a 14:1 ratio of diastereomers **38a** to **38b**. The diastereomers were separated by preparative TLC (silica gel) using 1:50 ethyl acetate/hexanes as eluent in a 9:1 ratio. The minor isomer **38b** was obtained as a yellow oil (23.3 mg, 0.053 mmol, 8%). The major isomer **38a** was obtained as a yellow solid (203 mg, 0.457 mmol, 65%) which was crystalized from hexanes at 0 °C to give crystals suitable for X-ray structure determination. The total yield of diastereomers was 73%.

Each of the two pure diastereomers **38a** (19.9 mg, 0.044 mmol) and **38b** (21.4 mg, 0.048 mmol) were placed in a NMR tube and dissolved in $CDCl_3$. The solutions were deoxygenated by the freeze–thaw method (3×) and sealed under vacuum. Each of the two tubes was monitored by NMR daily, and after 10 days at room temperature each diastereomer epimerized to give a 1:1.65 ratio in favor of the minor isomer **38b**. After the 10 days the tubes were opened and TLC showed only the two diastereomer spots present. Thus no side products could be detected by TLC, and no side reactions had apparently occurred. After chromatography of the solution in each tube, the mass recovery of the 1:1.65 mixture of **38a** and **38b** starting from **38a** was 62% (12.0 mg, 0.027 mmol) and starting from **28b** the mass recovery was 77% (16.3 mg, 0.037 mmol).

38a: mp 71–72 °C; ^1H NMR ($CDCl_3$) δ 1.59 (d, 3 H), 3.94 (s, 3 H), 4.87 (q, 1 H), 7.10 (m, 3 H), 7.21 (m, 5 H), 7.37 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.16 (q), 55.28 (q), 61.61 (d), 125.72 (d), 127.26 (d), 127.52 (d), 128.49 (d), 128.68 (d), 131.88 (d), 132.19 (s), 139.20 (s), 139.30 (s), 217.48 (s), 223.14 (s), 256.78 (s); IR ($CHCl_3$) 2927 w, 2053 w, 1977 w, 1929 s, 1795 w, 1262 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 443 M^+ (4), 415 (2), 359 (18), 303 (23), 288 (6), 199 (13), 172 (17), 155 (7), 131 (41), 116 (100), 103 (21), 89 (13), 77 (24). Anal. Calcd for $C_{22}H_{17}O_6NCr$: C, 59.59; H, 3.84. Found: C, 59.65; H, 4.05.

38b: ^1H NMR ($CDCl_3$) δ 1.59 (d, 3 H), 3.03 (s, 3 H), 4.87 (q, 1 H), 7.12 (d, 2 H), 7.25 (m, 3 H), 7.50 (m, 3 H), 7.66 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.30 (q), 54.81 (q), 62.49 (d), 126.47 (d), 127.36 (d), 127.39 (d), 127.48 (d), 128.53 (d), 129.19 (d), 131.93 (s), 132.25 (s), 140.35 (s), 217.61 (s), 223.17 (s), 253.27 (s); IR ($CHCl_3$) 2937 w, 2054 w, 1978 w, 1929 s, 1801 w, 1248 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 443 M^+ (4), 415 (2), 359 (16), 303 (21), 288 (5), 199 (12), 172 (18), 155 (6), 131 (39), 116 (100), 103 (15), 89 (13), 77 (20).

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Registry No. **2**, 27436-93-7; **4**, 111847-85-9; **9**, 20540-69-6; **10**, 111847-86-0; **11**, 111847-87-1; **12**, 111847-88-2; **13**, 111847-89-3; **14**, 111847-90-6; **15**, 111847-91-7; **16**, 111847-92-8; **17**, 111847-93-9; **18**, 34491-84-4; **21**, 32370-44-8; **22**, 121809-08-3; **23**, 121809-06-1; **24**, 22852-50-2; **25**, 121809-42-5; **26**, 121809-43-6; **27**, 121809-44-7; **29**, 117497-95-7; **30**, 121809-11-8; **31**, 121809-45-8; **32**, 121809-46-9; **32a**, 121809-51-6; **33**, 121844-92-6; **34**, 121809-47-0; **35**, 121809-48-1; **36**, 121809-49-2; **37**, 121809-50-5; **38a**, 111847-94-0; **38b**, 111954-65-5; **39**, 77662-03-4; MeCN, 75-05-8; *n*-PrCN, 109-74-0; *i*-PrCN, 78-82-0; *t*-BuCN, 630-18-2; $PhCH_2CN$, 140-29-4; PhCN, 100-47-0; *p*-$MeOC_6H_4CN$, 874-90-8; $Ph^{13}COCl$, 52947-05-4; 2-cyanofuran, 617-90-3; 1-pentyne, 627-19-0.

Supplementary Material Available: X-ray crystallographic data for compound **32** including a VERSORT and tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (9 pages); a listing of F_o and F_c (7 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of the Cationic Thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$. Reactions of the Thiocarbene $[HC(pz)_3](CO)_2W[\eta^2\text{-}CHSMe]^{2+}$ with Nucleophiles

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The thiocarbonyl complex $[HC(pz)_3](CO)_2W(CS)$ (**1**) is prepared by reaction of *trans*-$IW(CO)_4(CS)^-$ with $HC(pz)_3$, tris(1-pyrazolyl)methane. The nucleophilic sulfur atom of the CS ligand is methylated with Me_3O^+ to give the thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (**2**). Reaction of the carbyne (**2**) with phosphorus nucleophiles (PR_3) gives the η^2-ketenyl derivatives $[HC(pz)_3](CO)(PR_3)W[C(O)CSMe]^+$. Methylation of $[HC(pz)_3](CO)(PMe_3)W[C(O)CSMe]^+$ at the ketenyl oxygen atom yields the acetylene complex $[HC(pz)_3](CO)(PMe_3)W(MeOC{\equiv}CSMe)^{2+}$. The title thiocarbene complex $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^{2+}$ (**3**) is prepared by protonation of the carbyne carbon atom in $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ with $HBF_4{\cdot}Et_2O$. Reactions of **3** with PR_3, SR^-, and $NaBH_4$ nucleophiles give the carbene adducts $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(L)SMe]^+$. These studies show that the reactivity of the cationic $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (**2**) is similar to that of electron-rich carbynes like $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ rather than to the reactivity of cationic Fischer carbynes.

Introduction

In recent years, the preparations and reactions of thiocarbene[1] and thiocarbyne[2] complexes have been studied extensively in this laboratory. The thiocarbyne complex $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$,[3] where $HB(pz)_3^-$ is the hydrotris(1-pyrazolyl)borato ligand, is similar in its reactivity to other electron-rich carbynes.[4] Thus, treating the

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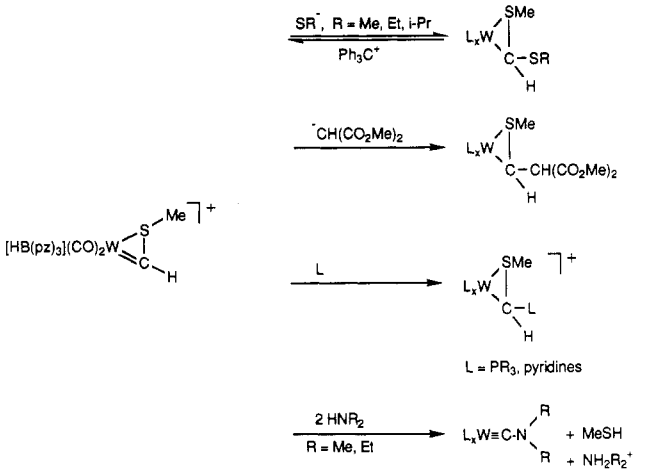
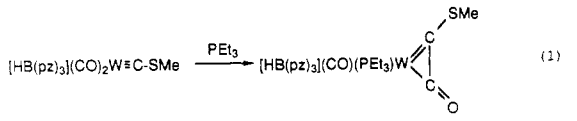
Scheme I

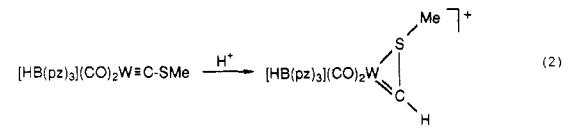


thiocarbyne with PEt_3 causes carbonylation of the carbyne to give the η^2-ketenyl compound (eq 1).[5] Electron-rich



