Thermal and Photolytic Promotion of α-Thiolate Migration in $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SR)_2SR]$ To Give Carbyne Complexes $[HB(pz)_3](RS)_2W{\equiv}CSR$

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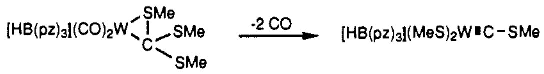
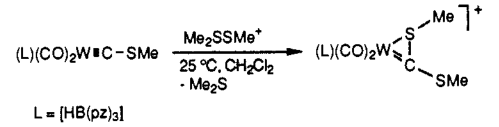
Abstract: Heating the complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SR)SMe]$ (**1**, R = Me; **3**, R = Et) above 60 °C results in CO loss, C–S bond cleavage, and MeS or EtS migration to give the carbynes $[HB(pz)_3](MeS)(RS)W{\equiv}CSR'$ (**2**, R = R' = Me; **4**, R = Me, Et, R' = Et, Me), e.g.,



In contrast, the analogous SAr complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SAr)SMe]$ (**5**, Ar = Ph; **7**, Ar = 4-C_6H_4Me) eliminate the disulfide ArSSMe upon heating, producing the known carbyne $[HB(pz)_3](CO)_2W{\equiv}CSMe$. However, photolysis of **5** and **7** gives the carbynes $[HB(pz)_3](MeS)(ArS)W{\equiv}CSMe$ (**6**, Ar = Ph; **8**, Ar = 4-C_6H_4Me) in a reaction very similar to the thermal reactions of **1** and **3**. Similarly, photolysis of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$ (**9**) yields $[HB(pz)_3](MeS)_2W{\equiv}CMe$ (**10**). Mechanisms of the reactions and structural features of the carbyne products are discussed.

The carbyne carbon in electron-rich transition-metal carbyne complexes is known to be susceptible to electrophilic attack.[1] Thus, treating the thiocarbyne $[HB(pz)_3](CO)_2W{\equiv}CSMe$ with $[Me_2SSMe]SO_3CF_3$ gives the η^2-dithiocarbene $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$ (eq 1).[2] This dithiocarbene reacts with a variety of nucleophiles to give a range of products (Scheme I).[2] In those reactions where the dithiocarbene adduct $[HB(pz)_3](CO)_2[\eta^2\text{-}C(SMe)(Nuc)SMe]$ is formed, both the carbon and sulfur atoms remain coordinated to tungsten and the C–S bond remains intact.



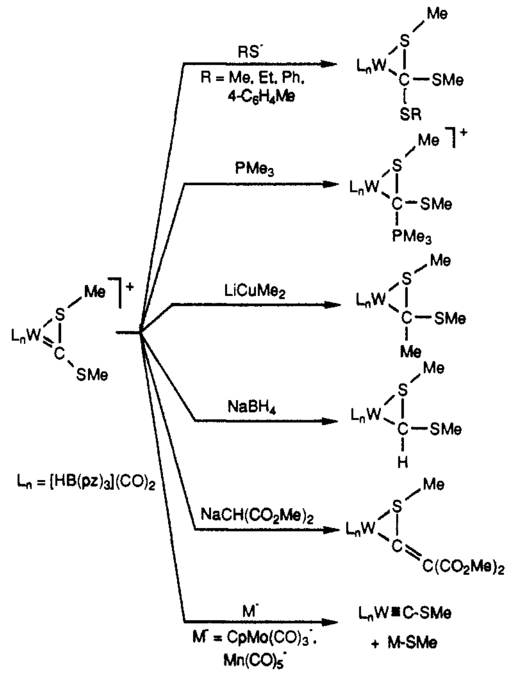
(1)

In this paper, we describe thermal and photolytic reactions of the complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ (Nuc = SMe, SEt, SPh, S-4-C_6H_4Me, Me),[2] which involve a novel migration of thiolate (RS) groups from the α-carbon to tungsten to generate a carbyne complex.

Experimental Section

General Procedures. All reactions, chromatography, distillations, and recrystallizations were carried out under an atmosphere of prepurified N_2 by using standard inert atmosphere and Schlenk techniques[3] unless stated otherwise. Tetrahydrofuran (THF) and Et_2O were distilled from Na/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. 1,2-Dichloroethane was distilled from P_2O_5. Reactions were carried out at room temperature unless stated otherwise. Neutral products were recrystallized by dissolving them in a mixture of CH_2Cl_2 or Et_2O (1-2 mL) and hexanes (40–60 mL) and slowly cooling the solution to low temperature (−20 to −78 °C) over 2–4 days.

Scheme 1



The ^1H and $^{13}C\{H\}$ NMR data were recorded on a Nicolet-NT 300-MHz spectrometer using the deuterated solvent as the internal reference (CD_2Cl_2: δ 5.32 and 53.8 ppm, respectively). Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Photochemical reactions were carried out under N_2 in a quartz tube, using a Canrad-Hanovia medium-pressure, 450-W, quartz mercury vapor lamp (40–48% UV, 40–43% visible, the balance is IR). Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ (Nuc = SMe, SEt, SPh, S–4-C_6H_4Me, Me) were prepared by using previously described procedures.[2] All other chemicals were used as received from commercial sources.

