# Reactions of the Thiocarbene Complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ with Sulfur, Carbon, and Nitrogen Nucleophiles

Heesook P. Kim and Robert J. Angelici*

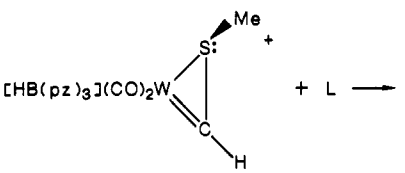
*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

*Received April 4, 1986*

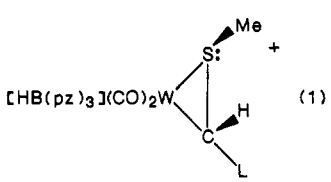
Nucleophiles add to the carbene carbon of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (**2**) in which the $\eta^2$-CH(SMe) group is coordinated via both the C and S atoms. In the products of these reactions, the C and S atoms remain coordinated. Thus, mercaptides ($SR^-$) and the malonate anion react with **2** to give air-stable adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]$ (L = SMe, SEt, S(*i*-Pr), $CH(CO_2Me)_2$). With 4-(dimethylamino)pyridine, **2** forms the air-stable carbene adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(NC_5H_4NMe_2)]^+$. With secondary amines ($HNMe_2$, $HNEt_2$), the carbene compound **2** reacts quite differently and forms air-stable aminocarbyne complexes $[HB(pz)_3](CO)_2W(\equiv CNR_2)$. Reactions of **2** with primary amines ($NH_2Me$, $NH_2Et$, $NH_2CH_2CH_2OH$, $NH_2(i\text{-}Pr)$, $NH_2(t\text{-}Bu)$, and $NH_2(4\text{-}C_6H_4CH_3)$) and $NH_3$ also produce aminocarbyne compounds $[HB(pz)_3](CO)_2W(\equiv CNHR)$, but they are in equilibrium with their hydride–isocyanide tautomers $[HB(pz)_3](CO)_2(H)W(CNR)$ (R = Me, Et, $CH_2CH_2OH$, *i*-Pr, *t*-Bu), the first examples of such a tautomerism. A variety of other bases simply deprotonate **2** to give the carbyne $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**). The fluxionality of the $HB(pz)_3$ ligand in these complexes is discussed.

## Introduction

The thiocarbene complex $Cp(CO)_2Fe[=CH(SMe)]^+$, Cp = $\eta^5$-$C_5H_5$, reacts with a variety of nucleophiles to give a range of products (Scheme I).[1,2] All of the reactions are presumed to proceed by initial attack at the carbene carbon atom. In recent papers,[3,4] we reported the preparation of the thiocarbene complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (**2**), in which the [CH(SMe)] carbene ligand is coordinated to the W via both the carbene C and S atoms. Only one other $\eta^2$-thiocarbene complex $\{(PPh_3)_2[CN(4\text{-}C_6H_4CH_3)](Cl)Os[\eta^2\text{-}C(SMe)(4\text{-}C_6H_4CH_3)]\}ClO_4$[5] has been reported. Very little is known about the reactivities of either of these complexes. Like the simple $\eta^1$-carbene complex $Cp(CO)_2Fe[CH(SMe)]^+$,[1,2] **2** reacts with phosphorus donors, L ($PPh_3$, $PEt_3$, $PPh_2H$, $P(OMe)_3$), to give carbene adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]^+$, in which both the C and S atoms remain coordinated to the W (eq 1).[4] The phosphonium proton in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2H)]^+$ is removed by $NEt_3$ to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$, whose structure was established by an X-ray diffraction study.[4] In the present report, we describe reactions of **2** with compounds having nucleophilic S, C, and N atoms.



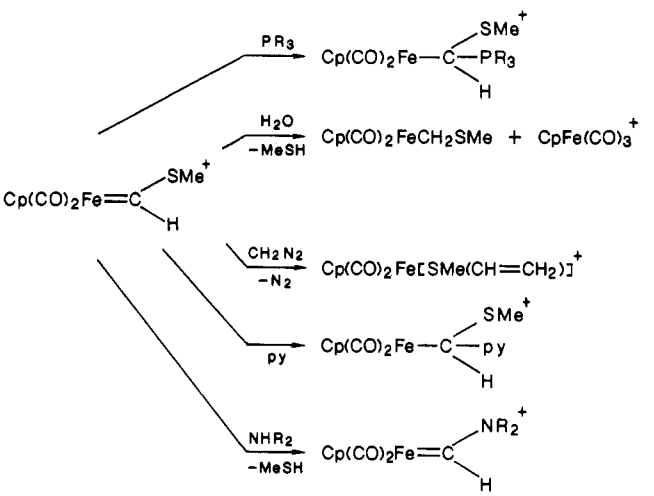
**2**



(1)

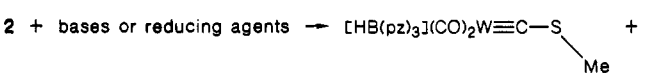
L = $PPh_3$, $PEt_3$, $PPh_2H$, $P(OMe)_3$

**Scheme I**

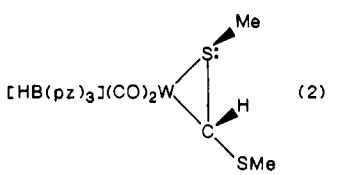


## Results and Discussion

**Reactions of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3CO_3$ (2) with Bases or Reducing Agents.** Most of the reactions of **2** described in the preceding paper involve nucleophilic addition to the carbene carbon atom. Nucleophiles are also bases. In fact, there are some Lewis bases that give no product resulting from nucleophilic addition. Thus, the bases, dry NaH, $NaBH_4$, NaOMe, NaOPh, PPNSH, $NaSCH_2Ph$, NaSePh, $LiCH_3$, $NEt_3$, $K_2CO_3$, $NH_2NH_2$, $NHMeNH_2$, and NHMeNHMe, react with **2** to give $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**; 10–20%), and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (**3**; 5–40%), according to eq 2. The highest yield of **1** (90%) is found when **2** is



**1**



(2)

**3**

reacted with $NaSCH_2Ph$. As discussed in the following

(1) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018.
(2) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1583.
(3) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124.
(4) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics*, preceding paper in this issue.
(5) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, *259*, 215.

0276-7333/86/2305-2489$01.50/0 © 1986 American Chemical Society

**Table I. IR Data for the Complexes in $CH_2Cl_2$ Solvent**

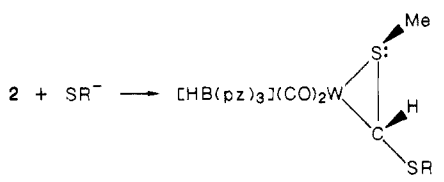
| complex | IR $\nu$(CO), $cm^{-1}$ |
|---|---|
| $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**) | 1980 s, 1888 s |
| $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (**2**) | 2067 m, 1996 s |
| $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (**3A**) | 1937 s, 1832 s[a] |
| $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (**3B**) | 1957 w, 1821 w[a] |
| $[HB(pz)_3](CO)_2W[CH(SMe)(SEt)]$ (**4A**) | 1936 s, 1833 s[a] |
| $[HB(pz)_3](CO)_2W[CH(SMe)(SEt)]$ (**4B**) | 1958 w, 1820 w[a] |
| $[HB(pz)_3](CO)_2W[CH(SMe)[SCH(Me)_2]]$ (**5A**) | 1935 s, 1832 s[a] |
| $[HB(pz)_3](CO)_2W[CH(SMe)[SCH(Me)_2]]$ (**5B**) | 1958 w, 1820 w[a] |
| $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SEt)]\}CF_3SO_3$ (**6**) | 2065 m, 1990 s |
| $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)[CH(CO_2Me)_2]]$ (**7**) | 1932 s, 1805 s, 1747 m, 1730 m |
| $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(NC_5H_5)]\}CF_3SO_3$ (**8**) | 1957 s, 1823 s |
| $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(4\text{-}NC_5H_4Me)]\}CF_3SO_3$ (**9**) | 1955 s, 1819 s |
| $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)[4\text{-}NC_5H_4NMe_2]]\}CF_3SO_3$ (**10**) | 1953 s, 1813 s |
| $[HB(pz)_3](CO)_2W(\equiv CNMe_2)$ (**11**) | 1941 s, 1837 s |
| $[HB(pz)_3](CO)_2W(\equiv CNEt_2)$ (**12**) | 1938 s, 1831 s |
| $[HB(pz)_3](CO)_2W(\equiv CNHMe)$ (**13**)[b,g] | 1943 s, 1837 s |
| $[HB(pz)_3](CO)_2W(\equiv CNHEt)$ (**14**)[c,g] | 1943 s, 1841 s |
| $[HB(pz)_3](CO)_2W(\equiv CNHCH_2CH_2OH)$ (**15**)[d,g] | 1942 s, 1844 s |
| $[HB(pz)_3](CO)_2W[\equiv CNHCH(Me)_2]$ (**16**)[e,g] | 1943 s, 1843 s |
| $[HB(pz)_3](CO)_2W[\equiv CNHC(Me)_3]$ (**17**)[f,g] | 1945 s, 1840 s |
| $[HB(pz)_3](CO)_2W[\equiv CNH(4\text{-}C_6H_4Me)]$ (**18**) | 1956 s, 1860 s |
| $[HB(pz)_3](CO)_2W(\equiv CNH_2)$ (**19**) | 1950 s, 1855 s |

[a] Hexane solvent. [b] $\nu$(CN) = 2125 $cm^{-1}$. [c] $\nu$(CN) = 2118 $cm^{-1}$. [d] $\nu$(CN) = 2090 $cm^{-1}$. [e] $\nu$(CN) = 2100 $cm^{-1}$. [f] $\nu$(CN) = 2100 $cm^{-1}$. [g] $[HB(pz)_3](CO)_2(H)W(CNR)$ tautomer present; see text.

sections, **1** and **3** are side products of reactions with other nucleophiles; presumably they are formed according to eq 2.