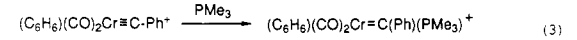
(1)

carbynes can also be protonated at the carbyne carbon. Roper and co-workers[6] reported the reaction of $Os[\equiv C(4\text{-}C_6H_4Me)](Cl)(CO)(PPh_3)_2$ with HCl that resulted in the formation of $Os[=CH(4\text{-}C_6H_4Me)](Cl)_2(CO)(PPh_3)_2$. Similarly, reactions of $Cp(CO)_2W{\equiv}CR$ (R = Me, tolyl) with HI give neutral carbenes $Cp(CO)_2IW{=}CHR$.[7] When $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ is treated with $HOSO_2CF_3$, it leads to the C- and S-coordinated thiocarbene complex (eq 2).[8] The η^2-thiocarbene $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ is attacked at the carbene carbon by a variety of nucleophiles (Scheme I).[5,9]



(2)

In contrast, Fischer-type cationic carbynes are electrophilic and are frequently observed to undergo attack at the carbyne carbon by a variety of nucleophiles.[10] The carbyne complex $(C_6H_6)(CO)_2Cr{\equiv}C(Ph)^+$ reacts with PMe_3 to produce the ylide (eq 3).[11] Other examples of



(3)

nucleophilic addition are the reactions of $Cp(CO)_2M{\equiv}C{-}Ph^+$ (M = Mn, Re) with F^-, Cl^-, Br^-, I^-, and $C_{10}H_7Se^-$ to give the corresponding neutral carbene compounds $Cp(CO)_2M[=C(Nu)(Ph)]$.[12] In this paper, we describe the preparation and reactions of the cationic carbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (an analogue of the neutral $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$), where $HC(pz)_3$ is the tris(1-pyrazolyl)methane ligand. One goal of this study was to determine whether $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ reacts like a cationic Fischer-type carbyne or like electron-rich carbynes such as $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$.

Table I. IR Data for the Complexes in CH_2Cl_2 Solvent

complex	IR ν_{CO}, cm^{-1}
$[HC(pz)_3](CO)_2W{-}C{\equiv}S$ (1)	1885 s, 1794 s[a]
$\{[HC(pz)_3](CO)_2W{\equiv}CSMe\}PF_6$ (2-PF_6)	1991 s, 1906 s
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]\}(BF_4)_2$ (3-2BF_4)	2079 s, 2010 s[b]
$\{[HC(pz)_3](CO)(PMe_3)W[C(O)CSMe]\}BF_4$ (4-BF_4)	1902 s, 1680 m
$\{[HC(pz)_3](CO)(PEt_3)W[C(O)CSMe]\}BF_4$ (5-BF_4)	1881 s, 1665 m
$\{[HC(pz)_3](CO)(PEt_2H)W[C(O)CSMe]\}BF_4$ (6-BF_4)	1905 s, 1680 m
$\{[HC(pz)_3](CO)(PMe_2Ph)W[C(O)CSMe]\}BF_4$ (7-BF_4)	1904 s, 1683 m
$\{[HC(pz)_3](CO)(PMe_3)W(\eta^2\text{-}MeOC{\equiv}CSMe)\}(BF_4)_2$ (8-2BF_4)	1970 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_3)SMe]\}(BF_4)_2$ (9-2BF_4)	1960 s, 1855 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(PMePh_2)SMe]\}(BF_4)_2$ (10-2BF_4)	1951 s, 1853 s
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(P(OMe)_3)SMe]\}(BF_4)_2$ (11-2BF_4)	1962 s, 1848 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH_2SMe]\}BF_4$ (12-BF_4)	1938 s, 1814 s[b]
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)SMe]\}BF_4$ (13-BF_4)	1938 s, 1827 vs[b]
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(S\text{-}t\text{-}Bu)SMe]\}BF_4$ (14-BF_4)	1937 s, 1828 s
$\{[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SPh)SMe]\}BF_4$ (15-BF_4)	1955 s, 1830 vs[b]

[a] Nujol mull; ν_{CS} 1178 cm^{-1}. [b] In $MeNO_2$.

Experimental Section

General Procedures. All reactions, filtrations, distillations, and recrystallizations were carried out under an atmosphere of prepurified N_2 using standard inert-atmosphere and Schlenk techniques[13,14] unless stated otherwise. Hexanes and CH_2Cl_2 were distilled from CaH_2. Diethyl ether was distilled from Na/benzophenone. Nitromethane was distilled from $CaCl_2$. Reagent grade acetone was stored over type 4A molecular sieves and degassed with N_2 before use. Reactions were carried out at room temperature unless stated otherwise. All solutions were air-sensitive, and the products slowly decomposed in solution even when under N_2. As solids, the products could be handled in air; however, they were best stored under an atmosphere of N_2 or Ar. The products were characterized by comparing their IR (Table I), ^1H NMR (Table II), and $^{13}C\{H\}$ NMR (Table III) spectra with those of their hydrotris(pyrazolyl)borato analogues.[5,9] In many cases, elemental analyses could not be obtained because the compounds partially decompose during recrystallization. Fast precipitation of the products by adding large amounts of Et_2O often trapped impurities in the solids.

Infrared spectra were obtained by using a Perkin-Elmer 681 spectrophotometer, and spectra were referenced to the 1601.0 cm^{-1} band of polystyrene. The ^1H and $^{13}C\{H\}$ NMR spectra were recorded on a Nicolet-NT-300 MHz spectrometer, using the deuterated solvent as the internal reference. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) mass spectra were

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Table II. ^1H NMR Data for the Complexes in CD_3CN Solvent at Room Temperature[a]

complex	[HC(pz)$_3$]	H3 of pz[b]	H5 of pz[b]	H4 of pz[b]	other
2-PF$_6$	8.89	8.28 (br)	8.02 (br)	6.58 (br)	2.79 (SMe)
3-2BF$_4$[c]	9.57	8.64 (m)	8.25 (d)	6.58 (m)	13.15 (WCH),[d] 2.57 (SMe)
4-BF$_4$	9.09	8.50 (d), 8.42 (d), 8.39 (d), 8.33 (d), 8.26 (d), 7.39 (d)		6.76 (t),[e] 6.64 (t),[e] 6.42 (t)[e]	2.73 (SMe), 1.36 (PMe$_3$)[f]
5-BF$_4$	9.30	8.51, 8.45, 8.37 (d), 8.30, 7.33 (d)		6.71, 6.62, 6.35	2.73 (SMe), 0.62 (Me),[g] 1.9–1.6 (m, P-CH$_2$)
6-BF$_4$	9.11	8.52 (d), 8.42 (d), 8.39 (d), 8.33 (d), 8.27 (d), 7.44 (d)		6.74 (t),[e] 6.63 (t),[e] 6.44 (t)[e]	5.11 (P-H),[h] 2.74 (SMe), 1.79 (m, PCH$_2$), 0.93 (Me),[i] 0.80 (Me)[i]
7-BF$_4$	9.03	8.37 (d), 8.33 (d), 8.20 (d), 7.83 (d), 7.71 (d)		6.60 (t),[e] 6.45 (t),[e] 6.38 (t)[e]	7.4–7.1 (m, Ph), 2.73 (SMe), 1.72 (d, J = 10.2, PMe), 1.69 (d, J = 9.8, PMe)
8-2BF$_4$	9.40	8.61 (d), 8.54 (d), 8.41 (d), 8.37 (d), 8.33 (d), 7.47 (d)		6.84 (t),[e] 6.71 (t),[e] 6.56 (t)[e]	4.51 (OMe), 2.43 (SMe), 1.48 (d, J_{PH} = 9.9, PMe)
9-2BF$_4$	9.78	8.65		6.81 (t)[e]	8.1–7.7 (m),[j] 5.85 (W-CH), 2.27 (SMe)
10-2BF$_4$	9.16	8.40		6.64	7.85 (m),[j] 5.08 (W-CH), 2.43 (PMe),[k] 1.83 (SMe)
11-2BF$_4$	9.11	8.36 (d)	8.31 (d)	6.62 (t),[e] 6.58 (t)[e]	4.39 (WCH),[l] 4.11 (POMe),[m] 1.85 (SMe)
12-BF$_4$	9.46	8.42 (d)	8.17	6.54 (t)[e]	4.09,[n] 3.59[n] (WCH$_2$), 2.46 (SMe)
13-BF$_4$ (A)	9.01	8.36 (d)	8.28 (d)	6.55 (t)[e]	5.05 (WCH), 2.50 (SMe), 2.37 (WSMe)
13-BF$_4$ (B)	9.11	not resolved	8.32 (d)	6.57 (t)[e]	5.56 (WCH), 2.60 (SMe), 1.78 (WSMe)
14-BF$_4$ (A)	8.96	8.44	8.27 (d)	6.54 (t)[e]	4.52 (WCH), 2.37 (WSMe), 1.40 (S-*t*-Bu)
14-BF$_4$ (B)	9.06	8.36	8.32 (d)	6.57 (t)[e]	5.35 (WCH), 1.88 (WSMe), 1.48 (S-*t*-Bu)
15-BF$_4$ (A)	8.94	8.41	8.28 (d)	6.56 (t)[e]	7.4–7.2 (m, Ph), 5.14 (WCH), 2.44 (WSMe)
15-BF$_4$ (B)	9.05	8.39	8.33 (d)	6.59 (t)[e]	7.6–7.4 (m, Ph), 5.79 (WCH), 1.87 (WSMe)