Thermal Reaction of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$ (1). A solution of $ClCH_2CH_2Cl$ (15 mL) containing **1** (0.137 g, 0.226 mmol) was refluxed for 8 h, giving a brown solution. The solution was concentrated to 5 mL. Hexanes (80 mL) were then layered on top, and the solution was allowed to stand at −20 °C for 18 h. This afforded air-stable, brown crystals of $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (**2**, 0.0845 g, 68%). Anal. Calcd for $C_{13}H_{19}BN_6S_3W$: C, 28.38; H, 3.48; S, 17.48. Found: C, 28.31; H, 3.47; S, 17.65. EIMS (70 eV): *m/e* 550 (M^+). ^1H NMR:[4]

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(1) (a) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124. (b) Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476. (c) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570. (d) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965. (e) Howard, J. A. K.; Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A.; Stringer, A. *Inorg. Chim. Acta* **1985**, *100*, 23. (f) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. *J. Organomet. Chem.* **1984**, *270*, C45. (g) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599. (h) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322.

(2) Doyle, R. A.; Angelici, R. J. *J. Organomet. Chem.*, in press.

(3) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

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δ 3.42 (s, 6 H, J_{WH} = 4.2 Hz, WSMe), 2.84 (s, 3 H, CSMe), 8.11 (d, J = 2.1 Hz, 2 H, H3), 8.07 (d, J = 1.9 Hz, 1 H, H3), 7.83 (d, J = 2.4 Hz, 1 H, H5), 7.69 (d, J = 1.9 Hz, 2 H, H5), 6.35 (pseudo-t, J = 2.2 Hz, 1 H, H4), 6.25 (pseudo-t, J = 2.2 Hz, 2 H, H4). ^{13}C NMR:[5] δ 268.3 (W≡C), 27.0 (WSMe), 19.7 (CS*Me*), 146.3, 144.1 (C3), 136.0, 135.3 (C5), 106.2, 105.9 (C4).

Thermal Reaction of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(SEt)SMe] (3). Refluxing a solution of ClCH$_2$CH$_2$Cl (20 mL) containing **3** (0.134 g, 0.216 mmol) for 18 h gave a brown solution. This solution was concentrated to 5 mL and chromatographed on neutral alumina (Grade 1, 1 × 10 cm). A brown band containing [HB(pz)$_3$](MeS)(RS)W≡CSR′ (**4**, R = Me, Et; R′ = Et, Me) was eluted with a 3:2 mixture of hexanes/CH$_2$Cl$_2$. A second green band sticks to the column. The eluate was evaporated to dryness, giving **4** as an air-stable, brown powder (0.484 g, 40%). Complex **4** is a mixture of two isomers (A, B) (see Discussion). Anal. Calcd for C$_{14}$H$_{21}$BN$_6$S$_3$W: C, 29.80; H, 3.75; N, 14.89. Found: C, 30.00; H, 3.88; N, 14.91. EIMS (70 eV): *m/e* 564 (M$^+$). ^{1}H NMR: δ 4.05 (m, WSCH$_2$, B), 3.45 (s, WSMe, B), 3.37 (s, WSMe, A), 3.20 (q, J = 7.4 Hz, CSCH$_2$, A), 2.83 (s, CSMe, B), 1.51 (t, J = 7.4 Hz, Me, A), 1.40 (t, J = 7.6 Hz, Me, B), 8.14 (m, H3, H5), 7.85 (d, J = 2.1 Hz, H3 or H5), 7.70 (m, H3, H5), 6.36 (m, H4), 6.26 (m, H4).

Photolysis of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(SPh)SMe] (5). A THF (10-mL) solution of **5** (0.177 g, 0.265 mmol) was photolyzed for 6.5 h, giving a brown solution. The solvent was removed in vacuo, and the residue dissolved in CH$_2$Cl$_2$ (5 mL) was chromatographed on neutral alumina (5% H$_2$O, 2 × 15 cm) by eluting with CH$_2$Cl$_2$/hexanes (1:2). Removal of the solvent gave the brown powder product [HB(pz)$_3$](PhS)(MeS)W≡CSMe (**6**, 0.119 g, 73%). Anal. Calcd for C$_{18}$H$_{21}$BN$_6$S$_3$W: C, 35.31; H, 3.46; N, 13.73. Found: C, 35.56; H, 3.58; N, 13.53. EIMS (70 eV): *m/e* 612 (M$^+$). ^{1}H NMR: δ 3.69 (s, 3 H, WSMe), 2.51 (s, 3 H, CSMe), 7.23 (m, 5 H, SPh), 8.09 (d, J = 2.0 Hz, 1 H, H3 or H5), 8.03 (d, J = 1.9 Hz, 1 H, H3 or H5), 7.84 (d, J = 1.4 Hz, 1 H, H3 or H5), 7.80 (d, J = 2.4 Hz, 1 H, H3 or H5), 7.73 (d, J = 1.8 Hz, 1 H, H3 or H5), 7.70 (d, J = 2.4 Hz, 1 H, H3 or H5), 6.27 (pseudo-t, J = 2.1, 2.3 Hz, 1 H, H4), 6.25 (pseudo-t, J = 2.4, 2.1 Hz, 1 H, H4), 6.22 (pseudo-t, J = 2.0, 2.2 Hz, 1 H, H4). ^{13}C NMR: δ 271.1 (W≡C), 150.1, 132.1, 128.0, 125.7 (WSPh), 29.1 (WSMe), 19.3 (CS*Me*), 151.5, 150.8, 150.5 (C3), 136.3, 135.7, 135.6 (C5), 106.7, 106.4, 106.2 (C4).

