Chapter 7: Diazoalkane complexes of cobalt

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7.1 Introduction

Diazoalkanes have been used as reagents for a wide range of metal-catalyzed transformations[1,2] including the cyclopropanation of olefins.[3] In addition, diazoalkanes can act as versatile ligands in transition metal complexes, as these ligands can adopt a plethora of monomeric bonding modes when bound to a metal center.[4] While all of the bonding modes shown in Figure 7.1 have been structurally characterized, type **B** is the most common.[5] The electronic nature of the ligand is highly dependent on the substituents on the carbon atom. For example, resonance stabilization from aryl substituents often provides more stable diazoalkane complexes.

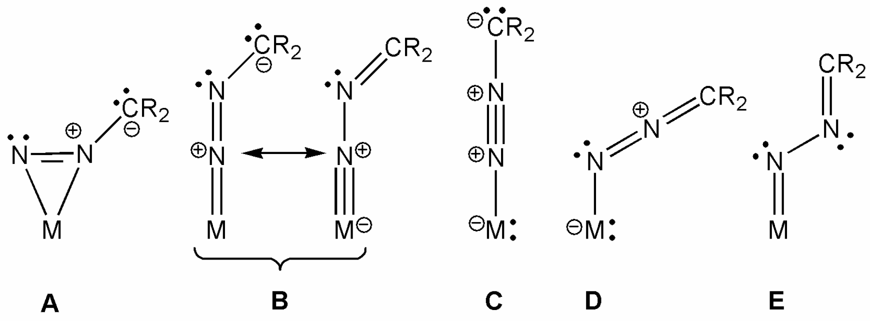


Figure 7.1. Structurally characterized examples have been prepared for each of these monomeric bonding modes of diazoalkanes (A-E). See reference 4.

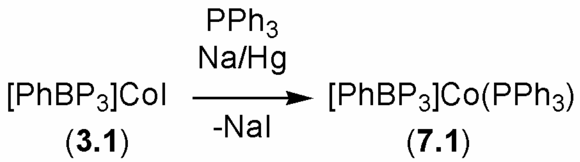
The degradation of metal-bound diazoalkanes is a common method for preparing transition metal carbenes.[6] A common application of carbene complexes is olefin metathesis.[7] For example, one of the most active olefin metathesis catalysts, Grubbs's catalyst ($RuCl_2(=CHPh)(PPh_3)_2$), is prepared by diazoalkane addition to the precursor ($RuCl_2(PPh_3)_3$) resulting in the carbene complex.[8] We chose to investigate the properties of cobalt diazoalkane complexes with the aspiration of synthesizing a related cobalt alkylidene complex. To date, there are no examples of structurally characterized Schrock-type cobalt carbenes; however, complexes with this ligand motif have been prepared for other first-row metals such as iron,[9] nickel,[10] and, more recently, copper.[11] Furthermore, Schrock-type carbenes have been prepared using the second- and third-row group 9 metals rhodium[12] and iridium.[13,14] This chapter discusses the synthesis of a number of cobalt diazoalkane complexes, including examples that adopt binding modes **A** and **B** and attempts to generate a cobalt alkylidene.

7.2 Results

7.2.1 Synthesis of diazoalkane complexes

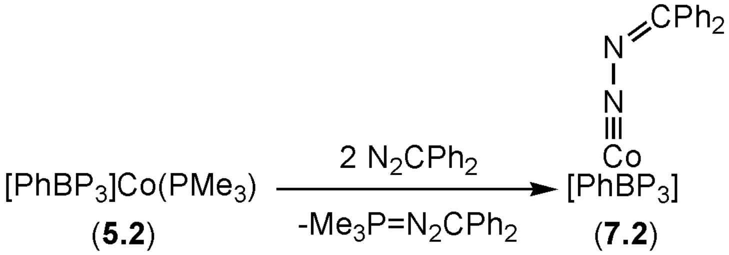
Based on our success in synthesizing imide species such as [PhBP$_3$]CoN^{t}Bu (**5.7**) through two electron oxidative degradation of organic azides, we were interested in generating a carbene from a free diazoalkane using a similar oxidative group transfer strategy.[15] A five coordinate cobalt(III) carbene complex such as [PhBP$_3$]Co(=CR$_2$)(PR$_3$) (R = aryl or alkyl; [PhBP$_3$] = [PhB(CH$_2$PPh$_2$)$_3$]$^-$) would be isoelectronic to Bergman's carbene, [Cp*]Ir(=CH$_2$)(PMe$_3$), suggesting that the target cobalt carbene complex would be a reasonable synthetic goal.