[a] Chemical shifts in δ and coupling constants in Hz. Resonances are singlets unless stated otherwise. [b] The hydrogen coupling constants for the pyrazolyl ligand are 0–3 Hz. [c] In CD_3NO_2. [d] J_{WH} = 19.3. [e] Due to overlapping d of d. [f] J_{PH} = 9.3. [g] dt, J = 7.6, J_{PH} = 15.2. [h] dt, J_{PH} = 335.8, J_{HH} = 5.5. [i] dt, J_{PH} = 17.1, J_{HH} = 7.6. [j] H5 of pz and Ph. [k] d, J_{PH} = 12.9. [l] d, J_{PH} = 2.6. [m] d, J_{PH} = 11.1. [n] d, J = 7.4.

Table III. ^{13}C NMR Data for the Complexes in CD_3NO_2 Solvent at Room Temperature

complex	CO	[HC(pz)$_3$]	C3 of pz	C5 of pz	C4 of pz	other
2-PF$_6$	223.0	68.5	149.9, 149.4	138.9	110.5	276.0 (W≡C), 26.5 (SMe)
3-2BF$_4$	210.2	78.2	149.4 (br)	136.4, 135.9, 135.8	110.1, 109.7, 108.9	223.3 (W=C), 26.1 (SMe)
4-BF$_4$[b]	222.6	77.3	148.9, 142.3	137.1, 130.9	110.6, 109.8, 108.1	217.2 (ketenyl C), 209.8 (ketenyl CO), 23.4 (SMe), 11.4 (d, J_{PC} = 53, PMe$_3$)
8-2BF$_4$	229.1	78.4	151.1, 150.0, 148.5	138.5, 137.1, 136.5	111.6, 110.9, 109.8	241.9 (MeO*C*≡), 205.3 (MeS*C*≡), 69.4 (OMe), 18.2 (SMe), 10.4 (d, J_{PC} = 56, PMe$_3$)
9-2BF$_4$[c]	241.7,[d] 216.7	78.0	152.4, 143.9	137.1, 136.6	110.9, 109.5, 108.8	40.4 (d, J_{PC} = 67, W-C), 25.2 (SMe)
10-2BF$_4$[e]	239.3,[f] 216.5	78.1	151.5	137.1	111.0	43.0 (d, J_{PC} = 58, W-C), 23.9 (SMe), 9.4 (PMe)[g]
11-2BF$_4$	236.2, 219.7	78.3	151.3	136.5, 136.2, 134.4	110.6, 109.6, 108.8	69.1 (d, J_{PC} = 38, W-C), 54.5 (d, J_{PC} = 20, POMe), 24.9 (SMe)
13-BF$_4$ (A)	231.3, 228.7	78.1	149.8	135.9	110.3	66.1 (W-C), 24.9, 21.5 (SMe)
13-BF$_4$ (B)	233.4, 220.7	78.3	150.8	136.2	110.5	71.2 (W-C), 26.5, 23.7 (SMe)

[a] Chemical shifts in δ and coupling constants in Hz. [b] In $(CD_3)_2CO$. [c] PPh_3: 135.4 (d, J_{PC} = 9), 131.6 (d, J_{PC} = 13), 122.7, 121.5. [d] J_{PC} = 8. [e] PPh_2: 136.5, 136.2, 134.0 (d, J_{PC} = 8), 133.5 (d, J_{PC} = 8), 131.5 (t, J_{PC} = 13), 125.0, 123.8, 122.7, 121.5. [f] d, J_{PC} = 5. [g] d, J_{PC} = 62.

obtained by using a Kratos MS-50 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Conductivity measurements were made by using a Markson 4402 conductivity meter and dip cell.

The compounds $Bu_4N[IW(CO)_4(CS)]$[15] and NaSR[9] were prepared by using previously described procedures. The ligand $HC(pz)_3$ was purchased from Columbia Organic Chemicals. All other chemicals were used as received from commercial sources.

[HC(pz)$_3$](CO)$_2$W(CS) (1). A solution of $Bu_4N[IW(CO)_4(CS)]$ (3.43 g, 4.84 mmol) in acetone (100 mL) was cooled to 0 °C. Silver tetrafluoroborate (0.941 g, 4.83 mmol) was then added and the mixture stirred for 1 h. The resulting orange solution was filtered under vacuum by using a coarse Schlenk frit containing Celite (2 × 7 cm) into a flask containing a solution of $HC(pz)_3$ (1.04 g, 4.85 mmol) in acetone (20 mL). Refluxing for 5 h caused a gold precipitate to form. The solution was then cooled to room temperature and the precipitate collected by suction filtration and washed with acetone (30 mL). Yield: 1.78 g (74%). This complex was insoluble in all organic solvents tried (hexanes, Et_2O, THF, CH_2Cl_2, acetone, MeCN, $MeNO_2$, DMSO) and could not be purified.

{[HC(pz)$_3$](CO)$_2$W≡C—SMe}PF$_6$ (2-PF$_6$). A CH_2Cl_2 (25 mL) suspension of 1 (0.304 g, 0.610 mmol) and $[Me_3O]PF_6$ (0.126 g, 0.611 mmol) was stirred at room temperature for 2 h, giving a brown solution. The solution was filtered, and hexanes (40 mL) were added to precipitate the orange product (0.305 g, 76%). Anal. Calcd for $C_{14}H_{13}F_6N_6O_2PSW$: C, 25.55; H, 1.99; N, 12.77; S, 4.87. Found: C, 25.49; H, 2.29; N, 12.65; S, 4.82. MS (FAB): m/e 513 (parent cation, M^+), 457 (M^+ – 2CO). Molar conductivity ($MeNO_2$): Λ_M = 89.5 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[16] The analogous tetrafluoroborate salt 2-BF$_4$ was synthesized from a CH_2Cl_2 (100 mL) suspension of 1 (2.12 g, 4.26 mmol) and $[Me_3O]BF_4$ (0.630 g, 4.26 mmol). After 15 h, the brown solution was filtered, and hexanes were added to the filtrate, thus precipitating the orange product powder (2.33 g, 91%). The IR and ^1H NMR spectra of 2-BF$_4$ and 2-PF$_6$ are identical.

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]}(BF$_4$)$_2$ (3-2BF$_4$). A solution of 2-BF$_4$ (0.100 g, 0.167 mmol) in $MeNO_2$ (10 mL) was treated with $HBF_4{\cdot}Et_2O$ (27.0 μL, 0.183 mmol). The solution turns from orange to purple in ca. 5 min. The complex 3-2BF$_4$ was not isolated (it tended to be a sticky oily solid, which was difficult to handle) but used in situ for further reactions.

