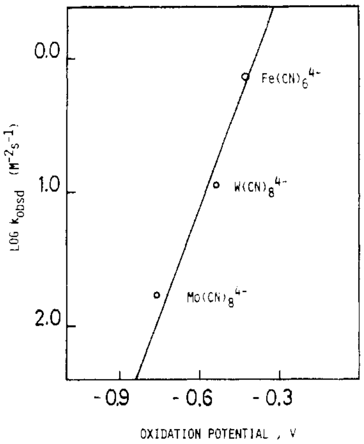

Figure 3. Plot of log k_{obsd} ($M^{-2}\ s^{-1}$; cation = K^+), for the oxidation of $M(CN)_n^{4-}$ by $S_2O_8^{2-}$, against the oxidation potential (vs. NHE) of the cyano complex (M = Fe, Mo, W). Values for $Fe(CN)_6^{4-}$ and $W(CN)_8^{4-}$ are from ref 3 and 5, respectively.

The variation in the ionic strength of the reaction mixture between 0.09 and 1.05 had very little effect on the rate constant (Table II). Application of the Davies equation[31]

$$-\log f^{\pm} = 0.5Z_1Z_2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \qquad (3)$$

to the individual ion activities shows that the effect of the ionic strength on the rate constants is given by

$$\log k = \log k_0 + 0.5(\Delta Z)^2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \qquad (4)$$

where

$$(\Delta Z)^2 = Z_x^2 - (pZ_p^2 + qZ_q^2 + rZ_r^2)^{32}$$

According to the observed rate law [Z_p, Z_q, Z_r, and Z_x are the electronic charges of $Mo(CN)_8^{4-}$, $S_2O_8^{2-}$, M^+, and the activated complex, respectively, and *p*, *q*, and *r* denote the order with respect to the species], $(\Delta Z)^2 = 4$ and

$$\log k = \log k_0 + 2[\mu^{1/2}/(1 + \mu^{1/2}) - 0.3\mu] \qquad (5)$$

According to eq 5 the value of *k* passes through a broad maximum at $\mu = 0.5$ M but varies only by about 20% between $\mu = 0.09$ M and $\mu = 1.05$ M. Our experimental observations (Table II) are in agreement with this calculated trend.

A correlation between the rate constants and the driving force for the reaction of peroxydisulfate with the cyano complexes of Fe, Mo, and W (Figure 3) was found. k_{obsd} is linearly dependent on the driving force, with a slope of 5.5 V^{-1}. The Marcus relation[33] (eq 6) predicts this type of linear behavior where k_{12} is the

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (6)$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (7)$$

cross-reaction rate constant, k_{11} and k_{22} are self-exchange rate constants, and K_{12} is the equilibrium constant. This predicts a slope of 8.46 V^{-1} for a plot of log k_{12} vs. $E°$. Our experimental results are thus reasonably consistent with the Marcus theory.

The dependency of k_{obsd} on the driving force, $E°$ (Figure 3), indicates that the electron-transfer step is rate-determining. This, as well as the first-order dependence in both oxidant and reductant (eq 2), shows an advantage of the electron transfer between $M(CN)_n^{3-}$ and $S_2O_8^{2-}$ via an outer-sphere pathway over the hydrolysis of the peroxydisulfate ion for these reactions.

Acknowledgment. We are grateful to the South African CSIR and the Research Fund of this University for financial support.

Registry No. $Mo(CN)_8^{4-}$, 17923-49-8; $S_2O_8^{2-}$, 15092-81-6; Cs, 7440-46-2; Rb, 7440-17-7; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2.

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Syntheses, Spectral Properties, and Substitution Reactions of $M(CO)_3(S_2CNC_4H_4)_2$ (M = Mo, W) Complexes Containing the Electronically Unique Pyrrole-*N*-carbodithioate Ligand