The reducing agent, sodium naphthalenide, also produces **1** (10%) and **3** (40%). Thus, it is possible that some or all of the nucleophiles noted above behave as reducing agents, although no attempt was made to identify oxidation products. There is no evidence for CO-containing products other than **1** and **3**. While the mechanism of reaction 2 is unclear, transfer of $MeS^-$ from **2** to form **3** must be involved and is presumably related to the demonstrated good leaving group ability of $MeS^-$ in thiocarbene complexes.[2,6]

**Reactions of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ with $SR^-$.** Complex **2** reacts readily with mercaptides to give the corresponding air-stable bis(organothio)methyl complexes **3**–**5** in about 90% yield (eq 3). The



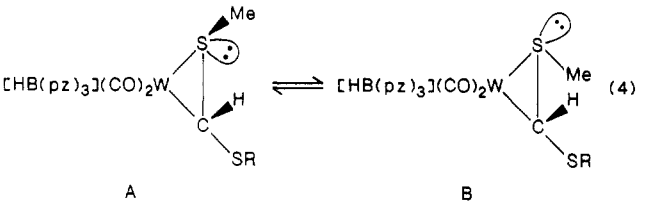

(3)

**3**, R = Me
**4**, R = Et
**5**, R = *i*-Pr

reaction appears to be a simple nucleophilic addition of the mercaptide to the carbene carbon.[7] Similar reactions of $Cp(CO)_2Fe[CH(SMe)]^+$ [2] and $Cp(CO)_2Fe[C(SMe)_2]^+$ [6a] have also been reported. The thiocarbyne compound **1** is also obtained from reaction 3 in 5% yield. With $SCH_2Ph^-$ and $SH^-$, only the base reaction (eq 2) occurs yielding **1** and **3**.

IR and $^1H$ and $^{13}C$ NMR spectra of **3** (Tables I–III) show two sets of peaks, suggesting the presence of two isomers. The isomers could not be separated by column chromatography or recrystallization. The relative ratio of the major isomer A to the minor isomer B was obtained by integration of the methine protons (CH). The ratio of these two isomers of **3** depends on the solvent and temperature; the ratio is 14:1 at 25 °C in $C_6D_6$, 7:1 at 25 °C in $CDCl_3$, 6:1 at 25 °C in $CD_2Cl_2$, 5:1 at 25 °C in $(CD_3)_2CO$, 4:1 at 25 °C in $CD_3NO_2$, and 3:1 at 50, 70, and 85 °C in $CD_3NO_2$ solution.

The isomers presumably result from inversion at the coordinated sulfur atom (eq 4). The major isomer A of




A B (4)

**3** probably has the structure in which the sulfur donor (SR, R = Me) adds to the carbene carbon on the side opposite the Me on the sulfur atom, which is also on the side opposite the bulky $[HB(pz)_3]$ group; this structure would be essentially the same as that of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ (see Figure 1 in the preceding paper),[4] except SMe replaces $PPh_2$. Inversion of the sulfur atom has been observed in numerous sulfide (e.g., $R_2S$ and $RSCH_2CH_2SR$) complexes;[8a] the coalescence temperatures for pyramidal inversion in the complexes $W(CO)_5(PhCH(Me)SCH_3)$[8b] and $(CO)_4W(PhCH_2SCH_2CH_2SCH_2Ph)$[8c] are −76.5 °C ($\Delta G^\ddagger$ = 28.0 kJ/mol) and 27 °C ($\Delta G^\ddagger$ = 51.5 kJ/mol), respectively. The SMe peaks of the two isomers of **3** do not coalesce up to 85 °C in $CD_3NO_2$. The high coalescence temperature for **3** may be caused by the three-membered ring which has been found to increase the inversion barrier in *trans*-$PdCl_2(SCMe_2CMe_2)_2$.[8d] Two noninterconverting isomers were also observed for the three-membered ring complex $(dppe)(CO)_3W[CH(SR)(SR)]^+$;[8e] these were likewise ascribed to *E* and *Z* isomers resulting from inversion at the coordinated sulfur atom. IR and $^1H$ NMR spectra (Tables I and II) reveal the presence of two isomers for **4** and **5** also. The relative ratios of the two isomers of **4** and **5** at 25 °C in $CD_2Cl_2$ are 8:1 and 3:1, respectively.

Although the isomers of **3**–**5** may result from inversion at the sulfur, it is not possible to discount the possibility that they arise from rotation of the whole $\eta^2$-CH(SMe)(SR) unit around an axis from the W to the center of the $\eta^2$-C–S bond. A similar three-membered ring ($\eta^2$-$CH_2PMe_2$) rotation was proposed in $(PMe_3)_4WH(\eta^2\text{-}CH_2PMe_2)$.[9]

A third isomerization process to be considered is that involving cleavage of the C–S bond in the $\eta^2$-CH(SMe)(SR) ligand to give the carbene–mercaptide complex W[=CH(SR)](SMe), which could interchange the positions of the H and SR groups by rotation around the W[=CH(SR)] carbene bond. In another context, Roper[10] has proposed

(6) (a) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108. (b) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1118.
(7) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(8) (a) Abel, E. W.; Orrell, K. J.; Bhargava, S. K. *Prog. Inorg. Chem.* **1984**, *32*, 1. (b) Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M.; Klei, E. *J. Organomet. Chem.* **1978**, *161*, 183. (c) Cross, R.; Hunter, G.; Massey, R. C. *J. Chem. Soc.*, Dalton *Trans.* **1976**, 2015. (d) Abel, E. W.; Booth, M.; Orrell, K. *J. Chem. Soc., Dalton Trans.* **1979**, 1994. (e) Schenk, W. A.; Schwietzke, T. *Organometallics* **1983**, *2*, 1905.
(9) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc.*, Dalton *Trans.* **1985**, 2025. Also, for $Cp_2Zr(X)[CH(SR')R]$, see: Ward, A. S.; Mintz, E. A.; Ayers, M. R. *Organometallics* **1986**, *5*, 1585.