{[HC(pz)$_3$](CO)(PMe$_3$)W[C(O)CSMe]}BF$_4$ (4-BF$_4$). A solution of 2-BF$_4$ (0.200 g, 0.334 mmol) in CH_2Cl_2 (15 ml) was treated with PMe_3 (36.0 μL, 0.353 mmol), which caused the solution to turn from orange to red. The solution was stirred for 30 min, and then Et_2O (100 mL) was added to precipitate the pale red powder product (0.212 g, 94%). Anal. Calcd for $C_{17}H_{22}BF_4N_6O_2PSW$: C, 30.20; H, 3.28. Found: C, 29.77; H, 3.49. MS (FAB): m/e 589 (parent cation, M^+), 561 (M^+ – CO), 513 (M^+ – PMe_3). Molar conductivity ($MeNO_2$): Λ_M = 95.0 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[16]

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{[HC(pz)$_3$](CO)(PR$_3$)W[C(O)CSMe]}BF$_4$ (PR$_3$ = PEt$_3$, 5-BF$_4$; PR$_3$ = PEt$_2$H, 6-BF$_4$; PR$_3$ = PMe$_2$Ph, 7-BF$_4$). Using a procedure similar to the one above, the ketenyl complexes **5**-BF$_4$, **6**-BF$_4$, and **7**-BF$_4$ were isolated in 61–68% yield. These complexes were characterized by their IR (Table I) and ^{1}H NMR (Table II) spectra.

{[HC(pz)$_3$](CO)(PMe$_3$)W(η^2-MeOC≡CSMe)}(BF$_4$)$_2$ (8-2BF$_4$). A solution of **4**-BF$_4$ (0.058 g, 0.086 mmol) in CH_2Cl_2 (20 mL) was treated with [Me$_3$O]BF$_4$ (0.013 g, 0.088 mmol). The mixture was stirred at room temperature for 18 h. The product precipitated from solution as a sticky solid. The solvent was removed in vacuo, and the residue was washed with CH_2Cl_2 (2 × 5 mL). Yield: 0.032 g (48%). MS (FAB): *m/e* 623 (parent dication + F$^-$). Even after repeated recrystallizations from acetone/Et$_2$O the product contained small amounts of impurities; therefore, a good elemental analysis could not be obtained.

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(PPh$_3$)SMe]}(BF$_4$)$_2$ (9-2BF$_4$). A solution of **3**-2BF$_4$ (0.254 mmol) in $MeNO_2$ (20 mL) was treated with PPh_3 (0.0666 g, 0.254 mmol). The solution was stirred at room temperature for 1 h. The solvent was then removed in vacuo and the residue extracted with CH_2Cl_2 (10 mL). Filtration, followed by addition of hexanes (80 mL) to the CH_2Cl_2 solution, precipitated the product as a pale red powder (0.167 g, 70%). Anal. Calcd for $C_{32}H_{29}B_2F_8N_6O_2PSW\cdot CH_2Cl_2$: C, 38.29; H, 3.02; N, 8.12. Found: C, 38.67; H, 3.44; N, 8.49. MS (FAB): *m/e* 863 (parent dication + BF$_4^-$), 795 (parent dication + F$^-$). Molar conductivity ($MeNO_2$): Λ_M = 164 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (2:1 electrolyte).[16]

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(PMePh$_2$)SMe]}(BF$_4$)$_2$ (10-2BF$_4$). Using the same procedure as above, **3**-2BF$_4$ (0.208 mmol) in $MeNO_2$ (20 mL), when treated with PPh_2Me (39 μL, 0.21 mmol), yielded **10**-2BF$_4$ (red powder, 0.0878 g, 48%). Anal. Calcd for $C_{27}H_{27}B_2F_8N_6O_2PSW$: C, 36.42; H, 3.06; N, 9.44. Found: C, 36.38; H, 3.56; N, 9.15. MS (FAB): *m/e* 801 (parent dication + BF$_4^-$), 733 (parent dication + F$^-$). Molar conductivity ($MeNO_2$): Λ_M = 163 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (2:1 electrolyte).[16]

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(P(OMe)$_3$)SMe]}(BF$_4$)$_2$ (11-2BF$_4$). A solution of **3**-2BF$_4$ (0.21 mmol) in $MeNO_2$ (15 mL) was treated with P(OMe)$_3$ (25 μL, 0.21 mmol). The solution was stirred at room temperature for 1 h. The solvent was then removed *in vacuo* and the residue extracted with CH_2Cl_2 (10 mL). Filtration, followed by addition of hexanes (75 mL) to the CH_2Cl_2 solution, precipitated the product as a red powder (0.094 g, 55%). This product was characterized by its IR, ^{1}H NMR, and ^{13}C{H} NMR spectra.

{[HC(pz)$_3$](CO)$_2$W[η^2-CH$_2$SMe]}(BF$_4$) (12-BF$_4$). Treatment of a solution of **3**-2BF$_4$ (0.338 mmol) in $MeNO_2$ (15 mL) with a solution of $NaBH_4$ (0.0250 g, 0.676 mmol) in H_2O (1 mL) gave an orange-brown solution after 1 h. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2 (20 mL). Filtration of the CH_2Cl_2 extract through Celite, followed by addition of hexanes (100 mL), precipitated the product as an orange powder (0.106 g, 52%). Anal. Calcd for $C_{14}H_{15}BF_4N_6O_2SW$: C, 27.93; H, 2.51; N, 13.96. Found: C, 27.78; H, 2.77; N, 13.97. MS (FAB): *m/e* 515 (parent cation). Molar conductivity ($MeNO_2$): Λ_M = 79 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[16]

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(SMe)SMe]}(BF$_4$) (13-BF$_4$). A solution of **3**-2BF$_4$ (0.502 mmol) in $MeNO_2$ (20 mL) was treated with NaSMe (0.0704 g, 1.00 mmol). The mixture was stirred at room temperature for 1 h. The solvent was then removed *in vacuo* and the residue extracted with CH_2Cl_2 (20 mL). Filtration of the CH_2Cl_2 extract through Celite was followed by addition of hexanes (100 mL). This precipitated the product as an orange powder (0.199 g, 61%). MS (FAB): *m/e* 561 (parent cation, M$^+$), 533 (M$^+$ – CO). Molar conductivity ($MeNO_2$): Λ_M = 80 Ω^{-1} cm^2 mol^{-1} at 10^{-3} M (1:1 electrolyte).[16]

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(S-*t*-Bu)SMe]}(BF$_4$) (14-BF$_4$). Using the procedure above, **3**-2BF$_4$ (0.167 mmol) in $MeNO_2$ (10 mL) when treated with Na(S-*t*-Bu) (0.0375 g, 0.334 mmol) yielded **14**-BF$_4$ (orange powder, 0.062 g, 54%). MS (FAB): *m/e* 603 (parent cation, M$^+$), 575 (M$^+$ – CO), 547 (M$^+$ – 2CO).

{[HC(pz)$_3$](CO)$_2$W[η^2-CH(SPh)SMe]}(BF$_4$) (15-BF$_4$). In a similar preparation, **3**-2BF$_4$ (0.169 mmol) in $MeNO_2$ (10 mL) when treated with NaSPh (0.0447 g, 0.338 mmol) yielded **15**-BF$_4$ (orange powder, 0.050 g, 41%). MS (FAB): *m/e* 623 (parent cation, M$^+$), 595 (M$^+$ – CO), 567 (M$^+$ – 2CO).

Results and Discussion

Preparation of [HC(pz)$_3$](CO)$_2$W(CS) (1). Refluxing a solution of HC(pz)$_3$ and Bu$_4$N[IW(CO)$_4$(CS)][15] in acetone produces a gold precipitate, which is formulated as [HC(pz)$_3$](CO)$_2$W(CS) (**1**). Its insolubility in a range of solvents precluded purification and characterization by NMR. The mass spectrum was also not very informative, showing only peaks due to HC(pz)$_3$. The IR spectrum (Nujol mull) shows two CO bands (1885 s, 1794 s cm^{-1}) and one terminal CS band (1178 s cm^{-1}), which are similar to those reported for Bu$_4$N{[HB(pz)$_3$](CO)$_2$W(CS)} (ν_{CO} 1884 s, 1787 s cm^{-1}; νCS 1149 s cm^{-1}) and Bu$_4$N[Cp(CO)$_2$W(CS)] (ν_{CO} 1890 s, 1804 vs cm^{-1}; ν_{CS} not reported).[17] It is interesting to note that on the basis of the CO band energies, HC(pz)$_3$ is a slightly more basic ligand than Cp$^-$. Because of the similarity of its preparation and its IR spectrum to Bu$_4$N{[HB(pz)$_3$](CO)$_2$W(CS)}, the gold powder is formulated as [HC(pz)$_3$](CO)$_2$W(CS) (**1**).

