent through a σ-allyl intermediate as shown in (19).

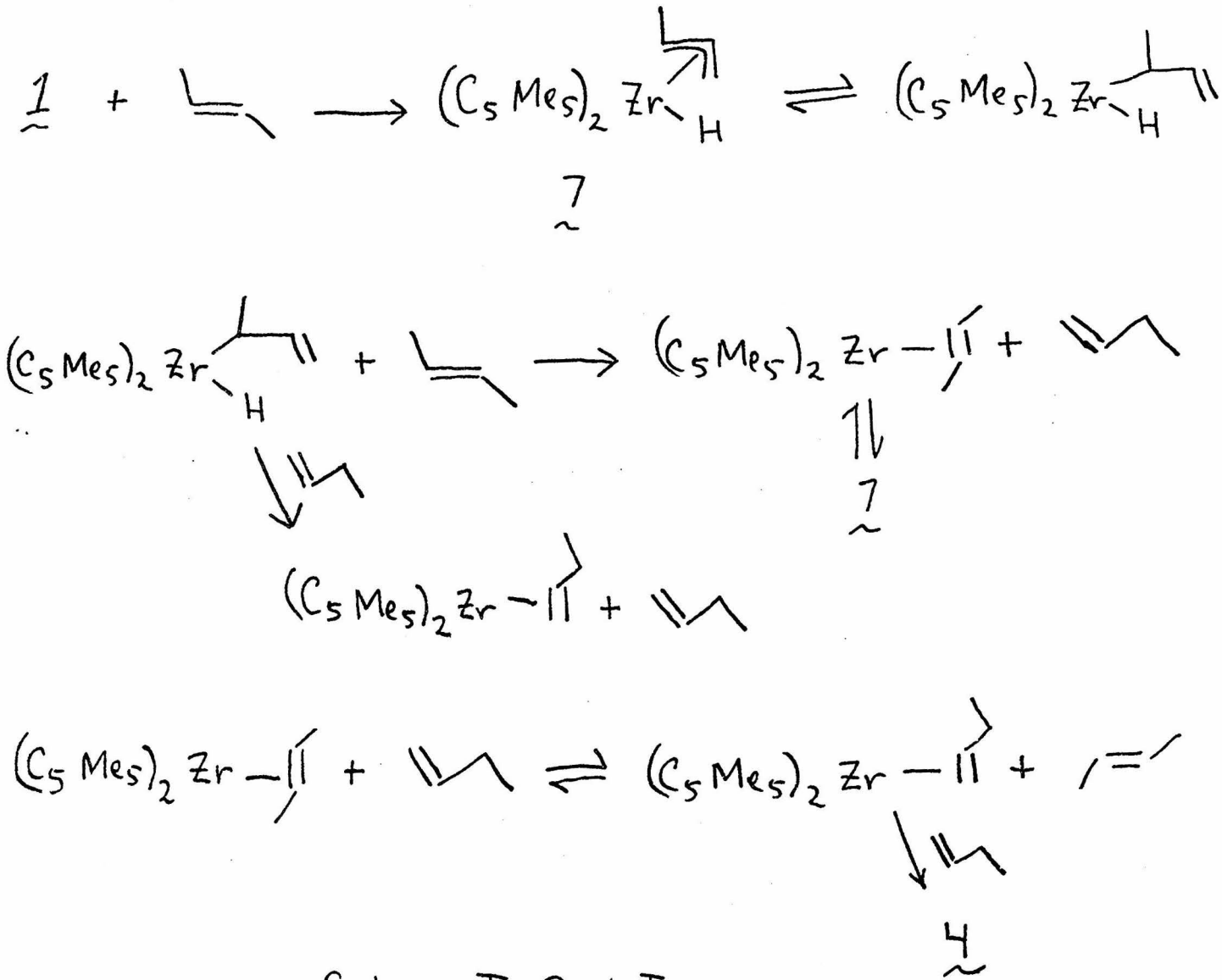


(19)

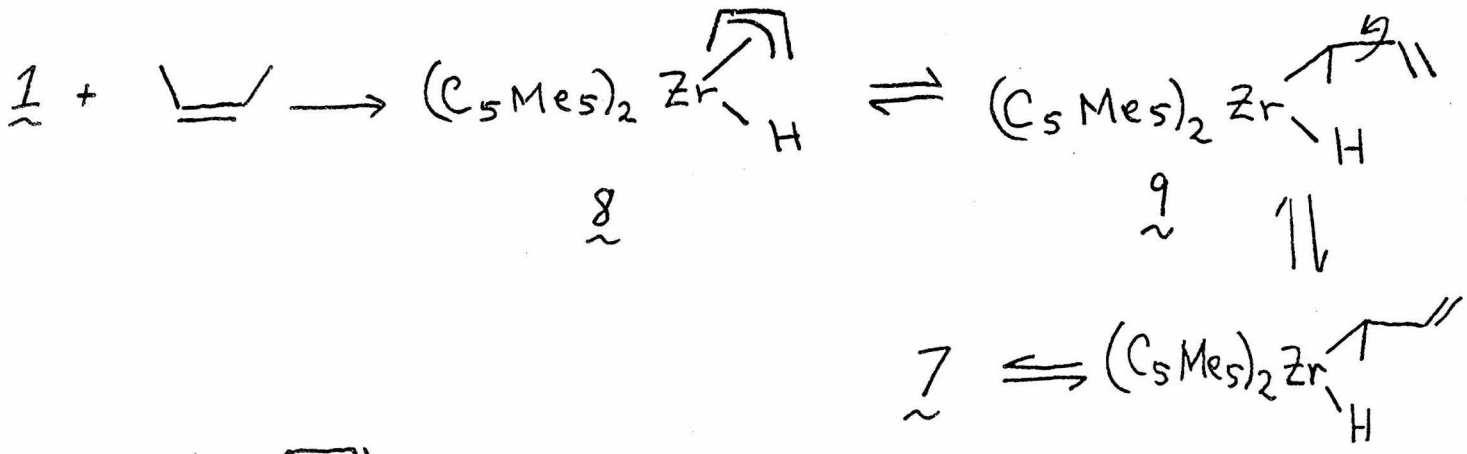
H_a and H_b have been interchanged without disturbing the trans orientation of the methyl group. In addition, the rings have been made equivalent due to the different orientation of the methyl group with respect to the rings in I and II. This type of syn-anti interchange is well documented[47] in organometallic systems having π-allyl groups although confirmation of such a process occurring in 7 would require a variable temperature NMR study. Figure 5 also shows a singlet at 1.81 δ due to the ring methyl groups but the remainder of the spectrum is fairly uninformative, consisting of various multiplets and overlapping peaks although it is possible that the multiplet centered at 2.58 δ is due to the doublet of quartets expected for H_d.

Further support for the π-allylic nature of 7 is provided by the infrared spectrum which shows a band at 1530 cm^{-1} tentatively assigned to the allyl C-C stretch. This may be compared to $Cp_2Zr(\pi\text{-}C_3H_5)(\sigma\text{-}C_3H_5)$ which has its π-allyl stretch at 1533 cm^{-1}.[48]

The various processes believed to be occurring in (17) are shown in Scheme I. Postulation of 7 as the trans, rather than cis allyl hydride is supported by the NMR results and the observation that 7 may be prepared quantitatively from trans-2-butene but not from cis-2-butene. The greater stability of 7 compared to 8 may be due to less steric crowding with the permethyl rings in 7 than in 8. Note that the proposed scheme requires that 8 pass through the σ-allyl complex 9 in order to form 7. This explains the observation that some metallocycle (4) is always formed from 1



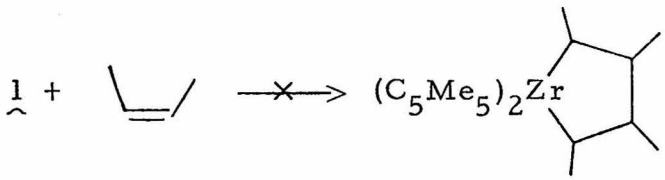
Scheme I - Part I
(from trans-2-butene)



Scheme I - Part II
(from cis-2-butene)

and cis-2-butene since 9 may reductively eliminate 1-butene with the formation of the olefin complexes 10 or 11 by reaction with cis-2-butene or 1-butene, respectively. Either 10 or 11 can then lead to metallocycle. The instability of 8 relative to 7 also explains the ease with which cis-2-butene is converted to 4 on reaction with 1 while trans-2-butene requires much longer reaction times. The scheme is also in agreement with the fact that 7 may be heated under argon for extended periods of time at 60° with little decomposition but addition of excess trans-2-butene will slowly drive the reaction to metallocycle (4). Recall that the syn-anti interchange shown in (19) is quite fast at room temperature while the interconversions shown in Scheme I require heating at 40°. This is in agreement with the expected slower addition of zirconium to a sterically crowded internal olefin as in Scheme I compared to the addition to a terminal olefin shown in (19).

It should be noted that the internal butenes do not close without rearrangement as shown in eq. 20. The observation of olefin



(20)

terminalization before closure to metallocycle is in agreement with the findings of Schwartz in his reactions of olefins with Cp_2Zr-(H)(Cl).[49] In these experiments, he always sees terminalization of internal olefins in the formation of the $Cp_2Zr(R)(Cl)$ species so that the α-carbon can become a primary carbon atom. We have found that reaction of 1 with an internal olefin which cannot terminalize -- namely cyclohexene -- results in no reaction with 1 up to 60° when 1 starts to decompose. Since cyclohexene is a fairly bulky olefin, it may be purely a steric problem although the inability to form a primary α-carbon in the resulting metallocycle may also contribute to its nonreactivity.

Finally, a word concerning the thermal stability of the metallocycles compared to their acyclic analogs is in order. Recent work[50] in our group by Don McAlister has shown that

reaction of BuLi or EtLi gives $(C_5Me_5)_2Zr(H)(Bu)$ or $(C_5Me_5)_2ZrH_2$ respectively, suggesting processes shown in eqs. 21 and 22.

$$(C_5Me_5)_2ZrCl_2 + 2\ BuLi \longrightarrow \left[(C_5Me_5)_2Zr\begin{matrix}Bu\\Bu\end{matrix}\right] \qquad (21)$$

$$\downarrow$$

$$(C_5Me_5)_2Zr\begin{matrix}Bu\\H\end{matrix} + \quad =\!\!\smile$$

$$(C_5Me_5)_2ZrCl_2 + 2\ EtLi \longrightarrow \left[(C_5Me_5)_2Zr\begin{matrix}Et\\Et\end{matrix}\right] \qquad (22)$$

$$\downarrow$$

$$C_2H_4 + (C_5Me_5)_2ZrH_2 \longleftarrow \left[(C_5Me_5)_2Zr\begin{matrix}H\\Et\end{matrix}\right] + C_2H_4$$

These processes involve the commonly observed β-elimination of olefins from transition metal alkyls. It is noteworthy that the zirconacyclopentanes may be recrystallized by heating to 50° with no decomposition whatsoever, suggesting efficient suppression of the β-elimination pathway in these complexes. This result is in agreement with findings by Whitesides[38,40] using metallocycles of platinum and titanium which show enhanced thermal stability over their acyclic counterparts. The decomposition products of Whitesides' metallocycles were observed to contain products characteristic of

C-C bond breaking. David Erwin[51] of our group has found that thermolysis of 2 at 120° yields ethylene and ethane (in addition to butenes) -- presumably from fracture of C-C bonds in the metallocycle. Thus, suppression of β-elimination allows one to observe alternate reactivity pathways not available to acyclic metal alkyls. The reaction of these metallocycles with CO will be the topic of the next chapter.

Experimental

Physical measurements.

^{1}H NMR spectra were recorded on a Varian A60-A, EM-390, or HR-220 spectrometer. 67.89-MHz ^{13}C spectra were obtained on a Bruker NMR Spectrometer at the Francis N. Bitter National Magnet Laboratory in Cambridge, Massachusetts. Infrared spectra were measured on Perkin-Elmer 180 or 457 models or on a Beckman IR-12 spectrophotometer. Infrared spectra of solids were recorded as Nujol mulls using NaCl plates and spectra of gases were measured using a 10 cm path length cell (NaCl windows) fitted with a stopcock and ball joint for attachment to a vacuum line. Molecular weight measurements were determined cryoscopically in benzene. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, or Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Materials

All manipulations were performed using high vacuum line or glove box techniques. Solvents were purified by vacuum transfer

first from $LiAlH_4$, then from "titanocene" prepared as described earlier.[52] NMR solvents -- benzene-$\underline{d}_6$ (Aldrich) and toluene-$\underline{d}_8$ (Stohler) -- were vacuum transferred from "titanocene." Hydrogen and argon were purified by passage over activated Linde 4 Å molecular sieves and MnO on vermiculite.[53] Carbon monoxide (Matheson) was used directly from the cylinder. Ethylene (Union Carbide), propylene, 1-butene, isobutylene, cis-2-butene, anhydrous HCl and trans-2-butene (all Matheson) were purified by at least two freeze-pump-thaw cycles using LN_2. 1,5-Hexadiene (K & K Laboratories), 1,6-heptadiene (Pfalz & Bauer), 1,7-octadiene (Chemicals Procurement Laboratories), and cyclohexene (MCB) were all vacuum transferred from activated Linde 4 Å molecular sieves. Methyl iodide (MCB) was vacuum transferred from calcium hydride. $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$[42,43] and $(\eta^5\text{-}C_5Me_5)_2ZrH_2$[44] were prepared as previously described.

Procedures

(1) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CH_2)_2CH_2)$. (a) from $\{(C_5Me_5)_2ZrN_2\}_2N_2$. 3.80 mol ethylene was added to a stirred solution of 380 mg (0.471 mmol) $\underset{\frown}{1}$ in 15 ml of toluene maintained at -78°. The dry ice-acetone bath was removed and the solution was allowed to warm slowly to 25°. After 2h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 1.35 mmol N_2 (2.86 mmol/mmol $\underset{\frown}{1}$) was collected by a Toepler pump and discarded. After warming all traps to -78°, 1.85 mmol ethylene was collected; thus 1.95 mmol C_2H_4 (2.07 mmol/mmol Zr)

were consumed. Toluene was removed and the bright yellow product recrystallized from petroleum ether. Calculated for $ZrC_{24}H_{38}$: C 69.00, H 9.17, Zr 21.84; found: C 68.76, H 8.92, Zr 21.57.

(b) from $(C_5Me_5)_2ZrH_2$. 4.19 mmol ethylene was added to a stirred solution of 253 mg (0.696 mmol) $(C_5Me_5)_2ZrH_2$ in 15 ml toluene maintained at -78°. The dry ice-acetone bath was removed and the solution was allowed to warm slowly to 25°. After 2h at 25°, the residual gases (2.36 mmol) were collected by a Toepler pump and identified as a mixture of ethane and ethylene by IR. The solid product was identified as $\underset{\sim}{2}$ by ^1H NMR spectrometry.

(c) reaction of ($\underset{\sim}{2}$) with HCl. 0.96 mmol anhydrous HCl was added to a frozen solution of 200 mg (0.478 mmol) $\underset{\sim}{2}$ in 10 ml toluene and the mixture was allowed to warm to 25°. After 2h at 25°, the gases were separated and collected by a series of traps and a Toepler pump. 0.406 mmol butane (0.85 mmol/mmol $\underset{\sim}{2}$) was collected and identified by its infrared spectrum.

(d) reaction of ($\underset{\sim}{2}$) with H_2. 30 mg (0.072 mmol) $\underset{\sim}{2}$ was dissolved in 0.4 ml benzne-$\underline{d}_6$ and sealed under 1 atm H_2 in an NMR tube. After several hours at 25°, the NMR spectrum indicated that $\underset{\sim}{2}$ was converted to $(C_5Me_5)_2ZrH_2$ and a 2:1 molar ratio of butane:ethane.

($\underset{\sim}{2}$) $(\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CHMe)_2CH_2)}$. 3.49 mmol propylene was added to a stirred solution of 238 mg (0.295 mmol) $\underset{\sim}{1}$ in 15 ml of toluene maintained at -78°. The mixture was allowed to warm

slowly to 25°. After 2h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 0.876 mmol N_2 (2.97 mmol/mmol 1) was collected by a Toepler pump and discarded. After warming all traps to -78°, 2.28 mmol propylene was collected; thus 1.22 mmol C_3H_6 (2.06 mmol/mmol Zr) were consumed. Toluene was removed and the bright yellow product recrystallized from petroleum ether. Calculated for $ZrC_{26}H_{42}$: C 70.04, H 9.50; found: C 70.29, H 9.62.

