possible to determine if the remaining donor atoms are coordinated to Zn(II) in 1 M D_2SO_4. No structural assignment could be made from the data available.

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Registry No. Cu(D-Pyala)$_2$·2H_2O, 77846-71-0; Zn(D-Pyala)$_2$, 60478-55-9; Ni(aib-D-Pyala), 77827-46-4; Cu(aib-D-Pyala), 77827-47-5; Zn(aib-D-Pyala), 77827-48-6; Ni(D-Pyala)$_2$, 77827-49-7; acetone, 67-64-1.

Supplementary Material Available: Tables listing observed and calculated structure factors for structure A and structure B and bond distances and angles for both structures (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Ames Laboratory–USDOE,[1]
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Preparation of Some Dithiocarbene Complexes, $W(CO)_5[C(SR)_2]$, and Their Reactions with Nucleophiles

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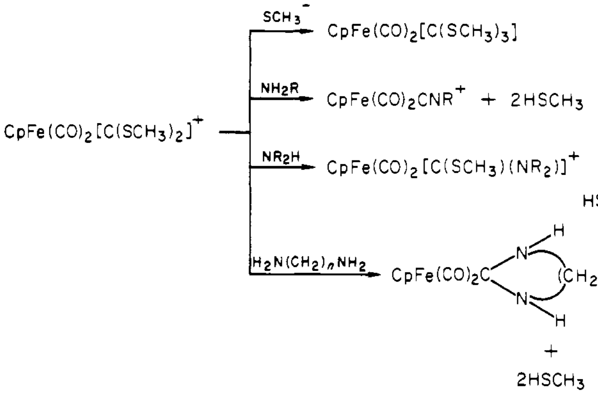
The reaction of $W(CO)_5CS$ with ^-SR (R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, or t-C_4H_9) followed by alkylation of the resulting dithioester anion, $W(CO)_5[C({=}S)SR]^-$, by R′I (R′ = CH_3 or C_2H_5) produces [bis(alkylthio)carbene]tungsten complexes, $W(CO)_5[C(SR)(SR')]$, in good yield. The substituted tetracarbonyl[bis(methylthio)carbene]tungsten complexes *cis*-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$ and *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ are prepared by an analogous route using *cis*-$W(CO)_4L(CS)$, where L = $P(OCH_3)_3$ or $P(OPh)_3$. (Cyclic dithiocarbene)tungsten complexes may be prepared in a similar manner from $W(CO)_5CS$, $NaS(CH_2)_nSH$ (n = 2, 3, 4), and CH_3I to give $W(CO)_5\overline{CS(CH_2)_nS}$. The carbene complex $W(CO)_5\{C(SCH_3)[SFe(CO)_2Cp]\}$ (Cp = $\eta^5C_5H_5$) is prepared by the reaction of $W(CO)_5[C({=}S)(SCH_3)]^-$ with $CpFe(CO)_2(THF)^+$. Isocyanide complexes, $W(CO)_5CN{-}R$, are formed when $W(CO)_5[C(SCH_3)_2]$ reacts with primary amines, RNH_2, where R = CH_3, $(CH_2)_2CH_3$, CH_2Ph, C_6H_{11}, and $(CH_2)_2N(CH_3)_2$, or the diamine $NH_2(CH_2)_3NH_2$. When *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ is reacted with NH_2CH_2Ph and $NH_2(CH_2)_3NH_2$, isocyanide complexes are also formed. The reaction of $W(CO)_5[C(SCH_3)_2]$ with secondary amines $NH(CH_3)_2$, $H\overline{N(CH_2)_2OCH_2CH_2}$, or $H\overline{N(CH_2)_4CH_2}$ yields (aminothiocarbene)tungsten complexes, $W(CO)_5[C(SCH_3)NR_2]$. The compound $[N(C_2H_5)_4{}^+][W(CO)_5CN^-]$ was formed from the reaction of $W(CO)_5[C(SCH_3)_2]$ with $[N(C_2H_5)_4{}^+][N_3{}^-]$.

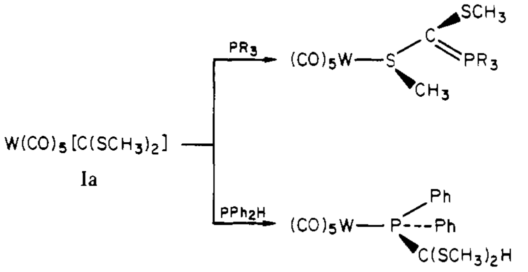
Introduction

It has been only recently that transition-metal complexes containing the dithiocarbene ligand $[C(SR)_2]$ have been isolated,[2-11] and only a few studies of their reactivity have been reported.[8,10,11] McCormick and Angelici[8,12] found that $CpFe(CO)_2[C(SCH_3)_2]^+$ (Cp = η^5-C_5H_5) reacts with mercaptides and amines according to eq 1.



(1)

Recently, we reported the preparation of $W(CO)_5[C(SCH_3)_2]$[11] and its remarkable reactions with secondary and tertiary phosphines (eq 2).



(2)

We would now like to report the preparations of other [bis(alkylthio)carbene]pentacarbonyltungsten complexes, $W(CO)_5[C(SR)_2]$, and their reactions with amines and other nucleophiles.

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Experimental Section

General Information. The thiocarbonyl and carbene complexes $W(CO)_5CS$,[13] $W(CO)_4(CS)P(OCH_3)_3$,[14] $W(CO)_4(CS)P(OPh)_3$,[14] $W(CO)_5[C(SCH_3)_2]$,[11] and $[CpFe(CO)_2(THF)^+][BF_4^-]$[15] were prepared as previously reported. A mixture[13] of $W(CO)_5CS$ ranging from 41 to 78% in $W(CO)_6$ was used in the preparations of the carbene products unless otherwise stated. The NaH used was a 57% oil dispersion. The grams and millimoles of $W(CO)_5CS$ and NaH listed below are the amounts of these compounds actually used. Tetrahydrofuran (THF) was distilled from sodium benzophenone under N_2 immediately before use. Hexanes were stored over 4A molecular sieves. All other chemicals were reagent grade and were used without further purification. All reactions were performed under prepurified N_2 with use of standard inert-atmosphere techniques.

Synthesis of Complexes. $W(CO)_5[C(SC_2H_5)(SCH_3)]$ (IIb). A solution of $NaSC_2H_5$ was made by adding HSC_2H_5 (0.037 g, 0.63 mmol) to a suspension of NaH (0.016 g, 0.65 mmol) in 15 mL of THF. The solution was allowed to stir for 45 min at room temperature. Then $W(CO)_5CS$[13] (0.15 g, 0.41 mmol) in 10 mL of THF was added to the $NaSC_2H_5$ solution. The resulting orange solution was allowed to stir for 5 min. To this solution was added CH_3I (0.089 g, 0.63 mmol), and the mixture was allowed to stir for an additional 10 min. At the end of this time the reaction mixture was evaporated to dryness under an N_2 stream. The remaining solid was extracted with hexanes, and the extracts were evaporated to dryness under reduced pressure. The resulting solid was taken up in CS_2 and placed on a 2 × 36 cm Florisil column. Slow elution with CS_2 led to the separation of two bands. The first eluted band was yellow and was identified as a mixture of $W(CO)_6$ and $W(CO)_5CS$. The second band was orange-red and contained $W(CO)_5[C(SC_2H_5)(SCH_3)]$. The $W(CO)_5[C(SC_2H_5)(SCH_3)]$ solution was evaporated to dryness under reduced pressure, and the tungsten dithiocarbene was recrystallized from pentane at −20 °C. A 47% (0.088 g, 0.20 mmol) yield of orange flakes was obtained; mp 56–61 °C. Anal. Calcd for $C_9H_8O_5S_2W$: C, 24.34; H, 1.82. Found: C, 24.52; H, 1.90.