**Table II. $^1$H NMR Data for the Complexes in $CD_2Cl_2$ Solvent at Room Temperature[a]**

| complex | H3 of pz | H4 of pz | H5 of pz | other |
|---|---|---|---|---|
| 1[b] | 7.91 (br) | 6.23 (br) | 7.65 (br) | 2.69 (SMe) |
| 2 | 8.07 (d, $J$ = 2.21), 7.94 (t, $J$ = 2.90)[c] | 6.50 (t, $J$ = 2.37),[c] 6.47 (t, $J$ = 2.35)[c] | 7.91 (d, $J$ = 2.36), 7.83 (d, $J$ = 2.14), 7.81 (d, $J$ = 2.07) | 12.78 (s, $J_{WH}$ = 19.83, CH), 2.37 (SMe) |
| 3A | 8.10 (d, $J$ = 1.58) | 6.24 (t, $J$ = 2.20)[c] | 7.65 (d, $J$ = 2.37) | 4.89 (s, $J_{WH}$ = 3.46, CH), 2.47 (CSMe), 2.35 (WSMe) |
| 3B | not resolved | 6.26 (br) | 7.69 (d, $J$ = 2.17) | 5.39 (CH), 2.59 (CSMe), 1.57 (WSMe) |
| 4A | 8.13 (br) | 6.23 (t, $J$ = 2.23)[c] | 7.65 (d, $J$ = 1.98) | 4.82 (s, $J_{WH}$ = 3.91, CH), 2.71 (q, $J$ = 7.42, $SCH_2$), 2.44 (SMe), 1.38 (t, $J$ = 7.44, Me) |
| 4B | not resolved | 6.25 (t, $J$ = 2.02)[c] | 7.68 (d, $J$ = 2.15) | 5.43 (CH), 2.97 (q, $J$ = 7.36, $SCH_2$), 1.57 (SMe), 1.15 (t, $J$ = 7.57, Me) |
| 5A | 8.16 (br) | 6.23 (t, $J$ = 2.19)[c] | 7.65 (d, $J$ = 2.08) | 4.71 (s, $J_{WH}$ = 4.39, WCH), 2.97 (h, $J$ = 6.76, CH), 2.40 (SMe), 1.41 (d, $J$ = 6.56, Me), 1.36 (d, $J$ = 6.81, Me) |
| 5B | not resolved | 6.25 (t, $J$ = 2.36)[c] | 7.69 (d, $J$ = 2.14) | 5.40 (WCH), 3.23 (h, $J$ = 6.84, CH), 1.57 (SMe), 1.49 (d, $J$ = 6.65, Me), 1.43 (d, $J$ = 6.50, Me) |
| 6 | 8.07 (d, $J$ = 2.22), 7.94 (t, $J$ = 2.29)[c] | 6.49 (t, $J$ = 2.39),[c] 6.47 (t, $J$ = 2.19)[c] | 7.91 (d, $J$ = 2.30), 7.81 (d, $J$ = 2.11), 7.78 (d, $J$ = 2.06) | 12.81 (s, $J_{WH}$ = 19.77, CH), 2.68 (m, $SCH_2$), 1.21 (t, $J$ = 7.54, Me) |
| 7 | 8.22 (br) | 6.26 (br) | 7.69 (br) | 4.87 (d, $J$ = 10.36, WCH), 3.80, 3.79 (OMe), 3.74 (d, $J$ = 10.35, CH), 1.52 (SMe) |
| 9[d] | 8.22 (br) | 6.43 (br) | 7.93 (br) | 8.62 (d, $J$ = 6.74, H2 and H6 of pic), 7.92 (d, $J$ = 6.62, H3 and H5 of pic), 7.58 (CH), 2.67 (Me), 1.96 (SMe) |
| 10[d] | 8.25 (br) | 6.41 (br) | 7.91 (br) | 8.11 (d, $J$ = 7.76, H2 and H6 of py), 7.01 (d, $J$ = 7.75, H3 and H5 of py), 7.34 (CH), 3.31 ($NMe_2$), 1.84 (SMe) |
| 11 | 7.79 (d, $J$ = 1.74) | 6.20 (t, $J$ = 1.99)[c] | 7.67 (d, $J$ = 2.03) | 3.21 ($NMe_2$) |
| 12 | 7.80 (d, $J$ = 1.57) | 6.20 (t, $J$ = 2.08)[c] | 7.67 (d, $J$ = 1.97) | 3.42 (q, $J$ = 7.23, $NCH_2$), 1.37 (t, $J$ = 7.28, Me) |
| 13[b] | 7.80 (d, $J$ = 1.79) | 6.16 (t, $J$ = 2.20)[c] | 7.64 (d, $J$ = 1.85) | 3.15 (d, $J$ = 4.27 NMe), [3.60 (NMe), −2.36 (WH)][e] |
| 14 | 7.79 (d, $J$ = 0.94) | 6.19 (t, $J$ = 1.81)[c] | 7.69 (d, $J$ = 1.59) | 3.44 (q, $J$ = 7.35, $NCH_2$), 1.88 (t, $J$ = 7.36, Me), [3.15 (q, $J$ = 7.11, $NCH_2$), 1.84 (t, $J$ = 7.36, Me), −2.36 (WH)][e] |
| 15 | 7.81 (br) | 6.20 (t, $J$ = 1.63)[c] | 7.71 (d, $J$ = 2.04) | 3.80 (t, $J$ = 5.08, $OCH_2$), 3.50 (t, $J$ = 5.22, $NCH_2$), [4.07 (t, $J$ = 5.08, $OCH_2$), 3.46 (t, $J$ = 5.00, $NCH_2$), −2.28(WH)][e] |
| 16 | 7.80 (d, $J$ = 1.15) | 6.20 (t, $J$ = 1.99)[c] | 7.67 (d, $J$ = 2.22) | 4.18 (h, $J$ = 6.43, CH), 1.30 (d, $J$ = 6.53, Me), [4.55 (h, $J$ = 6.43, CH), 1.40 (d, $J$ = 6.86, Me), −2.36 (WH)][e] |
| 17 | 7.81 (d, $J$ = 1.49) | 6.19 (t, $J$ = 2.21)[c] | 7.67 (d, $J$ = 2.11) | 1.37 (Me), [1.47 (Me), −2.34 (WH)][e] |
| 18 | 7.86 (d, $J$ = 2.23) | 6.21 (t, $J$ = 2.16)[c] | 7.69 (d, $J$ = 2.14) | 7.23 (d, $J$ = 8.34, Ph), 7.14 (d, $J$ = 8.35, Ph), 2.32 (Me) |
| 19 | 7.98 (d, $J$ = 0.94) | 6.27 (t, $J$ = 2.08)[c] | 7.67 (d, $J$ = 2.39) | |

[a] Chemical shifts in $\delta$ and coupling constants in Hz. [b] $CDCl_3$ solvent. [c] Due to overlapping d of d. [d] $CD_3NO_2$ solvent. [e] Values in square brackets correspond to the $[HB(pz)_3](CO)_2(H)W(CNR)$ tautomer; other values are for $[HB(pz)_3](CO)_2W(\equiv CNHR)$ tautomer.

**Table III. $^{13}$C NMR Data for the Complexes in $CD_2Cl_2$ Solvent at Room Temperature[a]**

| complex | CO | C3 of pz | C4 of pz | C5 of pz | other |
|---|---|---|---|---|---|
| 1[b] | 224.7 | 144.9 | 105.7 | 135.2 | 264.4 (WCS), 17.4 (SMe) |
| 2 | 212.98, 212.55 | 147.21, 146.31, 145.95 | 106.06, 108.48, 108.33 | 138.76, 138.51, 138.27 | 227.95 (CH), 28.40 (SMe) |
| 3A | 232.58 ($J_{WC}$ = 151.67), 230.66 ($J_{WC}$ = 151.67) | 144.81 | 105.89 | 135.38 | 61.79 ($J_{W-C}$ = 32.17, CH), 22.44 (SMe), 20.44 (WSMe) |
| 3B | 236.04, 220.02 | not resolved | 106.05 | 135.59 | 71.69 (CH), 26.20 (SMe), 21.35 (WSMe) |
| 12[b] | 225.83 | 144.46 | 105.03 | 134.39 | 254.61 (WC), 44.66 ($NCH_2$), 14.46 (Me) |

[a] Chemical shifts in ppm and coupling constants in Hz. [b] $CDCl_3$ solvent.

such a C–X (X = O, Se, Te) cleavage. Although this type of isomerization cannot be dismissed, it seems less likely than the previous two possibilities.

A fourth isomerization mechanism, involving dissociation of $SR^-$ to give **2** which can readd $SR^-$ on the same or opposite side, can be excluded. This conclusion is based on the observation there is no exchange of the $SMe^-$ group in **3** (0.023 mmol) with added $Na^+SEt^-$ (0.036 mmol) and HSEt (0.044 mmol) in 0.5 mL of $CD_2Cl_2$ over a period of 22 h at 25 °C; there was also no other reaction.

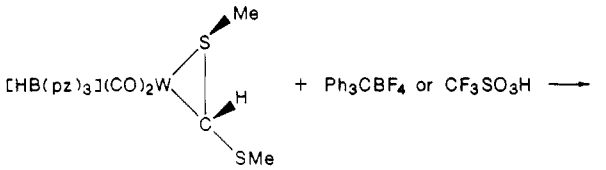
The SMe carbene compound **2**, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, reacts with $SEt^-$ to give $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ (**4**); no $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ is detected in this reaction. Likewise, the SEt carbene compound **6**, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SEt)]^+$, reacts with $SMe^-$ to give $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$;[11] no **4** is detected in this reaction. No interconversion of **4** to $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ or vice versa occurs at room temperature. Therefore, scrambling

(10) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53.