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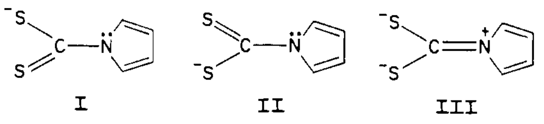
A series of seven-coordinate $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ (*n* = 0-2) molybdenum(II) and tungsten(II) complexes have been synthesized with the electronically unique pyrrole-*N*-carbodithioate chelating ligand [$M(CO)_2L(S_2CNC_4H_4)_2$: M = Mo, W, L = PPh_3, PEt_3, $P(OMe)_3$; M = Mo, L = OC_4H_8, SC_4H_8, $AsPh_3$, $SbPh_3$. $M(CO)L_2(S_2CNC_4H_4)_2$: M = Mo, W, L = $P(OMe)_3$; M = Mo, L = PEt_3, $^1/_2$ $Ph_2PCH_2CHPPh_2$. $[R_4N][M(CO)_2X(S_2CNC_4H_4)_2]$: M = Mo, W, X = F; M = Mo, X = Cl, Br, I]. The decreased electron donor ability of the pyrrole-*N*-carbodithioate ligand relative to alkyl analogues is evident in increased infrared ν_{CO} frequencies and in increased lability of carbon monoxide ligands in $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ complexes with *n* = 0 and 1. The 16-electron $Mo(CO)_2(S_2CNC_4H_4)_2$ complex is significantly more electrophilic than $Mo(CO)_2(S_2CNEt_2)_2$ as reflected in isolation of the stable halide complexes listed above. Carbon-13 enriched carbon monoxide ligands in $W(CO)_3(S_2CNC_4H_4)_2$ and $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ have been used to probe intramolecular rearrangements by variable-temperature ^{13}C NMR. Two low-temperature fluxional processes are observed for the parent tricarbonyl; the first exchanges two of the three inequivalent carbonyl ligands, and the second averages all three carbonyl signals. The (triphenylphosphine)tungsten derivative exhibits a single carbon monoxide ^{13}C NMR signal at room temperature, which is frozen into two signals at low temperature.

Introduction

Dithiocarbamate anions can be represented by the three resonance forms shown in Chart I. Contributions from these resonance forms are relatively insensitive to alkyl substituent variations on the nitrogen atom.[1] The pyrrole-*N*-carbodithioate ligand ($^-S_2CNC_4H_4$) prepared by Kellner et al.[2] exhibits unusual bonding

Chart I



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properties in homoleptic pyrrole-*N*-carbodithioate complexes. Various workers have confirmed the hypothesis that resonance form III is unfavorable for $S_2CNC_4H_4$ ligands (R_2 = –CHCHCHCH–) due to loss of pyrrole aromaticity upon delocalization of the nitrogen lone pair into the CS_2 fragment.[3] The pyrrole-*N*-carbodithioate ligand is therefore an inferior electron donor relative to *N*,*N*-dialkyldithiocarbamate ligands.

We initiated a study of $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ (n = 1, 2) complexes in an effort to systematically modify the molecular properties of these compounds relative to those of previously reported dialkyldithiocarbamate analogues.[4] Reported here are (1) the preparation and isolation of $M(CO)_3(S_2CNC_4H_4)_2$ (M = Mo, W), $Mo(CO)_2(S_2CNC_4H_4)_2$, and $M(CO)_2L(S_2CNC_4H_4)_2$ complexes for various phosphorus, sulfur, arsenic, and antimony two-electron donor ligands, (2) facile syntheses of several $Mo(CO)(PR_3)_2(S_2CNC_4H_4)_2$ derivatives, (3) syntheses of $[R_4N][Mo(CO)_2X(S_2CNC_4H_4)_2]$ derivatives (X = F, Cl, Br, I), (4) infrared spectroscopic data for these bis(pyrrole-*N*-carbodithioato) complexes, and (5) temperature-dependent ^{13}C NMR spectra for $W(CO)_3(S_2CNC_4H_4)_2$ and $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$.

Experimental Section

Materials and Methods. All manipulations involving air- or moisture-sensitive reagents were performed under an oxygen-free atmosphere of nitrogen or argon by using standard Schlenk techniques. All solvents were degassed by a nitrogen sparge to remove dissolved oxygen. When necessary, solvents were purified by distillation under nitrogen gas in the presence of an appropriate drying agent. Chemical reagents were obtained from commercial sources and used without further purification. $K[S_2CNC_4H_4]\cdot{}^1/_2OC_4H_8$ was prepared by using Bereman's method.[5] The ligand crystallized with a $^1/_2$ mol of THF solvate/mol of ligand. $Mo(CO)_4Cl_2$,[6] $W(CO)_4Cl_2$,[7] $[(C_2H_5)_4N][Mo(CO)_5I]$,[8] $W(CO)_3(PR_3)_2Cl_2$,[9] and $[(C_3H_7)_4N][W(CO)_4I_3]$[10] were prepared as described previously.

Physical Measurements. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a WM Bruker 250 spectrometer. Proton and carbon-13 chemical shifts are reported as parts per million downfield of Me_4Si, and phosphorus-31 chemical shifts are reported relative to an external H_3PO_4 standard. NMR sample temperatures were measured by a thermocouple located near the probe. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer and calibrated with a polystyrene standard. Visible absorption spectra were measured on a Perkin-Elmer 552 spectrophotometer using matched 1.0-cm cells.