$W(CO)_5[C(S\text{-}i\text{-}C_3H_7)(SCH_3)]$ (IIc). Following the method of preparation for IIb, we used the following reactants and quantities: NaH (0.015 g, 0.64 mmol), $HSCH(CH_3)_2$ (0.049 g, 0.64 mmol), $W(CO)_5CS$ (0.16 g, 0.44 mmol), and CH_3I (0.091 g, 0.64 mmol). $W(CO)_5[C(SCH(CH_3)_2)(SCH_3)]$ was obtained as orange crystals in 59% (0.12 g, 0.26 mmol) yield; mp 78–81 °C. Anal. Calcd for $C_{10}H_{10}O_5S_2W$: C, 26.21; H, 2.20. Found: C, 26.24; H, 2.16.

$W(CO)_5[C(S\text{-}n\text{-}C_4H_9)(SCH_3)]$ (IId). This complex was prepared by the same method as was used for IIb, using NaH (0.015 g, 0.64 mmol), $HS(CH_2)_3CH_3$ (0.067 g, 0.64 mmol), $W(CO)_5CS$ (0.16 g, 0.44 mmol), and CH_3I (0.091 g, 0.64 mmol). The product IId was obtained as a red oil.

$W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$ (IIe). This complex was prepared by a route analogous to that used for IIb. Starting with NaH (0.016 g, 0.67 mmol), $HSC(CH_3)_3$ (0.060 g, 0.67 mmol), $W(CO)_5CS$ (0.16 g, 0.44 mmol), and CH_3I (0.095 g, 0.67 mmol), we obtained 0.072 g (0.15 mmol, 45%) of orange needles of $W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$, mp 113–118 °C. Anal. Calcd for $C_{11}H_{12}O_5S_2W$: C, 27.98; H, 2.52. Found: C, 28.44; H, 2.79.

$W(CO)_5[C(SC_2H_5)_2]$ (IIf). A route similar to the one used for the preparation of IIb was used to make this complex. Starting with NaH (0.015 g, 0.64 mmol), HSC_2H_5 (0.037 g, 0.64 mmol), $W(CO)_5CS$ (0.15 g, 0.41 mmol), and C_2H_5I (0.094 g, 0.64 mmol), we obtained 0.036 g (0.079 mmol, 19%) of $W(CO)_5[C(SC_2H_5)_2]$ as red crystals, mp 58–63 °C. This complex displayed IR and ^1H NMR spectra similar to those reported earlier.[2a]

***cis*-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$ (IIg).** A solution of $NaSCH_3$ was made by bubbling $HSCH_3$ through a suspension of NaH (0.0055 g, 0.23 mmol) in 20 mL of THF for 30 min. The solution was allowed to stir for an additional 30 min. Then a mixture of *cis*- and *trans*-$W(CO)_4(CS)[P(OCH_3)_3]$[14] (0.17 g, 0.37 mmol) in 15 mL of THF was added. The yellow reaction mixture turned orange after being stirred approximately 15 min. At this time CH_3I (0.034 g, 0.24 mmol) was added; the solution was stirred for 15 min and then evaporated to dryness. The residue was extracted with hexanes, and the hexane extracts were evaporated to dryness. The residue was taken up in CS_2 and placed on a 2 × 36 cm Florisil column. Elution with CS_2 led to the separation of two bands. A yellow band identified as *cis*- and *trans*-$W(CO)_4[P(OCH_3)_3]CS$ was eluted first. The second band was orange-red and contained 0.042 g (0.076 mmol, 21%) of *cis*-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$, as a red oil.

***cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ (IIh).** The same method used to prepare IIg was used for this complex. Starting with NaH (0.048 g, 2.0 mmol), $HSCH_3$ gas, *cis*- and *trans*-$W(CO)_4[P(OPh)_3]CS$[14] (0.920 g, 1.41 mmol), and CH_3I (0.296 g, 2.09 mmol), we obtained 0.24 g (0.32 mmol, 42%) of *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ as red crystals, mp 106–108 °C. Anal. Calcd for $C_{25}H_{21}O_7PS_2W$: C, 42.15; H, 2.98. Found: C, 42.08; H, 3.05.

$W(CO)_5\overline{CS(CH_2)_2S}$ (IIIa). This complex was prepared in the same manner as was used for IIb, by the reaction of NaH (0.016 g, 0.66 mmol), $HS(CH_2)_2SH$ (0.62 g, 0.66 mmol), $W(CO)_5CS$ (0.15 g, 0.63 mmol), and CH_3I (0.093 g, 0.66 mmol) in THF. After crystallization from hexanes 0.14 g (0.33 mmol, 51%) of $W(CO)_5\overline{CS(CH_2)_2S}$ was obtained as red crystals, mp 110–115 °C. Anal. Calcd for $C_8H_4O_5S_2W$: C, 22.44; H, 0.94. Found: C, 22.73; H, 1.03.

$W(CO)_5\overline{CS(CH_2)_3S}$ (IIIb). This complex was prepared from NaH (0.016 g, 0.68 mmol), $HS(CH_2)_3SH$ (0.073 g, 0.68 mmol), $W(CO)_5CS$ (0.24 g, 0.64 mmol), and CH_3I (0.096 g, 0.67 mmol) by a procedure analogous to the one used for IIb. The product $W(CO)_5\overline{CS(CH_2)_3S}$ (0.088 g, 0.20 mmol, 31%) was obtained as orange-red crystals, mp 113–128 °C. Anal. Calcd for $C_9H_6O_5S_2W$: C, 24.45; H, 1.37. Found: C, 24.42; H, 1.38.

$W(CO)_5\overline{CS(CH_2)_4S}$ (IIIc). The method used for the preparation of IIb was followed for this complex using NaH (0.014, 0.57 mmol), $HS(CH_2)_4SH$ (0.070 g, 0.57 mmol), $W(CO)_5CS$ (0.20 g, 0.55 mmol), and CH_3I (0.082 g, 0.58 mmol). Orange flakes of $W(CO)_5\overline{CS(CH_2)_4S}$ (0.10 g, 0.22 mmol, 41%) were obtained; mp 112–116 °C. Anal. Calcd for $C_{10}H_8O_5S_2W$: C, 26.33; H, 1.77. Found: C, 26.33; H, 1.76.