(3) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHEt)_2CH_2)$. 3.11 mmol 1-butene was added to a stirred solution of 250 mg (0.310 mmol) 1 in 15 ml of toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 0.878 mmol N_2 (2.82 mmol/mmol 1) was collected by a Toepler pump and discarded. After warming all traps to -64°, 1.89 mmol 1-butene was collected; thus 1.22 mmol C_4H_8 (1.97 mmol/mmol Zr) were consumed. Toluene was removed and the bright yellow product recrystallized from petroleum ether. Calculated for $ZrC_{28}H_{46}$: C 70.96, H 9.79; found: C 70.19, H 9.79.

Molecular weight determined cryoscopically for 75.5 mg 4 per g of C_6H_6: 484 ± 30 (calcd 474).

(4) Reaction of (1) with isobutylene. 3.79 mmol isobutylene was added to a stirred solution of 256 mg (0.317 mmol) 1 in 15 ml of toluene at -78°. The mixture was allowed to warm slowly to 25°. After 2h at 25°, no color change had been observed. The reaction mixture was heated at 60° for 2h but the only color change

observed was characteristic of thermal decomposition of 1. The ^{1}H NMR spectrum of the residue which remained after removal of the toluene showed a complex mixture of products.

(5) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH(CH_2)_3CHCH_2)$. 1.86 mmol 1,6-heptadiene was added to a stirred solution of 250 mg (0.310 mmol) 1 in 15 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2 h at 25°, toluene was removed and the bright yellow product recrystallized from petroleum ether. Molecular weight determined cryoscopically for 80.4 mg 5 per g of C_6H_6: 484 ± 35 (calcd 458). The ^{1}H NMR of 5 shows signals at 1.80 δ (s), 1.82 δ (s), -0.39 δ (double doublet), 2.50 δ, 2.00 δ, 1.37 δ, 1.10 δ, 0.88 δ, 0.49 δ (all multiplets).

(6) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH(CH_2)_4CHCH_2)$. 1.73 mmol 1,7-octadiene was added to a stirred solution of 233 mg (0.289 mmol) 1 in 15 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2h at 25°, toluene was removed leaving an oily yellow product. Attempts to obtain a crystalline product with petroleum ether proved unsuccessful. For this reason, no elemental analysis of this compound could be obtained. The ^{1}H NMR of 6 shows signals at 1.82 δ (s), 1.87 δ (s), -0.09 δ (double doublet), 2.49 δ, 2.04 δ, 1.62 δ, 1.34 δ, 1.14 δ, 0.84 δ (all multiplets).

(7) Reaction of (1) with 1,5-hexadiene. 1.80 mmol 1,5-hexadiene was added to a stirred solution of 242 mg (0.300 mmol)

1 in 15 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. During the reaction, solid products (probably dimeric or polymeric) precipitated out of solution. After 2h at 25°, toluene was removed and the solid residue was examined by ^{1}H NMR. The spectrum indicated that a complex mixture of products had formed in the reaction.

(8) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHEt)_2CH_2)$ from cis-2-butene. 3.60 mmol cis-2-butene was added to a stirred solution of 236 mg (0.292 mmol) 1 in 15 ml toluene maintained at -78°. The mixture was slowly warmed to 40° and stirred overnight at this temperature followed by removal of toluene. The bright yellow product was recrystallized from petroleum ether and shown by ^{1}H NMR to be 4.

(9) $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHEt)_2CH_2)$ from trans-2-butene. 0.45 mmol trans-2-butene was condensed onto a frozen solution of 30 mg (0.037 mmol) 1 dissolved in 0.4 ml benzene-d_6 contained in an NMR tube sealed onto a ground glass joint. The tube was sealed closed and the mixture allowed to warm slowly to 25°. The progress of the reaction was monitored periodically by ^{1}H NMR and was judged to be complete after 5 days at 25°.

(10) (a) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^3\text{-}C_4H_7)$. 0.909 mmol trans-2-butene was added to a stirred solution of 121 mg (0.150 mmol) 1 in 10 ml of toluene maintained at -78°. The mixture was allowed to warm slowly to 40°. As soon as a color change from purple to orange took place, the reaction was quenched by cooling to -78°. This color change typically took 5-10 minutes at 40°. It is essential that the reaction be immediately quenched or contamination

by 4 will result. Residual gases were removed and passed through a series of LN_2 cooled traps. 0.393 mmol N_2 (2.61 mmol/mmol 1) was collected by a Toepler pump and discarded. After warming all traps to -64°, 0.664 mmol trans-2-butene and 0.051 mmol more N_2 was collected; thus 0.245 mmol C_4H_8 (0.939 mmol/mmol Zr) was consumed. Toluene was removed and the orange-brown product recrystallized from petroleum ether. The infrared spectrum of 7 has bands at 1575 cm^{-1} (m), 1530 cm^{-1} (m), 1025 cm^{-1} (s), 1000 cm^{-1} (m), 970 cm^{-1} (m), 845 cm^{-1} (s), 775 cm^{-1} (m), 670 cm^{-1} (m).

(10) (b) reaction of (7) with MeI. 0.600 mmol MeI was added to a stirred solution of 81.8 mg (0.196 mmol) 7 in 10 ml of toluene at -78°. The mixture was allowed to warm slowly to 25°. After 2h at 25°, the residual gases were removed and passed through a series of LN_2 cooled traps. 0.117 mmol gas (0.597 mmol/mmol 7) was collected by a Toepler pump and identified as methane by its infrared spectrum. The solid residue of the reaction was examined by ^1H NMR spectroscopy and appeared to be a complex mixture of products. The infrared spectrum of the solid has bands at 1070 cm^{-1} (m), 1030 cm^{-1} (vs), 960 cm^{-1} (m), 850 cm^{-1} (w), 815 cm^{-1} (w), 740 cm^{-1} (w), 670 cm^{-1} (m).

(11) Reaction of (1) with cyclohexene. 2.17 mmol cyclohexene was added to a stirred solution of 146 mg (.181 mmol) 1 in 10 ml of toluene at -78°. The mixture was allowed to warm slowly to 25°. After 2h at 25°, no color change indicative of metallocycle

formation had occurred. The solution was heated for 2h at 60° but the only color change observed was that characteristic of decomposition of 1.

References

1. F. D. Mango, Coord. Chem. Rev., 15, 109 (1975).
2. P. Binger, Angew. Chem., Int. Ed. Engl., 11, 309 (1972).
3. N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and I. C. Paul, J. Am. Chem. Soc., 94, 5446 (1972).
4. R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, J. Am. Chem. Soc., 95, 1674 (1973).
5. M. J. Doyle, J. McMeeking, and P. Binger, J. Chem. Soc., Chem. Commun., 376 (1976).
6. P. Binger, M. J. Doyle, J. McMeeking, C. Krüger, and Y.-H. Tsay, J. Organomet. Chem., 135, 405 (1977).
7. F.-W. Grevels, D. Schulz, and E. K. von Gustorf, Angew. Chem., Int. Ed. Engl., 13, 534 (1974).
8. M. A. Bennett, R. N. Johnson, and I. B. Tomkins, J. Am. Chem. Soc., 96, 61 (1974).
9. A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, J. Am. Chem. Soc., 95, 597 (1973).
10. S. J. McLain, C. D. Wood, and R. R. Schrock, J. Am. Chem. Soc., 99, 3519 (1977).
11. H. Hogeveen and H. C. Volger, J. Am. Chem. Soc., 89, 2486 (1967).
12. L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).
13. D. M. Roundhill, D. N. Lawson, and G. Wilkinson, J. Chem. Soc. A, 845 (1968).

14. P. G. Gassman and J. A. Nikora, J. Organomet. Chem., 92, 81 (1975).

15. R. M. Moriarty, K.-N. Chen, C.-L. Yeh, J. L. Flippen, and J. Karle, J. Am. Chem. Soc., 94, 8944 (1972).

16. R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, J. Organomet. Chem., 33, 247 (1971).

17. D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, J. Organomet. Chem., 70, 133 (1974).

18. J. A. McGinnety, J. Organomet. Chem., 59, 429 (1973).

19. R. Noyori, Y. Kumagai, H. Takaya, J. Am. Chem. Soc., 96, 634 (1974).

20. T. J. Katz and S. A. Cerefice, J. Am. Chem. Soc., 91, 6519 (1969).

21. T. J. Katz and S. A. Cerefice, J. Am. Chem. Soc., 91, 2405 (1969).

22. H. C. Volger, H. Hogeveen, and M.M.P. Gaasbeek, J. Am. Chem. Soc., 91, 218 (1969).

23. P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel," Vol. II, Academic Press, New York, N.Y., 1975, pp. 146-151.

24. G. K. Barker, M. Green, J.A.K. Howard, J. L. Spencer, and F.G.A. Stone, J. Am. Chem. Soc., 98, 3373 (1976).

25. F. L. Bowden and R. Giles, Coord. Chem. Rev., 20, 81 (1976).

26. S. Otsuka, K. Tani, and J. Yamagata, J. Chem. Soc., Dalton Trans., 2491 (1973).

27. R. J. De Pasquale, J. Organomet. Chem., 32, 381 (1971).

28. G. Ingrosso, L. Porri, G. Pantini, and P. Racanelli, J. Organomet. Chem., 84, 75 (1975).

29. G. Ingrosso, A. Immirzi, and L. Porri, J. Organomet. Chem., 60, C35 (1973).

30. N. Calderon, E. A. Olfstead, and W. A. Judy, Angew. Chem., Int. Ed. Engl., 15, 401 (1976).

31. J. L. Herrisson and Y. Chauvin, Makromol. Chem., 141, 161 (1970).

32. C. P. Casey and T. J. Burkhardt, J. Am. Chem. Soc., 7808 (1974).

33. E. L. Muetterties, Inorg. Chem., 14, 951 (1975).

34. T. J. Katz and J. McGinnis, J. Am. Chem. Soc., 97, 1592 (1975).

35. R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, J. Am. Chem. Soc., 98, 3478 (1976).

36. C. P. Casey and S. W. Polichnowski, J. Am. Chem. Soc., 99, 6097 (1977).

37. G. G. Biefeld, E. A. Eick, and R. H. Grubbs, Inorg. Chem., 12, 2166 (1973).

38. J. X. McDermott, J. F. White, and G. M. Whitesides, J. Am. Chem. Soc., 98, 6521 (1976).

39. R. H. Grubbs, A. Miyashita, M.-I. M. Liu, and P. L. Burk, J. Am. Chem. Soc., 99, 3863 (1977).

40. J. X. McDermott, M. E. Wilson, and G. M. Whitesides, J. Am. Chem. Soc., 98, 6529 (1976).

41. P. Diversi, G. Ingrosso, and A. Lucherini, J. Chem. Soc., Chem. Commun., 52 (1977).

42. J. M. Manriquez and J. E. Bercaw, J. Am. Chem. Soc., 96, 6229 (1974).

43. R. D. Sanner, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 8351 (1976).

44. J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, submitted for publication.

45. P. Laszlo and P. Stang, "Organic Spectroscopy," Harper and Row, New York, N.Y., 1971, pp. 39-48.

46. J. W. Byrne, H. U. Blaser, and J. A. Osborn, J. Am. Chem. Soc., 97, 3871 (1975).

47. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd Ed., Interscience, New York, N.Y., 1972, pp. 763-766.

48. H. J. de Liefde Meijer and F. Jellinek, Inorg. Chim. Acta, 4, 651 (1970).

49. D. W. Hart and J. Schwartz, J. Am. Chem. Soc., 96, 8115 (1974).

50. D. R. McAlister, private communication.

51. D. K. Erwin, private communication.

52. R. H. Marvich and H. H. Brintzinger, J. Am. Chem. Soc., 93, 2046 (1971).

53. T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

CHAPTER V

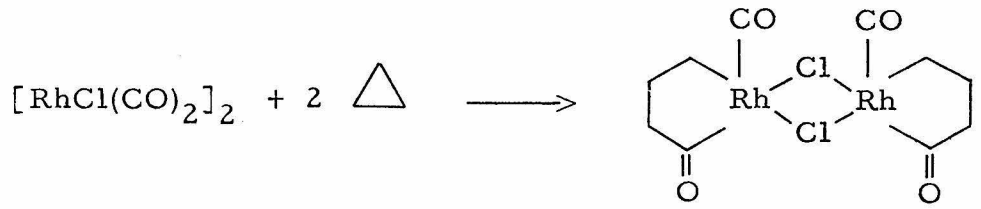
THE REDUCTION OF CARBON MONOXIDE PROMOTED BY ALKYL AND HYDRIDE DERIVATIVES OF PERMETHYLZIRCONOCENE

Introduction

Recent interest has been shown in the desire to develop selective homogeneous analogs to the Fischer-Tropsch process[1-7] which converts CO/H_2 mixtures into a variety of hydrocarbon products by the use of heterogeneous catalysts. Little is known about the mechanism of this reaction although it has been suggested[7] that metal formyl complexes are involved in the reduction. Recent papers[8,9] by Muetterties have reported the production of hydrocarbons from synthesis gas using $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, or a mixture of $Ir_4(CO)_{12}$ and $NaCl \cdot 2AlCl_3$ as homogeneous catalysts. A related process, which also involves the reduction of CO by hydrogen, is the synthesis of ethylene glycol using rhodium complexes as catalysts.[10] Schwartz[11] and Caulton[12] have been able to stoichiometrically reduce CO with hydrogen, producing linear alcohols and methane, respectively. This chapter reports our work[13] in this area using reaction systems based on bis(pentamethylcyclopentadienyl)zirconium complexes.

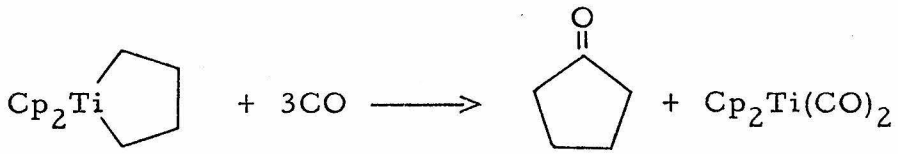
This chapter also reports on the reaction of carbon monoxide with the zirconacyclopentanes whose syntheses were described in the preceding chapter. Several reports[14-17] have appeared in which transition metal carbonyl complexes react with strained rings

to produce products formally arising from CO "insertion" into a metallocycle (eq. 1). In some cases, CO has been added to a



(1)

metallocyclopentane complex to yield free cyclopentanone (eq. 2)[18-20] or a transition metal acyl compound (eq. 3).[21]



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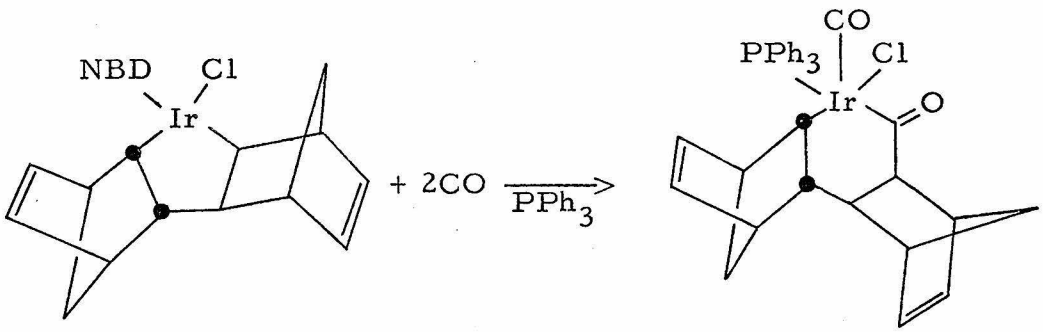


(3)

Results

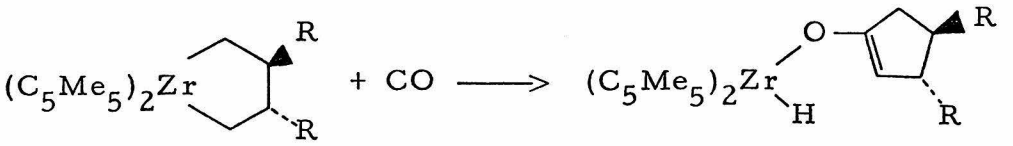
1. Reactions of $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ with H_2. Photolysis (Pyrex filtered) or thermoloysis (110°) of toluene solutions of $(C_5Me_5)_2Zr(CO)_2$ (1)[13] with H_2 (~ 1 atm) affords $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (2) in nearly quantitative yield as a white solid (eq. 4).

$$(C_5Me_5)_2Zr(CO)_2 + 2H_2 \longrightarrow (C_5Me_5)_2Zr(H)(OCH_3) + CO \qquad (4)$$