Syntheses. **$Mo(CO)_n(S_2CNC_4H_4)_2$ (n = 2, 3).** $K[S_2CNC_4H_4]\cdot{}^1/_2OC_4H_8$ was weighed into a Schlenk tube in the drybox. Methylene chloride (50 mL) was added to a stoichiometric amount of $Mo(CO)_4Cl_2$, freshly generated from $Mo(CO)_6$, causing carbon monoxide evolution. The pyrrole-*N*-carbodithioate was removed from the drybox and added to the $Mo(CO)_4Cl_2$ solution by connecting the neck joints of the two Schlenk flasks and inverting to drop the ligand into solution. The solution immediately turned dark red, and gas evolved. A solution IR spectrum showed bands at 2042 (s), 1966 (s), and 1943 (sh) cm^{-1}. The product was chromatographed through a short alumina column (under an atmosphere of carbon monoxide) using methylene chloride as the eluent. Solvent was reduced in vacuo to 5–10 mL, and a green oil, $Mo(CO)_2(S_2CNC_4H_4)_2$, was produced. A stream of carbon monoxide gas was introduced through the side arm for 5 min. The product turned orange as CO was added, and crystals of $Mo(CO)_3(S_2CNC_4H_4)_2$ grew in the flask. The solution was cooled with an ice bath for 30 min before the product was isolated by filtration as red crystals in greater than 80% yield. ^1H NMR ($CDCl_3$): δ 7.56 (m, 4 H, α-H), 6.35 (m, 4 H, β-H). The tricarbonyl compound does not appear to lose CO under dynamic vacuum in the solid state.

$Mo(CO)_2(S_2CNC_4H_4)_2$ can be prepared in essentially quantitative amounts from methylene chloride solutions of $Mo(CO)_3(S_2CNC_4H_4)_2$. Solvent removal in vacuo leaves a green oil. Further drying results in a green amorphous solid. The compound is extremely air-sensitive and attempts to recrystallize it using nondonor solvents were unsuccessful. Donor solvents such as diethyl ether, tetrahydrofuran, and acetone instantly dissolve $Mo(CO)_2(S_2CNC_4H_4)_2$ to give purple solutions of $Mo(CO)_2(solvent)(S_2CNC_4H_4)_2$. $Mo(CO)_2(S_2CNC_4H_4)_2$ can also be prepared quantitatively by a solid-state reaction. Grinding $[(C_2H_5)_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ (vide infra) in a Nujol mull causes a color change from brown to green due to formation of $Mo(CO)_2(S_2CNC_4H_4)_2$ by elimination of $[(C_2H_5)_4N]I$.

$W(CO)_3(S_2CNC_4H_4)_2$. Methylene chloride (100 mL) was added to freshly prepared $W(CO)_4Cl_2$, causing CO evolution. $K[S_2CNC_4H_4]\cdot{}^1/_2OC_4H_8$ was added as described above. Carbon monoxide rapidly evolved, and the solution color turned dark red. After 15 min the solution IR showed bands at 2034, 1948, and 1928 cm^{-1}. The solution was chromatographed on a short alumina column as described for $Mo(CO)_3(S_2CNC_4H_4)_2$ (the tungsten derivative can be chromatographed under nitrogen). The orange-brown eluent was reduced in vacuo, pentane was added, and the flask was placed in a refrigerator. The solution was later filtered to isolate the dark red crystals which had formed in greater than 85% yield. ^1H NMR ($CDCl_3$): δ 7.53 (m, 4 H, α-H), 6.40 (m, 4 H, β-H).

$W(CO)_3(S_2CNC_4H_4)_2$, ^{13}CO Enriched. A solution of $W(CO)_3(S_2CNC_4H_4)_2$ (0.84 g, 1.52 mmol) in CH_2Cl_2 (35 mL) was prepared and frozen in a liquid-nitrogen bath. The flask was evacuated and the matrix slowly thawed. The gases liberated were removed under dynamic vacuum. The process was repeated. Carbon monoxide (90%, ^{13}CO enriched, Mound Laboratory) was introduced into the Schlenk flask to a pressure of approximately 1 atm. The solution was stirred for 3 h. The solution IR spectrum showed significant enrichment (subsequent formation of $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ from this material showed approximately 25% ^{13}CO enrichment). The solvent volume was reduced to 5 mL, pentane was added, and the flask was cooled to induce crystallization. The product was filtered, washed with pentane, and dried to yield the enriched product in crystalline form.

$[(C_2H_5)_4N][M(CO)_2X(S_2CNC_4H_4)_2]$ (M = Mo, X = F, Cl, Br; M = W, X = F). The preparative procedure for the tungsten fluoride derivative is representative of the syntheses of the molybdenum derivatives, too. Tetraethylammonium fluoride dihydrate (0.32 g, 1.73 mmol) was added to a tared Schlenk tube in the drybox. A solution of $W(CO)_3(S_2CNC_4H_4)_2$ (0.95 g, 1.72 mmol) in methylene chloride (25 mL) was prepared in a Schlenk flask. The complex salt was prepared by connecting the necks of the two Schlenk flasks, after removal from the drybox, and rotating the $[Et_4N]F$ flask to drop the salt into the solution. Carbon monoxide began to evolve after 1 min of stirring. After 5 min the solution color had changed from orange-red to red-purple. After 15 min the solution IR indicated that the product was the major species in solution (ν(CO) 1904 (s), 1811 (s) cm^{-1}). The flask was placed in a refrigerator to induce crystallization. After the solid was isolated by filtration, a second crop was obtained from the filtrate by adding ether and cooling. The combined yield of the dark red crystalline product was 65%. ^1H NMR (THF-d_8): δ 7.62 (m, 4 H, α-H), 6.15 (m, 4 H, β-H), 3.08 (q, 8 H, CH_2), 1.80 (3 t, $^3J_{HH}$ = 7 Hz, $^3J_{HN}$ = 2 Hz, 12 H, CH_3).