Photolysis of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(S-4-C$_6$H$_4$Me)SMe] (7). Similar to the procedure directly above, photolysis of **7** (0.143 g, 0.210 mmol) in THF (10 mL) for 3.5 h gave a brown solution. The solvent was removed in vacuo, and the residue was dissolved in CH$_2$Cl$_2$ (5 mL); the CH$_2$Cl$_2$ solution was chromatographed on neutral alumina (5% H$_2$O, 2 × 15 cm). Elution with CH$_2$Cl$_2$/hexanes (2:3) gave a single brown band containing the product [HB(pz)$_3$](4-MeC$_6$H$_4$S)(MeS)W≡CSMe (**8**). A green band remained at the top of the column. Recrystallization gave brown microcrystals of **8** (0.0684 g, 52%). Anal. Calcd for C$_{19}$H$_{23}$BN$_6$S$_3$W: C, 36.44; H, 3.70; N, 13.42. Found: C, 36.75; H, 3.85; N, 13.05. EIMS (70 eV): *m/e* 626 (M$^+$). ^{1}H NMR: δ 3.65 (s, 3 H, WSMe), 2.51 (s, 3 H, CSMe), 2.36 (s, 3 H, Ar*Me*), 7.13 (m, 4 H, SAr), 8.09 (d, J = 2.0 Hz, 1 H, H3 or H5), 8.01 (d, J = 1.9 Hz, 1 H, H3 or H5), 7.86 (d, J = 1.3 Hz, 1 H, H3 or H5), 7.80 (d, J = 2.2 Hz, 1 H, H3 or H5), 7.72 (d, J = 2.2 Hz, 1 H, H3 or H5), 7.70 (d, J = 2.2 Hz, 1 H, H3 or H5), 6.26 (m, 3 H, H4). ^{13}C NMR: δ 270.8 (W≡C), 145.5, 131.8, 130.1, 128.7 (WSAr), 28.8 (WSMe), 21.1 (Ar*Me*), 19.3 (CS*Me*), 147.1, 146.6, 144.7 (C3), 136.3, 135.7, 135.5 (C5), 106.7, 106.4, 106.2 (C4).

Photolysis of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(Me)SMe] (9). A THF (20 mL) solution of **9** (0.0966 g, 0.168 mmol) was photolyzed for 8 h, giving a brown solution. The solvent was removed in vacuo, and the residue was dissolved in CH$_2$Cl$_2$ (10 mL); the solution was filtered through neutral alumina (Grade 1, 5 cm). Addition of hexanes, followed by slow removal of the solvent in vacuo to dryness, gave the orange powder product [HB(pz)$_3$](MeS)$_2$W≡CMe (**10**, 0.0681 g, 78%). Anal. Calcd for C$_{13}$H$_{19}$BN$_6$S$_2$W: C, 30.14; H, 3.70; S, 12.38. Found: C, 30.18; H, 3.91; S, 12.14. EIMS (70 eV): *m/e* 518 (M$^+$), 471 (M$^+$ − SMe). ^{1}H NMR: δ 4.38 (s, J_{WH} = 9.3 Hz, 3 H, CMe), 3.37 (s, 6 H, WSMe), 8.08 (d, J = 1.6 Hz, 2 H, H3), 8.04 (d, J = 1.7 Hz, 1 H, H3), 7.82 (d, J = 2.1 Hz, 1 H, H5), 7.68 (d, J = 2.0 Hz, 2 H, H5), 6.34 (pseudo-t, J = 2.1 Hz, 1 H, H4), 6.24 (pseudo-t, J = 2.1 Hz, 2 H, H4). ^{13}C NMR: δ 303.9 (W≡C), 32.8 (C*Me*), 26.2 (WSMe), 146.8, 144.3 (C3), 136.1, 135.5 (C5), 106.5, 106.1 (C4).

Structure Determination of [HB(pz)$_3$](MeS)$_2$W≡CSMe (2). A dark brown block-shaped crystal of **2** was mounted on a glass fiber in a random orientation. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table I.