Ideally, synthesis of a Co(III) carbene could begin with the same type of Co(I) precursor as used for the imide synthesis. It was necessary to prepare an additional Co(I) starting material, in addition to the previously described [PhBP$_3$]CoPMe$_3$ (**5.2**), since a more sterically bulky apical phosphine ligand such as PPh$_3$ may be required to stabilize the proposed five-coordinate carbene. Addition of free PPh$_3$ to a solution of [PhBP$_3$]CoI (**3.1**) in the presence of sodium/mercury amalgam gives [PhBP$_3$]Co(PPh$_3$), **7.1** (Eq. 7.1). This species is paramagnetic ($S = 1$) and has a similar pale green color to **5.2**.



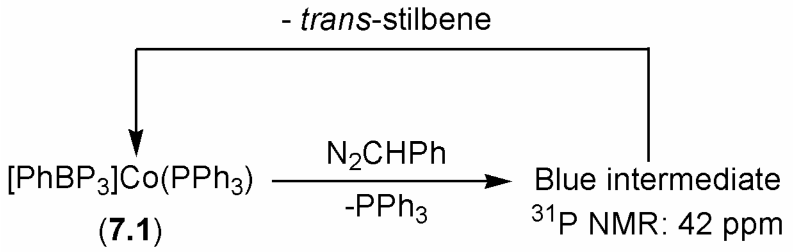
$$\underset{(\mathbf{3.1})}{[PhBP_3]CoI} \xrightarrow[\text{-NaI}]{\text{PPh}_3,\ \text{Na/Hg}} \underset{(\mathbf{7.1})}{[PhBP_3]Co(PPh_3)} \quad (7.1)$$

It was found that two equivalents of N_2CPh_2 react with $[PhBP_3]CoPMe_3$ (**5.2**) to generate the diazophosphazene $Me_3P{=}N_2CPh_2$ and the thermally stable diazoalkane adduct, $[PhBP_3]CoN_2CPh_2$, **7.2** (Eq. 7.2), rather than undergo carbene transfer and concomitant expulsion of N_2. Complex **7.2** is a red diamagnetic solid with a single ^{31}P NMR peak at 60 ppm, indicative of local C_3 symmetry about the cobalt center. Evidence for a diazoalkane adduct included a positive test for nitrogen upon combustion analysis and the lack of the signature $^{13}C\{^1H\}$ NMR peak (> 200 ppm) expected for a carbene moiety. Neither heating the complex nor adding Lewis acids such as $Sm(OTf)_3$ (OTf = $-OSO_2CF_3$) triggered the loss of N_2 to yield a carbene complex. Furthermore, addition of an alkene, such as styrene, to the diazoalkane complex does not lead to cyclopropanation, even with elevated temperature (100 °C).