$W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$ (IV). To a solution of $Na[W(CO)_5C(S)(SCH_3)^-]$, prepared from NaH (0.024 g, 1.0 mmol), CH_3SH, and pure $W(CO)_5CS$ (0.38 g, 1.0 mmol) in 25 mL of THF, was added a solution of $[CpFe(CO)_2(THF)][BF_4]$[15] (0.34 g, 1.0 mmol) in 5 mL of CH_2Cl_2. After the solution was stirred for 30 min, it was evaporated to dryness. The residue was extracted with hexanes. The remaining solid was taken up in a minimum amount of CH_2Cl_2 and filtered. The product IV was crystallized by adding hexanes to the CH_2Cl_2 filtrate and cooling to −20 °C. A yield of 40% (0.23 g, 40 mmol) of IV was obtained; mp 154 °C dec. Anal. Calcd for $C_{14}H_8FeO_7S_2W$: C, 28.40; H, 1.36. Found: C, 28.08; H, 1.43.

Reactions of $W(CO)_5[C(SCH_3)_2]$. With H_2NCH_3. Methylamine was bubbled through a solution of IIa (0.102 g, 0.238 mmol) in 20 mL of hexane for 30 s. During this time the solution faded from orange-red to pale yellow. The reaction mixture was allowed to stir for 1 h. The solution was then evaporated to a white solid. A 70% yield of $W(CO)_5CNCH_3$ (Va) was obtained after crystallization from hexanes at −20 °C. This complex displayed the same IR and ^1H NMR spectra as were reported earlier.[16]

With $H_2N(CH_2)_2CH_3$. To a solution of IIa (0.077 g, 0.25 mmol) in 25 mL of hexanes was added $NH_2(CH_2)_2CH_3$ (0.39 g, 6.6 mmol). The solution was allowed to stir for 12 h. The resulting pale yellow solution was evaporated to dryness under reduced pressure. A yield of 0.083 g (84%) of $W(CO)_5CN(CH_2)_2CH_3$ (Vb) was collected after crystallization from hexanes at −20 °C, mp 88–93 °C.

With H_2NCH_2Ph. Benzylamine (0.073 g, 0.68 mmol) was added to a solution of IIa (0.12 g, 0.29 mmol) in 10 mL of hexanes. The solution was allowed to stir for 10 min. The orange reaction mixture was reduced to dryness, and a pale yellow solid remained. The solid residue was crystallized from hexanes at −20 °C, yielding 0.099 g (77%) of pale yellow $W(CO)_5CNCH_2Ph$ (Vc), mp 79–82 °C. Anal. Calcd for $C_{13}H_7NO_5W$: C, 35.40; H, 1.60. Found: C, 35.66; H, 1.63.

With $H_2NC_6H_{11}$. This complex was prepared by the same method as was used for Vc, starting with IIa (0.12 g, 0.27 mmol) and $NH_2C_6H_{11}$ (0.12 g, 1.2 mmol). After crystallization a 52% yield of $W(CO)_5CNC_6H_{11}$ (Vd) was isolated as white crystals, mp 92–95 °C.

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This complex displayed the same IR spectrum as was reported previously.[16]

With $H_2N(CH_2)_2N(CH_3)_2$. Following the method of preparation for Vb, we used IIa (0.10 g, 0.24 mmol) and $NH_2(CH_2)_2N(CH_3)_2$ (0.043 g, 0.48 mmol) in 20 mL of hexane. Crystallization from hexanes at −20 °C yielded 0.062 g (61%) of $W(CO)_5CN(CH_2)_2N(CH_3)_2$ (Ve), mp 36–37 °C. Anal. Calcd for $C_{10}H_{10}N_2O_5W$: C, 28.45; H, 2.39. Found: C, 28.22; H, 2.36.

With $HN(CH_3)_2$. The complex $W(CO)_5[C(SCH_3)N(CH_3)_2]$ (VIa) was prepared by a method similar to that used for Va. Dimethylamine was bubbled through a solution of IIa (0.10 g, 0.24 mmol) in 20 mL of hexanes for 10 min. Crystallization from hexanes yielded 0.075 g (74%) of $W(CO)_5[C(SCH_3)N(CH_3)_2]$ (VIa) as yellow crystals, mp 62–69 °C. Anal. Calcd for $C_9H_9NO_5SW$: C, 25.31; H, 2.13. Found: C, 25.25; H, 2.16.

With $HN(CH_2)_4CH_2$. To a solution of IIa (0.10 g, 0.23 mmol) in 20 mL of hexanes was added piperidine (0.434 g, 5.11 mmol). The solution was allowed to stir for 5 h. The reaction mixture was then evaporated to dryness. The residue was taken up in CS_2 and placed on a 2 × 36 cm Woelm alumina (Activity Grade III) column. A yellow band containing the aminothiocarbene product developed and was collected. The complex was crystallized from hexane at −20 °C. Yellow crystals of $W(CO)_5\{C(SCH_3)[N(CH_2)_4CH_2]\}$ (VIb) (0.058 g, 53%) were isolated; mp 97–103 °C. Anal. Calcd for $C_{12}H_{13}NO_5SW$: C, 30.85; H, 2.81. Found: C, 31.03; H, 2.84.

With $HN(CH_2)_2OCH_2CH_2$. The method used to prepare VIb was followed in the preparation of $W(CO)_5\{C(SCH_3)[N(CH_2)_2OCH_2CH_2]\}$ (VIc) using IIa (0.100 g, 0.233 mmol) and morpholine (0.539 g, 6.19 mmol). Yellow crystals of VIc were obtained in a 48% yield.

With $H_2N(CH_2)_3NH_2$. As was done for Vb, $W(CO)_5CN(CH_2)_3NH_2$ (VIIa) was isolated from the reaction of IIa (0.10 g, 0.24 mmol) and $H_2N(CH_2)_3NH_2$ (0.035 g, 0.48 mmol). Crystallization from hexanes yielded 0.066 g (67%) of VIIa as a white powder. Anal. Calcd for $C_9H_5N_2O_5W$: C, 26.49; H, 1.98. Found: C, 26.83; H, 1.90.

With $[N(C_2H_5)_4^+][N_3^-]$. A mixture of IIa (0.0763 g, 0.177 mmol) and $[N(C_2H_5)_4^+][N_3^-]$[17] (0.0305 g, 0.177 mmol) in 20 mL of THF was stirred for approximately 12 h. The resulting yellow solution was evaporated to dryness. The residue was washed with hexanes and crystallized from a mixture of CH_2Cl_2 and hexanes at −20 °C. A 61% yield of the yellow crystalline product $[N(C_2H_5)_4^+][W(CO)_5CN^-]$ (VIII) was obtained, mp 119–126 °C. Anal. Calcd for $C_{14}H_{20}N_2O_5W$: C, 35.01; H, 4.21. Found: C, 34.85; H, 4.25.

Reactions of *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$. With H_2NCH_2Ph. The complex *cis*-$W(CO)_4[P(OPh)_3]CNCH_2Ph$ (Vf) was prepared in the same manner as was used for Vb from the reaction of IIh (0.092 g, 0.13 mmol) and H_2NCH_2Ph (0.080 g, 0.75 mmol). The product, Vf (0.068 g, 73%), was obtained as a white powder, mp 68–70 °C. Anal. Calcd for $C_{30}H_{22}NO_7PW$: C, 49.81; H, 3.07. Found: C, 49.70; H, 2.96.