Table I. Crystal and Data Collection Parameters for the X-ray Diffraction Study of [HB(pz)$_3$](MeS)$_2$W≡CSMe (2)

formula	WS$_3$N$_6$C$_{13}$BH$_{24}$
fw	550.19
space group	$P2_1/n$
a, Å	10.059 (2)
b, Å	13.192 (3)
c, Å	14.649 (3)
β, deg	91.90 (2)
V, Å^3	1943 (1)
Z	4
d_{calcd}, g/cm^3	1.881
cryst size, mm	0.30 × 0.25 × 0.20
μ(Mo Kα), cm^{-1}	63.92
diffractometer	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα
orientation reflections, no. range (2θ)	25, 19° < 2θ < 35°
temp, °C	23 ± 1
scan method	θ–2θ
max 2θ, deg	55.0
total unique reflections	4443
unique reflections obsd ($F_o^2 > 3\sigma(F_o^2)$)	3091
no. of parameters refined	217
T_{min}/T_{max}	1.00/0.747
R^a	0.0358
$R_w{}^b$	0.0452
quality of fit indicator^c	0.966
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	2.85, 0.76 Å from W

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\sum\omega(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

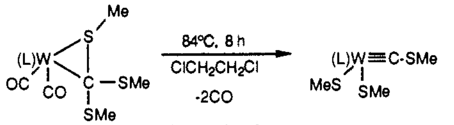
A total of 8867 reflections were collected in the ±*h*,+*k*,±l hemisphere. The average intensity of three intensity standards, measured every hour of exposure time, increased about 7% over the entire data collection period. Therefore, a nonlinear intensity correction was made based on the three standards. An empirical absorption correction was made, based on a series of ψ scans.

Structure Solution and Refinement. The position of the W atom was taken from a Patterson map, and all of the remaining non-hydrogen atoms were then found in a difference Fourier map. Full matrix least-squares refinement converged smoothly and, in the later stages, included anisotropic thermal parameters for every atom. The final cycle of refinement included 217 variable parameters.

The X-ray data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. All calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP package (Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, Holland).

Results and Discussion

Thermal Reactions of [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)(Nuc)SMe] Complexes. Upon heating above 65 °C, [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)$_2$SMe] (**1**) undergoes irreversible C–S bond cleavage, SMe migration to the tungsten, and CO loss to form the 16-electron terminal thiocarbyne [HB(pz)$_3$](MeS)$_2$W≡CSMe (**2**, eq 2) in 68% isolated yield. No other products are identified by



1 **2** (2)

^{1}H NMR spectroscopy in the reaction mixture; however, a small amount (5–10%) of an uncharacterized insoluble green material is also formed. The ^{13}C{H} NMR spectrum of **2** shows the carbyne carbon resonance at δ 268.3 ppm, which is similar to the chemical shifts reported for the 18-electron thiocarbyne complexes [HB(pz)$_3$](CO)$_2$W≡CSMe and Cp(CO)$_2$W≡CS[2,4-C$_6$H$_3$(NO$_2$)$_2$] (δ 264.4 and 261.7 ppm, respectively).[5] Thus, the carbyne ^{13}C chemical shift is essentially unaffected by the change in the oxidation state of tungsten. This suggests that **2**, like the 18-electron

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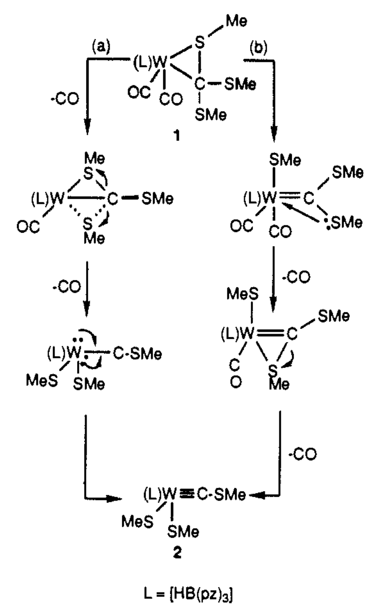
(4) The assignment of the pyrazolyl ring positions is as given by: Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 187.

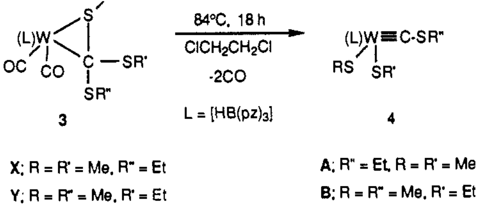
(5) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

Scheme II



complexes, is an electron-rich carbyne as compared to the electron-poor carbyne $(t\text{-BuO})_3W{\equiv}CS{-}t\text{-Bu}$, in which the carbyne ^{13}C shift occurs ~40 ppm further upfield at δ 222.7 ppm.[6] The structure of **2** was established by X-ray analysis and will be discussed later. Although **2** is a 16-electron complex, it does not react with PMe_3 (25 °C, 72 h) to form an adduct nor does it displace the MeS^- group as in the reaction of $Tp'(CO)_2W{\equiv}C{-}SMe$ with PR_3 to give the cationic phosphinocarbyne, $Tp'(CO)_2W{\equiv}CPR_3^+$ (R = Me, Et).[7] Complex **2** also does not react with CO (250 psi, 25 or 85 °C) to form either an adduct or complex **1** by the reverse of eq 2.

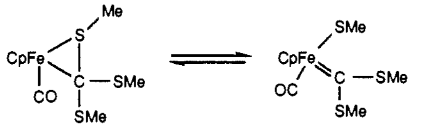
Upon heating, $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SEt)SMe]$ (**3**), which is a mixture of three isomers (X, Y, and Z), also loses both CO ligands, and two thiolate groups migrate to tungsten, forming **4** (eq 3), which exists as two isomers, $[HB(pz)_3](MeS)_2W{\equiv}CSEt$



(3)

(A) and $[HB(pz)_3](MeS)(EtS)W{\equiv}CSMe$ (B). These isomers could not be separated by chromatography or recrystallization. The resonances in the ^1H NMR spectrum of the mixture of isomers were assigned by comparison with those of **2**, in which the two MeS groups bound to tungsten occur further downfield than the MeS group bound to the carbyne carbon.