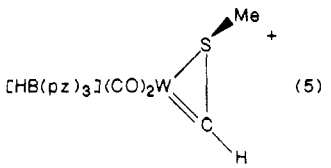
(11) The $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ complex is prepared by a procedure similar to the one used (see Experimental Section) for **3**. The $^1$H NMR spectrum of the major isomer of $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ taken in $CD_2Cl_2$ solution shows peaks at $\delta$ 8.14 (H3 of pz), 7.65 (d, $J$ = 1.85 Hz, H5 of pz), 6.24 (t, $J$ = 2.22 Hz, H4 of pz), 4.79 (s, $J_{WH}$ = 4.91, CH), 2.66 (m, $SCH_2$), 2.42 (s, SMe), and 1.16 (t, $J$ = 7.57 Hz, Me).

of the bound (SMe) and dangling sulfide (SEt) groups does not occur in **4** and probably also not in **3** and **5**. Other results also suggest the W–S bond is inert; **3** does not react with CO (1 atm, 30 °C, 30 min, $CH_2Cl_2$) nor $PEt_3$ (25 °C, 1 h, $CH_2Cl_2$). An attempt to cleave the W–S bond in **2** with CO (80 psig, 40 °C, 22 h) was also not successful. Thus, the W–S bond is robust in **3** and **2**.

One of the $MeS^-$ groups is removed quantitatively from $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ upon treatment with $Ph_3CBF_4$ (eq 5). The reaction of **3** with $CF_3SO_3H$ also



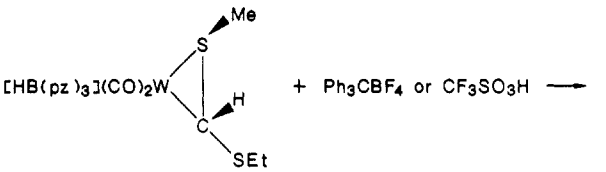

**3**



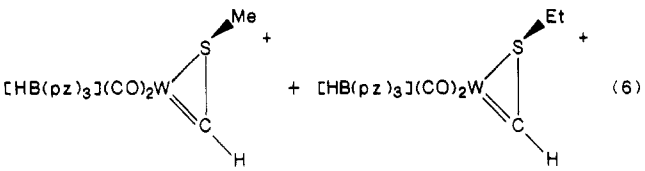

(5)

**2**

yields **2** (eq 5) but in only 20% yield; decomposition is also observed. Compound **4** reacts with $Ph_3CBF_4$ to form both the thiomethyl **2** (30%) and thioethyl **6** carbene (70%) products (eq 6). The reaction of **4** with $CF_3SO_3H$ also




**4**

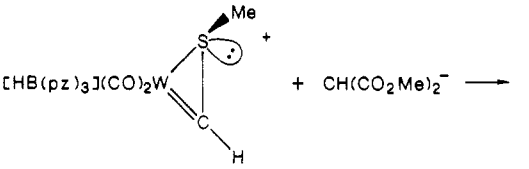



(6)

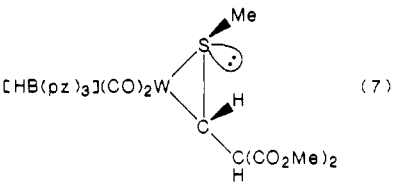
**2** **6**

gives **2** (10%) and **6** (10%) (eq 6). The identity of **6** was established by comparing its $^1H$ NMR spectrum with an authentic sample of this compound prepared by the reaction of $[HB(pz)_3](CO)_2W(\equiv CSEt)$ with $CF_3SO_3H$. Although it might seem that the uncoordinated SEt would be abstracted by $Ph_3CBF_4$ or $CF_3SO_3H$ more readily than the bound sulfide (SMe), the product distribution establishes that the SMe group is removed preferentially. As noted above, **4** does not isomerize to $[HB(pz)_3](CO)_2W[CH(SMe)(SEt)]$ at these temperatures: thus, this isomerization of **4** cannot account for the formation of both **2** and **6**. It is possible that both the coordinated (SMe) and uncoordinated (SEt) groups are abstracted at about the same rates or $Ph_3C^+$ and $H^+$ oxidiize **4** to give a radical intermediate which interconverts the SMe and SEt groups. There is, however, no direct evidence for either of these mechanistic possibilities.

**Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (2) with $CH(CO_2Me)_2^-$.** Carbanions are known to add to carbene carbon centers.[12] Similarly, the $\eta^2$-carbene of **2** reacts with the carbanion $CH(CO_2Me)_2^-$ to produce the air-stable malonate adduct **7** in 92% yield (eq 7). The




**2**



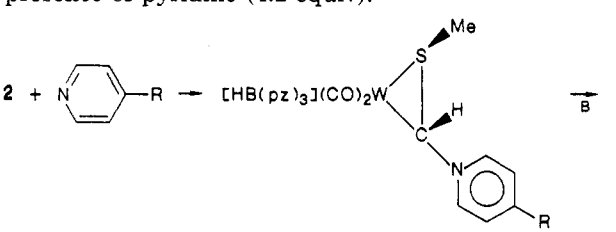

(7)

**7**

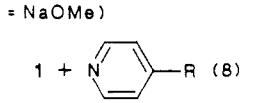
more nucleophilic MeLi, however, does not form an adduct but gives the typical base reaction (eq 2) products, **1** and **3**. In the $^1H$ NMR spectrum of **7**, the two Me groups of the malonate are nonequivalent (δ 3.80, 3.79) due to the chiral center at the methine carbon.[13] The large coupling constant ($^3J_{HH}$ = 10.35 Hz) of the two methine hydrogens suggests that the H atoms are anti to each other;[14] this configuration minimizes repulsion between the two $CO_2Me$ groups and the CO ligands.

**Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (2) with Pyridines.** Pyridine (py) is known to form carbene adducts such as $Cp(CO)_2Fe[CH(SMe)(py)]^+$[2] and $Cp(NO)(PPh_3)Re[CH_2(py)]^+$.[15] In contrast to these adduct-forming reactions, **2** reacts at room temperature with tertiary amines such as $Et_3N$ to give **1** (10%) and **3** (30%) according to eq 2. Even though there is no spectroscopic evidence for it, **3** probably results from initial formation of the adduct $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(NEt_3)]^+$ followed by transfer of a $MeS^-$ group to another carbene ligand, as suggested for related reactions of iron thiocarbene complexes with tertiary amines.[2,6]

The $\eta^2$-carbene compound **2** combines with pyridine ($pK_a$ = 5.2) at room temperature (eq 8) to form an unstable adduct, **8**, which was only characterized by its IR spectrum (Table I). Even with excess pyridine (4.2 equiv), the reaction is not complete after 2 h of stirring. The pyridine adduct **8** decomposes (eq 8) to the thiocarbyne compound **1** within 2 h at room temperature in solution in the presence of pyridine (4.2 equiv).




**8**, R = H (B = py)
**9**, R = Me (B = 4-picoline)
**10**, R = $NMe_2$ (B = NaOMe)




(8)

Compound **2** also forms an adduct, **9** with 4-picoline ($pK_a$ = 6.1) according to eq 8. The 4-picoline complex **9**

(12) (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833. (b) Fischer, E. O.; Reidmüller, S. *Chem. Ber.* **1976**, *109*, 3358. (c) Fischer, E. O.; Held, W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 3842.

(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 207.

(14) Reference 13, pp 208–10.

(15) Tam, W.; Lin, G. Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

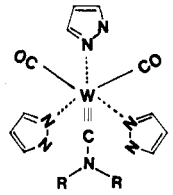
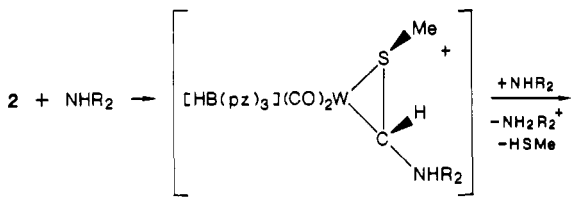


**Figure 1.** Proposed structure of $[HB(pz)_3](CO)_2W(\equiv CNR_2)$ (R = Me (**11**) or Et (**12**)). H and B atoms are omitted.

undergoes transformation to the thiocarbyne compound **1** in the presence of 4-picoline (1 equiv) in $CD_2Cl_2$ solution within 5 h. The reaction of **2** with 4-dimethylaminopyridine ($pK_a$ = 9.7) gives an air-stable isolable adduct, **10** (eq 8), in 90% yield. No conversion of **10** to **1** in the presence of excess 4-(dimethylamino)pyridine (10 equiv) is observed. However, the reaction of **10** with 4 equiv of NaOMe ($pK_a$ = 16) gives **1** within 5 min. Thus, the conversion of **8**, **9**, and **10** to **1** (eq 8) requires a base, presumably to remove the methine proton. The strength of the base required appears to depend on the donor ability of the pyridine in the adduct. For pyridine and 4-picoline which are relatively weak donors, excess pyridine or 4-picoline are sufficiently strong bases to cause the conversion of **8** and **9** to **1**. For the adduct **10** of the much more basic 4-(dimethylamino)pyridine, the much stronger base NaOMe is required. Related to the conversion of **8**, **9**, and **10** to **1** is the similar deprotonation of the methine hydrogen in $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$ with NaH to give **1** in 90% yield.[4] In all of these reactions, it appears that deprotonation of the adduct gives an unstable intermediate which loses the pyridine or phosphine and rearranges to carbyne **1**. In contrast to these deprotonations, base reactions of **2** with NaH or NaOMe (eq 2) produce both **1** (10%) and **3** (40% and 30%, respectively). The formation of **3** in the latter reaction is apparently blocked in the deprotonation reactions of the adducts of **2**.