With $H_2N(CH_2)NH_2$. The complex $W(CO)_4[P(OPh)_3]CN(CH_2)_3NH_2$ (VIIb) was prepared by the same method as was used for Vc. A trace of CH_2Cl_2 was added to 25 mL of hexane to dissolve IIh (0.090 g, 0.13 mmol). To this was added $NH_2(CH_2)_3NH_2$ (0.057 g, 0.77 mmol); VIIb (0.0560 g, 64%) was isolated as a white powder.

Reactions of $W(CO)_5CS(CH_2)_2S$ with $H_2N(CH_2)_3NH_2$. Approximately 2–3 mg of IIIa was dissolved in 2 mL of hexanes. A large excess of $H_2N(CH_2)_3NH_2$ was added to the solution. An IR spectrum taken after the solution turned colorless was identical with that of VIIa obtained from the reaction of IIa with $H_2N(CH_2)_3NH_2$.

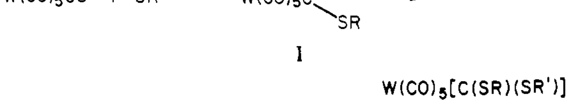
Reactions of $W(CO)_5CS(CH_2)_3S$ with H_2NCH_3, H_2NCH_2Ph, $H_2N(CH_2)_2N(CH_3)_2$, and $H_2N(CH_2)_3NH_2$. Approximately 2–3 mg of IIIb was dissolved in 2 mL of hexanes followed by the addition of a large excess of the primary amine. Although the isocyanide products were never isolated from these reactions, the IR spectra of the reaction mixtures were identical with those of Va, Vc, Ve, and VIIa obtained from the reaction of the corresponding amine with IIa.

Reactions of $W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$ with H_2NCH_3. Methylamine was bubbled through a solution of IV (0.0955 g, 0.161 mmol) in 20 mL of CH_2Cl_2 for approximately 45 min. The solution was allowed to stir for an additional 1 h. It was then evaporated to dryness, and the residue was extracted with hexanes. The hexanes extracts contained only Va.

Spectral Data. Proton NMR spectra were recorded at room temperature on a Varian HA 100 spectrometer in $CDCl_3$ with $CHCl_3$ as the internal reference and Me_4Si as the internal lock; temperature-dependent ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer. The ^{13}C NMR spectra were also recorded on the JEOL FX-90Q spectrophotometer; $Cr(acac)_3$ (~0.1 M) was added to the solutions to reduce data collection time. Infrared spectra were recorded on a Perkin-Elmer 281 spectrometer.

Results and Discussion

Preparation and Characterization of $W(CO)_5[C(SR)(SR')]$ Dithiocarbene Complexes. The room-temperature preparation of pentacarbonyl[bis(methyldithio)carbene]tungsten (IIa), described in a previous paper,[11] has been found to be a general method for the preparation of [bis(alkylthio)carbene]tungsten complexes, simply by varying the mercaptide and alkyl halide (eq 3). In the first step, the mercaptide anion attacks the carbon atom of the thiocarbonyl ligand, forming a dithioester anion (I). Preferential attack of nucleophiles on the thiocarbonyl carbon atom rather than the CO carbon has been seen before.[16,18–21] Intermediate I has not been isolated, but infrared spectra of reaction mixtures show that I (R = CH_3; 2049 w, 1911 s, 1869 m cm^{-1}) is formed almost quantitatively. However, when PhS^-, $PhSe^-$, CH_3O^-, Ph_3Sn^-, and Ph_2P^- were used, no intermediates of type I were seen. The second step in eq 3 has been found to proceed with CH_3I, C_2H_5I, *i*-C_3H_7I, and *n*-C_4H_9I, but best results are obtained when CH_3I is used. Yields are lower by approximately 30% when alkyl iodides other than CH_3I are used, and there is often an impurity in these reactions, which makes crystallization more difficult. When CH_3COBr, $BrCH_2CO_2H$, or allyl bromide is reacted with $[W(CO)_5C({=}S)(SCH_3)^-]$, the only product isolated is IIa. In an attempt to make $W(CO)_5[C(SCH_3)(SH)]$ the methyl dithioester anion was reacted with H_3PO_4 and CF_3SO_3H. In both cases no carbene was formed and $W(CO)_5CS$ was the only isolated carbonyl-containing compound.



I

$$W(CO)_5[C(SR)(SR')] \qquad (3)$$

IIa, R = R′ = CH_3
b, R = C_2H_5, R′ = CH_3
b, R = CH_3, R′ = C_2H_5
c, R = *i*-C_3H_7, R′ = CH_3
c, R = CH_3, R′ = *i*-C_3H_7
d, R = *n*-C_4H_9, R′ = CH_3
d, R = CH_3, R′ = *n*-C_4H_9
e, R = *t*-C_4H_9, R′ = CH_3
f, R = R′ = C_2H_5

This same procedure has also been used to make the substituted tungsten dithiocarbene complexes *cis*-$W(CO)_4L[C(SCH_3)_2]$ [L = $P(OCH_3)_3$ (IIg) and $P(OPh)_3$ (IIh)] by starting with a substituted tetracarbonyl(thiocarbonyl)tungsten complex, *cis*- and *trans*-$W(CO)_4L(CS)$. The reaction proceeds satisfactorily where L is $P(OCH_3)_3$ or $P(OPh)_3$ (ν(CS) = 1247 and 1257 cm^{-1}, respectively).[14] However, when L is PPh_3 (ν(CS) = 1241 cm^{-1} [14]) no reaction occurs. It therefore appears that nucleophilic attack by the mercaptide ion does not occur when ν(CS) is lower than 1247 cm^{-1}. Although a mixture of *cis*- and *trans*-$W(CO)_4L(CS)$ is used in these re-

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Table I. Infrared Spectra of the Carbene and Isocyanide Complexes in Hexanes