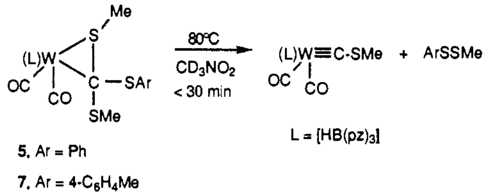
No intermediates are detected by ^1H NMR spectroscopy during the reactions (eq 2 and 3) of **1** and **3**. Two possible pathways for reaction 2 are shown in Scheme II. In pathway a, the first step involves CO loss and coordination of a second SMe group to tungsten. The resulting intermediate with an $\eta^3\text{-}C(SMe)_3$ ligand is similar to the known complexes. $\{Cp(CO)_2W[C(SMe)_2(4\text{-}C_6H_4Me)]\}(BF_4)_2$[8] and $I(CO)_3W[C(SMe)_2(Me)]$,[9] each with a carbon and two sulfur donors coordinated to tungsten. Subsequent cleavage of both C–S bonds in this intermediate with loss of a second CO gives the carbyne product **2**. In pathway b, C–S bond cleavage occurs first, producing a WSMe group and an η^2-carbene, in a process that is essentially the same as that (eq 4) for $Cp(CO)Fe[\eta^2\text{-}C(SMe)_2SMe]$ for which there is substantial evidence.[10] This is followed by loss of CO and coordination of one of the carbene SMe groups to tungsten, thus forming an η^2-carbene.



(4)

Similar η^2-carbenes, $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$,[2] $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}SO_3CF_3$,[11] $\{Cp(CO)_2W[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}BF_4$,[8] and $\{(PPh_3)_2[CN(4\text{-}C_6H_4Me)](Cl)Os[\eta^2\text{-}C(4\text{-}C_6H_4Me)SMe]\}ClO_4$,[12] have been reported in the literature. Additional CO loss and C–S bond cleavage give the carbyne product **2**. There are no results that exclude either pathway a or b as the mechanism of these reactions. A mechanism involving elimination of RSSR (see eq 5), followed by oxidative addition of this species to the metal, is not possible since $[HB(pz)_3](CO)_2W{\equiv}CSMe$ does not react with MeSSMe over 24 h in refluxing THF nor does it react photolytically with MeSSMe or PhSSPh to give **2** (only slow decomposition occurs).

The SAr complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SAr)SMe]$[2] (**5**, Ar = Ph; **7**, Ar = $4\text{-}C_6H_4Me$) do not lose CO upon heating but quantitatively eliminate the disulfides ArSSMe (identified by ^1H NMR and mass spectroscopies) and form the known thiocarbyne complex $[HB(pz)_3](CO)_2W{\equiv}CSMe$[5] (eq 5).



(5)

5, Ar = Ph

7, Ar = $4\text{-}C_6H_4Me$

A mechanism involving thiolate radicals (ArS•) seems unlikely since no ArSSAr or MeSSMe is produced in the reaction. A more likely pathway is a concerted α-elimination of the disulfide. To our knowledge, no analogous α-eliminations of disulfides from organic thioketals $(R_2C(SR')_2)$ to generate carbenes $(R_2C{:})$ have been reported.

One might ask why the alkyl sulfide compounds (**1** and **3**) undergo RS migration (eq 2 and 3) while the aryl sulfide derivatives (**5** and **7**) eliminate disulfide (eq 5). If reactions 2 and 3 proceed by either mechanism a or b in Scheme II, the SR group that is not coordinated to the tungsten must become coordinated at some point. Since the aryl sulfide groups (SAr) are less nucleophilic and basic than the SMe and SEt groups, it seems that they will be less likely to coordinate to the metal and give products of the type in eq 2 and 3. Apparently the elimination of the disulfide in the aryl sulfide then is the favored reaction. The weaker nucleophilicity (or basicity) of the SAr groups is also seen in the lack of scrambling of the SMe and SAr groups in **5** or **7** to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SAr]$, whereas **3** does show scrambling of the SMe and SEt groups to give $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SEt]$ in less than 1 h at 25 °C.[2]

Photolytic Reactions of $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Nuc)SMe]$ Complexes. In contrast to their thermal reactions (eq 5), **5** and **7** under UV photolysis at room temperature, lose two CO ligands, undergo C–S cleavage, and undergo migration of the SAr group from the carbon to the tungsten to form the thiocarbynes

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Table II. Selected Bond Distances (Å)[a] and Angles (deg)[a] in $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (**2**)