The IR spectra of **8**–**10** show two strong $\nu$(CO) absorptions (**8**; 1957, 1823 $cm^{-1}$) close to those observed for the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]^+$ (e.g., L = P(OMe)$_3$; 1955, 1826 $cm^{-1}$).[4] However, the methine proton resonance of **10** at $\delta$ 7.34 is considerably more deshielded than the corresponding signal in the adducts $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)L]$ (e.g., L = P(OMe)$_3$; $\delta$ 5.45).[4]

**Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (2) with $NHR_2$.** Secondary amines ($HNR_2$) replace[6b,16] a thioalkoxy group in $Cp(CO)_2Fe[C(SMe)_2]^+$ to give aminothiocarbenes $Cp(CO)_2Fe[C(SMe)(NR_2)]^+$ and MeSH. Similar reactions of other $\eta^1$-thiocarbene complexes have also been reported.[2,17] In contrast, **2** reacts with $NHR_2$ (R = Me, Et) to produce air-stable aminocarbyne compounds in about 30% yield (eq 9). Compound **3** is also




$[HB(pz)_3](CO)_2W{\equiv}CNR_2$ (9)

**11**, R = Me
**12**, R = Et

obtained as a side product in this reaction. The amine,

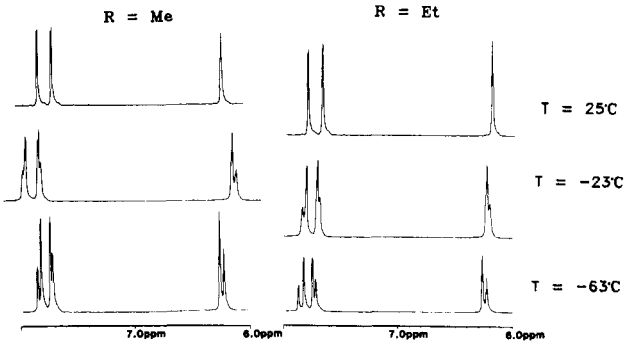



**Figure 2.** Temperature-dependent $^1H$ NMR spectra of $[HB(pz)_3](CO)_2W(\equiv CNR_2)$ (R = Me (**11**) or Et (**12**)) in $CD_2Cl_2$ solvent.

$NHR_2$, presumably initially gives the adduct (eq 9), and then deprotonation of $NHR_2$ takes place with another mole of $NHR_2$. Finally, ring opening with elimination of HSMe yields the aminocarbyne product. The average $\nu$(CO) frequency of $[HB(pz)_3](CO)_2W(\equiv CNEt_2)$ (1956, 1864 $cm^{-1}$ (hexane)) is 9 $cm^{-1}$ lower than that of the corresponding Cp complex $Cp(CO)_2W(\equiv CNEt_2)$ (1958, 1880 $cm^{-1}$ (hexane)),[18] suggesting that $HB(pz)_3$ is a better electron donor than Cp, as observed previously.[19] The chemical shift of the carbyne carbon atom ($\delta$ 254.61) in the $^{13}C$ NMR spectrum of **12** is similar to those in $[HB(pz)_3](CO)_2W(\equiv CSMe)$ ($\delta$ 264.4)[20] and $Br(CO)_4W(\equiv CNEt_2)$ ($\delta$ 235.62).[21] The structures of **11** and **12** (Figure 1) suggest that two of the pyrazolyl groups are different than the other. Indeed, $^1H$ NMR spectra of **11** and **12** at −63 °C show two identical and one different pyrazolyl group (Figure 2). As the temperature is increased, the pyrazolyl signals broaden and coalesce and are equivalent at room temperature (Table II). These spectral changes suggest the $HB(pz)_3$ ligand is rotating or the two CO and the carbyne groups are rapidly exchanging positions at room temperature. Rapid rotation of the $HB(pz)_3$ group has been proposed in $[HB(pz)_3](CO)_2Mo(\eta^3\text{-}CH_2CRCH_2)$ (R = Me or Ph);[22] the limiting high- and low-temperature spectra (R = Me) were obtained at +50 and −40 °C, respectively.

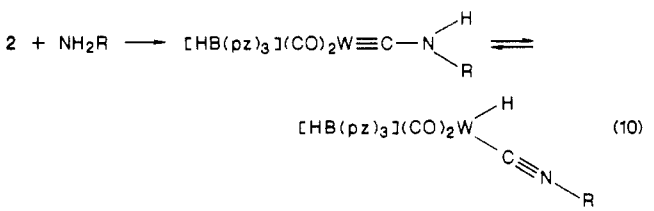
Varying degrees of $HB(pz)_3$ ligand fluxionality have been observed in other compounds in our studies. The energy barrier for rotation of the $HB(pz)_3$ ligand around the B–H axis is found to be sensitive to the electronic environment at the metal center. Most cationic complexes such as $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$, $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]^+$,[4] and $[HB(pz)_3](CO)(PEt_3)W(MeOC{\equiv}CSMe)^+$ [4] show inequivalence of all three pyrazolyl rings in $^1H$ NMR spectra taken at room temperature, suggesting that rotation is slow on the NMR time scale. Whereas electron-rich neutral complexes such as **3**, **11**, **12**, $[HB(pz)_3](CO)_3WX$ (X = Cl, I),[4] and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$[4] show equivalence of all three pyrazolyl rings in $^1H$ NMR spectra taken at room temperature. The intermediate stage, broadening of the pyrazolyl ring peaks, is observed in the room-temperature $^1H$ NMR spectra of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$,[4] **9**, and **10**.

The above variations of $HB(pz)_3$ fluxionality may, in general, reflect the Lewis acidity of the metal center. In cases where the metal has the highest acidity, the N donors of the $HB(pz)_3$ ligand are bound more strongly, and fluxionality is not observed at room temperature. In more

(16) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231.
(17) (a) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73. (b) Pickering R. A.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2977.
(18) Fischer, E. O.; Lindner, T. L.; Huttner, G.; Friedrich, P.; Kreissl, R. F.; Besenhard, J. O. *Chem. Ber.* **1977**, *110*, 3397.
(19) Curtis, M. D.; Shiu, K. B. *Inorg. Chem.* **1985**, *24*, 1213.
(20) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.
(21) Fischer, E. O.; Kreis, G.; Kreissl, F. R.; Kalbfus, W.; Winkler, E. *J. Organomet. Chem.* **1974**, *65*, C53.
(22) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 3183.

electron-rich complexes, which generally have a zero charge and the metal is not as acidic, the pyrazolyl groups are not bound to the metal as strongly and fluxionality is observed. These trends are illustrated by **2** and its adducts: (1) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_3)]^+$ are not fluxional at room temperature; (2) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PEt_3)]^+$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(4\text{-}NC_5H_4R)]^+$ (R = Me, $NMe_2$) have broadened pyrazolyl protons indicating some fluxionality; (3) $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)(PPh_2)]$ are completely fluxional at room temperature (25 °C). The importance of the electron richness of the metal is supported by a correlation of the average $\nu$(CO) values of **2** and its adducts with the fluxionality of the $HB(pz)_3$ ligand. Carbene compound **2** and the $PPh_3$ adduct show relatively high average $\nu$(CO) values at 2032 and 1894 $cm^{-1}$, respectively. The intermediate complexes have lower average $\nu$(CO) values at 1887 (4-picoline complex **9**), 1883 ($4\text{-}NC_5H_4NMe_2$ compound **10**), and 1882 $cm^{-1}$ ($PEt_3$ complex). The neutral SMe, **3**, and $PPh_2$ compounds show the lowest average $\nu$(CO) values at 1872 and 1864 $cm^{-1}$, respectively.

**Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ (2) with Primary Amines and $NH_3$.** Like secondary amines, a variety of primary amines and $NH_3$ react with **2** at room temperature to produce the corresponding aminocarbyne compounds in 25–35% yield (eq 10). The usual side




(10)

**13**, R = Me
**14**, R = Et
**15**, R = $CH_2CH_2OH$
**16**, R = $CH(Me)_2$
**17**, R = $C(Me)_3$
**18**, R = 4-$C_6H_4Me$
**19**, R = H

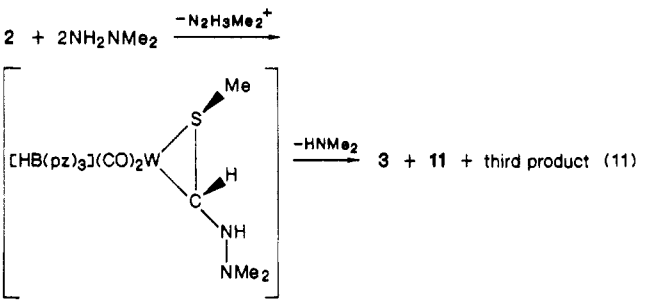
products **1** (0–5%)[23] and **3** (30–50%) are also formed. The aminocarbyne compounds **13–19** are so air-sensitive that they were not isolated; however, they were characterized by the similarity of their IR and $^1H$ NMR spectra (Tables I and II) to those of **11** and **12**. The $\nu$(CO) frequencies of **13–19** are very close to those of **11** and **12**. However, IR spectra of **13–17** show an extra weak band in the $\nu$(CN) region (2090–2125 $cm^{-1}$), suggesting the presence of a CNR ligand; there are only two $\nu$(CO) bands in both $CH_2Cl_2$ and hexane solvents. In the $^1H$ NMR spectra of **13–17**, there are peaks for the aminocarbyne compound along with additional peaks for another type of R group and a metal hydride (ca. $\delta$ −2.3). The additional peaks in the IR and $^1H$ NMR spectra of **13–17** indicate the carbyne complexes $[HB(pz)_3](CO)_2W(\equiv CNHR)$ are in equilibrium with the isocyanide–hydride tautomer $[HB(pz)_3](CO)_2(H)W(CNR)$. In contrast, the absence of $\nu$(CN) and a hydride resonance in the spectra of compounds **18** and **19** shows that these compounds exist only in the aminocarbyne structure. It thus appears that the electron-rich alkyl R groups in **13–17** promote formation of the isocyanide–hydride tautomer. The relative ratio of the aminocarbyne to isocyanide–hydride tautomer is obtained by integration of the peaks for the R groups. The ratio of the amount of the aminocarbyne to the hydride compound is dependent on the solvent but not on the bulkiness of R; the ratio is 4:1 in $CDCl_3$ for **13**, 5:1 in $CD_2Cl_2$ for **14**, 4:1 in $CD_2Cl_2$ for **15**, 4:1 in $CD_2Cl_2$ for **16**, 4:1 in $CD_2Cl_2$ for **17**, and 9:1 in $CD_3NO_2$ for **17**. It is interesting that the related Cp complex $Cp(CO)_2Mo(H)(C\equiv NMe)$ shows no evidence for the carbyne tautomer $Cp(CO)_2Mo\equiv CNHMe$.[24] Perhaps, it is the preference of $HB(pz)_3$ complexes for 6-, rather than 7-coordination,[19] or the greater electron-donor ability of $HB(pz)_3$ which favors the aminocarbyne structure in compounds **13–19**, as contrasted with the Cp system.

Compounds **13–19** slowly decompose in solution even under an $N_2$ atmosphere. During the decomposition of **17**, the relative amounts of the aminocarbyne and hydride tautomers remain constant at 4:1 during a 52-h period, during which time 50% of **17** had decomposed. Thus, the equilibrium process between the tautomers is faster than the rate of decomposition.

To our knowledge, the tautomerism described here is the only example of an equilibrium between aminocarbyne and isocyanide–hydride isomers, although Pombeiro[25] has suggested $Mo(dppe)_2(CNR)(\equiv CNHR)^+$ as an intermediate in the protonation of $Mo(dppe)_2(CNR)_2$ to give $Mo(dppe)_2(CNR)_2(H)^+$.

The secondary aminocarbyne $[HB(pz)_3](CO)_2W(\equiv CNMe_2)$ (**11**) does not undergo methyl transfer analogous to the above tautomerism to give $[HB(pz)_3](CO)_2(Me)W(CNMe)$; even at 70 °C for 5 h there is no reaction.

Reaction of **2** with the hydrazine $NH_2NMe_2$ (eq 11) produces **3** (28%), **11** (28%), and a third product which is not sufficiently stable to be isolated. This reaction




(11)

I

possibly involves $NH_2NMe_2$ addition to the carbene carbon and deprotonation with another mole of $NH_2NMe_2$ to form intermediate I. Migration of the proton from N–H to $NMe_2$ and fission of the N–N bond liberates free $NHMe_2$. The $NHMe_2$ could react with **2** to form the observed **3** and **11**. According to eq 11, the third product would then have the chemical formula $[HB(pz)_3](CO)_2W[CH(SMe)N]$, which is consistent with the IR and $^1H$ NMR spectra reported in the Experimental Section. This same compound (10%) is also formed in the reaction of **2** and $NaN_3$ which also gives **1** (10%) and **3** (10%). It is not unreasonable that $N_3^-$ addition to the carbene carbon of **2** followed by loss of $N_2$ would also lead to the composition $[HB(pz)_3](CO)_2W[CH(SMe)N]$ for the third product; unfortunately, this compound could not be characterized further.

With other hydrazines, $NH_2NH_2$, $NHMeNH_2$, and NHMeNHMe, only the base reaction (eq 2) occurs, yielding **1** (2–20%) and **3** (40%). A reaction related to (11) is that of *asy*-dimethylhydrazine with $(CO)_5Cr[C(OMe)(Me)]$ to give the likely intermediate $(CO)_5Cr[C(NHNMe_2)(Me)]$, which rearranges to $(CO)_5Cr(NCMe)$

(23) The $NH_2CH_2CH_2OH$ and $NH_2$-*t*-Bu reactions do not produce the thiocarbyne compound **1**.

(24) Adams, R. D. *Inorg. Chem.* **1976**, *15*, 169.

(25) Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 55.

with loss of $HNMe_2$.[26] Similarly, $CpFe(CO)_3^+$ reacts with $NH_2NMe_2$ or $N_3^-$ to give an intermediate adduct, which rearranges to $CpFe(CO)_2(NCO)$.[27]

## Experimental Section

**General Procedures.** Methods and instrumentation were the same as described in the previous paper.[4] THF was distilled from Na–benzophenone under $N_2$. All amines, except $Me_2NH$, $MeNH_2$, $EtNH_2$, $H_2NCH_2CH_2OH$, and $NH_3$, were stored over KOH overnight and distilled from KOH. Ethanolamine ($H_2NCH_2CH_2OH$) was purified by vacuum distillation (5 mm, 40 °C) before use. The complexes $NaCpFe(CO)_2$,[28] $PPNCo(CO)_4$,[29] $[HB(pz)_3](CO)_2W(\equiv CSMe)$,[20] and $[HB(pz)_3](CO)_2W(\equiv CSEt)$[20] were prepared by using the previously described procedures. Synthesis of the complex $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (**2**) was described previously.[3,4] $NaC_{10}H_8$,[30] NaSePh,[31] $NaCH(CO_2Me)_2$,[32] (PPN)SH,[33] and NHMeNHMe[27] were synthesized according to the literature references given. 4-(Dimethylamino)pyridine was recrystallized from $CH_2Cl_2$/hexane. All other chemicals were commercial products of the highest purity available and were used as received.

**Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (2) with Bases.** The thiocarbene compound **2** (47 mg, 0.071 mmol) in 10 mL of $CH_2Cl_2$ was treated with $KOCMe_3$ (49 mg, 0.44 mmol). The reaction mixture was allowed to stir for 3 h. The solution was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate ($KCF_3SO_3$). After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The resulting residue was redissolved in a minimum amount of $CH_2Cl_2$. This solution was chromatographed on a 1 × 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**) was eluted first with a 1:2 mixture of $CH_2Cl_2$/hexane; yield 40%. Then, a yellow band was eluted with a 2:1 mixture of $CH_2Cl_2$/hexane. The yellow eluate was evaporated to dryness, and the resulting solid was recrystallized from $CH_2Cl_2$/hexane at −20 °C to give air-stable, orange crystals of **3** (8 mg, 20%), whose spectra were identical with those of an authentic sample (see below).

In a procedure similar to the one above, the reactions of **2** (ca. 30 mg, 0.045 mmol) in 5–10 mL of solvent with 1–2 equiv of various bases gave the following yields of **1** and **3**, respectively, in parentheses: dry NaH (10, 40%), $NaBH_4$ (10, 40%), NaOMe (10, 30%), NaOPh (15, 30%), (PPN)SH (10, 5%), NaSePh (5, 40%), $LiCH_3$ (10, 10%)/THF, $NEt_3$ (10, 30%), $K_2CO_3$ (10, 30%), $NH_2NH_2$ (2, 40%), $NHMeNH_2$ (20, 40%), and NHMeNHMe (20, 40%)/$CH_2Cl_2$.