Toepler pump analysis of the thermal reaction shows that 0.961 mol CO/mol 1 is evolved and 1.78 mol H_2/mol 1 (1.85 mol H_2/mol CO evolved) is absorbed in the reaction. Molecular weight measurements of 2 indicate that it is a monomer in benzene. The ^1H NMR spectrum of 2 in benzene-d_6 shows resonances at 1.96 δ (s, 30H) due to the permethyl rings, 3.87 δ (s, 3H) due to the methoxide ligand, and 5.70 δ (s, 1H) due to the hydride. The infrared spectrum shows bands at 1590 cm^{-1} (ν (Zr-H)) and 1140 cm^{-1} (ν (C-O)); the deuteride analog of 2 shows its Zr-D stretch at ~1130 cm^{-1}. Hydrolysis of 2 with aqueous HCl (performed by Juan Manriquez in our group[13]) leads to $(C_5Me_5)_2ZrCl_2$, H_2 (0.74 mol/mol 2), and CH_3OH (0.78 mol/mol 2) in approximate agreement with eq. (5).

$$(C_5Me_5)_2Zr(H)(OCH_3) + 2HCl \longrightarrow (C_5Me_5)_2ZrCl_2 + H_2 + CH_3OH \qquad (5)$$

2. Reactions of zirconacyclopentanes with CO. The zirconacyclopentanes described in Chapter IV react with 1 atm CO at 25° in toluene according to eq. (6). White crystalline products $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OC(=O)CH(CHR)_2CH_2)$ (6, R = H; 7, R = CH_3; 8, R = CH_2CH_3) are obtained in greater than 90% yield in all cases (a small amount of $(C_5Me_5)_2Zr(CO)_2$ (1) is always formed). Toepler pump analysis of these reactions indicate that 1.05 ± 0.05 mol CO/mol Zr is consumed. The trans-3,4-dialkyl stereochemistry is



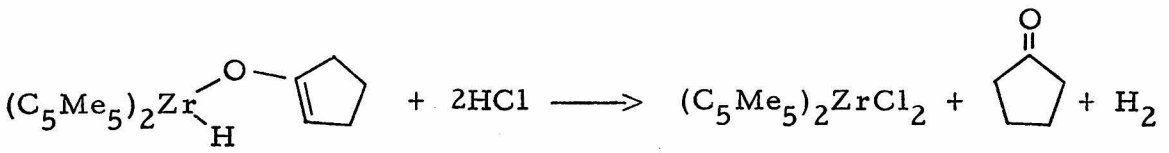
(6)

3	R = H	6	R = H
4	R = CH_3	7	R = CH_3
5	R = CH_2CH_3	8	R = CH_2CH_3

supported by the isolation of the corresponding ketone (vide infra). 6 has also been synthesized by prolonged photolysis ($\lambda > 480$ nm) of 1 and ethylene in toluene. The ^{1}H NMR spectrum of 6 in benzene-d_6 has signals at 1.97 δ (s, 30H) due to the permethyl rings, 6.07 δ (s, 1H) due to the Zr-H moiety, 4.42 δ (t, 1H, $^3J_{H-H} \sim 2$ Hz) assigned to the vinylic hydrogen, and a broad multiplet in the region 2.0-2.5 δ (6H) attributable to the methylene hydrogens of the cyclopentene ring. The ^{1}H NMR spectrum of 6 prepared from 3 and ^{13}CO shows no large splitting of any resonances, indicating that no hydrogen atoms are bonded directly to the ^{13}C atom in 6. The infrared spectrum of 6 has characteristic bands at 1628 cm^{-1} (ν (C=C)), 1275 cm^{-1} (ν (C-O)), and 1538 cm^{-1} (ν (Zr-H)), the first two bands shifting to 1595 cm^{-1} and 1250 cm^{-1} for 6 prepared from 3 and ^{13}CO. Furthermore, 6 reacts smoothly with methyl iodide to yield $(\eta^5\text{-}C_5Me_5)_2Zr(I)\text{-}(\overline{OC=CH(CH_2)_2CH_2})$ (9) with evolution of methane (0.94 mol/mol 6) according to eq. (7). As expected, infrared and ^{1}H NMR spectra for 9 are nearly identical to those for 6 with the notable absences of the Zr-H stretch at 1538 cm^{-1} in the infrared and the hydride

(7)

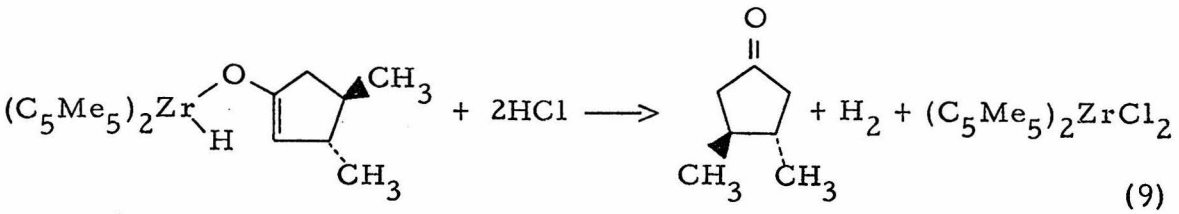
resonance at 6.07 δ in the ^{1}H NMR. Treatment of 6 with HCl in diethyl ether affords cyclopentanone in moderate yields (55%, glc) as shown in eq. (8).



(8)

The ^{1}H NMR spectrum of 7 in benzene-d_6 shows signals at 1.98 δ (s, 30H) attributable to the permethyl rings, 6.06 δ (s, 1H) due to the hydride, 4.33 δ (d, 1H, $^3J_{H-H}$ = 2 Hz) assigned to the vinylic proton, 1.13 δ (d, 6H, $^3J_{H-H}$ = 7 Hz) due to the overlap of the two doublets expected for the methyl groups bonded to the cyclopentene ring (vide infra), and multiplets at 2.30 δ and 1.39 δ. The assignment of the doublet at 1.13 δ as due to nearly perfect overlap of the doublets expected for the methyl groups bound to the cyclopentene ring is based on the intensity of this doublet (6H) and the observation that spectra run on both 90 MHz and 220 MHz instruments show the same coupling constant for this doublet (i.e. it is really a doublet and not just two singlets). Further support for this assignment comes from the observation that the methyl groups in 8 have a chemical shift difference of only 0.02 ppm (see below). Treatment of 7 with anhydrous HCl in diethyl ether affords

trans-3,4-dimethylcyclopentanone (10) as shown below. 10 was identified by the preparation of its semicarbazone and comparison of



(9)

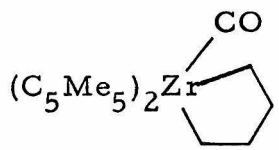
the melting point of this derivative (203-205°) with the reported melting points of the semicarbazones of the cis (176.5-177.5°) and trans (204-205°)-3,4-dimethylcyclopentanones.[22]

The ^{1}H NMR spectrum of 8 in benzene-d_6 has resonances at 1.98 δ (s, 30H) due to the permethyl rings, 6.02 δ (s, 1H) assigned to the hydride, 4.34 δ (d, 1H, $^3J_{H-H}$ = 2 Hz) attributable to the vinylic hydrogen, 0.98 δ (t, 3H, $^3J_{H-H}$ = 7 Hz) and 0.96 δ (t, 3H, $^3J_{H-H}$ = 7 Hz) due to the methyls on the ethyl groups attached to the cyclopentene ring, and multiplets at 2.28 δ and 1.14-1.64 δ. Note that the two methyl groups have nearly identical chemical shifts which supports the assignment given for 7 in which it was proposed that the methyls had identical chemical shifts (vide supra).

Discussion

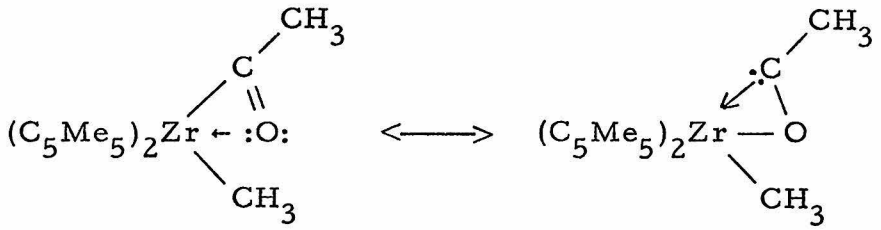
The results presented here, along with experiments performed by others in our group, show that alkyl and hydride derivatives of bis(pentamethylcyclopentadienyl)zirconium undergo facile reactions with carbon monoxide to yield final products in which the carbonyl oxygen is bound to zirconium. In the case of $(C_5Me_5)_2ZrH_2$ the

initial carbonyl adduct, $(C_5Me_5)_2ZrH_2(CO)$, has been identified at low temperature and shown to have a structure with CO carbon-bonded to zirconium in the central equatorial position (Scheme I).[13] Similar structures may be assumed for the (proposed) initial carbonyl adducts of $(C_5Me_5)_2Zr(CH_3)_2$ and $(C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ although these adducts have not been observed.[13] However, for the zirconacyclopentanes, it appears more reasonable that the adduct has the structure shown below, since the alternative with CO positioned within the five-membered ring should be highly unfavorable.



The subsequent migratory insertion of CO into Zr-alkyl or Zr-H bonds occurs with ease in all cases. The results of a study of the reaction of $(C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ with ^{13}CO established that alkyl migration is favored over hydride migration for this system.[13] In addition, the initial conversion of $(C_5Me_5)_2ZrH_2$ to $(C_5Me_5)_2ZrH_2(CO)$ compared to the direct formation of acyls from CO and $(C_5Me_5)_2Zr(CH_3)_3$ or $(C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ without buildup of detectable concentrations of their carbonyl adducts[13] points out the relative ease of alkyl as compared to hydride migration.

The facility of these migratory insertions and the subsequent reactivity of these acyl and formyl complexes may be due to the unusual bonding mode of these groups with zirconium. A "side-on" coordination of the acyl group has recently been established by Floriani and Fachinetti for $Cp_2Zr(CH_3)(COCH_3)$[23] and $Cp_2TiCl(COCH_3)$.[24] Analogous "side-on" bonding of acyl and formyl groups is indicated in these $(C_5Me_5)_2Zr$ systems in light of the structural features shared by all these compounds. Thus, the similarity of infrared and ^1H NMR data for $(C_5Me_5)_2Zr(CH_3)$-$(COCH_3)$[13] to those for $Cp_2Zr(CH_3)(COCH_3)$ dictates nearly identical structures. Interaction of an acyl oxygen lone pair of electrons with the empty, low-lying orbital located in the equatorial plane of the $(C_5Me_5)_2Zr$ grouping enables the zirconium to achieve a full 18 electron valence shell (structure I). An additional resonance structure (II) can also contribute to the bonding, however. In this form

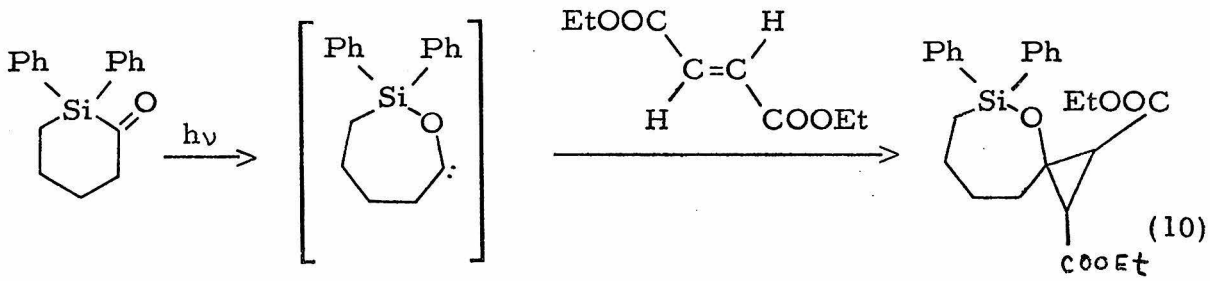


I II

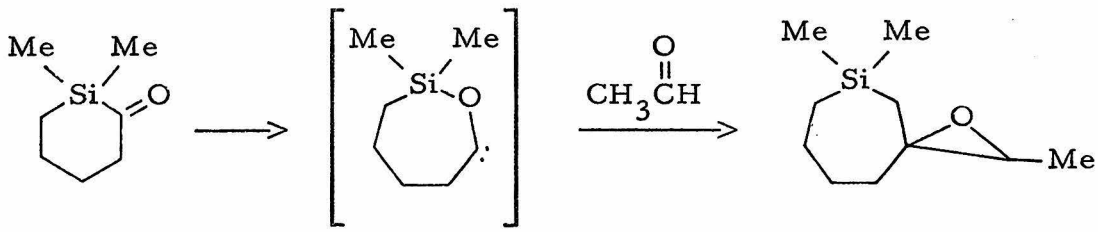
the acyl group is bonded to the zirconium both by a covalent zirconium-oxygen bond and a dative interaction of the "oxycarbene" lone pair on carbon completing the valence shell at zirconium. The resultant carbenoid character of the acyl center allows rationalization of the reaction patterns observed in these systems.

Photolysis or pyrolysis of acylsilanes yields unstable siloxycarbene intermediates which undergo subsequent reactions including insertion into H-X bonds of polar solvents (e.g. CH_3OH, CH_3COOH, HCN, HCl, PhSH, and H_2O) (eq. (9)),[25] nucleophilic attack on electron deficient olefins (eq. (10)),[26] nucleophilic attack on carbonyl groups (eq. (11)),[27] and insertion into β or α C-H bonds (eqs. (12) and (13)).[28]

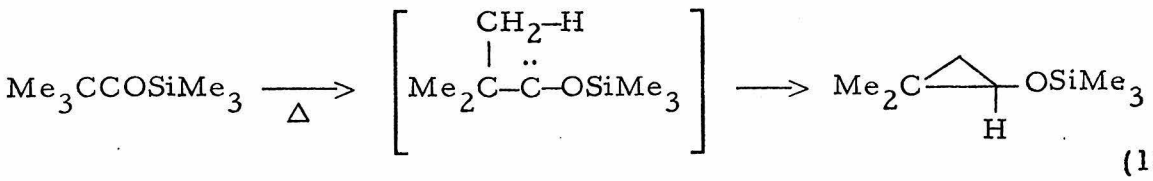
$$R_3SiCOR' \xrightarrow{h\nu} [R_3SiO\ddot{C}R'] \xrightarrow{R''OH} R_3SiO\underset{\underset{OR''}{|}}{\overset{\overset{H}{|}}{C}}R' \qquad (9)$$



(10)



(11)



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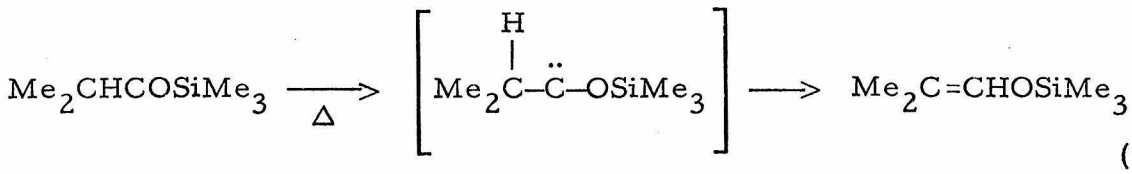
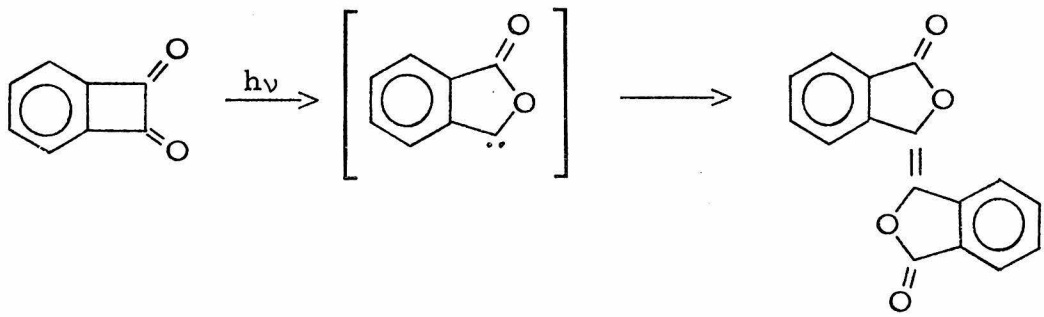
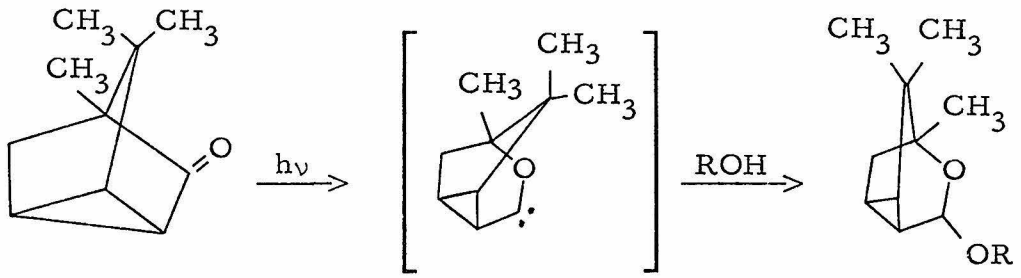