W-C(1)	1.788 (7)	W-C(1)-S(1)	171.6 (5)	S(2)-W-N(2)	86.1 (2)
C(1)-S(1)	1.700 (7)	C(1)-S(1)-C(2)	103.2 (5)	S(2)-W-N(3)	163.2 (2)
S(1)-C(2)	1.82 (1)	W-S(2)-C(3)	110.7 (3)	S(2)-W-C(1)	90.6 (2)
W-S(2)	2.338 (2)	W-S(3)-C(4)	110.9 (3)	S(3)-W-C(1)	95.3 (2)
W-S(3)	2.343 (2)	N(1)-W-N(2)	82.0 (2)	S(3)-W-N(1)	80.4 (1)
S(2)-C(3)	1.81 (1)	N(1)-W-N(3)	81.1 (2)	S(3)-W-N(2)	160.5 (1)
S(3)-C(4)	1.831 (8)	N(2)-W-N(3)	77.2 (2)	S(3)-W-N(3)	91.8 (1)
W-N(1)	2.288 (5)	S(2)-W-S(3)	103.65 (7)	N(2)-W-C(1)	101.4 (2)
W-N(2)	2.222 (5)	S(2)-W-N(1)	94.9 (2)	N(3)-W-C(1)	94.5 (3)
W-N(3)	2.196 (6)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

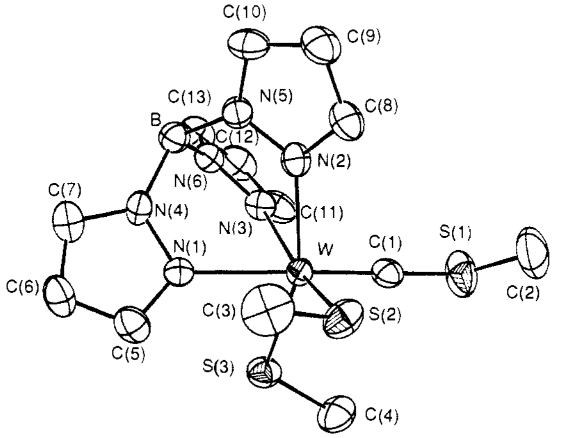
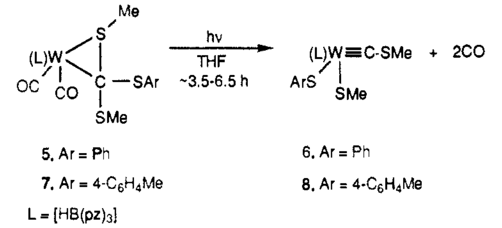


Figure 1. ORTEP plot of $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (**2**).

$[HB(pz)_3](ArS)(MeS)W{\equiv}CSMe$ (**6**, Ar = Ph, 73%; **8**, Ar = 4-C_6H_4Me, 52%) (eq 6). These reactions are similar to the

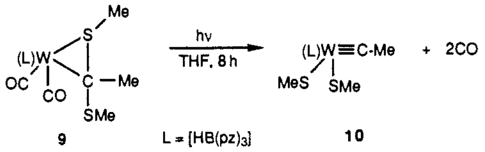


(6)

thermolysis reactions (eq 2 and 3) of **1** and **3**. As in those reactions, an uncharacterized insoluble green material (10–30%) is also formed. Complexes **6** and **8** were characterized by their elemental analyses and MS, ^1H NMR, and $^{13}C\{H\}$ NMR spectra. The ^1H NMR spectra of **6** and **8** show two different SMe groups (δ 3.69 and 2.51 ppm, δ 3.65 and 2.51 ppm, respectively). As in complexes **2** and **4**, the MeS group bound to tungsten occurs further downfield than the MeS group bound to carbon. Unlike complex **4**, **6** and **8** exist as only one isomer, the one in which an SMe and the SAr group are bound to tungsten. The $^{13}C\{H\}$ NMR spectra of **6** and **8** show carbyne carbon resonances at δ 271.1 and 270.8 ppm, respectively, which are similar to that of $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (**2**) at δ 268.3 ppm (vide supra).

While compounds **1** and **3** produce the carbyne complexes **2** and **4**, respectively, upon heating (eq 2 and 3), these reactions also occur under photolysis; however, the yields (**2**, 34%; **4**, 26%) are lower than those (**2**, 68%; **4**, 40%) obtained from the thermolysis reactions. In addition, a larger amount (30–40%) of the uncharacterized green product is obtained.

The methyl complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(Me)SMe]$ (**9**)[2] upon photolysis also undergoes loss of two CO ligands and transfer of the two MeS groups to the tungsten to give the methyl carbyne complex **10** in 78% yield (eq 7). It was somewhat



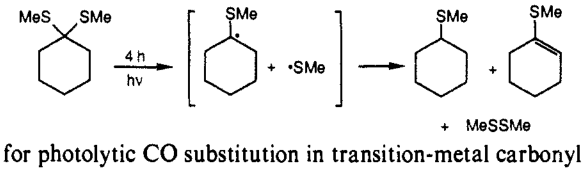
(7)