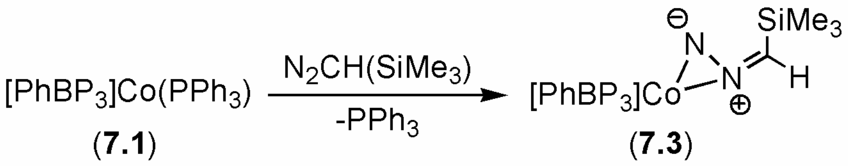
(7.2)

Interestingly, the addition of less sterically hindered diazoalkanes, such as N_2CHPh to $[PhBP_3]CoPMe_3$ (**5.2**), does not result in the formation of a clean diazoalkane complex. In an attempt to trap the potential carbene, a more sterically encumbered Co(I) precursor, $[PhBP_3]Co(PPh_3)$ (**7.1**), was used. Addition of excess N_2CHPh to **7.1** at -30 °C yielded a blue product that had a single new peak in the ^{31}P NMR spectrum at 42 ppm. The observation of PPh_3 at -6 ppm in the ^{31}P NMR spectrum suggests that the product formed was not a species like $[PhBP_3]Co(=CHPh)(PPh_3)$, but either the diazoalkane adduct $[PhBP_3]CoN_2CHPh$ or possibly the carbene $[PhBP_3]Co=CHPh$ (Eq. 7.3). Upon warming to room temperature, the reaction mixture returned to a pale green color, and **7.1** was evident as the only metal containing species detected by ^{1}H NMR and UV-vis spectroscopy. The organic byproduct was determined by GC/MS to be *trans*-stilbene (by fragmentation). Although we have been unable to isolate the product, spectroscopic differences (^{31}P NMR, UV-vis) suggest that the reaction with N_2CHPh did not result in the same type of diazoalkane adduct as $[PhBP_3]CoN_2CPh_2$, **7.2**.



(7.3)

With this in mind, we set out to synthesize a *stable* diazoalkane adduct with a different bonding mode from **7.2** (vide infra) or perhaps with a carbene complex. Addition of $N_2CH(TMS)$ (TMS = $SiMe_3$) as a 2.0 M hexanes solution to a THF solution of **7.1** yields a stable blue product, $[PhBP_3]CoN_2CH(TMS)$ (**7.3**), based on structural characterization (vide infra) (Eq. 7.4). Complex **7.3** can be purified by crystallization from THF and petroleum ether at -30 °C. This species gives a nearly identical ^{31}P NMR resonance (42 ppm) and UV-vis absorption spectra (λ_{max} = 583 nm) as the blue intermediate of the reaction between **7.1** and N_2CHPh, indicating that the blue product is most likely $[PhBP_3]CoN_2CHPh$. Complex **7.3** is stable in the solid state at -30 °C for days although it decomposes at ambient temperature.



(**7.1**) (**7.3**) (7.4)

7.2.2 Solid-state structures of the diazoalkane complexes

The collection of single crystal X-ray diffraction data was necessary to unambiguously assign the bonding mode of the different diazoalkane complexes $[PhBP_3]CoN_2CPh_2$ (**7.2**) and $[PhBP_3]CoN_2CH(TMS)$ (**7.3**). The solid-state structures of **7.2** and **7.3** show very different bonding modes and are consistent with their different colors and ^{31}P NMR spectra. Complex **7.2** has a similar Co-N1 distance (1.667(2) Å) as the imido complexes $[PhBP_3]CoN$-*p*-tolyl, **5.4**, and $[PhBP_3]CoN^tBu$, **5.7** (1.658(2) and 1.633(2) Å, respectively) and exhibits a similar slightly bent Co-N1-N2 angle of 163.1(2)° (Figure 7.2). The very short Co-N bond in **7.2** is the second shortest metal-nitrogen bond structurally characterized for an end-on bound diazoalkane.[16] Furthermore, the N1-N2 bond (1.280(2) Å) is elongated in comparison to other group 9 terminally bound diazoalkane adducts (~ 1.16 Å)[14c,17] and significantly shorter than a true N-N single bond (~ 1.45 Å).[18] This suggests that the terminal nitrogen of the diazoalkane possesses significant metal-ligand multiple bond character, with the $-NCPh_2$ moiety effectively acting as the terminal functional group of an imide (i.e., $Co{\equiv}N\text{-}N{=}CPh_2$). This bonding mode has been well described before by Haymore and is common for Group 6 transition metals. Notably, this complex is the first example that displays end-on bonding of a diazoalkane ligand to cobalt.