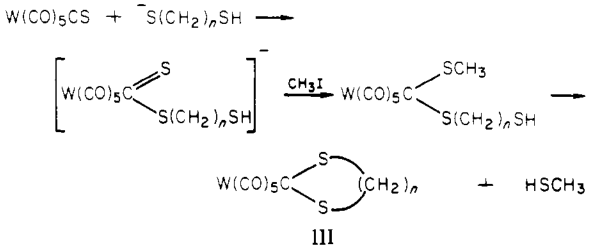
complex	no.	ν(CO), cm^{-1}	ν(CN), cm^{-1}
$W(CO)_5[C(SCH_3)_2]$	IIa[a]	2067 m, 1984 w, 1950 s, 1941 s	
$W(CO)_5[C(SCH_3)_2]$	IIa[b]	2066 m, 1935 s	
$W(CO)_5[C(SC_2H_5)(SCH_3)]$	IIb	2066 m, 1984 w, 1949 s, 1941 s	
$W(CO)_5[C(S\text{-}i\text{-}C_3H_7)(SCH_3)]$	IIc	2067 m, 1983 w, 1949 s, 1941 s	
$W(CO)_5[C(S\text{-}n\text{-}C_4H_9)(SCH_3)]$	IId	2067 m, 1983 w, 1949 s, 1940 s	
$W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$	IIe	2066 m, 1984 w, 1949 s, 1939 s	
$W(CO)_5[C(SC_2H_5)_2]$	IIf	2066 m, 1983 w, 1948 s, 1941 s	
cis-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$	IIg	2026 m, 1946 m, 1914 s, 1903 sh	
cis-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$	IIh	2027 s, 1944 s, 1921 s, 1908 s	
$W(CO)_5CS(CH_2)_2S$	IIIa	2069 w, 1950 s	
$W(CO)_5CS(CH_2)_3S$	IIIb	2067 w, 1944 s	
$W(CO)_5CS(CH_2)_4S$	IIIc	2067 w, 1950 sh, 1944 s	
$W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$	IV[b]	2062 m, 2038 m, 1997 m, 1927 s	
$W(CO)_5CNCH_3$	Va	2068 w, 1956 s	2177 w
$W(CO)_5CN(CH_2)_2CH_3$	Vb	2066 m, 1955 s	2166 w
$W(CO)_5CNCH_2Ph$	Vc	2066 m, 1956 s	2164 w
$W(CO)_5CNC_6H_{11}$	Vd	2064 m, 1954 s	2158 w
$W(CO)_5CN(CH_2)_2N(CH_3)_2$	Ve	2066 m, 1954 s	2166 w
$W(CO)_4[P(OPh)_3]CNCH_2Ph$	Vf	2028 s, 1949 s, 1928 vs	2150 w
$W(CO)_5\{C(SCH_3)[N(CH_3)_2]\}$	VIa	2064 w, 1956 m, 1929 s	
$W(CO)_5\{C(SCH_3)[N(CH_2)_4CH_2]\}$	VIb	2063 m, 1927 s	
$W(CO)_5\{C(SCH_3)[N(CH_2)_2OCH_2CH_2]\}$	VIc	2059 w, 1923 s	
$W(CO)_5CN(CH_2)_3NH_2$	VIIa	2066 m, 1953 s	2166 w
$W(CO)_4[P(OPh)_3]CN(CH_2)_3NH_2$	VIIb	2028 s, 1952 s, 1032 vs	2164 w
$[N(C_2H_5)_4{}^+][W(CO)_5CN^-]$	VIII[b]	2055 w, 1921 s, 1886 sh	

[a] Reference 11. [b] Solvent CH_2Cl_2.

actions, only the cis isomer reacts. The trans isomer, together with small amounts of the unreacted cis isomer, is isolated upon workup of the reaction mixture. The cis configuration of the products, IIg and IIh, is confirmed by their infrared and ^{13}C NMR spectra. The infrared spectra of IIg and IIh contain four ν(CO) bands, which is consistent with the cis isomer but not the trans, whose spectrum should contain only two ν(CO) absorptions. The ^{13}C NMR spectrum (Table III) of IIh shows three CO resonances. Again this is consistent with only the cis isomer.

Although the ν(CS) frequency appears to be a useful indicator of the reactivity of a CS ligand toward nucleophiles, the small difference in values for *cis*- (1257 cm^{-1}) and *trans*-$W(CO)_4[P(OPh)_3](CS)$ (1254 cm^{-1}) would not allow one to predict with certainty the observed reactivity of the cis and nonreactivity of the trans isomer with MeS^-. Perhaps for these cis–trans isomers, the ν(CS) values do not reflect the actual difference in electron density on the CS ligand, as discussed in earlier papers.[14,16]

Cyclic dithiocarbenes may be prepared by reacting dimercaptans with 0.5 equiv of NaH, forming the monoanion, which is then reacted with $W(CO)_5CS$. Methyl iodide is added to the resulting dithioester anion, presumably forming a carbene, which then undergoes loss of methylmercaptan to form the cyclic dithiocarbene (eq 4). This procedure has been used to form five-, six-, and seven-membered rings in yields ranging from 30 to 50%.



(4)

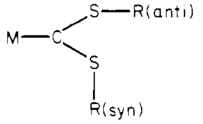
III

n = 2 (IIIa), 3 (IIIb), 4 (IIIc)

The solid orange tungsten dithiocarbene complexes are stable for months on exposure to air at room temperature. They are soluble in common organic solvents ranging in polarity from pentane to acetone. Their solutions when exposed to air at room temperature show some decomposition after 2 or 3 days.

Infrared spectra (Table I) of complexes IIb–f are very similar to that of IIa.[11] The four ν(CO) absorptions for complexes IIa–f are observed in the ranges 2066–2067 m, 1983–1984 w, 1948–1950 s, and 1939–1941 s cm^{-1}, with calculated ν(CO) approximate force constants[22] of k_1 = 15.56–15.60 and k_2 = 15.90 mdyn/Å, which indicate that the bis(alkylthio)carbene ligand has a π-acceptor/σ-donor ratio lower than that of CO ($W(CO)_6$, k = 17.7 mdyn/Å[23]) but similar to that of PPh_3 ($W(CO)_5PPh_3$, k = 15.5 mdyn/Å; k_2 = 15.9 mdyn/Å[14]). A similar conclusion was reached previously for the analogous $CpFe(CO)_2L^+$ complexes.[10]

The ^1H NMR spectra (Table II) of the tungsten dithiocarbenes show a single resonance for the alkyl groups of the carbene ligand at room temperature. Other dithiocarbenes of chromium,[2a,3] tungsten,[2a,3,11] and iron[8,9] also show equivalent alkyl groups in their room-temperature ^1H NMR spectra. This indicates that the restricted rotation about the C(carbene)–S bond, which presumably gives rise to the inequivalent syn- and anti-alkyl groups in some platinum dithiocarbene complexes,[6,7] is not observed in the chromium, tungsten, and iron complexes at this temperature.



However, restricted rotation is observed for some tungsten and iron dithiocarbenes at low temperatures.[8-11] Rationalizations for the differences in the rates of rotation around the C-

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Table II. ^{1}H NMR Spectra of the Carbene and Isocyanide Complexes in $CDCl_3$ (τ)

complex	SCH_3[a]	SCH_2	NCH_2	other resonances
IIa[b]	7.04			
IIb	7.04	6.46 (q)		8.47 (t, CH_3)
IIc	7.06			5.66 (m, SCH), 8.44 (d, CH_3)
IId	7.04	6.46 (t)		8.28 (m, CH_2-CH_2), 8.94 (t, CH_3)
IIe	6.80			8.31 (s, CH_3)
IIf		6.48 (q)		8.49 (t, CH_3)
IIg	7.08			6.36 (d, OCH_3)
IIh	7.35			2.78 (s, OPh)
IIIa		6.36 (s)		
IIIb		7.06 (m)		7.48 (m, CH_2)
IIIc		6.74 (m)		7.63 (m, CH_2)
IV	6.76			4.88 (s, Cp)
Va				6.52 (s, NCH_3)
Vb			6.32 (t)	8.16 (m, CH_2), 8.88 (t, CH_3)
Vc			5.06 (s)	2.63 (m, Ph)
Ve			6.20 (t)	7.24 (t, CH_2), 7.60 (s, CH_3)
Vf			5.40 (s)	2.75 (m, Ph)
VIa	7.06			6.06 (s, CH_3), 6.45 (s, CH_3)
VIb	7.06			5.55, 5.81, and 8.13 (m, m, m, $N(CH_2)_4CH_2$)
VIc	7.01			5.46, 5.70, and 6.08 (t, t, m, $N(CH_2CH_2)_2O$)
VIIa			6.16 (t)	7.06 (t, CH_2), 8.05 (m, CH_2)
VIIb			6.49 (t)	2.67 (s, Ph), 7.16 (t, CH_2), 8.28 (m, CH_2)
VIII[c]				6.47 (q, CH_2), 8.58 (m, CH_3)

[a] All resonances are singlets. [b] Reference 11. [c] Solvent acetone-d_6.