surprising that complex **9** did not undergo any type of thermolysis reaction (85 °C, CD_3NO_2, 2 h). The product of the photolytic reaction, $[HB(pz)_3](MeS)_2W{\equiv}CMe$ (**10**), was characterized by its elemental analysis and MS, ^1H NMR, and $^{13}C\{H\}$ NMR spectra. In the ^1H NMR spectrum of **10**, the two SMe groups exhibit a single resonance at δ 3.37 ppm, which is similar to that (δ 3.42 ppm) observed for the two SMe groups bound to tungsten in $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (**2**) (vide supra). The resonance at δ 4.38 ppm (J_{WH} = 9.3 Hz) is assigned to the Me group bound to the carbyne carbon. This is much further downfield than the resonance observed for the carbyne Me group in the 18-electron complex $[HB(pz)_3](CO)_2W{\equiv}CMe$ (δ 2.43 ppm).[4] However, similar downfield Me resonances have been reported for the alkylidyne complexes $(t\text{-}BuO)_3(py)W{\equiv}CMe$ (δ 3.89 ppm, J_{WH} = 8.1 Hz) and $(t\text{-}BuO)_3W{\equiv}CMe$ (δ 3.56 ppm, J_{WH} = 7.13 Hz).[6] The carbyne $^{13}C\{H\}$ resonance in **10** occurs at δ 303.9 ppm, which compares with the shift reported for the 18-electron complex $[HB(pz)_3](CO)_2W{\equiv}CMe$ (δ 295.2 ppm).[4] Thus, as in the thiocarbynes (**2**, **4**, **6**, and **8**), an increase in the oxidation state of tungsten changes the carbyne carbon chemical shift very little. This suggests that the carbyne carbon in **10** is more similar to the carbyne in the electron-rich $[HB(pz)_3](CO)_2W{\equiv}CMe$ than to the Schrock-type carbyne in $(t\text{-}BuO)_3W{\equiv}CMe$, in which the carbyne carbon shift occurs ~50 ppm further upfield at δ 254.3 ppm.[6]

Photolysis of the phosphine complexes $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(PR_3)SMe]\}SO_3CF_3$ (PR_3 = PMe_3, PEt_2H)[2] at 25 °C in THF for 3 h gives a mixture of products, one of which was identified by IR and ^1H NMR as the η^2-dithiocarbene $\{[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)SMe]\}SO_3CF_3$.[2] Under similar conditions, photolysis of the complex $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]$[2] also gives a mixture of uncharacterized products.

A possible mechanism for the photolytic reactions (eq 6 and 7) of **5**, **7**, and **9** could involve UV-promoted CO loss, followed by coordination of a second SR group to tungsten. This is basically the same as path a in Scheme II, one of the mechanisms proposed for the thermal reactions. Photolytic CO substitution is well-known in transition-metal carbonyl complexes.[13] King et al. have reported[14] UV photolytic CO substitution in $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ by $(Et_2N)PF_2$ to give $CpMo(CO)(\eta^3\text{-}C_3H_5)(PF_2NEt_2)$. Similarly, photolyzing $CpMo(CO)_2(NO)$ in the presence of PPh_3 produces $CpMo(CO)(NO)(PPh_3)$.[15]

Another possible mechanism could involve light-promoted homolytic C–S bond cleavage as the initial step. Berchtold and Kohrman have reported[16] the photolysis of a series of thioketal compounds that give products resulting from homolytic C–S bond cleavage. An example is shown in eq 8. On the basis of precedent



(8)

for photolytic CO substitution in transition-metal carbonyl com-

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Table III. Comparative Structural Data for Molybdenum and Tungsten Thiolate Complexes

complex	no. of electrons	M–S, Å	ref
$[HB(pz)_3](MeS)_2W{\equiv}CSMe$	16	2.338 (2) 2.343 (2)	this work
trans-$[Mo(S{-}n{-}Bu)_2(dppe)_2]$	16	2.361 (1)	24
$Mo(S{-}t{-}Bu)_2(CN{-}t{-}Bu)_2(PhC{\equiv}CPh)$	16	2.338 (3)	25
cis-$[Mo(S{-}t{-}Bu)_2(CN{-}t{-}Bu)_4]$	16	2.374 (3)	26
$CpMo(NO)(SPh)_2$	16	2.345 (1) 2.339 (1)	27
$[Na(18\text{-crown-}6)][W(CO)_5(SH)]$	18	2.567 (5)	28
$[NEt_4][W_2(CO)_{10}(\mu\text{-}SC_6Cl_5)]$	18	2.568 (4)	29
$W_2(CO)_8(\mu\text{-}S{-}t\text{-}Bu)_2{}^a$	18	2.480 (2)	30
$W_2(CO)_8(\mu\text{-}SMe)_2{}^a$	18	2.47 (1) 2.477 (6)	31
$[NEt_4]_2[W_2(CO)_8(\mu\text{-}SPh)_2]$	18	2.582 (2) 2.599 (2)	32
$[NEt_4]_2[Mo_2(CO)_8(\mu\text{-}SCH_2CO_2Et)_2]$	18	2.586 (1) 2.587 (1)	33
$Mo_2(CO)_6(\mu\text{-}SCH_2CO_2Et)_2(CH_3CN)_2{}^a$	18	2.455 (2) 2.467 (2)	33
$\{[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}OSO_2CF_3$	18	2.481 (6)	11

[a] This complex contains a M–M bond.

plexes, the mechanism shown in path a of Scheme II seems more likely. However, there are no results that unequivocally eliminate a mechanism involving homolytic C–S bond cleavage.