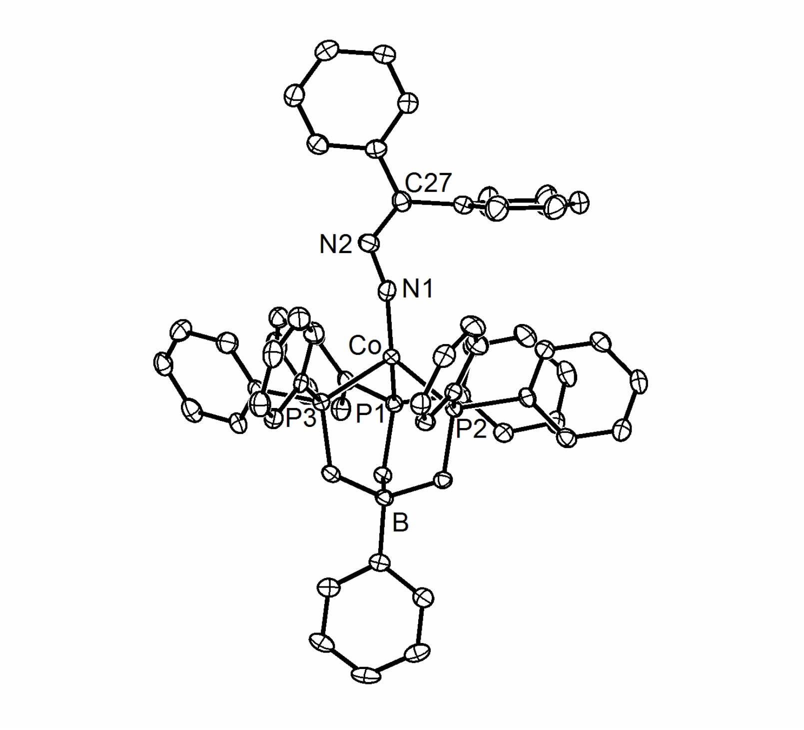


Figure 7.2. Displacement ellipsoid representation (50%) for [PhBP$_3$]CoN$_2$CPh$_2$ (**7.2**). Selected interatomic distances (Å) and angles (deg): Co-N1, 1.667(2); N1-N2 1.280(2); N2-C27, 1.311(2); Co-P1, 2.157(1); Co-P2, 2.184(1); Co-P3, 2.181(1). P1-Co-P2, 90.09(2); P1-Co-P3, 92.31(2); P2-Co-P3, 94.07(2); N1-Co-P1, 125.00(6); N1-Co-P2, 128.86(6); N1-Co-P3, 117.13(6); Co-N1-N2, 163.1(2); N1-N2-C27, 123.1(2).

In contrast, [PhBP$_3$]CoN$_2$CH(TMS) (**7.3**) is a side-bound diazoalkane adduct, with a Co-N1 bond distance of 1.788(3) Å and a Co-N2 bond distance of 1.857(4) Å (Figure 7.3). These distances are significantly shorter than the only other reported side-bound diazoalkane of cobalt, (PMe$_3$)$_3$Co(CH$_3$)(N$_2$C$_5$H$_4$), which had bond lengths of 1.994 and 1.914 Å for Co-N1 and Co-N2, respectively.[19] Moreover, these Co-N distances are the shortest nitrogen-metal linkages reported for any side-bound diazoalkane complex found in the literature. The shortest M-N1 and M-N2 distances reported previously are 1.874(3) Å and 1.834(3) Å, for $(^tBuNC)_2Ni$(diazofluorene) (diazofluorene = $N_2C_{13}H_8$).[20] Furthermore, the N1-N2 bond distance in **7.3** of 1.289(4) Å is slightly elongated when compared to the N-N bond distances within similar side-bound diazoalkanes, which typically fall between 1.21 and 1.27 Å.[21] These bond distances suggest that the π-bond is quite strong and that the π* orbital is also quite substantial, weakening the N1-N2 bond.