(13)

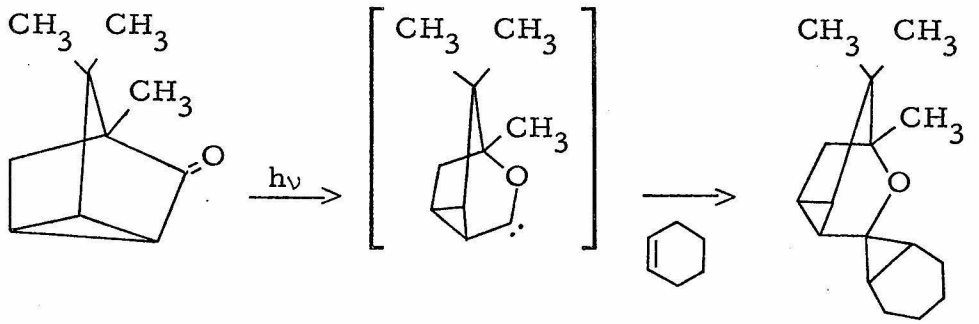
Photolysis of cyclic ketones also leads to the formation of unstable oxycarbene intermediates. These ketones undergo ring expansion in the formation of the oxycarbene analogous to the intermediates shown in eqs. (10) and (11) for cyclic silylketones. Subsequent reactions of these ring-expanded oxycarbenes include dimerization (eq. (14)),[29] insertion into the O-H bond of alcohols (eq. (15)),[30-34] addition to double bonds (eq. (16)),[30] and insertion into α C-H bonds (eq. (17)).[34]



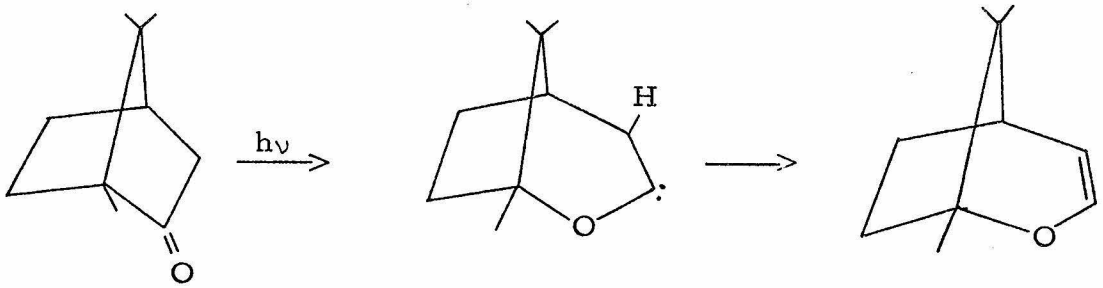
(14)


CH3
CH3
CH3
O
hν
CH3
CH3
CH3
O
ROH
CH3
CH3
CH3
O
OR

(15)


CH3
CH3
CH3
O
hν
CH3
CH3
CH3
O
CH3
CH3
CH3
O

(16)

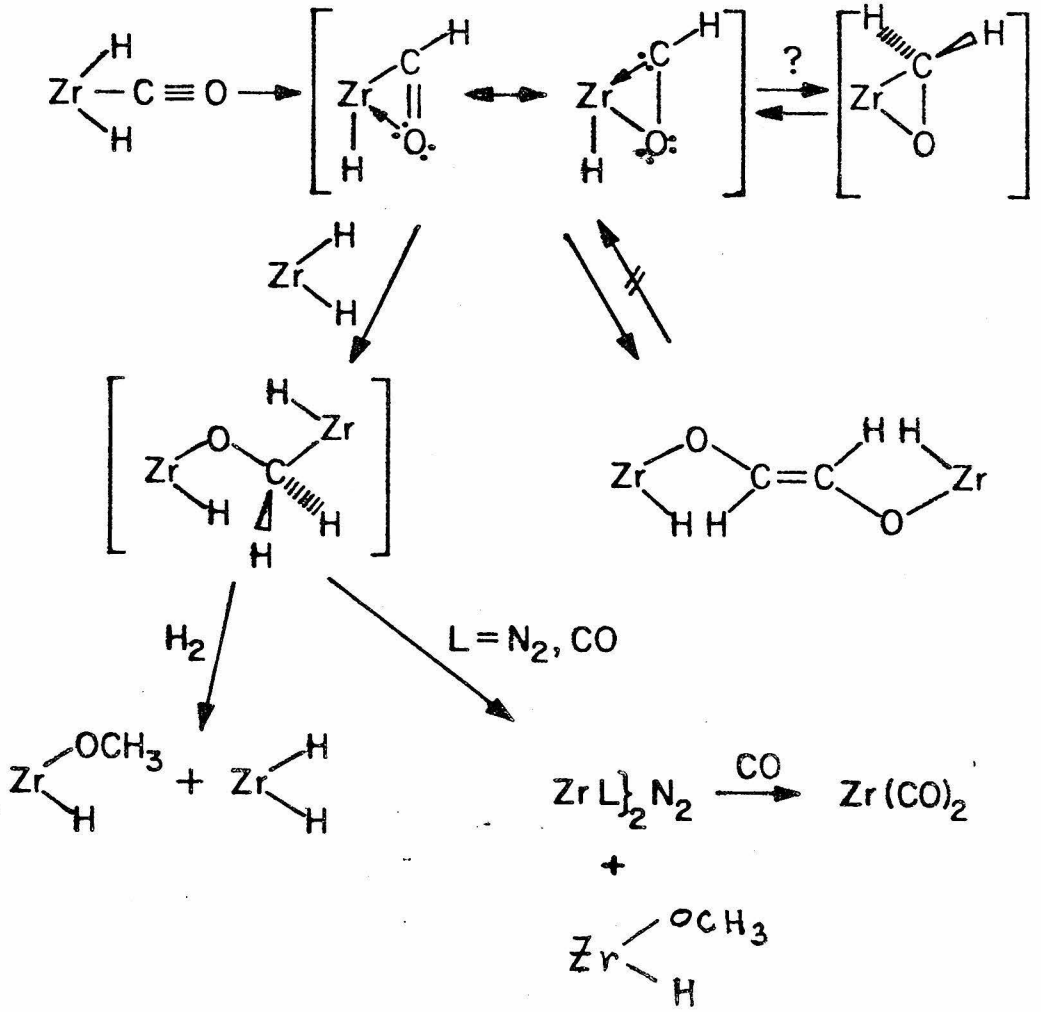

O
hν
H
O
O

(17)

The products which we obtain from reactions of permethylzirconocene acyl and formyl intermediates appear to show reactivity patterns similar to those found for siloxycarbenes and oxycarbenes.

Although we have not yet directly detected the postulated formyl hydride intermediate shown in Scheme I, dimerization of the oxycarbene, $(C_5Me_5)_2Zr(H)(\ddot{O}\dot{C}H)$, would provide a reasonable pathway to the product, $\{(C_5Me_5)_2ZrH\}_2$ (μ-OCH=CHO). This product is obtained when solutions of $(C_5Me_5)_2ZrH_2(CO)$ are allowed to warm <u>without</u> any $(C_5Me_5)_2ZrH_2$ (11) present.[13] In the presence of $(C_5Me_5)_2ZrH_2$, however, $(C_5Me_5)_2Zr(H)(OCH_3)$ (2) is obtained with 11 recovered unchanged.[13] We may explain this result by assuming that the oxycarbene will insert into a Zr-H bond of $(C_5Me_5)_2ZrH_2$ (11) as shown in Scheme I. Subsequent reductive elimination of 2 induced by H_2 or by good π-acid ligands such as CO and N_2 would simultaneously yield 11 or $\{(C_5Me_5)_2ZrL\}_2N_2$ (L = CO, N_2), respectively (Scheme I). Formation of $\{(C_5Me_5)_2ZrL\}_2N_2$ (L = CO, N_2) is observed when CO slowly diffuses into an N_2-blanketed solution of $(C_5Me_5)_2ZrH_2$ at 25°. Further reaction at 25° leads to $(C_5Me_5)_2Zr(H)(OCH_3)$ and $(C_5Me_5)_2Zr(CO)_2$ (1).[13]

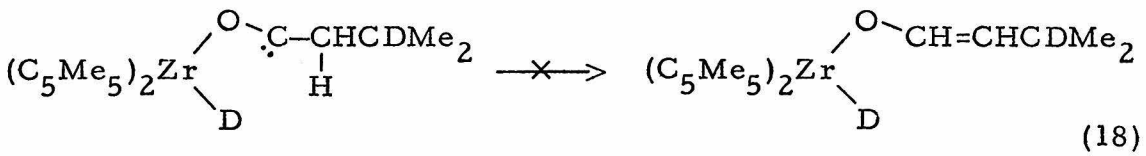
We propose that $ZrH_2(CO)$ is generated from $Zr(CO)_2$ and H_2 by photochemical or thermal loss of CO followed by addition of H_2. Support for this claim was provided by reaction of $\{(C_5Me_5)_2Zr(CO)\}_2N_2$[35] with H_2 at 25° leading predominantly to $(C_5Me_5)_2Zr(H)(OCH_3)$ (2).[13] Even with this support, however, there is still some question whether this Scheme is operative for the H_2 reduction of 1 to 2 since we have no direct evidence for the presence of



Scheme I

$(C_5Me_5)_2ZrH_2$ (11) in this system. It may be, however, that sufficient 11 is formed to catalyze the reduction of 1 to 2 via the same pathway as that shown in Scheme I.

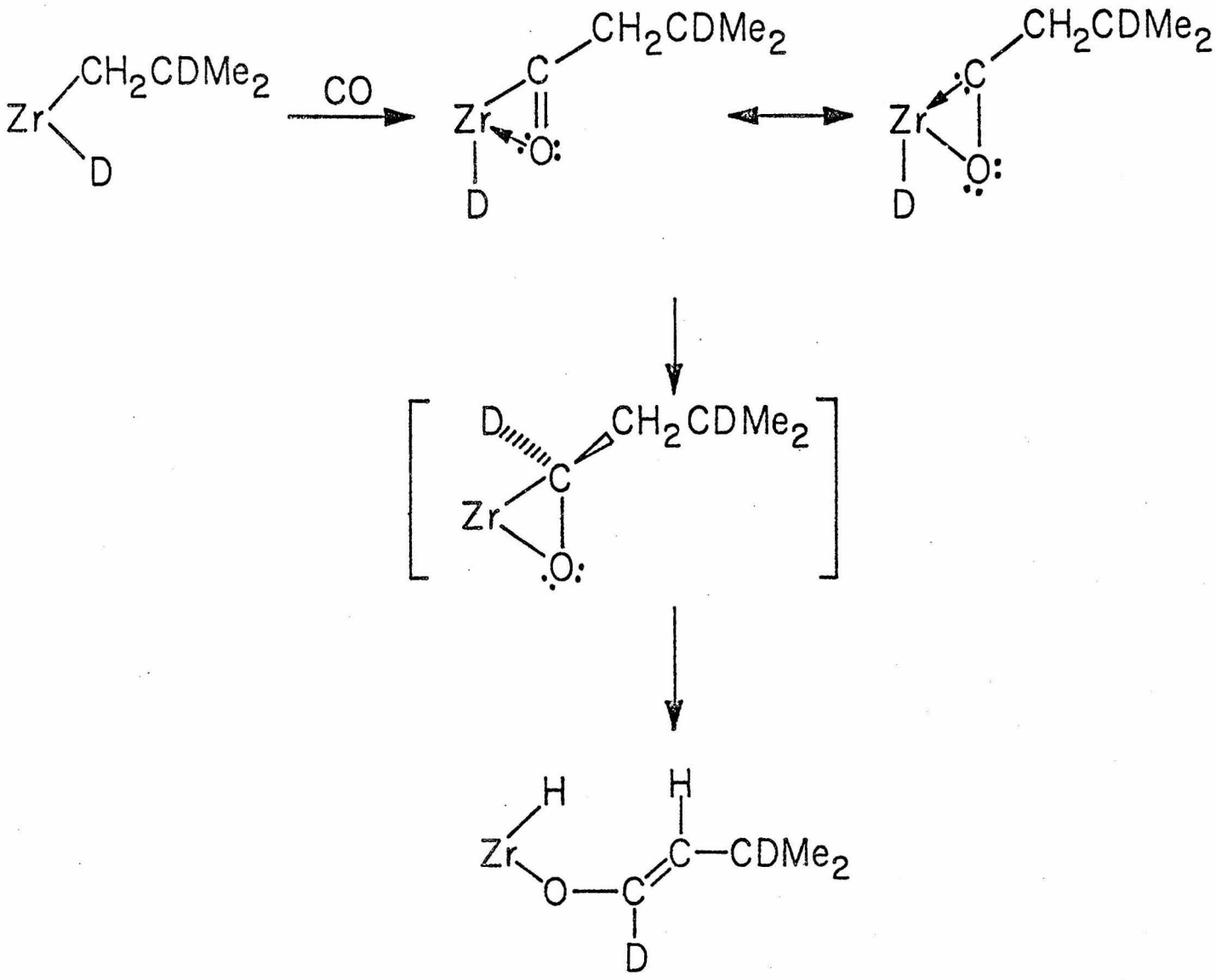
Scheme II shows the proposed mechanism for the reaction of the isobutyl hydride derivative $(C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (12) with CO.[36] The initial product, observed at -50°, is the acyl complex $(C_5Me_5)_2Zr(H)(COCH_2CHMe_2)$ (13) which rearranges to the enolate hydride $(C_5Me_5)_2Zr(H)(OCH=CHCHMe_2)$ (14) as the solution warms. The transformation of 13 to 14 could be rationalized as involving inseration of the oxycarbene species into the α C-H bond (eq. (18)) as has been observed for organic oxycarbenes and siloxycarbenes (vide supra). The results of a labeling study show that $(C_5Me_5)_2Zr(D)(OCH=CHCDMe_2)$ (eq. (18)) is not formed, however. Rather



(18)

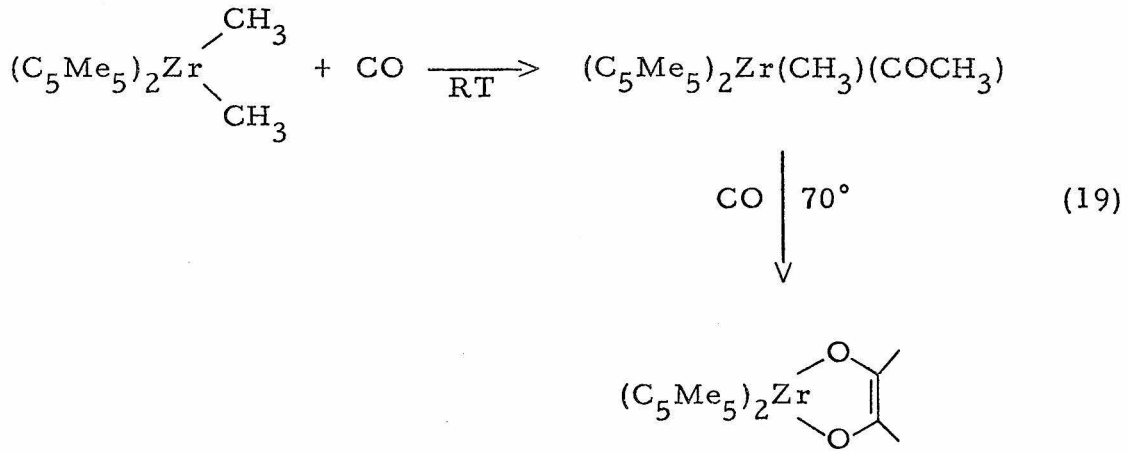
$Zr(H)(OCD=CHCDMe_2)$ is the product of this reaction. Scheme II shows that this result may be explained by assuming that the oxycarbene inserts into the Zr-H bond forming an aldehyde adduct which can undergo β-hydride abstraction yielding the enolate hydride 14.