Structure of $[HB(pz)_3](MeS)_2W{\equiv}CSMe$ (2). Crystals of **2** suitable for X-ray analysis were grown from CD_2Cl_2 by layering with hexanes at −20 °C. The coordination geometry is pseudooctahedral as shown in Figure 1. Selected bond distances and angles are given in Table II. The W–C(1) bond distance (1.788 (7) Å) is within experimental error of the metal–carbyne carbon distances reported for the electron-rich carbyne complexes $Cp(PPh_3)(CO)W{\equiv}CSPh$ (1.807 (18) Å)[17] and $[HB(3,5\text{-}Me_2C_3HN_2)_3](CO)_2Mo{\equiv}CS(4\text{-}C_6H_4NO_2)$ (1.801 (4) Å).[18] It is interesting to note that these W–C distances are slightly longer than the W–C distance (1.759 (6) Å)[19] found in the Schrock-type carbyne $[(t\text{-}BuO)_3W{\equiv}CMe]_2$. The W–C–S angle (171.6 (5)°) is within the range (170–180°)[20] typical for terminal carbynes. The C(1)–S(1) distance (1.700 (7) Å) appears to be slightly longer than the C(sp)–S distance in $MeSC{\equiv}CSMe$ (1.671 (2) Å)[21] determined by electron diffraction in the gas phase; however, it is similar to the C(carbyne)–S distances in $Cp(PPh_3)(CO)W{\equiv}CSPh$ (1.716 (10) Å)[17] and in $[HB(3,5\text{-}Me_2C_3HN_2)_3](CO)_2Mo{\equiv}CS(4\text{-}C_6H_4NO_2)$ (1.712 (4) Å).[18] The S(1)–C(2) (1.81 (1) Å), S(2)–C(3) (1.81 (1) Å), and S(3)–C(4) (1.831 (8) Å) distances compare well with S–C(sp^3) single-bond distances obtained in microwave studies of MeSH (1.819 Å),[22] Me_2S (1.802 Å),[23] and $MeSC{\equiv}CSMe$ (1.806 (2) Å).[21] The W–S(2) (2.338 (2) Å) and W–S(3) (2.343 (2) Å) distances are similar to the Mo–S distances in *trans*-$[Mo(S{-}n\text{-}Bu)_2(dppe)_2]$ (2.361 (1) Å),[24] $Mo(S{-}t\text{-}Bu)_2(CN{-}t\text{-}Bu)_2(PhC{\equiv}CPh)$ (2.338 (3) Å),[25] and *cis*-$[Mo(S{-}t\text{-}Bu)_2(CN{-}t\text{-}Bu)_4]$ (2.374 (3) Å).[26] Since all of these complexes are formally 16-electron species, the sulfur atoms of the thiolate ligands could donate π-electron density to the metal, thus shortening the M–S distances. The M–S distances for a variety of molybdenum and tungsten 16- and 18-electron complexes are listed in Table III. The M–S distances in the 16-electron compounds are 0.1–0.2 Å shorter than in the 18-electron compounds, thus indicating some degree of sulfur donation of π-electron density into vacant metal d orbitals. Perhaps it is the electron-donating ability of the RS groups in the carbyne complexes (**2**, **4**, **6**, **8**, and **10**) reported in this paper that makes the carbyne ligands so similar in these formally 16-electron complexes and in the related 18-electron analogues, e.g., $[HB(pz)_3](CO)_2W{\equiv}CSMe$, $[HB(pz)_3](CO)_2W{\equiv}CMe$, and $[HB(3,5\text{-}Me_2C_3HN_2)_3](CO)_2Mo{\equiv}CS(4\text{-}C_6H_4NO_2)$.

Conclusion. Migration of an α-hydrogen from an alkylidene ligand to produce an alkylidyne has been reported in several reactions by Schrock and co-workers.[20] For example, when PMe_3 is added to $Cp(Cl)[(t\text{-}Bu)CH_2]Ta{=}CH(t\text{-}Bu)$, the carbyne complex $Cp(Cl)(Me_3P)_2Ta{\equiv}C(t\text{-}Bu)$ and neopentane are formed.[34] In this paper, we have shown that a novel α-thiolate (RS) migration occurs when solutions of the complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)(SR)SMe]$ are heated or irradiated. The resulting carbyne complexes $[HB(pz)_3](MeS)(RS)W{\equiv}CSMe$ (R = Me, Et, Ph, $4\text{-}C_6H_4Me$) contain carbyne ligands that are spectroscopically and crystallographically similar to those of related $L(CO)_2W{\equiv}CX$ (L = $HB(pz)_3$ or Cp; X = SR, Me) derivatives despite the difference in oxidation state and formal electron count (16 vs 18 electrons) of the metal.

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Registry No. 1, 123813-07-0; **2**, 123813-08-1; **3X,Y**, 123834-60-6; **3Z**, 123813-09-2; **4A**, 123834-61-7; **4B**, 123834-64-0; **5**, 123834-62-8; **6**, 123834-63-9; **7**, 123813-10-5; **8**, 123813-11-6; **9**, 123813-12-7; **10**, 123813-13-8.

Supplementary Material Available: Tables of positional and thermal parameters, additional bond angles and distances, and general displacement parameters (6 pages); table of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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