Synthesis of [HC(pz)$_3$](CO)$_2$W≡C—SMe$^+$ (2). The sulfur atom in electron-rich tungsten thiocarbonyl complexes is known to act as a nucleophile toward a variety of electrophiles.[17,18] When a suspension of the thiocarbonyl **1** in CH_2Cl_2 is treated with Me_3O^+, it gives the S-alkylated product **2** (eq 4). Consistent with the com-

$$\underset{\mathbf{1}}{[HC(pz)_3](CO)_2W(CS)} \xrightarrow[CH_2Cl_2,\ 18\ h]{Me_3O^+} \underset{\mathbf{2}}{[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+} \quad (4)$$

plex's formulation as a thiocarbyne is the lack of a ν_{CS} absorption and the presence of two ν_{CO} absorptions (Table I). Its ^{13}C NMR spectrum (Table III) exhibits a resonance at δ 276.0 ppm which is assigned to the carbyne carbon. This is similar to those of other tungsten thiocarbyne complexes: [HB(pz)$_3$](CO)$_2$W≡C—SMe (δ 264.4 ppm)[3] and Cp(CO)$_2$W≡C—S[2,4-C$_6$H$_3$(NO$_2$)$_2$] (δ 261.7 ppm).[3] Complex **2** was further characterized by its FAB mass spectrum which showed the parent cation (M$^+$, *m/e* 513) and M$^+$ – 2CO (*m/e* 457). In addition, its molar conductivity in $MeNO_2$ (Λ_M = 89.5 Ω^{-1} cm^2 mol^{-1}) is consistent with a 1:1 electrolyte.[16]

Reactions of [HC(pz)$_3$](CO)$_2$W≡C—SMe$^+$ with Phosphorus Donors. Terminal carbyne ligands in cationic transition-metal complexes are reported to undergo attack by phosphines (e.g., eq 3) at the carbyne carbon.[19] However, in an electron-rich complex such as [HB(pz)$_3$](CO)$_2$W≡C—SMe, where the carbyne ligand is not susceptible to nucleophilic attack, PEt_3 causes carbonylation of the carbyne to give the η^2-ketenyl compound (eq 1).[5] Similarly, we observed that the thiocarbyne **2** reacts with a variety of phosphines to give the η^2-ketenyl complexes [HC(pz)$_3$](CO)(PR$_3$)W[C(O)CSMe]$^+$ (eq 5). The

$$\underset{\mathbf{2}}{[HC(pz)_3](CO)_2W{\equiv}C\text{-}SMe^+} \xrightarrow[CH_2Cl_2,\ 1\ h]{PR_3} \underset{\mathbf{4\text{-}7}}{[HC(pz)_3](CO)(PR_3)W\langle C(=O)CSMe\rangle^+} \quad (5)$$

PR$_3$ = PMe$_3$ (**4**), PEt$_3$ (**5**), PEt$_2$H (**6**), PMe$_2$Ph (**7**)

characteristic ν_{CO} of the ketenyl CO was observed (Table I) between 1685 and 1660 cm^{-1}.[4b,20] The chemical shifts

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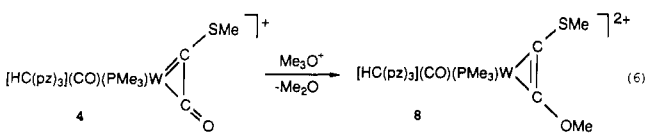
in the ^{1}H NMR (Table II) and ^{13}C NMR (Table III) spectra were assigned by comparison with assignments for the complex [HB(pz)$_3$](CO)(PEt$_3$)W[C(O)CSMe].[5]

In addition to complexes **4–7**, a ketenyl complex is also observed by solution IR (ν_{CO} 1915, 1685 cm^{-1}) when the thiocarbyne **2** is reacted with 1 equiv of P(OMe)$_3$ for 8 h at room temperature. In contrast, an equilibrium between **2** and the ketenyl complex is observed when **2** is treated with 1 equiv of P(O-*i*-Pr)$_3$ or PPh$_2$Me at 25 °C in CH_2Cl_2 (IR for the ketenyl complexes, ν_{CO} 1911, 1680, and 1905, 1682 cm^{-1}, respectively). Using 5 equiv of the phosphite or phosphine shifts the equilibrium almost completely toward the ketenyl complex. By isolating the product and then redissolving it in CD_2Cl_2 in the absence of excess phosphorus ligand, it is observed by ^{1}H NMR that the equilibrium shifts back toward the thiocarbyne **2** (~90%) within 2–3 h. The phosphine donors PCy$_3$, PPh$_3$, P(OPh)$_3$, and dppe do not react with **2** even when present in a 10-fold excess. Thus the tendency of **2** to undergo reaction 5 decreases with the P-donor ligand in the order: PMe$_3$ > PEt$_2$H > PEt$_3$ ~ PMe$_2$Ph > P(OMe)$_3$ > P(O-*i*-Pr)$_3$ ~ PPh$_2$Me ≫ PCy$_3$ ~ PPh$_3$ ~ P(OPh)$_3$. This trend suggests that the formation of the ketenyl complex is influenced by both the electronic and steric properties of the phosphorus nucleophile. Although P(OPh)$_3$ has a smaller cone angle (128°)[21] than PPh$_2$Me (136°),[21] it is not basic enough to form the ketenyl complex. Tricyclohexylphosphine (PCy$_3$) is more basic than any of the phosphines which do form the ketenyl complex; however, its large cone angle (170°)[21] inhibits formation of the ketenyl complex.

Kreissl and co-workers report[4a,b] the reaction of Cp(CO)$_2$M≡CR (M = Mo, W; R = Me, tolyl) with 1 equiv of PMe$_3$ produces η^2-ketenyl compounds. Addition of another equivalent of PMe$_3$ to the η^2-ketenyl compound or addition of 2 equiv of PMe$_3$ directly to the carbyne gives η^1-ketenyl compounds. All of the ketenyl complexes formed from the thiocarbyne **2** exist only as the η^2-form even in the presence of a large excess of the phosphorus donor. This is attributed to the crowded environment around the metal caused by the bulky HC(pz)$_3$ ligand, which apparently prohibits the second phosphorus ligand access to tungsten. No reaction was observed between the thiocarbyne and SMe$^-$, CN$^-$, I$^-$, or NH$_2$Me at room temperature or in refluxing CH_2Cl_2.

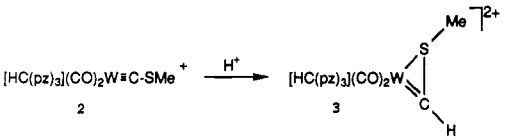
Reaction of [HC(pz)$_3$](CO)(PMe$_3$)W[C(O)CSMe]$^+$ (4) with [Me$_3$O]BF$_4$. Kreissl et al.[22] reported the methylation and addition of XCl$_3$ (X = B, Al, or In) to the ketenyl CO in Cp(CO)(PMe$_3$)W[C(O)CR] (R = Me, 4-C$_6$H$_4$CH$_3$) to give Cp(CO)(PMe$_3$)W(RC≡COMe)$^+$ and Cp(CO)(PMe$_3$)W(RC≡COXCl$_3$). A similar carbyne-to-alkyne transformation was observed in the methylation reaction of [HB(pz)$_3$](CO)(PEt$_3$)W[C(O)CSMe] to give [HB(pz)$_3$](CO)(PEt$_3$)W(MeOC≡SMe)$^+$.[5] Likewise, the ketenyl complex **4** reacts with Me$_3$O$^+$ to produce the violet complex [HC(pz)$_3$](CO)(PMe$_3$)W(MeOC≡CSMe)$^{2+}$ (**8**) (eq 6). The IR, ^{1}H NMR, and ^{13}C NMR data for **8** are similar