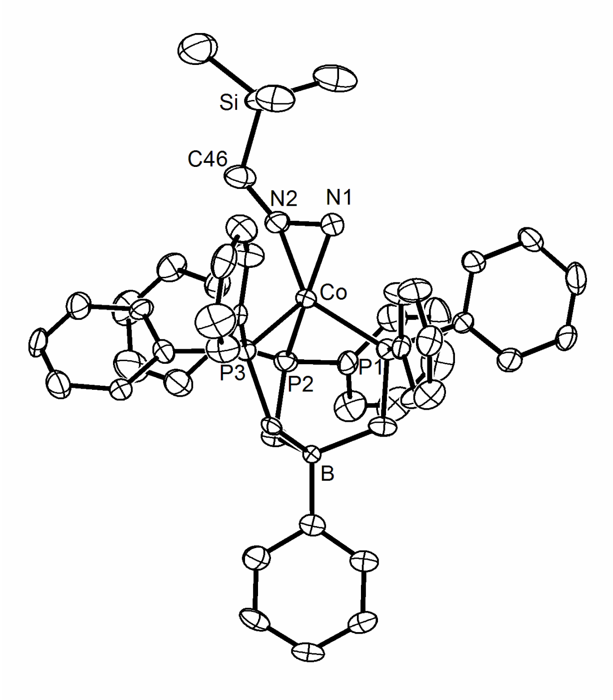


Figure 7.3. Displacement ellipsoid representation (50%) for $[PhBP_3]CoN_2CH(TMS)$ (**7.3**). Selected interatomic distances (Å) and angles (deg): Co-N1, 1.788(3); Co-N2, 1.857(4); N1-N2, 1.289(4); N2-C46, 1.324(5); Co-P1, 2.214(1); Co-P2, 2.212(1); Co-P3, 2.182(1). Co-N1-N2, 72.2(2); Co-N2-C46, 161.6(3); N1-N2-C46, 131.4(4); N2-C46-Si, 121.3(4); P1-Co-P2, 92.97(5); P1-Co-P3, 91.20(5); P2-Co-P3, 88.34(5).

7.3 Discussion

The end-on diazoalkane $[PhBP_3]CoN_2CPh_2$ (**7.2**), which is best represented by the type **B** bonding mode in Figure 7.1, is remarkably stable, and we have been unable to induce the loss of N_2 under any condition. Given the stability and lack of reactivity of the isolobal imide complexes we have prepared such as $[PhBP_3]$CoN-*p*-tolyl, **5.4**, it is not surprising that **7.2** is so stable. Furthermore, it is noteworthy that this complex is the first example of a type **B** bonding mode involving a group 9 metal. This lack of type **B** diazoalkanes complexes of group 9 metals is not unexpected since type **B** complexes are electronically similar to imides, and few group 9 imides have been prepared until very recently.[22] What is particularly significant in assigning **7.2** as a type **B** complex is the expanded N1-N2 bond distance of 1.280(2) Å. Other group 9 end-on diazoalkanes feature N-N bond distances that are much closer to 1.15 Å, suggesting more N-N multiple bond character as seen in the type **C** bonding mode.[5d,23]

The reaction between N_2CHPh and $[PhBP_3]Co(PPh_3)$ (**7.1**) suggests that sterics and electronics play some role in determining the bonding mode of the diazoalkane ligand. The less sterically encumbered N_2CHPh diazoalkane appears to be going through a side-bound intermediate similar to **7.3** prior to loss of N_2 and formation of stilbene. It is perhaps surprising that we have been unable to trap a carbene in this case. A Co(I) species such as $[PhBP_3]Co(PMe_3)$ should be poised to make $[PhBP_3]Co(=CHPh)(PMe_3)$, which is isoelectronic to Bergman's carbene $[Cp^*]Ir(=CH_2)(PMe_3)$. It is intriguing that a side-bound diazoalkane is formed given the inherent stability of the previously reported imides and the ability of a similar diazoalkane **7.2** to form an imide-like structure similar to $[PhBP_3]$CoN-*p*-tolyl, **5.4**. The lack of a second phenyl ring on the diazoalkane may destabilize the anionic resonance form of type **B** (Figure 7.1B, left), allowing other bonding modes to be electronically favored.