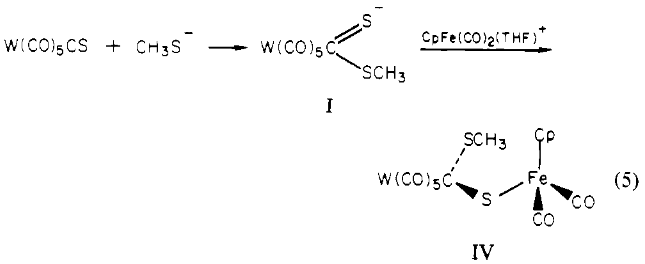
Table III. ^{13}C NMR Spectra of the Carbene Complexes in $CDCl_3$ (ppm)[a]

complex	carbene C	trans CO	cis CO	SCH_3	other resonances
IIa[b]	300.0	204.4	197.4	29.5	
IIb	298.9	204.3	197.4	29.5	40.2 (SCH_2), 12.1 (CH_3)
IIc	296.9	204.2	197.4	29.7	50.8 (CH), 22.1 (CH_3)
IIe	301.0	204.2	197.6	32.1	62.1 (SC), 28.9 (CH_3)
IIh	300.1			29.0	207.6,[c] 203.1,[d] and 199.9[e] (CO), 151.2,[f] 129.4, 124.5, and 121.0[g] (Ph)
IIIa	282.2	204.6	196.0		47.8 (SCH_2)
IIIb	277.5	204.3	196.7		36.3 (SCH_2), 17.4 (CH_2)
IIIc	291.1	205.3	197.5		44.3 (SCH_2), 26.7 (CH_2)
IV	323.4	206.6	199.2	31.3, 28.8	211.4 ($Fe(CO)_2$), 87.6 and 86.7 (C_5H_5)
VIa	249.8	201.9	198.3	25.7	56.3 (NCH_3), 45.1 (NCH_3)
VIb	245.6	202.0	198.1	25.4	65.6 and 54.4 (NCH_2), 27.8, 26.4, and 23.9 (CH_2)
VIc	250.5	209.2	198.1	25.4	67.9, 66.5, 84.3, and 54.0 (OCH_2), (NCH_2)

[a] All resonances are singlets unless otherwise noted. [b] Reference 11. [c] $J_{PWC} = 9.8$ Hz. [d] $J_{PWC} = 9.8$ Hz. [e] $J_{PWC} = 52.7$ Hz. [f] $J_{PC} = 5.9$ Hz. [g] $J_{PC} = 5.9$ Hz.

(carbene)-S bond of platinum vs. tungsten and iron complexes have been discussed previously.[8,11] The ^{13}C NMR spectra of IIa-h (Table III) at room temperature show single resonances for the alkyl groups of the carbene ligand, which also indicates rapid rotation about the C(carbene)-S bond. They also show a resonance near 300 ppm for the dithiocarbene carbon atom, which is consistent with previous reports[8,9,11] of dithiocarbene complexes.

The reaction of the methyl dithioester anion I with metal species to form a stable dithiocarbene has so far been limited to a reaction with $[CpFe(CO)_2(THF)^+][BF_4^-]$ to form IV (eq 5). In the solid state IV is stable for months on exposure to air. It is only slightly soluble in nonpolar solvents (hexane) but is very soluble in polar solvents (CH_2Cl_2, acetone). Solutions of IV at room temperature in air decompose in 3-4 h.



I

IV

(5)

The infrared spectrum of IV (Table I) contains four ν(CO) absorptions. The two ν(CO) bands at 2062 and 1927 cm^{-1} correspond to those of IIa in CH_2Cl_2 (Table I). The ^{13}C NMR spectrum contains two resonances (Table III) for both the methyl group and the cyclopentadienyl ring, indicating the presence of more than one isomer. However, the ^{1}H NMR spectrum (Table II) consists of only two resonances, one each for the methyl group and the cyclopentadienyl ring. There is no splitting of these ^{1}H singlets upon cooling an acetone-d_6 solution of IV to -50 °C. The reason for the difference between the splitting in the ^{1}H and ^{13}C NMR spectra remains unclear; however, ^{1}H resonances of the methyl groups and the rings in the different isomers may fortuitously occur at the same positions.

Other metal cations, $\{CpFe(CO)[P(OPh)_3](THF)^+\}$ and $[Re(CO)_5(NCCH_3)^+]$, have been tried in reaction 5, but no carbene products were isolated. Group 4A metal halides $[(CH_3)_3C](CH_3)_2SiCl$, Ph_3GeBr, Ph_3SnCl, and Ph_3PbCl have also been reacted with $[W(CO)_5C(=S)(SCH_3)^-]$. The only isolated carbonyl complex was $W(CO)_5CS$, which was obtained almost quantitatively. In the cases of the Ge, Sn, and Pb derivatives the reactions were complete in 5 min or less. The reaction with $[(CH_3)_3C](CH_3)_2SiCl$ required 20-30 min to reach completion. No carbene intermediates were detected in any of these reactions.

Reactions of $W(CO)_4L[C(SR_2)]$ with Primary Amines. The tungsten dithiocarbene complexes IIa,IIh, and IIIb were found to undergo reactions with primary amines at room temperature in hexanes to form tungsten isocyanide derivatives (eq 6). The

$$W(CO)_4L[C(SR)_2] + NH_2R' \rightarrow W(CO)_4L(CNR') + 2HSR \quad (6)$$

$$\begin{aligned}
&\text{Va}, L = CO, R = R' = CH_3\\
&\text{a}, L = CO, RR = (CH_2)_3, R' = CH_3\\
&\text{b}, L = CO, R = CH_3, R' = (CH_2)_2CH_3\\
&\text{c}, L = CO, R = CH_3, R' = CH_2Ph\\
&\text{c}, L = CO, RR = (CH_2)_3, R' = CH_2Ph\\
&\text{d}, L = CO, R = CH_3, R' = C_6H_{11}\\
&\text{e}, L = CO, R = CH_3, R' = (CH_2)_2N(CH_3)_2\\
&\text{e}, L = CO, RR = (CH_2)_3, R' = (CH_2)_2N(CH_3)_2\\
&\text{f}, L = P(OPh)_3, R = CH_3, R' = CH_2Ph
\end{aligned}$$

formation of the isocyanide presumably proceeds by nucleophilic attack of the amine on the p_z orbital of the carbene carbon to form an adduct, which then splits off two mercaptans to form the product. The reactions of the six-membered cyclic dithiocarbene complex IIIb with primary amines are slower than those of either the substituted (IIh) or the unsubstituted (IIa) bis(methylthio)carbene complexes. This slower reactivity of the cyclic dithiocarbenes was also observed in the $CpFe(CO)_2[C(SR)_2]^+$ system.[9] This is probably due to the poorer leaving-group ability of the dithiols and the stability of six-membered rings. Methylamine was also found to react with IV to form Va and a carbonyl-containing product whose infrared spectrum contained one band in the carbonyl stretching region ($\nu(CO)$ = 1933 cm^{-1}). The infrared spectrum of this product is very similar to those of *trans*-$[CpFe(CO)SR]_2$ complexes (R = CH_3, C_2H_5, Ph; $\nu(CO)$ = 1929, 1929, 1938 cm^{-1}, respectively)[24] and may indicate the formation of *trans*-$[CpFe(CO)SH]_2$.