(6)

to those for the related complexes [HB(pz)$_3$](CO)(PEt$_3$)W(MeOC≡CSMe)$^+$[5] and Cp(CO)(PMe$_3$)W(MeOC≡CMe)$^+$.[22] The low-field positions of the alkyne carbon atoms (δ 241.9, 205.3 ppm) in the ^{13}C NMR spectrum of **8** are comparable with shifts reported for [HB(pz)$_3$](CO)(PEt$_3$)W(MeOC≡CSMe)$^+$ (δ 231.1, 198.0 ppm),[5] Cp(CO)(PMe$_3$)W(MeOC≡CMe)$^+$ (δ 227.1, 197.7 ppm)[22] and (CO)(η^2-S$_2$CNEt$_2$)$_2$W(HC≡CH) (δ 206.6, 207.1 ppm),[23] where the acetylene moiety is proposed to be a four-electron donor. The highest mass +1 ion in the FAB mass spectrum of **8** occurs at *m/e* 623 and corresponds to the parent dication +F$^-$, and it has the correct isotope pattern. In our experience in using FAB for dications, we never see the parent dication at M^{2+}/2; instead +1 ions with *m/e* values equal to the parent dication plus one anion (i.e., for BF$_4^-$ salts the anion is either BF$_4^-$ or F$^-$) are observed.

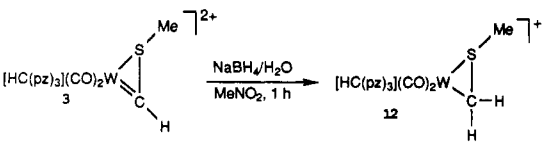
Preparation of {[HC(pz$_3$)](CO)$_2$W[η^2-CH(SMe)]}$^{2+}$ (3). Whereas the carbyne carbon in electron-rich complexes is not susceptibile to nucleophilic attack, it can be protonated. Protonation (eq 2) of the carbyne carbon in [HB(pz)$_3$](CO)$_2$W≡C—SMe leads to the C- and S-coordinated thiocarbene complex [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$, whose structure was established by an X-ray diffraction study.[8] Similarly, the addition of an equimolar amount of HBF$_4$·Et$_2$O to a MeNO$_2$ solution of the thiocarbyne **2** produces an immediate color change from orange to violet concomitant with the production of the thiocarbene [HC(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^{2+}$ (eq 7). The



(7)

thiocarbene **3** was characterized by comparison of its IR, ^{1}H NMR, and ^{13}C NMR to the related complex [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$.[5] The IR bands of **3** (ν_{CO} 2079 s, 2010 s cm^{-1}) are shifted to higher energy as compared with **2** (ν_{CO} 1991 s, 1906 s cm^{-1}), reflecting the increasing positive charge on the metal. The ^{1}H NMR of **3** exhibits a new resonance at δ 13.15 ppm, indicating that the proton is attached to the carbene carbon and not the metal, analogous to the carbene hydrogen in [HB(pz)$_3$](CO)$_2$W-[η^2-CH(SMe)]$^+$ (δ 12.78 ppm).[5] The ^{13}C NMR shows the characteristic downfield shift for the carbene carbon (δ 223.3 ppm), which is similar to the shifts reported for other thiocarbenes, [HB(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^+$ (δ 227.8 ppm),[8] [HB(pz)$_3$](CO)$_2$W[η^2-C(SMe)SMe]$^+$ (δ 230.5 ppm),[24] and Cp(CO)$_2$W[η^2-C(4-C$_6$H$_4$Me)SMe]$^+$ (δ 233.1 ppm).[25] Because attempts to precipitate **2** resulted in a sticky oily solid, it was not isolated and its subsequent reactions were performed *in situ*.

Reaction of [HC(pz)$_3$](CO)$_2$W[η^2-CH(SMe)]$^{2+}$ (3) with NaBH$_4$. The carbene carbon atom in transition-metal carbene complexes is frequently the site of attack by nucleophiles.[26] Similarly the thiocarbene **3**, when treated with NaBH$_4$, forms the hydride adduct **12** in 48% yield (eq 8). No other carbonyl-containing products are



(8)

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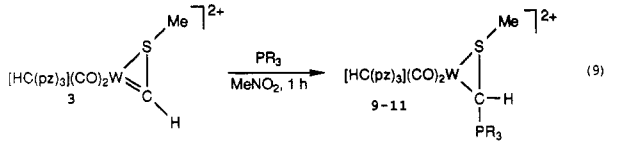
observed by IR during the reaction. The low yield is due to decomposition during the reaction and workup. Upon addition of the hydride, the carbonyl bands in the IR shift to lower energy (ν_{CO} 2079 s, 2010 s cm^{-1} to 1938 s, 1814 s cm^{-1}), which is consistent with decreasing the positive charge on the metal. The ^1H NMR spectrum exhibits two doublets at δ 4.09 and 3.59 ppm, J = 7.4 Hz, which are assigned to the methylene protons (CH_2). Nonequivalence of the two methylene protons is also observed in the analogous complexes $Cp(CO)_2W[\eta^2\text{-}CH_2SMe]$[27] ($\delta$ 2.64, 2.05 ppm; J = 6.0 Hz) and $(CO)_4Mn[\eta^2\text{-}CH_2SMe]$ (δ 2.35, 1.85; J = 5.5 Hz)[27] at 25 °C.

Reactions of $[HC(pz)_3](CO)_2W[CH(SMe)]^{2+}$ (3) with Phosphorus Donors. Phosphorus donors are among the nucleophiles that attack the carbene carbon in transition-metal carbene complexes. Examples include the reactions of $Cp(CO)_2Fe[CH(SMe)]^+$ [1d] and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^+$ [9] with phosphines and phosphites to give the adducts $Cp(CO)_2Fe[CH(L)SMe]^+$ (L = PPh_2Me, PPh_3, PPh_2Cl, PPh_2H, $P(OPh)_3$) and $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(L)SMe]^+$ (L = PPh_3, PEt_3, $P(OMe)_3$, PPh_2H). Similarly, $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(SMe)]^{2+}$ reacts at room temperature with phosphorus donors to give the adducts $[HC(pz)_3](CO)_2W[\eta^2\text{-}CH(L)SMe]^{2+}$ (eq 9).



(9)

PR_3 = PPh_3 (9), PPh_2Me (10), $P(OMe)_3$ (11)

The ^1H NMR resonance of the methine hydrogen in **9** and **10** occurs as a singlet. The absence of coupling to the phosphorus atom may be due to a Karplus-like dependence of $^2J_{PH}$ on the angle between the hydrogen and phosphorus atoms;[28] the coupling constant $^2J_{PH}$ ranges from 0 to 26 Hz depending on the angle between them. In contrast to the phosphine adducts, the methine hydrogen in the $P(OMe)_3$ adduct **11** does occur as a doublet (J_{PH} = 2.6 Hz) due to coupling with the phosphorus atom. In the ^{13}C NMR spectrum of **9**, **10**, and **11**, the methine carbon is coupled to the phosphorus atom giving a doublet. A carbene adduct was also observed by IR and ^1H NMR to form when a $MeNO_2$ solution of **3** was treated with PCl_3 at room temperature; however, attempts to isolate the adduct resulted in its decomposition.