While [PhBP$_3$]CoN$_2$CH(TMS) (**7.3**) is more stable than the product of **7.1** and N$_2$CHPh, it also degrades at ambient temperature over a period of hours. This species is best described as a type **A** diazoalkane. The bonding mode of the species makes the assignment of the cobalt oxidation state ambiguous. Since it is diamagnetic, the bonding scheme in this compound can be compared to related complexes, such as [PhBP$_3$]Co^{I}(CO)$_2$ (**5.10**) or [PhBP$_3$]Co^{III}Cl$_2$ (**5.9**). The bonding mode can either be described as one of two limiting cases: type **A** in Figure 7.1, suggesting Co(I), or as the resonance structure shown in Eq. 7.4, suggesting Co(III). The very short Co-N bonds do not necessarily favor one limiting resonance structure type over another.

The energy difference between the two structure types is noticeable upon the addition of N$_2$CH(Mes) (Mes = mesityl) to [PhBP$_3$]Co(PMe$_3$) (**5.2**) in benzene. The solution turns red immediately, but the ^{31}P NMR spectrum suggests that the reaction is quite complicated, as peaks at 59 (br), 40.5, 23.5, and 16.2 are observed. A control reaction between free PMe$_3$ and N$_2$CH(Mes) confirmed that the peak at 23.5 ppm is due to Me$_3$P=N$_2$CH(Mes). N$_2$CH(Mes) was added to [PhBP$_3$]Co(NCCH$_3$) (**6.4**), to simplify the reaction and to suppress the formation of the byproduct, which resulted in two peaks in the ^{31}P NMR at 59 (br) and 40.5 in a ratio of 3:2. This suggests that both the end-on (59 ppm) and side-on (40 ppm) diazoalkane species were formed by the addition of N$_2$CH(Mes) to a Co(I) precursor. The implication is that the two species are close in energy if both bonding modes can be formed with a single diazoalkne. The ability to observe both the side-bound and end-on conformational isomers of a diazoalkane is notable since only one other transition metal system, $[Cp^*]_2Ti$, can accommodate both end-on[24] and side-on[21a,25] bonding modes without significant ligand modifications.

7.4 Conclusions

Cobalt diazoalkanes complexes that exhibit two different bonding modes, side-on and end-on, have been prepared with the same auxiliary ligand, $[PhBP_3]$. The end-on diazoalkane complex is the first of this type involving cobalt and shows one of the shortest metal-nitrogen bonds for this ligand class. The side-bound diazoalkane is stable at low temperature and features the shortest metal-nitrogen bonds for a structurally characterized side-bound diazoalkane. Although it is rare to stabilize more than one bonding mode on a single transition metal system, it appears that the energy difference between the end-on and side-on bonding modes is small enough that the nature of the specific diazoalkane ligand dictates the bonding mode.

7.5 Experimental section

7.5.1 General considerations

General procedures were performed according to Sections 2.4.1 and 3.5.1.

7.5.2 Starting materials and reagents

The preparation of $[PhBP_3]CoI$ (**3.1**), $[PhBP_3]Co(PMe_3)$ (**5.2**), and $[PhBP_3]Co(NCCH_3)$ (**6.4**) are described in Chapters 3, 5, and 6, respectively. The reagents PPh_3, 2.0 M $N_2CH(TMS)$ in hexanes, sodium, and mercury metal were purchased from commercial vendors and used without further purification. The reagents N_2CPh_2,[26] N_2CHPh,[27] and $N_2CH(Mes)$[28] were prepared according to literature procedures.