The reaction of the zirconacyclopentane complexes with carbon monoxide must take a different course than that shown in Schemes I or II since these compounds have no Zr-H bonds available for oxycarbene insertions. The formation of the final product 6 may be

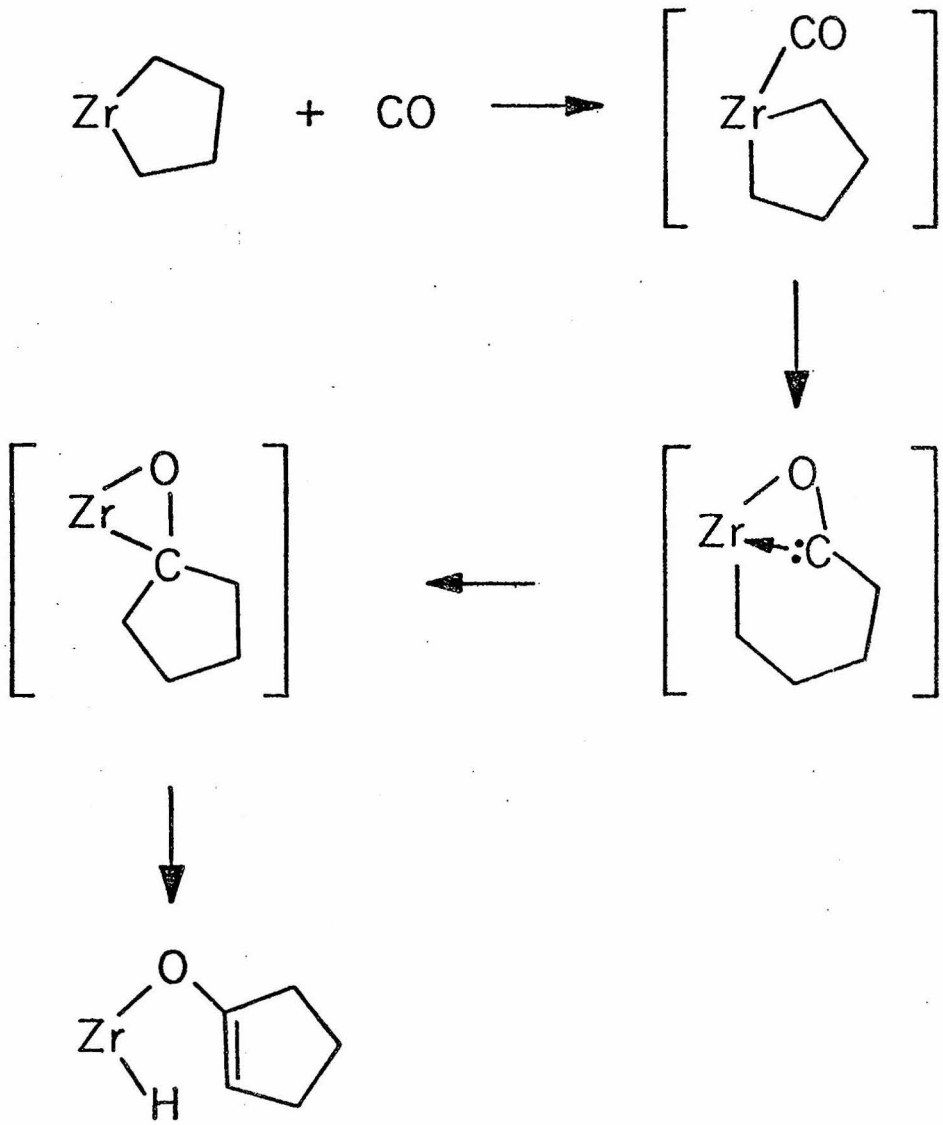

CH2CDMe2
Zr
D
CO
C
O
CH2CDMe2
Zr
D
C
O
CH2CDMe2
Zr
D
D
CH2CDMe2
C
Zr
O
H
H
Zr
O
C
C
CDMe2
D

rationalized by assuming the mechanism shown in Scheme III. We propose that insertion of CO into the zirconacyclopentane ring would generate an acyl complex but the constraints of the ring will force the carbene carbon to be cis to the remaining zirconium-carbon bond of the metallocycle. This proximity and the chance to form a five membered ring may encourage insertion of the oxycarbene into the Zr-C bond, thus affording a cyclopentanone adduct of permethylzirconocene. The final step would involve β-hydride abstraction (as suggested in Scheme II above) to yield the observed enolate hydride derivative. It should also be noted that the stereochemistry at the 3 and 4 positions in the ring is maintained, as expected according to this mechanism. Thus trans-3,4-dimethylzirconacyclopentane (4) yields trans-3,4-dimethylcyclopentene in 7.

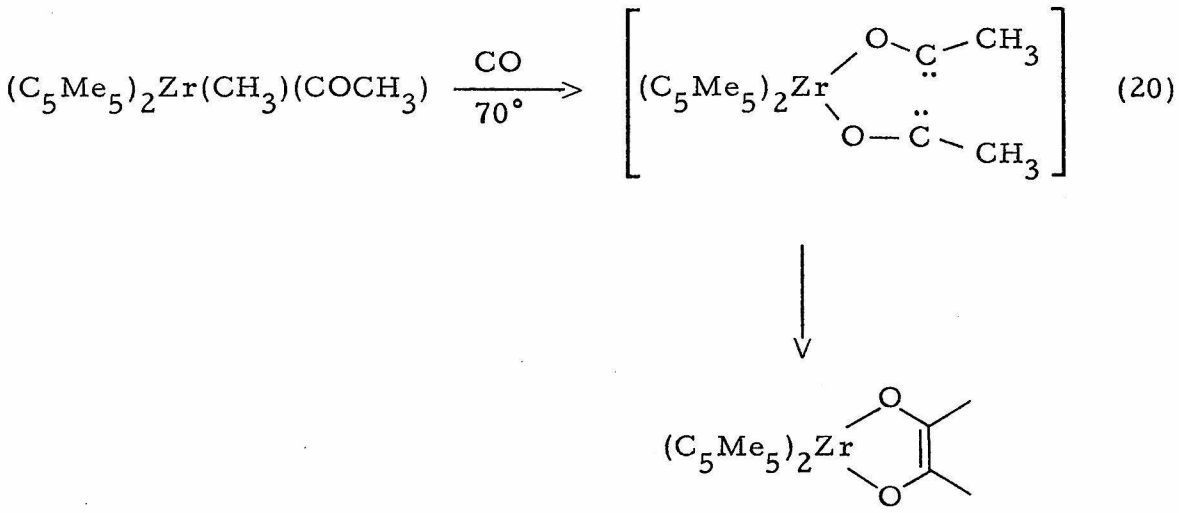
It is interesting to examine the reactivity with CO of an acyclic analog of 3, namely $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$ (15).[13] It was found[36] that addition of CO to 15 led to the formation of $(C_5Me_5)_2Zr(CH_3)(COCH_3)$ (16) which could be converted to $(C_5Me_5)_2Zr(O(CH_3)C{=}C(CH_3)O)$ (17) by heating at 70° (eq. (19)).



(19)


Zr
+ CO
CO
Zr
O
Zr
C
O
Zr
:C
O
Zr
H

The formation of this product may be rationalized on the basis of a second insertion of CO into the zirconium alkyl bond of 16 leading to a bis(acetyl) or functionally a bis(oxycarbene) complex which may undergo intramolecular dimerization to yield 17 (eq. (20)).



(20)

Thus the acyclic mono(acetyl) complex 16 shows no proclivity for insertion into the remaining Zr-C bond as is found for the cyclic analog. The stability of the acyclic acyl complex 16 compared to that of the unobservable cyclic acyl intermediate is in agreement with the results of Whitesides et al.[20] They observed the formation of free cyclopentanone, presumably by reductive elimination from a cyclic acyl intermediate, upon addition of CO to $Cp_2\overline{TiCH_2(CH_2)_2CH_2}$ at low temperature; however, the reaction of $Cp_2Ti(CH_3)_2$ with carbon monoxide was quite slow. While we observe no free cyclopentanone in our system, this ketone may be obtained in good yield by treatment of 6 with HCl. Thus it seems as though metallocycles provide a more reactive grouping for coordinated CO, encouraging insertion into M-C bonds and/or

reductive elimination, whereas acyclic dimethyl analogs do not promote such reactivity under similar conditions. This enhanced reactivity may be provided by (1) the cis orientation of the acyl carbon and the other metal-bound carbon required by ring constraints and (2) the formation of a five membered ring by insertion of the oxycarbene into the M-C bond.

In summary, then, carbonylation of hydride and alkyl derivatives of permethylzirconocene leads in some instances to products similar to those which might have been expected with more familiar (e.g. Group VIII) organometallic compounds, although enolate hydrides rather than aldehydes or ketones are produced. In other cases, products which are derived from the coupling of carbonyl carbon atoms (such as $\{(C_5Me_5)_2ZrH\}_2$ (μ-OCH=CHO) and 17) are observed. We believe these reactivity patterns may be rationalized most simply on the basis of an "oxycarbenoid" reactivity imparted to carbon by the unusual coordination of the acyl (or formyl) group to the permethylzirconocene moiety.

Transition metal formyl complexes formed by CO "insertion" into a metal-hydride bond have been postulated as intermediates in the Fischer-Tropsch reaction[7] and have been invoked in order to explain the unusual lability of transition metal carbonyl hydrides in substitution and exchange reactions.[37,38] The only isolated formyl complexes prepared to date, however, have involved intermolecular addition of hydride to transition metal carbonyl compounds (eq. (21))[39,40] or treatment of $Fe(CO_4)^{2-}$ with acetic formic anhydride (eq. (22)).[41] Thus, no formyl compounds have been

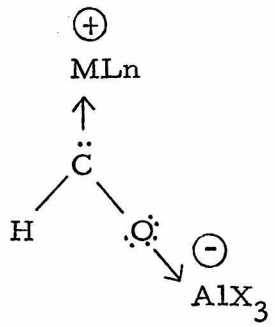
$$Fe(CO)_5 + NaHB(OCH_3)_3 \xrightarrow[[(Ph_3P)_2N]^{\oplus}\,Cl^{\ominus}]{} [(Ph_3P)_2N]^{\oplus}[(CO)_4Fe(CHO)]^{\ominus} + NaCl + B(OCH_3)_3 \quad (21)$$

$$Na_2Fe(CO)_4 + HCOCCH_3 \xrightarrow[[(Ph_3P)_2N]^{\oplus}\,Cl^{\ominus}]{} [(Ph_3P)_2N]^{\oplus}[(CO)_4Fe(CHO)]^{\ominus} + NaCl + NaOCOCH_3 \quad (22)$$

found by intramolecular ligand migration although Collman has reported observation of the reverse reaction (eq. (23)).

$$Na[Fe(CO)_4CHO] \xrightarrow[\text{slow}]{} Na[HFe(CO)_4] + CO \quad (23)$$

The reductive coupling of CO that we observe in our systems is reminiscent of the Fischer-Tropsch synthesis and may indicate the presence of "side-on" formyl and acyl intermediates in this important process. It is interesting to note that the homogeneous reduction of CO to produce alcohols or hydrocarbons recently observed by Schwartz[11] and Muetterties[8] used systems containing alkyl aluminum hydrides and aluminum chloride, respectively. Both of these reagents may function as Lewis acids, suggesting that oxycarbenes such as that shown below may be involved in the reactions.



Experimental

For a description of physical measurements and materials see Chapter IV. $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ was prepared as previously described.[13] The zirconacyclopentanes were prepared as described in Chapter IV.

Procedures

(1) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$. (a) by photolysis. 30 mg (0.072 mmol) 1 was dissolved in 0.4 ml benzene-d_6 and sealed under 1 atm H_2 in an NMR tube. The tube was photolyzed at 25° with a 200 watt mercury-xenon lamp using a Pyrex filter and the reaction was monitored by NMR. After 7 days of photolysis, the NMR spectrum indicated an equimolar mixture of 1 and 2. An identical sample stored in the dark showed no reaction.

(b) by thermolysis. 1.81 mmol H_2 was added to a stirred solution of 138 mg (0.330 mmol) 1 in 15 ml of toluene maintained at -78°. The mixture was heated for 14 h at 120°, then residual gases were removed and passed through a series of LN_2 cooled traps. 1.54 mmol gas ($CO + H_2$) was collected by a Toepler pump followed by cycling this mixture of gases over CuO at 320° to

convert H_2 to H_2O and CO to CO_2. The mixture of CO_2 and H_2O was passed through a dry ice-acetone trap which removed the H_2O. The amount of gas left was 0.317 mmol which means that 1.22 mmol H_2 was originally present so 0.587 mmol H_2 was used in the reaction. In summary, 0.317 mmol CO (0.961 mol/mol 1) was released and 0.587 mmol H_2 (1.85 mol/mol CO released) was consumed. Toluene was removed and the white product recrystallized from petroleum ether. Alternatively, the product may be purified by sublimation at 130° (10^{-3} Torr). Calculated for $ZrC_{21}H_{34}O$: C 64.06, H 8.71, Zr 23.17; found C 64.14, H 8.90, Zr 23.12. Molecular weight determined cryoscopically for 85.7 mg 2 per g of C_6H_6: 402 ± 30 (calcd 394).

(2) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCCH(CH_2)_2CH_2)$. (a) from (3). 3.78 mmol CO was added to a stirred solution of 400 mg (0.958 mmol) 3 in 15 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2 h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 2.75 mmol CO was collected by a Toepler pump; thus 1.03 mmol CO (1.08 mol/mol 3) was consumed in the reaction. Toluene was removed and the light tan product recrystallized from petroleum ether. Calculated for $ZrC_{25}H_{38}O$: C 67.35, H 8.59, Zr 20.46; found: C 67.56, H 8.50, Zr 21.03.

(b) from (1). 0.35 mmol ethylene was added to a frozen solution of 40 mg (0.096 mmol) 1 in 0.4 ml toluene-d_8 contained in an NMR tube and the tube was sealed. Photolysis at 25° was carried out using a Hanovia medium pressure mercury lamp filtered

through a # 3-71 Corning yellow sharp-cut filter ($\lambda > 490$ nm). The progress of the reaction was monitored by NMR and was judged to be complete after 72 h. An identical sample stored in the dark showed no reaction.

(c) reaction of (6) with HCl - formation of cyclopentanone. 0.80 mmol anhydrous HCl was added to a frozen solution of 173 mg (0.39 mmol) 6 in 10 ml diethyl ether. The mixture was allowed to warm slowly to 25° with stirring. After 2 h at 25°, volatiles were transferred to a flask in vacuo and this solution was concentrated to 1 ml by removing diethyl ether at -78°. The remaining solution, analyzed by glc using an OV-101 column and decane as an internal standard, contained 0.21 mmol cyclopentanone (55% yield).

(3) $(\eta^5\text{-}C_5Me_5)_2Zr(I)(OCCH(CH_2)_2CH_2)$. 1.04 mmol CH_3I was added to a stirred solution of 131 mg (0.294 mmol) 6 in 10 ml toluene maintained at -78°. The solution was allowed to warm slowly to 25°. After 2 h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 0.276 mmol methane (0.94 mol/mol 6) was collected by a Toepler pump and identified by its infrared spectrum. Toluene was removed and the product was recrystallized from petroleum ether.

(4) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCCH(CHCH_3)_2CH_2)$. (a) synthesis. 1.78 mmol CO was added to a stirred solution of 280 mg (0.590 mmol) 4 in 10 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2 h at 25°, residual gases were collected and passed through a series of LN_2 cooled traps.

1.13 mmol unreacted CO was collected by a Toepler pump; thus 0.650 mmol (1.10 mol/mol 4) was consumed in this reaction. Toluene was removed and the light tan product recrystallized from petroleum ether. Calculated for $ZrC_{27}OH_{42}$: C 68.44, H 8.93, Zr 19.25; found: C 68.75, H 9.07, Zr 19.78.

(b) reaction of (7) with HCl. 1.40 mmol anhydrous HCl was added to a frozen solution of 329 mg (0.694 mmol) 7 in 20 ml diethyl ether. The mixture was allowed to warm slowly to 25° with stirring. After 2 h at 25°, volatiles were transferred to a flask in vacuo and this solution was concentrated to 1 ml by removing diethyl ether at -78°. The semicarbazone derivative of the ketone was prepared from this solution using the standard procedure.[42] The melting point of this semicarbazone (203-5°) was in excellent agreement with the published value of 204-5° for the trans-3,4-dimethylcyclopentanone derivative.[22]

(5) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(O\overline{CCH(CHCH_2CH_3)_2CH_2})$. 1.30 mmol CO was added to a stirred solution of 184 mg (0.388 mmol) 5 dissolved in 10 ml toluene maintained at -78°. The mixture was allowed to warm slowly to 25°. After 2 h at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. 0.910 mmol CO were collected by a Toepler pump; thus, 0.390 mmol (1.00 mol/mol 5) CO was consumed in the reaction. Toluene was removed and the light tan product recrystallized from petroleum ether.