**Reaction of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (2) with Reducing Agents.** A THF solution of **2** (38 mg, 0.057 mmol) with $NaC_{10}H_8$ (1.5 mL, 0.039 M) was stirred at 0 °C for 10 min. According to the IR spectrum of the reaction mixture, the products included **1** (10%) and **3** (40%).

In a procedure similar to the one above, **2** (ca. 30 mg, 0.045 mmol) was reacted in 5–10 mL of THF with 1–1.6 equiv of various reducing agents to give **1** and **3**, respectively, in yields noted in parentheses: $NaCpFe(CO)_2$ (10, 40%), $PPNCo(CO)_4$ (10, 30%).

**$[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (3).** Dry NaH (42 mg, 1.8 mmol) was dissolved in 30 mL of THF, and $CH_3SH$ was slowly bubbled through the solution for 1 h. The solution was stirred for another 6 h, until $H_2$ production ceased. Then, THF was decanted from the white NaSMe precipitate, which was washed with THF and dried under vacuum. A THF solution (15 mL) containing $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (**2**; 60 mg, 0.091 mmol) and NaSMe (8 mg, 0.11 mmol) was allowed to stir for 15 min. Purification as for the $KOCMe_3$ reaction mixture described earlier afforded **1** (5%) and air-stable, orange crystals of **3** (46 mg, 90%). Anal. Calcd for $C_{14}H_{17}BN_6O_2S_2W$: C, 30.02; H, 3.06; N, 15.00; S, 11.45. Found: C, 29.81; H, 3.13; N, 14.83; S, 11.45. EIMS (18 eV): $m/e$ 560 ($M^+$), 512 ($M^+$ − HSMe), 504 ($M^+$ − 2CO), 473 ($M^+$ − 2CO − 2Me − H). IR ($CH_2Cl_2$): 1925 (s), 1802 (s) $cm^{-1}$.

**$[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ (4).** A 40-mL solution of THF containing dry NaH (1.24 g, 0.052 mol) and ethanethiol (8.1 mL, 0.11 mol) was stirred for 8 h, yielding a white precipitate (NaSEt). The THF was decanted from the precipitate, and the resulting solid was washed with THF and dried under vacuum. In a procedure similar to the one used for the synthesis of **3**, a mixture of $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}CF_3SO_3$ (**2**; 66 mg, 0.10 mmol) and NaSEt (9 mg, 0.11 mmol) in 40 mL of THF was stirred for 30 min. Then, hexane (20 mL) was added to the reaction mixture, and the solution volume was reduced, giving a white precipitate ($NaCF_3SO_3$). After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The residue was redissolved in a minimum amount of $CH_2Cl_2$. This solution was chromatographed on a 1 × 30 cm silica gel column. $[HB(pz)_3](CO)_2W(\equiv CSMe)$ (**1**) eluted first with a 1:2 mixture of $CH_2Cl_2$/hexane; yield 5%. Then, a yellow band which eluted with a 2:1 mixture of $CH_2Cl_2$/hexane was evaporated to give a solid. Air-stable, orange crystals of $[HB(pz)_3](CO)_2\overline{W[CH(SMe)(SEt)]}$ (**4**) were obtained by recrystallizing the solid from $CH_2Cl_2$/hexane at −20 °C (54 mg, 94%). The thioethyl compound **4** was always contaminated with some $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (**3**; 5%); neither recrystallization nor repeated chromatography separated the two completely. EIMS (18 eV): $m/e$ 574 ($M^+$), 518 ($M^+$ − 2CO), 489 ($M^+$ − 2CO − Et).

**$[HB(pz)_3](CO)_2\overline{W\{CH(SMe)[SCH(Me)_2]\}}$ (5).** A mixture of dry NaH (0.42 g, 0.018 mol) and $(CH_3)_2CHSH$ (4.7 mL, 0.050 mol) in 20 mL of THF was stirred for 8 h, yielding a white precipitate ($NaSCHMe_2$). The THF was decanted from the white solid, which was washed with THF and dried under vacuum. Analogous to the preparation of **3**, a THF solution (5 mL) containing **2** (21 mg, 0.032 mmol) and $NaSCH(CH_3)_2$ (4 mg, 0.041 mmol) was stirred for 15 min. Purification as for **4** afforded **1** (5%) and air-stable, orange crystals of **5** (17 mg, 90%). The product **5** was always contaminated with **3** (5%). EIMS (18 eV): $m/e$ 588 ($M^+$), 532 ($M^+$ − 2CO), 489 ($M^+$ − 2CO − $CH(Me)_2$).

**Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (3) with $CPh_3BF_4$.** Into a 4-mL $CH_2Cl_2$ solution of **3** (15 mg, 0.027 mmol) was added $CPh_3BF_4$ (12 mg, 0.036 mmol) at 0 °C. After the solution was warmed to room temperature, it was stirred for 30 min. The solvent was removed under vacuum, and the resulting residue was washed with diethyl ether and hexane. The (thiomethyl)carbene compound **2** was obtained in essentially quantitative yield.

**Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)_2]$ (3) with $CF_3SO_3H$.** A 0.4-mL $CD_2Cl_2$ solution of **3** (20 mg, 0.036 mmol) was placed in an NMR tube. Upon addition of $CF_3SO_3H$ (3.2 μL, 0.036 mmol) to the solution, the color changed to violet. The IR and $^1H$ NMR spectra of the reaction mixture showed that the (thiomethyl)carbene compound **2** was produced in 20% yield.

**$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SEt)]\}CF_3SO_3$ (6).** In a procedure similar to the one used for the preparation of **2**, addition of $CF_3SO_3H$ (10 μL, 0.11 mmol) to a solution of $[HB(pz)_3](CO)_2W(\equiv CSEt)$ (60 mg, 0.11 mmol) in 6 mL of $CH_2Cl_2$ at 0 °C produced an immediate color change from orange to the violet color of product **6**. After the solvent was removed under vacuum, the resulting solid was washed several times with hexane and diethyl ether. Air-stable, violet crystals of **6** were obtained by recrystallizing the solid from $CH_2Cl_2/Et_2O$ at −20 °C in essentially quantitative yield. Anal. Calcd for $C_{15}H_{16}BF_3N_6O_5S_2W$: C, 26.64; H, 2.39; N, 12.43. Found: C, 26.39; H, 2.52; N, 12.15. MS (FAB): $m/e$ 527 ($M^+$), 458 ($M^+$ − 2CO − CH), 429 ($M^+$ − 2CO − CH − Et).

**$[HB(pz)_3](CO)_2W\{\eta^2\text{-}CH(SMe)[CH(CO_2Me)_2]\}$ (7).** A solution of **2** (88 mg, 0.13 mmol) and $NaCH(CO_2Me)_2$ (1.0 mL, 0.13 M) in 5 mL of THF was allowed to stir for 15 min. The solvent was removed under vacuum, and the residue was redissolved in a minimum amount of $CH_2Cl_2$. This solution was chromatographed on a 1 × 30 cm column of silica gel with a 1:5 mixture of hexane/$CH_2Cl_2$; a single yellow band was collected. The eluate was concentrated, diluted with hexane, and cooled to −20 °C.

(26) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 963.
(27) Angelici, R. J.; Busetto, L. *J. Am. Chem. Soc.* **1969**, *91*, 3197.
(28) Dombek, B. D.; Angelici, R. J. *Inorg. Synth.* **1977**, *17*, 100.
(29) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.
(30) Closson, W. D.; Wriede, P.; Bank, S. *J. Am. Chem. Soc.* **1966**, *88*, 1581.
(31) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1111.
(32) Hegedus, L. S.; Inoue, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4917.
(33) Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604.

Air-stable, yellow crystals of **7** resulted (77 mg, 92%). Anal. Calcd for $C_{18}H_{21}BN_6O_6SW$: C, 33.56; H, 3.29; N, 13.05. Found: C, 33.64; H, 3.54; N, 12.98. EIMS (18 eV): $m/e$ 644 ($M^+$), 616 ($M^+ - CO$), 588 ($M^+ - 2CO$), 573 ($M^+ - 2CO - Me$).

**{[HB(pz)$_3$](CO)$_2$W[$\eta^2$-CH(SMe)(4-NC$_5$H$_4$Me)]}CF$_3$SO$_3$ (9).** A 0.4-mL $CD_2Cl_2$ solution of **2** (13 mg, 0.020 mmol) was placed in an NMR tube. The solution was degassed and purged with $N_2$. Upon addition of 4-picoline (3.7 μL, 0.038 mmol), the color of the solution changed to dark red to give complete conversion of **2** to **9**. After $^1H$ NMR spectra of the reaction mixture were taken, the solvent was removed under vacuum and the resulting residue was washed with ether. Air-stable, maroon crystals of **9** were obtained by recrystallizing the solid from $CH_2Cl_2/Et_2O$ at −20 °C (12 mg, 80%). The product **9** decomposed in the presence of $NC_5H_4Me$ (1 equiv) in $CD_2Cl_2$ solution within 5 h to give **1** (10%). MS (FAB): $m/e$ 606 (parent cation), 559 (parent cation − SMe), 513 (parent cation − 4-picoline).