7.5.3 Synthesis of compounds

Synthesis of [PhBP$_3$]Co(PPh$_3$), 7.1. A 0.60% Na/Hg amalgam was prepared by dissolving 6.0 mg (0.26 mmol) of sodium into 1.0 g of mercury. A THF (3 mL) solution of PPh$_3$ (67.9 mg, 0.259 mmol) was then added to the stirring amalgam followed by the addition of a THF (15 mL) solution of [PhBP$_3$]CoI, **3.1**, (215 mg, 0.247 mmol). The mixture was stirred for 12 h as the color changed from green to brown. The reaction mixture was then filtered through Celite to remove the amalgam, and the filtrate was dried in vacuo, affording a fine brown powder. This brown powder was dissolved in benzene (15 mL) and stirred vigorously. After 1 h, white precipitate (NaI) was observed, which was removed by filtration though Celite. The brown filtrate was frozen and dried to a fine brown powder through lyophilization and was washed with petroleum ether (2 x 10 mL) and dried. The powder was then dissolved in benzene (2 mL) and triturated with petroleum ether (15 mL), which caused a green powder to crash out of solution. The supernatant was decanted, and the green powder was washed with petroleum ether (2 x 10 mL) and then dried in vacuo leaving the pure green product (118 mg, 48% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 18.5 (br), 14.7, 11.7, 8.5, 8.1, 7.6, 4.3, 3.6, -4.0, -5.7 (br). UV-vis (C_6H_6) λ_{max}, nm (ε): 694 (220). Anal. Calcd for $C_{63}H_{56}BCoP_4$: C, 75.16; H, 5.61. Found: C, 75.17; H, 5.30.

Synthesis of [PhBP$_3$]CoN$_2$CPh$_2$, 7.2. A benzene (2 mL) solution of diazodiphenylmethane (N_2CPh_2) (55.4 mg, 0.285 mmol) was added dropwise to a stirring benzene (4 mL) solution of [PhBP$_3$]Co(PMe$_3$), **5.2**, (117 mg, 0.143 mmol). During the first 10 min the brown solution turned deep red. The solution was stirred for an additional 4 h to ensure completion, and the solvent was then removed via lyophilization. The resulting red powder was washed with petroleum ether (2 x 10 mL) to remove the byproduct, $Me_3P(N_2CPh_2)$. The red powder was taken up in benzene and crystallized by vapor diffusion of petroleum ether to afford analytically pure crystals (67 mg, 50 %). ^1H NMR (C_6D_6, 500 MHz): δ 8.14 (d, J = 7.0 Hz, 2 H), 7.89 (br, 4 H), 7.72 (t, J = 7.0 Hz, 2 H), 7.57 (m, 12 H), 7.48 (t, J = 7.0 Hz, 1 H), 7.18 (m, 6 H), 6.76 (m, 18 H), 1.48 (br, 6 H). $^{31}P\{H\}$ NMR (C_6D_6, 121.4 MHz): δ 60.1 (br). $^{13}C\{H\}$ NMR (C_6D_6, 209.5 MHz): δ 163.5, 139.5, 139.2, 138.2, 132.7, 132.6, 129.6, 129.2, 128.9, 128.8, 128.3, 124.9, 13.4 (br). UV-vis (C_6H_6) λ_{max}, nm (ε): 454 (6400), 520 (5400), 712 (4300). Anal. Calcd for $C_{58}H_{51}BCoN_2P_3$: C, 74.21; H, 5.48; N, 2.98. Found: C, 74.56; H, 5.47; N, 3.05.