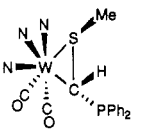
Reactions of the Thiocarbene (3) with Thiolates (SR^-). Complex **3** reacts readily with thiolates (SR^-) at room temperature to give the corresponding adducts **13–15** (eq 10). The low yields (40–65%) are due to decomposition during the reaction and workup. No other carbonyl-containing complexes were observed by IR during the reaction. Although the products were too unstable to obtain analytically pure, they were characterized by comparison of their IR, ^1H NMR, and ^{13}C NMR spectra to those of the analogous complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(SR)SMe]$.[9]

(10)

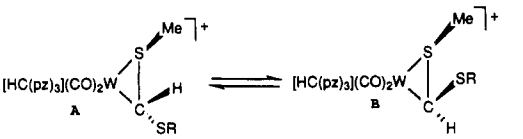
R = Me (13), *t*-Bu (14), Ph (15)

The ^1H and ^{13}C NMR spectra of **13** and the ^1H NMR spectra of **14** and **15** show two sets of resonances, suggesting the presence of two isomers, designated A and B. The IR spectra of **13**, **14**, and **15** show only one set of CO bands. However, the bands are very broad, suggesting the possible presence of $[HB(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_2)SMe]$, isomers. The relative ratio of the major isomer A to the minor isomer B for **13** is 8:1 at 25 °C and was obtained by integration of the methine (CH) protons. This ratio was not observed to change with time at 25 °C. The relative ratio A:B for **14** is initially 2:1 at 25 °C. After 4 h, the ratio changes to 6:1. Equilibrium was not observed due to some decomposition of the complex. However, the change in the isomer ratio is not the result of the decomposition of one isomer since the signal intensity decreases only slightly during the isomerization process. Similarly, the relative ratio A:B for **15** also changed from 1:12 to 5:1 after 9 days to 25 °C.

Attempts to grow single crystals of **13**, **14**, or **15** were unsuccessful. In all three compounds, the thermodynamically favored isomer is A. Presumably the structure of A is the same as that of $[Hb(pz)_3](CO)_2W[\eta^2\text{-}CH(PPh_2)SMe]$, which was determined by X-ray analysis.[5]



The structure shows that the Me group on the sulfur coordinated to tungsten is oriented above the WCS ring toward the pyrazolyl groups, whereas the PPh_2 group is positioned below the WCS ring toward the carbonyls and away from the bulky pyrazolyl groups. On the basis of this structure, there are three possible sets of isomers for **13–15** (assuming that the stereochemistry of the pyrazolyl and carbonyl groups around tungsten does not change). One set of two isomers would result if attack of the nucleophile at the carbene carbon atom of **3** occurs from above and below the WCS ring (eq 11). In reactions of phosphorus donors with the thiocarbene **3** (eq 9) only one isomer is formed. If A and B are the isomers shown in eq 11, the lack of isomers in **9–11** may be due to the larger size of the phosphorus ligand, causing it to attack the carbene carbon only from the side opposite the bulky $HC(pz)_3$ group. In support of isomers A and B (eq 11) is the lack of isomers in the hydride adduct **12** which does not have a stereogenic ring carbon atom.



(11)

As noted above, the isomers of **14** and **15** interconvert; one might consider three possible mechanisms for this isomerization. One, involving dissociation of SR^- to give **3** which can re-add SR^- on the same or opposite side, is unlikely. This conclusion is based on the observation (by ^1H NMR) that there is no exchange of the SPh^- group in **15** with excess added Na^+SMe^- in 0.5 mL of CD_2Cl_2 over a period of 36 h at 25 °C; also, no other reactions are observed.

An alternate isomerization process involves dissociation of the coordinated SMe to give a 16-electron species in which the W–C bond freely rotates (eq 12). Closure of the

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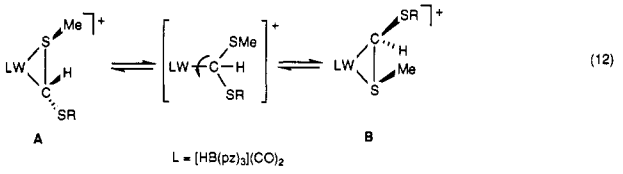
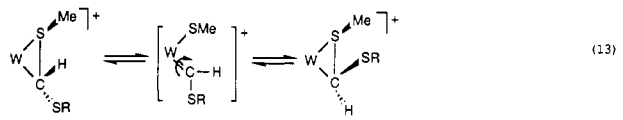
ring either gives back A or isomer B.



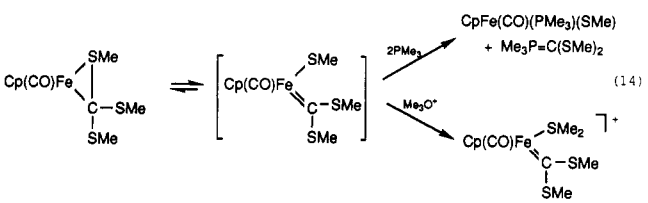
(12)

Another possible isomerization process involves cleavage of the C–S bond in the η^2-CH(SR)SMe 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 (eq 13). A related iron analogue, $Cp(CO)Fe[\eta^2\text{-}C(SMe)_2SMe]$,



(13)

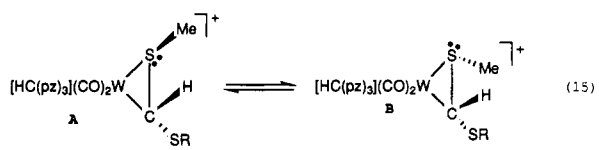
which is not a carbene itself, appears to convert to and react as a carbene (eq 14).[29] Presumably, the presence



(14)

of two thiolate groups on the ring carbon in the iron complex helps to stabilize the carbene form. Fast rotation around the iron–carbene bond gives one resonance in the ^{1}H NMR spectrum at 25 °C for the two SMe groups not bound to iron. In complex **15**, the isomerization process was observed to be slow (vide supra). Possibly the hydrogen atom on the ring carbon destabilizes the carbene form, thus causing the rate of C–S bond cleavage to be slower than in the iron complex.

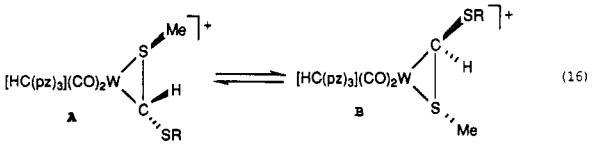
A different set of isomers for **13**, **14**, and **15** could result from the stereogenic center at the coordinated sulfur atom (eq 15). A mechanism for this isomerization is inversion



(15)

at the coordinated sulfur. Inversion at pyramidal sulfur has been observed in (2,5-dihydrothiophene)$W(CO)_5$ and [PhCH(Me)SMe]$W(CO)_5$ (T_c = −49 and −76.5 °C, respectively).[30] If the isomers of **13–15** result from inversion at sulfur, one would expect that similar isomers would be seen for the hydride adduct **12**, for which only one isomer is observed in the ^{1}H NMR spectrum at 25 °C. Similarly, only one isomer is observed in the ^{1}H NMR spectrum at 25 °C for the analogous complexes $[HB(pz)_3](CO)_2W[\eta^2\text{-}C(SMe)_2SMe]$[24] and $Cp(CO)_2M[\eta^2\text{-}CH_2(SMe)]$ (M = Mo, W),[27] where there are equivalent groups on the ring carbon.

A third set of isomers could be derived by changing the configurations at both the ring carbon and sulfur atoms (eq 16). Rotation of the whole η^2-CH(SR)SMe unit around an axis from the tungsten to the center of the η^2-C–S bond would interconvert isomers A and B, assuming inversion at sulfur is slow. A similar three-membered MCS ring



(16)

rotation was proposed by Mintz and co-workers for a series of zirconium complexes $Cp_2ClZr[\eta^2\text{-}CH(R)SR']$[31] which show one set of resonances in the ^{1}H NMR spectrum at room temperature and two sets at −80 °C. As in the case of sulfur inversion, if rotation of the η^2-CH(SR)SMe unit is occurring in **13–15**, one might also expect to see two isomers for the hydride adduct **12**, for which only one isomer is observed (vide supra).

Of the three possible sets of A, B isomers, it seems that isomers of the type in eq 11 are most likely, but there are no data that unequivocally eliminate the isomers in eq 15 and 16.

The thiocarbene **3** reacts with a number of amines (NEt_3, 4-$NC_5H_4(NMe_2)$, 4-NC_5H_4Me, NEt_2H, and NH_2CMe_3) in $MeNO_2$ at 25 °C. The IR spectra of the reaction solutions show two ν_{CO} bands similar in position to those observed for the PR_3, SR^-, and H^- adducts. However, attempts to isolate the products only gave free $HC(pz)_3$ ligand and free amine.