**{[HB(pz)$_3$](CO)$_2$W[$\eta^2$-CH(SMe)(4-NC$_5$H$_4$NMe$_2$)]}CF$_3$SO$_3$ (10).** Into a 10-mL $CH_2Cl_2$ solution of **2** (43 mg, 0.065 mmol) was added 4-(dimethylamino) pyridine (10 mg, 0.082 mmol). After the reaction mixture was stirred for 10 min, the solvent was removed under vacuum and the resulting residue was washed with ether. Air-stable, orange crystals of **10** were obtained by recrystallizing the solid from $CH_2Cl_2/Et_2O$ at −20 °C (46 mg, 90%). Anal. Calcd for $C_{21}H_{24}BF_3N_8O_5S_2W$: C, 32.16; H, 3.08; N, 14.29. Found: C, 31.71; H, 3.33; N, 13.75. MS (FAB): $m/e$ 635 (parent cation), 513 (parent cation − 4-(dimethylamino)pyridine).

**Reaction of {[HB(pz)$_3$](CO)$_2$W[$\eta^2$-CH(SMe)(4-NC$_5$H$_4$NMe$_2$)]}CF$_3$SO$_3$ (10) with NaOMe.** A 2-mL THF solution containing **10** (15 mg, 0.019 mmol) and NaOMe (4 mg, 0.074 mmol) was allowed to stir for 5 min. Complete conversion of **10** to **1** occurred as indicated by the IR spectrum of the reaction mixture.

**[HB(pz)$_3$](CO)$_2$W(≡CNMe$_2$) (11).** Into a 20-mL $CH_2Cl_2$ solution of **2** (94 mg, 0.14 mmol) was injected $NHMe_2$ vapor (7 mL, ca. 0.28 mmol) by using a syringe. After the reaction mixture was stirred for 10 min, it was diluted with 20 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate, $(NMe_2H_2)CF_3SO_3$. After the salt was removed by filtration through Celite, the solution was evaporated to dryness. The residue was redissolved in a minimum amount of $CH_2Cl_2$ and chromatographed on a 3 × 30 cm silica gel column. [HB(pz)$_3$](CO)$_2$W(≡CNMe$_2$) (**11**) eluted first with a 5:2 mixture of hexane and $CH_2Cl_2$. This fraction was evaporated to dryness, and the resulting residue was recrystallized from $CH_2Cl_2$/hexane, giving **11** (21 mg, 29%) as an air-stable, yellow solid. Anal. Calcd for $C_{14}H_{16}BN_7O_2W$: C, 33.04; H, 3.17; N, 19.26. Found: C, 32.84; H, 3.20; N, 18.99. EIMS (21 EV): $m/e$ 509 ($M^+$), 481 ($M^+ - CO$), 453 ($M^+ - 2CO$), 438 ($M^+ - 2CO - Me$), 397 ($M^+ - 2CO - CNMe_2$). A second band (orange) was eluted with a 2:1 mixture of $CH_2Cl_2$/hexane. Evaporation of this fraction and recrystallization of the residue from $CH_2Cl_2$/hexane gave orange crystals of **3** (24 mg, 31%).

**[HB(pz)$_3$](CO)$_2$W(≡CNEt$_2$) (12).** The method used to prepare **11** was also used for this complex. A 20-mL $CH_2Cl_2$ solution containing **2** (91 mg, 0.14 mmol) and $NHEt_2$ (22 μL, 0.21 mmol) was stirred for 10 min. The same workup as in the synthesis of **11** was employed to give air-stable, yellow crystals of **3** (24 mg, 31%) and **12** (23 mg, 31%). Anal. Calcd. for $C_{16}H_{20}BN_7O_2W$: C, 35.78; H, 3.75; N, 18.26. Found: C, 35.69; H, 3.79; N, 18.07. EIMS (21 eV): $m/e$ 537 ($M^+$), 509 ($M^+ - CO$), 481 ($M^+ - 2CO$), 452 ($M^+ - 2CO - Et$), 397 ($M^+ - 2CO - CNEt_2$).

**[HB(pz)$_3$](CO)$_2$W(≡CNHMe) (13).** Into a 5-mL $CH_2Cl_2$ solution of **2** (35 mg, 0.053 mmol) was injected $NH_2Me$ vapor (12 mL, ca. 0.48 mmol). After the reaction had proceeded for 15 min, hexane (10 mL) was added. The solution volume was reduced, giving a white precipitate, $(NH_3Me)CF_3SO_3$. The salt was removed by filtration through Celite, and the solution was evaporated to dryness to give a yellow solid. Compounds **1** (5%), **3** (30%), and [HB(pz)$_3$](CO)$_2$W(≡CNHMe) (**13**; 25%) were identified from IR and $^1H$ NMR spectra of the reaction mixture. The aminocarbyne compound **13** was not sufficiently stable to be isolated.

**[HB(pz)$_3$](CO)$_2$W[≡CNHC(Me)$_3$] (17).** A 0.4-mL $CD_2Cl_2$ solution of **2** (16 mg, 0.024 mmol) was placed in an NMR tube. The solution was degassed and purged with $N_2$, and $NH_2C(Me)_3$ (2.6 μL, 0.025 mmol) was injected into the solution yielding a yellow solution. IR and $^1H$ NMR spectra of the reaction mixture showed the presence of **3** (40%) and **17** (35%). The aminocarbyne compound **17** was not sufficiently stable to be isolated.

**Reaction of {[HB(pz)$_3$](CO)$_2$W[$\eta^2$-CH(SMe)]}CF$_3$SO$_3$ (2) with NH$_2$NMe$_2$.** A 5-mL $CH_2Cl_2$ solution containing **2** (46 mg, 0.070 mmol) and $NH_2NMe_2$ (6.9 μL, 0.091 mmol) was stirred for 5 min, yielding a greenish yellow solution. It was diluted with 30 mL of hexane; slow evaporation under reduced pressure furnished a white precipitate $NH_2NMe_2{\cdot}nCF_3SO_3H$, $n$ = 1 or 2, which was removed by filtration through Celite. The solution was evaporated to dryness, and the resulting residue was redissolved in a minimum amount of $CH_2Cl_2$. This $CH_2Cl_2$ solution was chromatographed on a 1 × 30 cm silica gel column. [HB(pz)$_3$](CO)$_2$W(≡CNMe$_2$) (**11**; 10 mg, 28%) was eluted first with a 5:2 mixture of hexane/$CH_2Cl_2$. Then an orange band, **3** (11 mg, 28%), was eluted with a 2:1 mixture of $CH_2Cl_2$/hexane. A third product (30%) decomposed on the column and could not be isolated. In the reaction mixture, this product had bands in its IR spectrum at 1951 and 1852 $cm^{-1}$ (hexane) and in the $^1H$ NMR ($CD_2Cl_2$) spectrum at δ 7.78 (3, d, $J$ = 2.61 Hz), 7.72 (3, d, $J$ = 1.88 Hz), 6.27 (3, t, $J$ = 2.18 Hz), 4.72 (1, s, $J_{WH}$ = 4.60 Hz), and 2.27 (3, s).

**Acknowledgment.** This material is based upon work supported by the National Science Foundation under Grant CHE-8100419 and CHE-8401844 (R.J.A.). We thank D. Scott for obtaining the variable-temperature NMR spectra.

**Registry No.** **1**, 77827-54-4; **2**, 90790-21-9; **3**, 104874-89-7; **4**, 104874-90-0; **5**, 104910-57-8; **6**, 104874-92-2; **7**, 104910-58-9; **8**, 104874-94-4; **9**, 104874-96-6; **10**, 104874-98-8; **11**, 104874-99-9; **12**, 104875-00-5; **13** (isomer 1), 104875-01-6; **13** (isomer 2), 104875-12-9; **14** (isomer 1), 104875-02-7; **14** (isomer 2), 104875-08-3; **15** (isomer 1), 104875-03-8; **15** (isomer 2), 104875-09-4; **16** (isomer 1), 104875-04-9; **16** (isomer 2), 104875-10-7; **17** (isomer 1), 104875-05-0; **17** (isomer 2), 104875-11-8; **18**, 104875-06-1; **19**, 104875-07-2; [HB(pz)$_3$](CO)$_2$W(≡CSEt), 77846-72-1.