References

1. H. Storch, N. Golumbic, and R. Anderson, "The Fischer-Tropsch and Related Syntheses," Wiley, New York, N.Y., 1951.
2. Y. T. Eidus, Russ. Chem. Rev., 36, 338 (1967).
3. M. A. Vannice, Catal. Rev. Sci. Eng., 14, 153 (1976).
4. M. A. Vannice, J. Catal., 37, 449, 462 (1975).
5. P. H. Emmett, Ed., "Catalysis," Vol. 4, Reinhold, New York, N.Y., 1956.
6. B. K. Nefedev and Y. T. Eidus, Russ. Chem. Rev., 34, 272 (1965).
7. G. Henrici-Olivé and S. Olivé, Angew. Chem., Int. Ed. Engl., 15, 136 (1976).
8. G. C. Demitras and E. L. Muetterties, J. Am. Chem. Soc., 99, 2796 (1977).
9. M. G. Thomas, B. F. Beier, and E. L. Muetterties, J. Am. Chem. Soc., 98, 1296 (1976).
10. R. L. Pruett and W. E. Walker (Union Carbide Corp.), West German Patent 2,262,318 (1973); Belgian Patent 815-841 (1974); U.S. Patents 3,878,214; 3,878,290; 3,878,292 (1975); and 3,833,634 (1974).
11. L. I. Shoer and J. Schwartz, J. Am. Chem. Soc., 99, 5831 (1977).
12. J. C. Huffman, J. G. Stone, W. C. Krussell, and K. G. Caulton, J. Am. Chem. Soc., 99, 5829 (1977).

13. (a) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, J. Am. Chem. Soc., 98, 6733 (1976);
(b) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, submitted for publication.

14. L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).

15. H. C. Volger, H. Hogeveen, and M.M.P. Gaasbeek, J. Am. Chem. Soc., 91, 218 (1969).

16. D. M. Roundhill, D. N. Lawson, and G. Wilkinson, J. Chem. Soc., Sect. A, 845 (1968).

17. P. G. Gassman and J. A. Nikora, J. Organomet. Chem., 92, 81 (1975).

18. F.-W. Grevels, D. Schulz, and E. K. von Gustorf, Angew. Chem., Int. Ed. Engl., 13, 534 (1974).

19. S. J. McLain, C. D. Wood, and R. R. Schrock, J. Am. Chem. Soc., 99, 3519 (1977).

20. J. X. McDermott, M. E. Wilson, and G. M. Whitesides, J. Am. Chem. Soc., 98, 6529 (1976).

21. A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, J. Am. Chem. Soc., 95, 597 (1973).

22. R. G. Haber and J. T. Klug, Bull. Res. Council Israel, 11A, 29 (1962).

23. G. Fachinetti, C. Floriani, F. Marchetti, and S. Merlino, J. Chem. Soc., Chem. Commun., 522 (1976).

24. F. Calderazzo, Angew. Chem., Int. Ed. Engl., 16, 299 (1977).

25. J. M. Duff and A. G. Brook, Can. J. Chem., 51, 2869 (1973).

26. A. G. Brook, H. W. Kucera, and R. Pearce, Can. J. Chem., 49, 1618 (1971).

27. A. G. Brook, R. Pearce, and J. B. Pierce, Can. J. Chem., 49, 1622 (1971).

28. A. R. Bassindale, A. G. Brook, and J. Harris, J. Organomet. Chem., 90, C6 (1975).

29. H. A. Staab and J. Ipaktschi, Tetrahedron Letters, 583 (1966).

30. P. Yates, Pure Appl. Chem., 16, 93 (1968) and references cited therein.

31. D. R. Morton and N. J. Turro, J. Am. Chem. Soc., 95, 3947 (1973) and references cited therein.

32. N. J. Turro and D. M. McDaniel, J. Am. Chem. Soc., 92, 5727 (1970).

33. G. Quickert, P. Jacobs, and W.-D. Stohrer, Angew. Chem., Int. Ed. Engl., 13, 197 (1974).

34. W. C. Agosta and D. K. Herron, J. Am. Chem. Soc., 90, 7025 (1968).

35. J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, J. Am. Chem. Soc., 98, 3042 (1976).

36. D. R. McAlister, Ph.D. Thesis, California Institute of Technology, 1977.

37. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, N.Y., 1967, p. 555.

38. A. Berry and T. L. Brown, J. Organomet. Chem., 33, C67 (1971).

39. C. P. Casey and S. M. Neumann, J. Am. Chem. Soc., 98, 5395 (1976).

40. S. R. Winter, G. W. Cornett and E. A. Thompson, J. Organomet. Chem., 133, 339 (1977).

41. J. P. Collman and S. R. Winter, J. Am. Chem. Soc., 95, 4089 (1973).

42. R. M. Roberts, J. C. Gilbert, L. B. Rodewald, A. S. Wingrove, "An Introduction to Modern Experimental Organic Chemistry," Holt, Rinehart, and Winston, New York, N.Y., 1969, pp. 232-233.

CHAPTER VI

CRYSTAL STRUCTURE DETERMINATIONS IN PROGRESS. STRUCTURES OF $(\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CH(CH_2CH_3))_2CH_2)}$, $\{(\eta^5\text{-}C_5Me_5)_2Zr(I)\}_2$ (μ-OCH=CHO), AND $(\eta^5\text{-}C_5Me_5)_2Zr$(BUTADIENE).

Introduction

This chapter describes the progress of work on the crystal structures of the three title compounds. Since all these compounds exhibit unsolved disorder of varying degrees, no attempt is made to describe the molecular conformation of these compounds in other than qualitative terms. The main purpose of this chapter is to describe the data collection procedures, note any unusual crystal features, explain the attempted solutions, and provide a prognosis for completion of the structures.

Part I. Crystal Structure Investigation of $(\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CH(CH_2CH_3))_2CH_2)}$

Experimental

$(\eta^5\text{-}C_5Me_5)_2\overline{Zr(CH_2(CH(CH_2CH_3))_2CH_2)}$ was prepared as described in Chapter IV and obtained as well-formed yellow crystals by slow removal of solvent from a 1:1 benzene:toluene solution of the complex at 0°. A series of Weissenberg and precession photographs (Cu-K_α and Mo-K_α radiation) showed monoclinic

symmetry with the systematic absences $hk\ell$, $h+k$ odd and $h0\ell$, ℓ odd so the space group C2/c was chosen.

A crystal of dimensions $0.35 \times 0.50 \times 0.75$ mm was mounted in a glass capillary under N_2 with its long axis (c) slightly skew to the ϕ axis of a Syntex $P\bar{1}$ full-circle automated diffractometer. Unit cell dimensions were obtained by a least-squares fit to the $\sin^2 \theta/\lambda^2$ values for fifteen reflections measured on the diffractometer. Crystal data are given in Table I.

Using Mo-K_α radiation monochromated with a graphite crystal, one quadrant of data ($hk\ell$ and $\bar{h}k\ell$) was measured between 2° and 60° in 2θ, using a θ-2θ scan technique at a scan rate of 2°/min; background counts were taken before and after each scan, with the total background counting time equal to the total scan time for the peak. The peak scan began 1.1° below $2\theta_1$ (2θ for Mo-$K_{\alpha 1}$) and continued to 1.1° above $2\theta_2$. Intensities of four check reflections measured every 100 reflections showed no crystal decomposition during data collection.

3808 independent reflections were measured and a variance $\sigma^2(F_o^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$, where S is the scan count. In addition, a small data set (200 reflections) was collected for the other twin so that the hk0 data for the twin which was used for intensity measurements could be scaled. (See the next section for details.) Intensities and their weights were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 4.3$ cm^{-1}). The data were then placed on an absolute scale by means of a Wilson

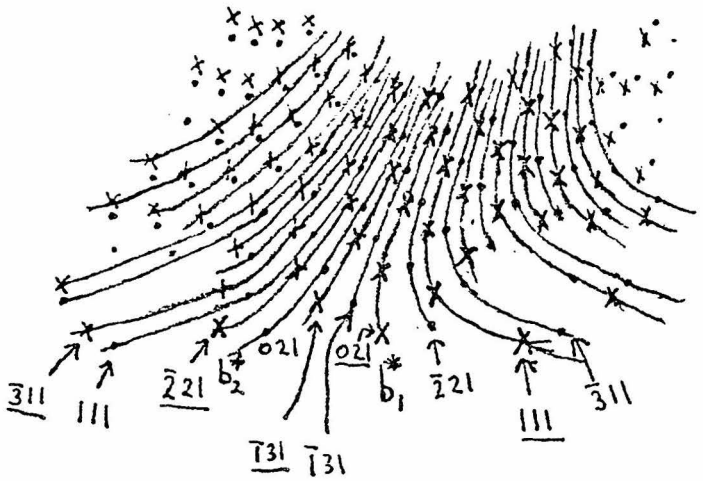
plot,[1] with scattering factors for all atoms calculated by the method of Cromer and Mann.[2] Reflections having $F_o^2 < 1.5\sigma(F_o^2)$ were deleted, leaving 2216 reflections for the working data set.

Solution Attempts and Discussion of the Structure

Figure 1 shows tracings of typical first and second layer Weissenberg photographs for crystals of this compound. It can be seen that the presence of a set of twins is indicated by the upper layer photographs, and several festoons have been drawn in to make this clearer. This twinning may be most simply described as due to the operation of a (100) twin plane so that (hkℓ) for twin 1 and (hkℓ) for twin 2 make up a twin pair. Several twin pairs have been labeled on the figure to illustrate this point. Luckily, the twins in this compound were well separated on the upper layers, making it possible to collect data on only one of the twins. However, the twins overlap on the zero layer since the b axis acts as a double mirror here. It is a mirror both between (hk0) and $(\bar{h}k0)$ in the same twin (due to monoclinic symmetry) and between $(hk0)_1$ and $(hk0)_2$ in a twin pair. This may be expressed as in eq. (1), where F_1 and F_2 are the structure factors for twins 1 and 2,

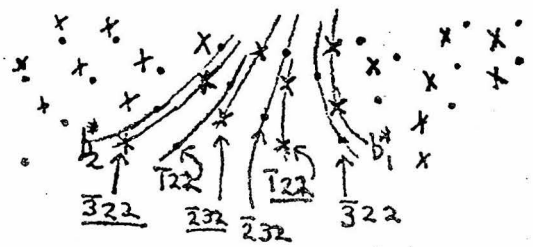
$$F_{obs}^2 = F_1^2(hk0) + F_2^2(\bar{h}k0) \qquad (1)$$

respectively. If we have equal quantities of the two twins, the intensity on the zero layer for one twin is simply half the observed intensity. In our case, however, one twin was of greater intensity so it was necessary to measure 200 upper layer reflections for



1st layer Weissenberg (ℓ=1)
X = twin 1 (underlined hkℓ)
• = twin 2

Figure 1. Tracings of first and second layer Weissenberg photographs of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CHEt)_2CH_2)$.



2nd layer Weissenberg (ℓ=2)

twin 2 in order to find a scale factor for use on the zero layer. In this way we could obtain the correct intensities for twin 1 (eqs. (2)-(5)).

$$F_2^2(hk\ell) = sF_1^2(hk\ell) \tag{2}$$

$$F_{obs}^2 = F_1^2(hk0) + sF_1^2(\bar{h}k0) \tag{3}$$

but for monoclinic crystals, $F_1^2(\bar{h}k0) = F_1^2(hk0)$ (4)

$$\therefore \quad F_1^2(hk0) = \frac{F_{obs}^2}{(1+s)} \tag{5}$$

This scaling was easily accomplished, providing us with a complete data set for twin 1.

A Patterson map was obtained from which the y coordinate of the zirconium atom was obtained (x and z are fixed since this atom lies on the twofold axis). A Fourier map was generated using the zirconium coordinates; examination of the map allowed us to find nine of the ten unique ring atoms (the two rings in one molecule are related by the twofold axis). A difference Fourier map was obtained using all located atoms, but only the tenth ring atom and the α-carbon in the metallocycle could be determined. All maps which had been calculated to this point showed a large (ca. 3.5 Å^2 cross section in the yz plane) area of electron density in the region of a special position ($\frac{1}{2}$, y, $\frac{1}{4}$) which apparently contains the β-carbons. Several disordered models were tried in an effort to fit the electron density in this region, but all disordered atoms seemed to

collapse into the special position upon least-squares refinement. The ethyl groups bonded to the β-carbons are also disordered and here, again, placement efforts were unsuccessful. Our "chemical intuition" was of little value in placing these ethyls since we were unable to locate the β-carbons to which they are bonded.

At this point it occurred to us that this disorder may be due to our choice of the centric rather than acentric (e.g. Cc) space group. Examination of a Fourier map in the plane of the permethyl rings indicated no disorder here, however. Attempted least-squares refinement in space group Cc proved to be unsuccessful, with the permethyl rings exhibiting unreasonable shifts.

The prognosis for this structure is good, we think, although some disordered atoms (especially the β-carbons) may have to be constrained in the refinement. The evidence suggests that it should be treated as centric with the permethyl rings as well as the α-carbon atoms related by a twofold axis. The "best" disordered model we have obtained (R = 0.18) indicates a "puckered" metallocyclic structure with ethyl groups at the β-carbon atoms in a trans arrangement.

Part II. Crystal Structure Investigation of $\{(\eta^5\text{-}C_5Me_5)_2Zr(I)\}_2$ (μ-OCH=CHO).

Experimental

$\{(\eta^5\text{-}C_5Me_5)_2Zr(I)\}_2$ (μ-OCH=CHO) was prepared by the method of Manriquez[3] and obtained as large, well-formed crystals by slow removal of solvent from a 1:1 toluene:benzene solution of

the complex at 0°. A series of Weissenberg and precession photographs (Cu-K_α and Mo-K_α radiation) showed monoclinic symmetry with the systematic absences $h0\ell$, $h+\ell$ odd, so space group Pn was chosen.

A crystal of dimensions 0.15 × 0.25 × 0.50 mm was mounted in a glass capillary under N_2 with its long axis (c) slightly skew to the ϕ axis of a G.E. XRD-5 quarter-circle diffractometer automated by Datex. Unit cell dimensions were obtained by a least squares fit of the $\sin^2\theta/\lambda^2$ values of 43 reflections measured on the diffractometer. Crystal data are given in Table II.

Using Mo-K_α radiation monochromated with a graphite crystal, one hemisphere of data was measured between 1.5° and 43° in 2θ, using a θ-2θ step scan technique at a scan rate of 1°/min; 30 sec background counts were taken before and after each scan. The scan width varied linearly from 2.2° at 2θ = 1.5° to 3.1° at 2θ = 43°. Intensities of three check reflections measured every 100 reflections showed no crystal decomposition during data collection.

Every reflection was collected in two equivalent octants and the data averaged to form a unique monoclinic data set containing 5026 reflections. A variance $\sigma^2(F_o^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$ where S is the scan count. Intensities and their weights were corrected for Lorentz and polarization effects but not for absorption (μ = 19.4 cm^{-1}). The data were then placed on an absolute scale by means of a Wilson plot,[1] with scattering factors for all atoms calculated by the method of Cromer and Mann.[2] The zirconium

and iodine atoms were treated as anomalous scatterers using values of $\Delta f'$ and $\Delta f''$ given by Cromer and Lieberman.[4] Reflections having $F_o^2 < 1.5\sigma(F_o^2)$ were deleted, leaving 4344 reflections for the working data set.

Attempted Solutions and Discussion of the Structure

A Patterson map was generated from which positions for all heavy atoms (4 zirconiums and 4 iodines) were derived. Several cycles of structure factors interspersed with Fourier maps revealed the approximate location of all the remaining atoms. It was a general feature of this structure that the light atoms were poorly defined on Fourier maps. Peaks were quite broad and overlapped, especially those of the permethyl ring carbons and the atoms bridging the two zirconiums. There were also peaks near three of the heavy atoms (I3, I4, Zr4) which we assumed were due to anomalous dispersion effects. Even after making an anomalous dispersion correction, though, these "mystery peaks" remained. Upon closer examination of the structure, it was discovered that the heavy atoms formed a nearly orthorhombic pseudolattice, with the two independent dimers almost related by an n-glide plane of this pseudolattice. It is possible that these "mystery peaks" are due to correlations between the two dimers imposed by this pseudosymmetry.