Attempts to react IIa with NH_2Ph, $NH_2C(=O)CH_3$, and $NH_2C(CH_3)_3$ resulted in no reaction. This is probably due to the lower nucleophilic character of NH_2Ph and $NH_2C(=O)CH_3$ and to steric hindrance in the case of $NH_2C(CH_3)_3$.

Reactions of $W(CO)_5[C(SR)_2]$ with Secondary Amines. When IIa is reacted with secondary amines at room temperature, 1 equiv of methyl mercaptan is evolved with the formation of an aminothiocarbene complex (eq 7). Steric hin-

$$\underset{\text{IIa}}{W(CO)_5[C(SCH_3)_2]} + HNR_2 \rightarrow W(CO)_5[C(SCH_3)(NR_2)] + HSCH_3 \quad (7)$$

$$\begin{aligned}
&\text{VIa}, HNR_2 = HN(CH_3)_2\\
&\text{b}, HNR_2 = H\overline{N(CH_2)_4CH_2}\\
&\text{c}, HNR_2 = H\overline{N(CH_2)_2OCH_2CH_2}
\end{aligned}$$

drance seems to exert a large influence over the reactions of IIa with secondary amines. The yields of aminothiocarbenes decrease as the steric bulk of the amine increases: $HN(CH_3)_2$ > piperidine ≥ morpholine > $HN(C_2H_5)_2$. No aminothiocarbene is formed with $HN(i\text{-}C_3H_7)_2$. Even with a large excess of the amine $HN(CH_3)_2$, piperidine, morpholine, or $HN(C_2H_5)_2$, there is no evidence for the replacement of two thiomethoxy groups to form diaminocarbene complexes $W(CO)_5[C(NR_2)_2]$. When IIIa is reacted with $HN(CH_3)_2$ or piperidine, no reaction occurs. Presumably the barrier to ring opening prevents formation of the aminothiocarbene.

The yellow aminothiocarbenes VIb and VIc show no noticeable decomposition upon exposure to air at room temperature for a period of months in the solid state. However, VIa starts to decompose slowly after 1 week at these conditions. It, VIa, may be stored in the solid state at −20 °C. The aminothiocarbenes are soluble in most common organic solvents.

The spectral characteristics of VIa–c are in general very similar. The IR spectra of VIa–c show two $\nu(CO)$ absorptions at 2059–2064 w and 1923–1929 s cm^{-1} (Table I). The greater tendency for nitrogen to donate electron density to the carbene carbon atom[10,25,26] as compared to sulfur is reflected in the lower $\nu(CO)$ frequencies of the aminothiocarbene as compared to $W(CO)_5[C(SCH_3)_2]$ (2066, 1983, 1949, 1940 cm^{-1}). The ^1H NMR spectra of VIa–c contain a singlet at τ 7.01–7.06 for the thiomethoxy group (Table II). The amine methyl groups of VIa and the four methylene groups of VIc are nonequivalent at room temperature. Nonequivalence of the amine methyl groups is also observed in $\{CpFe(CO)_2[C(SCH_3)[N(CH_3)_2]]\}PF_6$[8,27] and is consistent with a large donation of π-electron density from nitrogen to the carbene carbon atom, which causes restricted rotation around the C(carbene)–N bond.

The ^{13}C NMR chemical shift of the carbene carbon, δ(carbene), is very sensitive to changes in the electronic environment[28] at the carbene carbon atom. An upfield shift of approximately 70 ppm for the δ(carbene) is observed when an alkoxy group is substituted by an amine group in complexes of the type $Cr(CO)_5C(YR)R$.[30] An upfield shift of at least 50 ppm is observed when a thiomethoxy group of IIa is replaced with an amine group to form complexes VIa–c (Table III). Upfield shifts of about 70 ppm are also observed upon replacing a SCH_3 group with piperidine in $CpFe(CO)L[C(SCH_3)_2]^+$ (L = CO or CH_3CN).[9,10]

Reactions of $W(CO)_5[C(SR)_2]$ with Diamines. It has been previously reported that $\{CpFe(CO)_2[C(SCH_3)_2]\}PF_6$ reacts with diamines to form cyclic diaminocarbene complexes (eq 1). However, when IIa and IIh are reacted with 1,3-diaminopropane, no cyclic diaminocarbene complex is formed. Instead only the monomeric isocyanides $W(CO)_4(L)CN(CH_2)_3NH_2$ (VIIa,b) result. This reaction is similar to that of IIa with primary amines (eq 6). (Cyclic dithiocarbene)tungsten complexes of the type $W(CO)_5\overline{CN(R)(CH_2)_2N}(R)$[29] (R = CH_3 and C_2H_5) are known, and it is not clear why the reactions of the iron and tungsten dithiocarbenes give different products with 1,3-diaminopropane.

The ^1H NMR spectra of VIIa and VIIb show three absorptions in a 1:1:1 ratio, for the three different methylene groups. The protons of the NH_2 groups are not observed, presumably due to quadrupolar broadening by the nitrogen atom.

Reactions of $W(CO)_5[C(SR)_2]$ with Azide Anion. The product obtained when IIa is reacted with $[N(C_2H_5)_4^+][N_3^-]$ at room temperature is $[N(C_2H_5)_4^+][W(CO)_5CN^-]$[30] (eq 8).

$$W(CO)_5[C(SCH_3)_2] + N_3^- \rightarrow \underset{\text{VIII}}{W(CO)_5CN^-} + N_2 + CH_3SSCH_3 \quad (8)$$

A similar reaction occurs between $CpFe(CO)_2[C(SCH_3)_2]^+$ and NaN_3. It yields $CpFe(CO)_2CN$ as one of several products.[8] Dimethyl disulfide was identified as a product formed from the reaction of IIa with N_3^- by comparing its ^1H NMR spectrum with that of an authentic sample. Evolution of a gas,

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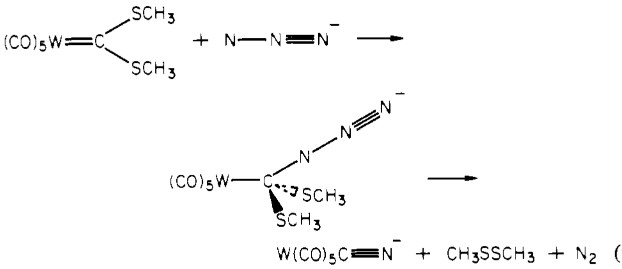
presumably N_2, was also observed during the reaction. A possible mechanism for this reaction is shown in eq 9.