Conclusions

The reactivity of the pyrazolylmethane thiocarbyne $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ (**2**) resembles that of electron-rich carbynes like $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ and $Cp(CO)_2W{\equiv}C{-}Ph$[32] rather than that of the cationic Fischer carbynes like $[Cp(CO)_2Re{\equiv}C{-}Ph]BCl_4$.[11] This is completely reasonable if one compares the ν(CO) absorptions of the complexes:

	ν_{CO}, cm^{-1}
$Cp(CO)_2Re{\equiv}C{-}Ph^+$	2098, 2038
$Cp(CO)_2W{\equiv}C{-}Ph$	1992, 1922
$Cp(CO)_2W{\equiv}C{-}SMe$	1985, 1911
$[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$	1991, 1906
$[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$	1980, 1888

The much higher ν(CO) values for the Re complex than any of W complexes indicate that Re and its associated carbyne ligand are substantially more positive than the same units in the W complexes; thus, it is not surprising that the Re–carbyne complex reacts by nucleophilic attack on the carbyne carbon and the W–carbyne complexes do not. The most important factor that causes this difference in reactivity is the +1 higher oxidation state of the Re. It is important to note that although the carbynes $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ and $Cp(CO)_2Re{\equiv}C{-}Ph^+$ are both cationic, the IR clearly indicates that there is much more electron density at the metal in the tungsten complex than in the rhenium.

Among the W complexes, the ν(CO) values are similar but decrease slightly with the tridentate ligand in the order: $Cp^- \geq HC(pz)_3 > HB(pz)_3^-$. This trend suggests that the tungsten in $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ is slightly more positive than in $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$. This difference shows up in the relative rates of phosphine attack on the two complexes (eq 1 and 5). Thus, under the same conditions, the $HC(pz)_3$ complex reacts approximately 10 times faster with PEt_3 than $[HB(pz)_3](CO)_2W{\equiv}C{-}SMe$ does. In addition, $[HC(pz)_3](CO)_2W{\equiv}C{-}SMe^+$ reacts with less basic phosphorus do-

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(32) Fischer, E. O.; Lindner, T. L.; Huttner, G.; Friedrich, P.; Kreissl, F. R.; Besenhard, J. O. *Chem. Ber.* **1977**, *110*, 3397.

nors (i.e., phosphites) which do not react with [HB(pz)$_3$](CO)$_2$W≡C—SMe.

Acknowledgment. We appreciate the support of this work by the National Science Foundation (Grant No. CHE-8719744).

Registry No. 1, 121866-67-9; 2-BF$_4$, 121866-90-8; 2-PF$_6$, 121866-69-1; 3-2BF$_4$, 121866-71-5; 4-BF$_4$, 121866-73-7; 5-BF$_4$, 121866-75-9; 6-BF$_4$, 121866-77-1; 7-BF$_4$, 121866-81-7; 9-2BF$_4$, 121866-96-4; 10-2BF$_4$, 121866-98-6; 11-2BF$_4$, 121867-00-3; 12-BF$_4$, 121866-83-9; 13-BF$_4$, 121866-85-1; 14-BF$_4$, 121866-87-3; 15-BF$_4$, 121866-89-5; Bu$_4$N[IW(CO)$_4$(CS)], 56031-00-6; {[HC(pz)$_3$(CO)P(O-*i*-Pr)$_3$W[C(O)CSMe]}BF$_4$, 121866-92-0; {[HC(pz)$_3$](CO)(PPh$_2$Me)W[C(O)CSMe]}BF$_4$, 121866-94-2.

Mesitylindium(III) Compounds. X-ray Crystal Structures of InMes$_3$, [NMe$_4$][InClMes$_3$], and [InClMes$_2$]$_2$

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The reaction of InCl$_3$ with 3 equiv of MesMgBr (Mes = mesityl, 2,4,6-Me$_3$C$_6$H$_2$) yields InMes$_3$ (**1**). The molecular structure of **1** consists of discrete monomeric units in which the three mesityl groups are crystallographically inequivalent. The possibility of an agostic C–H—In interaction is discussed. The addition of 1 equiv of Me$_4$NCl to **1** results in the formation of [Me$_4$N][InClMes$_3$] (**2**). The compounds InClMes$_2$ (**3**) and InCl$_2$Mes (**4**) were prepared from InMes$_3$ by means of exchange reactions with InCl$_3$. The reaction of InMes$_3$ with 2 equiv of Me$_3$NHCl yields InCl$_2$Mes(NMe$_3$) (**5**), which slowly redistributes to give a mixture of **4** and InCl$_2$Mes(NMe$_3$)$_2$ (**6**). The structures of **1**, **2**, and **3** have been confirmed by X-ray crystallography. InMe$_3$: monoclinic $P2_1/n$, a = 8.704 (2) Å, b = 21.888 (6) Å, c = 12.492 (4) Å, β = 95.06 (2)°, Z = 4, observed data 2542, R = 0.0348, R_w = 0.0391. [Me$_4$N][InClMes$_3$]·MeCN: monoclinic $P2_1/n$, a = 16.938 (5) Å, b = 9.154 (5) Å, c = 20.895 (5) Å, β = 94.49 (2)°, Z = 4, observed data 3400, R = 0.0783, R_w = 0.1040. [InClMes$_2$]$_2$: monoclinic, $P2_1/a$, a = 9.113 (2) Å, b = 16.083 (4) Å, c = 12.360 (3) Å, β = 109.90 (2)°, Z = 2, observed data 1824, R = 0.0449, R_w = 0.0658.

Introduction

Not withstanding the renewed interest in the chemistry of the heavier group 13 (Ölander numbering) elements aluminum, gallium, and indium, the relative importance of steric and electronic effects in determining the structure and reactivity of their compounds is still poorly understood. A study of phosphine adducts of trimethylaluminum showed that the steric bulk of the phosphine predominates in defining the geometry around both aluminum and phosphorus,[1,2] while the presence of π-bonding between aluminum and oxygen accounts for the short Al–O distances and large Al–O–C angles in monomeric four-coordinate aluminum alkoxide compounds.[3]

The use of sterically demanding ligands should increase the steric control over the structure of group 13 compounds. The compounds AlMes$_3$[4a] and GaMes$_3$[4b] (Mes = mesityl; 2,4,6-Me$_3$C$_6$H$_2$) were found to be monomeric, and their low Lewis acidities were proposed to be due to the steric bulk of the mesityl ligands. We report here that electronic effects, however, appear to influence the structure of the indium analogue InMes$_3$, whereas steric factors dominate the structures of [Me$_4$N][InClMes$_3$] and [InClMes$_2$]$_2$.

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Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in InMes$_3$

In–C(11)	2.170 (5)	In–C(21)	2.163 (5)
In–C(31)	2.170 (5)		
C(11)–In–C(21)	116.8 (2)	C(11)–In–C(31)	122.3 (2)
C(21)–In–C(31)	120.8 (2)	In–C(11)–C(12)	120.8 (3)
In–C(11)–C(16)	120.8 (3)	In–C(21)–C(22)	121.6 (3)
In–C(21)–C(26)	120.2 (4)	In–C(31)–C(32)	120.6 (4)
In–C(31)–C(36)	120.6 (3)		

Table II. Selected Intramolecular Nonbonded Distances (Å) in InMes$_3$

In···C(17)	3.340 (5)	In···C(19)	3.348 (5)
In···C(27)	3.338 (6)	In···C(29)	3.297 (6)
In···C(37)	3.363 (6)	In···C(39)	3.363 (6)
C(17)···C(27)	4.825 (8)	C(17)···C(37)	5.278 (8)
C(17)···C(39)	3.810 (8)	C(19)···C(27)	4.850 (8)
C(19)···C(29)	3.983 (8)	C(19)···C(39)	5.057 (9)
C(27)···C(37)	4.182 (9)	C(29)···C(37)	4.528 (8)
C(29)···C(39)	5.096 (8)		

Results and Discussion

The interaction of InCl$_3$ with 3 equiv of MesMgBr in Et$_2$O allows the formation of InMes$_3$ (**1**), the structure of which has been confirmed by X-ray crystallography (see below). Compound **1** is a colorless, crystalline solid that can be handled in air for several minutes without appreciable decomposition. InMes$_3$ is soluble in both Et$_2$O and THF, but it does not form a stable (i.e. isolable) adduct with either donor.

The molecular structure of InMes$_3$ is shown in Figure 1; selected bond lengths and angles are given in Table I.

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