Least-squares refinement was attempted with the approximate positions derived from Fourier maps. During refinement, it seemed as though the light atoms wandered aimlessly and distances and

angles in the permethyl rings became unreasonable. Since we were mainly interested in the bridging system, we fixed the rings at their pre-refinement positions and concentrated our refinement efforts on the remaining atoms. It is quite possible that the rings are disordered in some way, although we have not checked this possibility with Fourier maps in these ring planes.

We generated a Fourier map and found the bridging region to be disordered. We derived a model for this disorder but refinement was unsatisfactory, with temperature factors and population parameters fluctuating wildly. Again, it seemed as though the light atoms had no guidance in the refinement.

It must be admitted that the prognosis for this structure is poor. There seems to be no way to obtain accurate parameters for the light atoms. If one is going to solve this structure he will have to face possible disorder in the rings, confirmed disorder in the bridges, "mystery peaks" near some heavy atoms, and the apparent insensitivity of light atoms to refinement. In regard to this latter point, it should be mentioned that $\Sigma Z^2_{heavy} / \Sigma Z^2_{light} = 5.18$ for this structure -- a value far above the optimal ratio of 1.0 for the heavy atom method.[5] Several attempts were made to prepare the chloride analog of this compound before the structure was begun because we felt we might have problems with too many heavy atoms by using the iodide derivative. We were unsuccessful in our attempts to prepare the chloride, but if it can be made in the future it may be free of some of the problems we encountered here since there will not be such a disparity between heavy and light atoms.

In view of all the problems we experienced, we can only say that the geometry about the double bond in the bridge is trans and it consists of a Zr–O–C–C–O–Zr substructure. At present the R factor stands at 0.090.

Part III. Crystal Structure Investigation of $(\eta^5\text{-}C_5Me_5)_2Zr(butadiene)$.

Experimental

$(\eta^5\text{-}C_5Me_5)_2Zr(butadiene)$ was prepared by Richard Threlkel in our group, who was also a coworker on this structure. Large, well-formed crystals were obtained by heating a toluene solution until all the compound was dissolved, the solution was then slowly cooled to room temperature. A series of Weissenberg and precession photographs (Cu-K_α and Mo-K_α radiation) showed monoclinic symmetry with the systematic absences 0k0, k odd. Reflections with h0ℓ, ℓ odd were systematically weak but not absent.

A crystal of dimensions 0.25 × 0.35 × 0.60 mm was mounted in a glass capillary under N_2 with its long axis (c) slightly skew to the ϕ axis of a Syntex $P2_1$ full-circle automated diffractometer. Unit cell dimensions were obtained by a least squares fit of the $\sin^2\theta/\lambda^2$ values of 15 reflections measured on the diffractometer. Crystal data are given in Table III.

Using Mo-K_α radiation monochromated with a graphite crystal, one quadrant of data was measured between 1.5° and 50° in 2θ, using a θ-2θ step scan technique at a scan rate of 2°/min. Background counts were taken before and after each scan; data collection

was begun with the total background counting time equal to the total scan time. However, as data collection progressed, it became evident that crystal decomposition was going to be a problem. Thus, after 1200 reflections had been collected, the background: scan time ratio was cut to 0.5. The scan width at the beginning of data collection was 1.0° below $2\theta_1$ (2θ for Mo-$K_{\alpha 1}$) and 1.0° above $2\theta_2$. Due to the decomposition of the crystal, both these values were changed to 0.8 after 1200 reflections had been collected. The intensities of four check reflections measured every 100 reflections showed some decomposition during data collection. After 1000 reflections, F_o had decreased by 4.92% based on the check reflections. (The check reflections seemed to all decrease at approximately the same rate.) After 2500 reflections, F_o was off by 9.50% and at the end of data collection, F_o had decreased by 14.35%. The data were scaled according to the function $F_{corr} = (A + NB)F_{obs}$ where B is the number used for a linear decomposition correction and N is incremented by one for each reflection. Thus, the scale factor applied to the first reflection is A+B, the second reflection is A+2B, etc. The data were divided up into four blocks with new values for A and B calculated for each block.

4592 reflections were measured and equivalent reflections were averaged to give a monoclinic data set containing 3813 unique reflections. A variance $\sigma^2(F_o^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$, where S is the scan count. Intensities and their weights were corrected for Lorentz and polarization effects but not for absorption ($\mu = 5.1$ cm^{-1}).

The data were then placed on an absolute scale by means of a Wilson plot,[1] with scattering factors for all atoms calculated by the method of Cromer and Mann.[2] Reflections having $F_o^2 < 1.5\sigma(F_o^2)$ were deleted, leaving 2481 reflections for the working data set.

Solution Attempts and Discussion of the Structure

The systematic absences for this structure indicate space groups $P2_1$ (acentric) or $P2_1/m$ (centric) while considering the systematic weaknesses to be absent indicates $P2_1/c$. We attempted to solve the Patterson in all three space groups but found that only $P2_1/c$ gave us a consistent set of peaks; thus we assigned the compound to space group $P2_1/c$. The proposed reason for these systematic weaknesses will be described below.

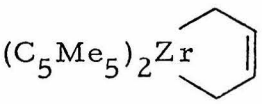
Using the zirconium position obtained from the Patterson map, we obtained a Fourier map which showed the position of 19 carbon atoms. Using all the atoms located to this point, we obtained a second Fourier and found the remaining 5 atoms. Both maps, however, were fairly inexact in the atomic positions but we decided to attempt least-squares refinement at this point anyway. This refinement seemed to proceed satisfactorily for one permethyl ring but the other ring and the butadiene adopted unacceptable geometries.

We obtained a Fourier map in the plane of the poorly refining ring and discovered this ring was disordered in a 1:1 ratio of two forms. We feel that this is the reason for the "systematic weaknesses" since this disorder indicates a deviation from $P2_1/c$

which would cause some h0ℓ, ℓ odd reflections to appear. It was decided to try refinement in $P2_1$ so that we could work with ordered rings. Least-squares refinement in this space group seemed to improve the previously disordered rings only marginally while the rest of the molecule became substantially worse.

We returned to $P2_1/c$ and continued refinement with our disordered model. Unfortunately, the geometry of the disordered rings still looked poor and the ordered ring was beginning to look bad as well. A difference map in the plane of the ordered ring showed that it, too, had disorder, although the ratio of the two forms appeared to be 1:4 here. Least-squares refinement was attempted using disordered models for both rings but population and temperature factors for these atoms were held constant. After three cycles, the R factor stands at 0.146, but the geometry of the rings is still poor and the butadiene ligand appears to be showing signs of disorder.

The prognosis for this structure is fair. It seems as though a slight twist of the ring around the zirconium-centroid axis while holding the methyls fixed will improve the current poor ring geometries. It is possible that refinement of the rings may not work due to disorder but hopefully once the geometries are improved as suggested, refinement will be smoother. The structure is definitely not a metallocycle (I); rather it seems to be a "side-on" bound adduct of butadiene (II). It is not possible to quote bond lengths of interest at this time due to disorder in the butadiene.



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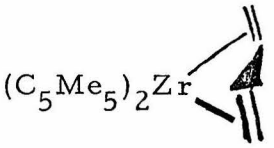


II

References

1. A.J.C. Wilson, Nature (London), 150, 151 (1942).

2. D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 24, 321 (1968).

3. J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, submitted for publication.

4. D. T. Cromer and D. Lieberman, J. Chem. Phys., 53, 1891 (1970).

5. G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N.Y., 1968, p. 278.

Table I. Crystal Data for

$(\eta^5\text{-}C_5Me_5)_2Zr(CH_2(CH(CH_2CH_3))_2CH_2$

$C_{28}H_{46}Zr$	Monoclinic space group C2/c
a = 18.133(8) Å	FW = 473.87
b = 11.258(3) Å	ρ_{calc} = 1.21 g·cm^{-3}
c = 16.171(7) Å	Z = 4
β = 128.17(3)°	μ = 4.3 cm^{-1}
V = 2595 Å^3	λ(Mo-K$_\alpha$) = 0.71069 Å

Table II. Crystal Data for

$\{(\eta^5\text{-}C_5Me_5)_2Zr(I)\}_2$ (μ-OCH=CHO)

$C_{42}H_{62}I_2O_2Zr_2$	Monoclinic Space Group Pn
a = 17.137(1) Å	FW = 1035.16
b = 16.308(1) Å	ρ_{calc} = 1.58 g·cm^{-3}
c = 17.179(1) Å	Z = 4
β = 114.65(1)°	μ = 19.4 cm^{-1}
V = 4364 Å^3	λ(Mo-K$_\alpha$) = 0.71069 Å

Table III. Crystal Data for $(\eta^5\text{-}C_5Me_5)_2Zr$(butadiene)

$C_{24}H_{36}Zr$	Monoclinic space group $P2_1/c$
a = 8.817(3) Å	FW = 415.75
b = 14.618(4) Å	ρ_{calc} = 1.28 g·cm^{-3}
c = 17.284(5) Å	Z = 4
β = 104.37(3)°	μ = 5.1 cm^{-1}
V = 2158 Å^3	λ(Mo-K$_\alpha$) = 0.71069

CHAPTER VII

SYNTHESIS AND REACTIONS OF POLYMER-BOUND $CpCo(CO)_2$ AND Cp_2ZrCl_2

Introduction

The synthesis of polymer-bound transition metal complexes is an area of considerable current interest.[1] The major appeal of this subject to us was the hope that metal centers could be kept monomeric on a highly cross-linked polymer.[2-6] Such isolation could allow one to see reactivity pathways that would be inaccessible in homogeneous systems due to coupling of metal centers to form dimers and larger clusters. For example, the generation of a coordinatively unsaturated species might be possible in a polymer-bound system whereas such a site might be quickly occupied by another metal in a homogeneous reaction. The availability of such an open site could allow one to develop a catalytic system based on a polymer-attached metal complex.

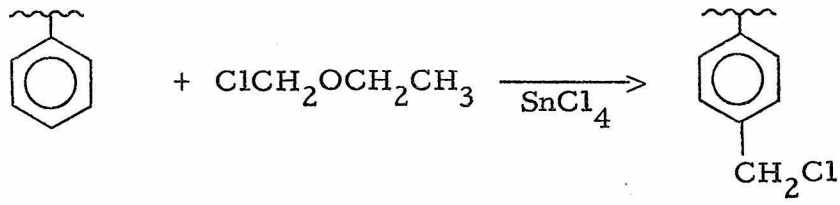
The first system we examined was polymer-bound $CpCo(CO)_2$ since recent reports[7-9] indicate that it is possible to photochemically labilize one of its carbonyl groups, although the resultant coordinatively unsaturated species forms dimers, trimers, or tetramers in the homogeneous system. We may be able to avoid these clusterification reactions, though, if the cobalt complex is immobilized on a polymer support. It was decided to use the hydroformylation reaction as a probe for catalytic activity since cobalt carbonyls are known to be active catalysts for this reaction.

We also decided to try the reaction of acetylenes with this polymer-bound complex since $CpCo(CO)_2$ is known to react with acetylenes both thermally[10] and photochemically[11-12] to yield stable organometallic products or organic compounds arising from cyclotrimerization of the acetylene.

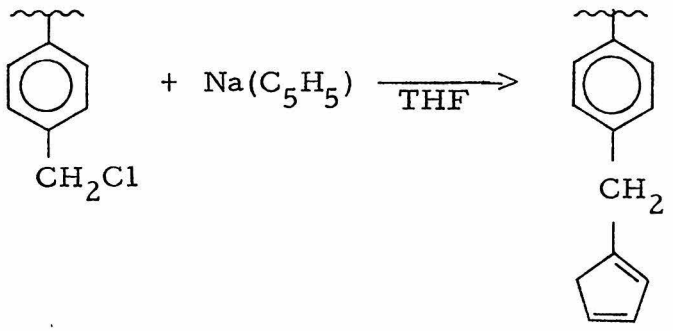
The other system we examined was polymer-bound Cp_2ZrCl_2. Our original aim was to prepare the dicarbonyl complex, $Cp_2Zr(CO)_2$, and study its reactivity toward H_2. We were interested to see whether the polymer-bound species would exhibit processes other than those seen in the homogeneous system (see Chapter V) due to its inability to undergo the intermolecular processes which we believe to be occurring in this reaction. This chapter reports the synthesis and results we have had with these various polymer-bound complexes.

Results and Discussion

We followed the approach of Grubbs,[2] with slight modifications, in order to prepare the polymer-bound cyclopentadiene (eqs. (1) and (2)).



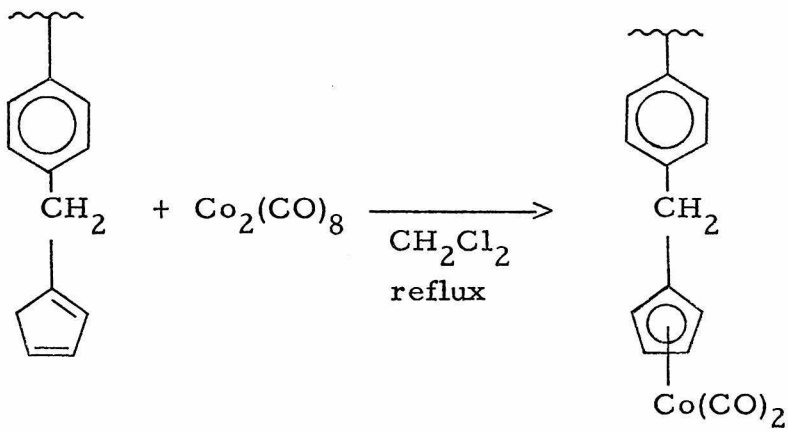
(1)



(2)

We found that Grubbs' suggested washing procedure did not free the ring-bound product of occluded NaCl so we made slight modifications in this step (see Experimental Section). We typically had chloride analyses of 1.70 meg Cl^-/g of beads after chloromethylation and 0.40 meg Cl^-/g of beads after ring attachment, indicating that ~75% of the available chloromethylated sites were cyclopentadienyl ring-bound (assuming the difference in chloride analyses is due to ring attachment).

Synthesis of polymer-bound $CpCo(CO)_2$ (1) was accomplished by modifications of the procedure published for the homogeneous reaction (eq. (3))[13] and went in ~35% yield based on available



(3)

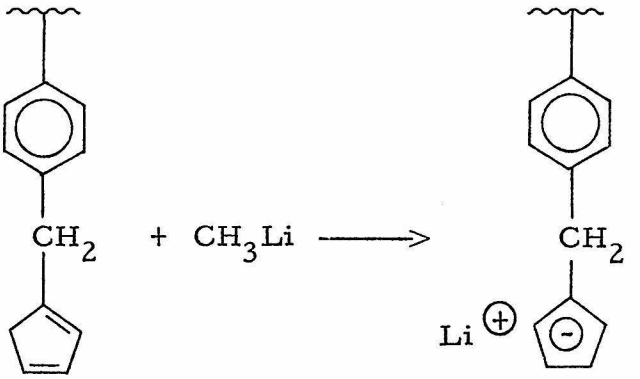
cyclopentadiene rings. $\underset{\wedge}{1}$ shows ν(C-O) bonds in the infrared at 2015 and 1955 cm^{-1} (Nujol mull). This is in good agreement with the reported[7] spectrum of the homogeneous compound which has bands at 2030 and 1970 cm^{-1} in heptane.

Unfortunately, $\underset{\wedge}{1}$ proved to be quite inert in our chosen reactions. It showed no reaction with 2-butyne either thermally or photochemically. We monitored both the solution (for possible cyclotrimerization of acetylenes) and the polymer bead (for possible new organometallic species) in these reactions but could find no evidence for any new products -- the polymer-bound species was always recovered unchanged. The attempted hydroformylation reaction was also unsuccessful, both photochemically and thermally, although a slight amount (< 5%) of hydrogenation of 1-pentene to pentane did take place. The starting complex was also recovered unchanged in these reactions.