Synthesis of [PhBP$_3$]CoN$_2$CH(TMS), 7.3. A 2.0 M solution of $N_2CH(TMS)$ (0.50 mL, 1.0 mmol) in hexanes was added to a stirring THF solution (3 mL) of $[PhBP_3]Co(PPh_3)$, **7.1**, (0.217 g, 0.216 mmol). The solution was stirred for 15 min and then petroleum ether (12 mL) was added. The solution was then cooled to -35 °C for 48 h until blue crystals formed (0.180 g, 97% yield). Elemental analysis failed due to decomposition. ^1H NMR (d_8-toluene, 300 MHz): δ 8.09 (d, J = 7.2 Hz, 2 H), 7.65 (t, J = 7.5 Hz, 2 H), 7.46 (m, 13 H), 6.74 (m, 18 H,), 6.66 (s, 1 H), 1.52 (br s, 6 H), 0.52 (s, 9 H). $^{31}P\{^1H\}$ NMR (d_8-toluene, 121.4 MHz): δ 42.5. UV-vis (C_6H_6) λ_{max}, nm (ε): 583 (2000).

Addition of N$_2$CHPh to [PhBP$_3$]Co(PPh$_3$), 7.1. Addition of excess (approximately 20 equiv.) N_2CHPh as a d_8-toluene solution to a d_8-toluene solution of $[PhBP_3]Co(PPh_3)$, **7.1**, at -30 °C gave a blue product that had ^{31}P NMR peaks at 42.1 and -6.8 (free PPh_3). The absorption spectrum of the reaction mixture showed a peak at 655 nm. After two hours at ambient temperature, ^1H NMR confirmed the return of **7.1**. A GC/MS trace of the reaction mixture confirmed the presence of *trans*-stilbene (m/z = 180).

Addition of $N_2CH(Mes)$ to $[PhBP_3]Co(PMe_3)$, 5.2. Addition of excess (approximately 10 equiv.) $N_2CH(Mes)$ as a C_6D_6 solution to a C_6D_6 solution of $[PhBP_3]Co(PMe_3)$, **5.2**, at ambient temperature gave a red mixture that had ^{31}P NMR peaks at 59 (br), 40.5, 23.5 and 16.2 ppm. The peak at 23.5 ppm was confirmed to be $Me_3P{=}N_2CH(Mes)$ by an independent synthesis.

Addition of $N_2CH(Mes)$ to $[PhBP_3]Co(NCCH_3)$, 6.4. Addition of excess (approximately 10 equiv.) $N_2CH(Mes)$ as a C_6D_6 solution to a C_6D_6 solution of $[PhBP_3]Co(NCCH_3)$, **6.4**, at ambient temperature gave a red mixture that had peaks at 59 (br) and 40.5 ppm in the ^{31}P NMR spectrum.

7.5.4 X-ray experimental information

The general X-ray experimental procedure was performed according to section 2.4.4. Crystallographic information is provided in Table 7.1.

Table 7.1. X-ray diffraction experimental details for $[PhBP_3]CoN_2CPh_2$ (**7.2**) and $[PhBP_3]CoN_2CH(SiMe_3)$ (**7.3**).

	$[PhBP_3]CoN_2CPh_2$ (**7.2**)	$[PhBP_3]CoN_2CH(SiMe_3)$ (**7.3**)
Chemical formula	$C_{58}H_{51}BCoN_2P_3$	$C_{57.5}H_{63}BCoN_2P_3Si$
Formula weight	938.66	778.27
T (ºC)	-177	-177
λ (Å)	0.71073	0.71073
a (Å)	13.1284(8)	16.5731(15)
b (Å)	16.5975(11)	13.2889(12)
c (Å)	21.8205(14)	23.277(2)
α (º)	90	90
β (º)	97.168(1)	97.231(2)
γ (º)	90	90
V ($Å^3$)	4717.5(5)	5085.7(8)
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
Dcalcd (g/cm^3)	1.322	1.271
$\mu(cm^{-1})$	5.07	5.00
R1, wR2 ($I>2\sigma(I)$)[a]	0.0466, 0.0693	0.0582, 0.0830

[a] $R1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$, $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

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