(9)

Other nucleophiles that did not react with IIa are $[N(C_4H_9)_4^+]I^-$, $N(C_2H_5)_3$, 1,4-diazabicyclo[2.2.2]octane, $CNCH_3$, and $S(CH_3)_2$.

Registry No. IIa, 76262-42-5; IIb, 77826-89-2; IIc, 77826-90-5; IId, 77826-91-6; IIe, 77826-92-7; IIf, 67517-56-0; IIg, 77846-65-2; IIh, 77826-93-8; IIIa, 77826-94-9; IIIb, 77826-95-0; IIIc, 77826-96-1; IV, 77826-97-2; Va, 50298-27-6; Vb, 77826-98-3; Vc, 77826-99-4; Vd, 15603-77-7; Ve, 77827-00-0; Vf, 77827-01-1; VIa, 77827-02-2; VIb, 77827-03-3; VIc, 77827-04-4; VIIa, 77827-05-5; VIIb, 77827-06-6; VIII, 77827-07-7; $W(CO)_5CS$, 50358-92-4; *cis*-$W(CO)_4(CS)[P(OCH_3)_3]$, 66007-60-1; *cis*-$W(CO)_4(CS)[P(OPh)_3]$, 65969-60-0; $Na[W(CO)_5C(S)(SCH_3)^-]$, 77846-66-3; $[CpFe(CO)_2(THF)][BF_4]$, 63313-71-3; HSC_2H_5, 75-08-1; $HSCH(CH_3)_2$, 75-33-2; $HS(CH_2)_3CH_3$, 109-79-5; $HSC(CH_3)_3$, 513-44-0; $HSCH_3$, 74-93-1; $HS(CH_2)_2SH$, 540-63-6; $HS(CH_2)_3SH$, 109-80-8; $HS(CH_2)_4SH$, 1191-08-8; CH_3I, 74-88-4; C_2H_5I, 75-03-6; H_2NCH_3, 74-89-5; $H_2N(CH_2)_2CH_3$, 107-10-8; H_2NCH_2Ph, 100-46-9; $H_2NC_6H_{11}$, 108-91-8; $H_2N(CH_2)_2N(CH_3)_2$, 108-00-9; $HN(CH_3)_2$, 124-40-3; $HN(CH_2)_4CH_2$, 110-89-4; $HN(CH_2)_2OCH_2CH_2$, 110-91-8; $H_2N(CH_2)_3NH_2$, 109-76-2; $[N(C_2H_5)_4^+][N_3^-]$, 993-20-4.

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Thiocarbonyl Complexes of Cyclopentadienyltungsten and [Hydrotris(1-pyrazolyl)borato]tungsten. Reactions at the CS Ligand Leading to Mercaptocarbyne and Isocyanide Complexes

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The anionic thiocarbonyl complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ reacted with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and acid or with $NOPF_6$ to give $CpW(CO)(CS)NO$ and $HB(pz)_3W(CO)(CS)NO$. The $CpW(CO)_2CS^-$ complex reacted with chloro-2,4-dinitrobenzene (DNP-Cl) to yield the mercaptocarbyne $Cp(CO)_2W{\equiv}C{-}S{-}DNP$. Analogous reactions of $CpW(CO)_2CS^-$ with MeI and EtI gave spectroscopic evidence for the formation of the less stable $CpW(CO)_2CS{-}R$ mercaptocarbyne complexes. The hydrotris(1-pyrazolyl)borate complex $HB(pz)_3W(CO)_2CS^-$ reacted with MeI, EtI, and DNP-Cl to give the stable mercaptocarbyne derivatives $HB(pz)_3W(CO)_2CS{-}R$. These reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ with alkyl halides contrast with those of $CpW(CO)_3^-$ and $HB(pz)_3W(CO)_3^-$, which give σ-bonded W–R complexes. Unexpectedly, $CpW(CO)(CS)(PPh_3)I$ reacted with LiPh to give the mercaptocarbyne $CpW(CO)(PPh_3)CS{-}Ph$, whose structure was established by an X-ray crystallographic determination. Evidence for the formation of $CpW(CO)_2CS{-}R$ complexes was also found in the reactions of *trans*-$CpW(CO)_2(CS)I$ with LiMe and LiPh. A stable mercaptocarbyne, $HB(pz)_3W(CO)_2CS{-}Me$, was isolated from the reaction of *trans*-$HB(pz)_3W(CO)_2(CS)I$ with LiMe. Possible mechanisms for the reactions of LiR with W(CS)I-containing complexes to give $W{\equiv}C{-}S{-}R$ and I^- are considered; a radical mechanism appears most likely. The conversion of CS groups to mercaptocarbynes involves the reduction of CS multiple bonds to C—S single bonds, a transformation that may have relevance for the catalytic cleavage of $C{\equiv}O$ bonds in carbon monoxide. Finally, reactions of $CpW(CO)(CS)NO$, $HB(pz)_3W(CO)(CS)NO$, *cis*-$CpW(CO)_2(CS)SnPh_3$, and *cis*-$CpW(CO)_2(CS)PbPh_3$ with H_2NMe smoothly transform the CS to the $C{\equiv}N{-}Me$ ligand in the products $CpW(CO)(CNMe)NO$, $HB(pz)_3W(CO)(CNMe)NO$, *cis*- and *trans*-$CpW(CO)_2(CNMe)SnPh_3$, and *cis*- and *trans*-$CpW(CO)_2(CNMe)PbPh_3$. Trends in the ν(CO) frequencies, the ^1H and ^{13}C NMR spectra, and the reactivities of the complexes are discussed.

Introduction

Recently, we reported[2] the preparation of the nucleophilic cyclopentadienyl and hydrotris(1-pyrazolyl)borate complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$. They were observed to react with a series of electrophiles E–X, where E = I, SePh, HgI, $SnPh_3$, or $PbPh_3$ and X = Cl, Br, or I, to yield products in which the E group was coordinated to the tungsten atom.

$$CpW(CO)_2CS^- \text{ or } HB(pz)_3W(CO)_2CS^- + E{-}X \rightarrow CpW(CO)_2(CS)E \text{ or } HB(pz)_3W(CO)_2(CS)E + X^- \quad (1)$$

In other electron-rich thiocarbonyl complexes, however, the sulfur atom of the CS group can act as the nucleophile. Thus, the reaction

$$IW(CO)_4CS^- + CH_3OSO_2F \rightarrow IW(CO)_4CS{-}CH_3 + SO_3F^- \quad (2)$$

yields the *S*-methyl product.[3] In the study reported here, we performed reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ with more electrophiles to determine whether addition occurs at the W or S atom. Also reported are reactions of the CS group in some complexes with the nucleophiles LiR and CH_3NH_2. Some of these results were communicated previously.[4]

Results and Discussion

Reactions at the Tungsten Atom. CpW(CO)(CS)NO and HB(pz)$_3$W(CO)(CS)NO. As in the procedure for the synthesis

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