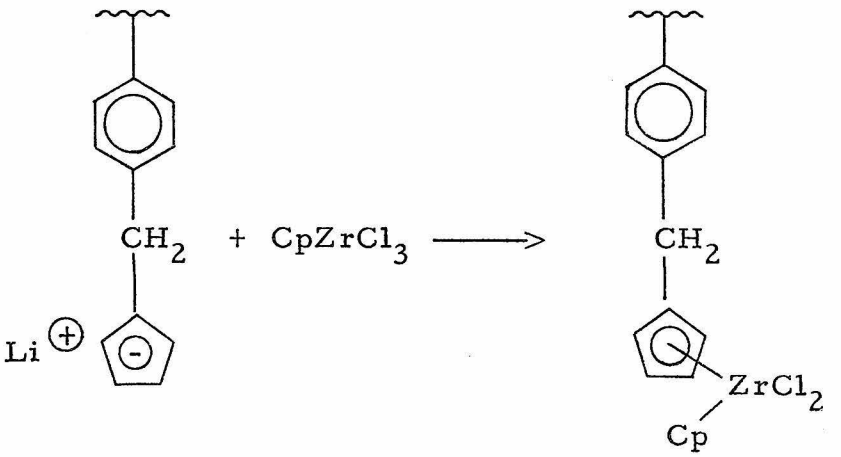
Although these results are certainly not encouraging, it is possible that we have not chosen the proper systems as probes to the reactivity of this polymer-bound complex. It <u>is</u> encouraging that this compound can be put on the polymer in fair yields in a manner completely analogous to the homogeneous case. A recent paper by Brintzinger[14] reports that photolysis of polymer-attached $CpCo(CO)_2$ leads to loss of both CO groups as evidenced by the disappearance of the ν(CO) bands in its infrared spectrum, although no mention is made of the length of time one must photolyze this complex to see such behavior. He has not yet attempted to utilize

this coordinative unsaturation to probe the reactivity of the compound.

Synthesis of polymer-bound Cp_2ZrCl_2 (2) was accomplished as shown in eqs. (4) and (5).



(4)



(5)

The zirconium complex is formed in ~ 25% yield and shows bands at 810, 820, 830, 1014, and 1025 cm^{-1} in the infrared (Nujol mull) in good agreement with the spectrum of an authentic sample of Cp_2ZrCl_2.

$Cp_2Zr(CO)_2$ has been synthesized only recently[15-17] and has never been made in yields greater than 15%, even when utilizing high pressure (200 atm) autoclave reactions. We believed that this might be due to the formation of polymeric side products such as the reported "$[Cp_2Zr(CO)_2]_n$"[18] and we thought that by immobilization of the metal centers on a polymer support, such side-reactions could be minimized.

The methods reported for the synthesis of $Cp_2Zr(CO)_2$ from Cp_2ZrCl_2 utilized either sodium amalgam[15] or lithium,[16] both of which would be difficult to separate from the beads. We favored lithium naphthalenide as a reducing agent[19] since the resultant naphthalene could be sublimed away from the polymer. The reaction of bound Cp_2ZrCl_2 with lithium naphthalenide at 25° and 1 atm CO did lead to polymer-bound $Cp_2Zr(CO)_2$ ($\underset{\sim}{3}$), with ν(CO) at 1865 and 1955 cm^{-1} (Nujol mull). This is in excellent agreement with the reported values of 1866 and 1964 cm^{-1} in THF.[15] Treatment of $\underset{\sim}{3}$ with I_2 liberated less than 5% of the expected CO, however. Thus it appears as though site isolation was not as important as we had hoped, although it may be possible to increase the yield by using autoclave conditions for the synthesis. We also tried MeLi and n-BuLi to make $Cp_2Zr(CO)_2$ since these reagents have been used to synthesize the titanium analog.[20,21] Unfortunately, these

compounds proved to be even less effective than lithium naphthalenide.

Since our attempts to synthesize a high yield of bound $Cp_2Zr(CO)_2$ met with failure, we decided to try making attached Cp_2ZrH_2 instead. Using this species, we could still realize our original goal of studying reduction of CO by H_2 using polymer-bound transition metals. $LiHBEt_3$ was chosen as the hydridic reagent but we obtained less than 6% dihydride in this way.

This chapter has reported the synthesis and characterization of polymer-bound $CpCo(CO)_2$ and Cp_2ZrCl_2. The desired reactivity for these compounds was not realized, although formation, albeit in small yield, of bound $Cp_2Zr(CO)_2$ suggests that this reaction might be worthy of further pursuit and Brintzinger's results suggest that $CpCo(CO)_2$ may be reactive in systems other than those we tried.

Experimental

Physical Measurements (see Chapter IV)

Materials.

Manipulations involving air-sensitive materials were performed using high vacuum line and glove box techniques. The 20% cross-linked polystyrene-divinylbenzene copolymer (Dow Chemical, # XFS-4022, 20-50 mesh) was extracted with dry benzene to remove any remaining styrene monomer. Chloromethyl ethyl ether (Aldrich Chemical Co.) was distilled immediately prior to use. Tetrahydrofuran was vacuum distilled from $LiAlH_4$ and hexane, 2-butyne,

and 1-pentene were vacuum distilled from activated Linde 4Å molecular sieves. Other solvents were treated as described in Chapter IV. $Co_2(CO)_8$ was obtained from Strem Chemical Co. and sublimed immediately before use. Cp_2Mg was prepared by the procedure of Barber[22] with the cyclopentadiene cracked immediately before use. The $ZrCl_4$ used in the synthesis of $CpZrCl_3$ (after the method of Wailes[23]) was sublimed before use. The beads were chloromethylated according to Grubbs' modification[2] of the method of Pepper.[24] The chloromethylated beads prepared in this manner had 1.70 meg Cl^-/g beads. Extreme caution should be exercised in handling chloromethyl ethyl ether as it is a known carcinogen!

Analyses

It was necessary to carry out chloride analysis on the beads at several times. The technique used was a modification of the Volhard method and is described for a typical sample. 6 ml of pyridine were added to 426 mg of beads in a test tube and the mixture was heated for 3 h at 100°. The contents of the tube were quantitatively washed into a 125 ml flask using 30 ml of 50% acetic acid/H_2O. 10 ml of concentrated HNO_3, 9.5 ml standardized $AgNO_3$ (accurately measured from a buret) and ca. 20 drops of $NH_4Fe(SO_4)_2$ were added. This solution was titrated with standardized KSCN until a color change from white to red-brown was observed. A sample sent to Galbraith Laboratories, Knoxville, Tennessee, was in satisfactory agreement with our analysis.

Procedures

(1) Preparation of cyclopentadienyl-substituted polymer. We followed the method of Grubbs[2] but found that substantial occluded chloride remained after the washing procedures recommended. We found it necessary to heat the beads for 1 h at 50° in a 2:1 H_2O:EtOH solution followed by filtration and further identical washing (5 washings were needed to get a negative test for chloride with concentrated $AgNO_3$). The beads were then washed twice with 1:1 THF:EtOH and finally twice with pure THF. The polymer was then vacuum dried for two days. Chloride analysis showed 0.39 meg Cl^-/g beads as residual bound chloride.

(2) Preparation of polymer-bound $CpCo(CO)_2$. We used the procedure Rausch and Genetti[13] followed when preparing $CpCo(CO)_2$ in homogeneous solution. Its modified form, as applied to polymer beads, is given here. 4 g ring-attached beads (5.24 meg ring) and 1.27 g (7.43 meg Co) freshly sublimed $Co_2(CO)_8$ were loaded into a frit assembly in the glove box. 25 ml CH_2Cl_2 were distilled onto the mixture on a vacuum line and the solution was heated at CH_2Cl_2 reflux for four days. The mixture was filtered and the solvent was removed. Fresh CH_2Cl_2 was distilled onto the beads and the mixture was stirred for 2 h, followed by filtration and removal of solvent. (Note: In all subsequent procedures, "washing" implies stirring for 2 h followed by filtration and removal of solvent.) This cycle was repeated three more times and the beads were allowed to stir overnight at 25°. This solution was filtered, followed by solvent removal, and a final washing with CH_2Cl_2. The filtrate at this time

was colorless so it was assumed that washing was complete. The CH_2Cl_2 was removed and the polymer dried *in vacuo* for three days yielding light green beads. These beads were analyzed (Galbraith) and found to contain 0.421 mmol Co/g beads.

(3) Preparation of polymer-bound Cp_2ZrCl_2. 20 ml of tetrahydrofuran were added to 1.17 g (1.53 meg ring) of ring-attached beads followed by the addition of 4.59 mmol MeLi. The reaction was stirred at 25° for 36 h followed by 3 THF washings and 3 benzene washings. 700 mg (2.66 mmol) of $CpZrCl_3$ was dissolved (as much as possible) in 20 ml THF and this solution was transferred to the beads *via* syringe (under counterflow of argon). 10 ml additional THF was distilled onto the reaction mixture and the suspension was heated overnight at 60°. The reaction was continued an additional 2 days at 25° followed by washing the beads three times with THF and three times with benzene (each wash was carried out at 40° for 2 h). The polymer was dried *in vacuo* for 3 days, yielding pale yellow beads which were shown by analysis (Galbraith) to contain 0.32 mmol Zr/g beads.

(4) Reaction of polymer-bound $CpCo(CO)_2$ with 2-butyne. (a) by photolysis. 688 mg (12.72 mmol) 2-butyne was added to a stirred suspension of 199 mg polymer-bound $CpCo(CO)_2$ (0.084 mmol Co) in 3 ml benzene-d_6 contained in a Schlenk tube having the sidearm fitted with a rubber septum cap. The tube was placed under an atmosphere of argon and positioned in front of a Pyrex-filtered Hanovia medium pressure lamp. The reaction was monitored periodically by withdrawal of *ca.* 0.3 ml of solution

under a counterflow of argon. This solution was then examined by ^{1}H NMR to determine whether any new species were present. After 48 h, no new liquid species could be detected in the NMR and an infrared spectrum obtained on the dried beads after removal of volatile species was identical to that of the starting complex.

(b) by thermolysis. 1.22 mmol 2-butyne was added to a suspension of 100 mg polymer (0.046 mmol Co) in 0.3 ml benzene-$\underline{d}_6$ contained in an NMR tube and the tube was sealed under an atmosphere of argon. The reaction was heated for 72 h at 120° with periodic monitoring by ^{1}H NMR but at no time was any new liquid species observed by NMR. An infrared spectrum run on the dried polymer after the reaction showed no change from the starting material.

(5) Attempted hydroformylation using polymer-bound $CpCo(CO)_2$. (a) by photolysis. 3.13 mmol 1-pentene was added to a suspension of 166 mg crushed polymer-bound $CpCo(CO)_2$ in 5 ml hexane contained in a quartz Schlenk tube having the sidearm fitted with a rubber septum cap. 0.85 mmol CO and 3.13 mmol H_2 were added to a 107 ml gas reservoir which was attached to the top of the Schlenk tube. The apparatus was placed in front of a Hanovia medium pressure mercury lamp and the stopcock opened to allow the gases into the Schlenk tube. The reaction was monitored periodically by carefully purging the area between the septum and the stopcock with argon followed by withdrawal of a small sample for examination by gas chromatography. After 72 h there was no evidence for the formation of any aldehydes although there was

a small amount (ca. 5%) of hydrogenation to pentane.

(b) by thermolysis. 3.25 mmol 1-pentene was added to a suspension of 177 mg (0.074 mmol Co) crushed polymer-bound $CpCo(CO)_2$ in 5 ml octane contained in a Schlenk tube having the sidearm fitted with a rubber septum cap. 0.813 mmol CO and 3.25 mmol H_2 were added to a gas reservoir which was attached to the Schlenk tube. The tube was placed in a 120° bath and the stopcock was opened to allow the gases into the Schlenk tube. The reaction was heated for 72 h with gas chromatography samples taken periodically as described in part (a). During the reaction period, no evidence was found for aldehyde formation and an infrared spectrum of the dried beads after the reaction showed no change from the starting material.

(6) Attempted synthesis of polymer-bound $Cp_2Zr(CO)_2$.

(a) with n-BuLi. 1.05 mmol n-BuLi was syringed into a stirred suspension of 520 mg (0.17 mmol) polymer-bound Cp_2ZrCl_2 in 20 ml toluene maintained at -78°. The mixture was placed under an atmosphere of CO and allowed to warm slowly to 25°. After 2 days at 25°, the beads were washed three times with toluene, twice with petroleum ether, and dried in vacuo. An infrared spectrum of the product showed no carbonyl bands, however.

(b) with lithium naphthalenide. 0.80 mmol lithium naphthalenide was syringed into a stirred suspension of 500 mg (0.16 mmol) polymer-bound Cp_2ZrCl_2 in 20 ml of THF maintained at -78°. The mixture was placed under a CO atmosphere and allowed to warm slowly to 25°. After 2 days at 25°, the beads were washed three

times with THF, twice with petroleum ether, and dried in vacuo. An infrared spectrum showed bands in the carbonyl region.

(c) treatment of "polymer-bound $Cp_2Zr(CO)_2$" with I_2. 40 mg I_2 was sublimed into a frozen mixture of 250 mg beads from part (b) in 10 ml toluene. The mixture was allowed to warm to 25°, with stirring. After 1 day at 25°, residual gases were removed and passed through a series of LN_2 cooled traps. The carbon monoxide collected by a Toepler pump amounted to less than 5% of that expected based on complete conversion of Cp_2ZrCl_2 to $Cp_2Zr(CO)_2$.

(d) with methyl lithium. 0.75 mmol MeLi was syringed into a stirred suspension of 370 mg (0.12 mmol) polymer-bound Cp_2ZrCl_2 in 20 ml toluene maintained at -78°. The mixture was placed under an atmosphere of carbon monoxide and allowed to warm slowly to 25°. After 2 days at 25°, the beads were washed three times with toluene, twice with petroleum ether, and dried in vacuo. An infrared spectrum of the product showed no carbonyl bands, however.

(7) Attempted synthesis of polymer-bound Cp_2ZrH_2. 1.0 mmol $LiHBEt_3$ was syringed into a stirred suspension of 505 mg (0.16 mmol) polymer-bound Cp_2ZrCl_2 in 20 ml toluene maintained at -78°. The mixture was allowed to slowly warm to 25°. After 2 days at 25°, the beads were washed three times with toluene, twice with petroleum ether, and dried in vacuo. 0.336 mmol MeI was added to a frozen mixture of 174 mg of the product of this reaction in 15 ml toluene. The mixture was allowed to warm slowly to 25°,

with stirring. After 2 days at 25°, residual gases were collected and passed through a series of LN_2 cooled traps. The methane collected by a Toepler pump amounted to less than 6% of that expected based on complete conversion of Cp_2ZrCl_2 to Cp_2ZrH_2.

References

1. See Proposition II of this thesis.
2. W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, J. Am. Chem. Soc., 97, 2128 (1975).
3. R. Grubbs, C. P. Lau, R. Cukier, and C. Brubaker, Jr., J. Am. Chem. Soc., 99, 4517 (1977).
4. E. S. Chandrasekaran, R. H. Grubbs, and C. H. Brubaker, Jr., J. Organomet. Chem., 120, 49 (1976).
5. R. Jackson, J. Ruddlesden, D. J. Thompson, and R. Whelan, J. Organomet. Chem., 125, 57 (1977).
6. J. I. Crowley and H. Rapaport, Acc. Chem. Res., 9, 135 (1976), and references cited therein.
7. K.P.C. Vollhardt, J. E. Bercaw, and R. G. Bergman, J. Organomet. Chem., 97, 283 (1975).
8. R. B. King, Inorg. Chem., 5, 2227 (1966).
9. W.-S. Lee and H. H. Brintzinger, J. Organomet. Chem., 127, 87 (1977).
10. R. S. Dickson and P. J. Fraser, Adv. in Organomet. Chem., 12, 323 (1974), and references cited therein.
11. W.-S. Lee and H. H. Brintzinger, J. Organomet. Chem., 127, 93 (1977).
12. R. Markby, H. W. Sternberg, and I. Wender, Chem. Ind., 1381 (1959).

13. M. D. Rausch and R. A. Genetti, J. Org. Chem., 35, 3888 (1970).

14. G. Gubitosa, M. Boldt, and H. H. Brintzinger, J. Am. Chem. Soc., 99, 5174 (1977).

15. J. L. Thomas and K. T. Brown, J. Organomet. Chem., 111, 297 (1976).

16. B. Demerseman, G. Bouquet, and M. Bigorgne, J. Organomet. Chem., 107, C19 (1976).

17. G. Fachinetti, G. Fochi, and C. Floriani, J. Chem. Soc., Chem. Commun., 230 (1976).

18. P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium," Academic Press, New York, N.Y., 1974, p. 242.

19. G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., J. Am. Chem. Soc., 88, 1138 (1966).

20. J. G. Murray, J. Am. Chem. Soc., 83, 1287 (1961).

21. Reference 18, p. 240.

22. W. A. Barber, J. Inorg. Nucl. Chem., 4, 373 (1957).

23. A. F. Reid and P. C. Wailes, J. Organomet. Chem., 2, 329 (1964).

24. K. W. Pepper, H. M. Paisley, and M. A. Young, J. Chem. Soc., 4097 (1953).