$[(C_2H_5)_4N][Mo(CO)_2Cl(S_2CNC_4H_4)_2]$. ^1H NMR ($CD_3C(O)CD_3$): δ 7.55 (m, 4 H, α-H), 6.30 (m, 4 H, β-H), 3.43 (q, 8 H, CH_2), 1.33 (3 t, $^3J_{HN}$ = 2 Hz, 12 H, CH_3).

$[(C_2H_5)_4N][Mo(CO)_2Br(S_2CNC_4H_4)_2]$. ^1H NMR $CD_3C(O)CD_3$): δ 7.55 (m, 4 H, α-H), 6.30 (m, 4 H, β-H), 3.44 (q, 8 H, CH_2), 1.34 (3 t, $^3J_{HH}$ = 7 Hz, $^3J_{HN}$ = 2 Hz, 12 H, CH_3).

$[R_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ (R = Et, *n*-Bu). The synthetic method described for the preparation of the tetraethylammonium derivative works equally well for the tetra-*n*-butylammonium derivative. $[(C_2H_5)_4N][Mo(CO)_5I]$ was generated and isolated. A solution of $[(C_2H_5)_4N][Mo(CO)_5I]$ (1.16 g, 2.36 mmol) in tetrahydrofuran (25 mL) was prepared. Iodine (0.60 g, 2.36 mmol) was added to generate $[(C_2H_5)_4N][Mo(CO)_4I_3]$. The potassium pyrrole-*N*-carbodithioate salt (1.10 g,

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4.71 mmol) was added and caused immediate gas evolution as the solution color turned red-purple. A solution IR spectrum showed the presence of both $Mo(CO)_3(S_2CNC_4H_4)_2$ and $[(C_2H_5)_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ at this stage of the reaction. A nitrogen stream was directed through the flask for 1 h to leave the iodo dicarbonyl complex as the only carbonyl-containing species in solution. IR: ν(CO) 1941 (s), 1877 (s) cm^{-1}. The solution was filtered through a Celite pad, and then the solvent volume was reduced and the flask was cooled. The product was isolated by filtration as a dark red-purple solid in 40% yield. When $[(C_2H_5)_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ was prepared in methylene chloride, the product produced a yellow solution (ν(CO) 1945 (s), 1860 (s) cm^{-1}). The visible spectrum of $[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ in CH_2Cl_2 has λ_{max} = 440 nm; the λ_{max} value of 549 nm observed in THF is believed to be due to displacement of iodide by THF in the coordination sphere.

$Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$. $Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$ was generated in solution by adding tetrahydrofuran to solid $Mo(CO)_2(S_2CNC_4H_4)_2$ or $Mo(CO)_2L(S_2CNC_4H_4)_2$ (L = CO, $AsPh_3$, $SbPh_3$, SC_4H_8, I^-) to produce a dark purple solution, which shows carbonyl stretching frequencies at 1946 (s) and 1878 (s) cm^{-1}. Each resultant THF solution exhibits a single visible absorption with λ_{max} = 547 nm. Solvent removal from a THF solution of the THF adduct that had been generated from $Mo(CO)_3(S_2CNC_4H_4)_2$ leaves a black amorphous solid. The infrared spectrum of a KBr pellet of this residue shows a weak tricarbonyl pattern, indicating that some $Mo(CO)_3(S_2CNC_4H_4)_2$ has been regenerated in this mixture.

$Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$. Addition of tetrahydrothiophene (0.13 mL, 0.13 g, 1.50 mmol) to $Mo(CO)_3(S_2CNC_4H_4)_2$, prepared as above, in 25 mL of CH_2Cl_2 caused gas evolution. After the mixture was stirred or 1 h, a solution infrared spectrum indicated the presence of both $Mo(CO)_3(S_2CNC_4H_4)_2$ and $Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$. A large excess of SC_4H_8 (5 mL) was added. Immediate gas evolution was accompanied by formation of a dark red solution. The reaction mixture was chromatographed on a short alumina column using methylene chloride/tetrahydrothiophene to elute a red band. The solvent volume was reduced in vacuo, a layer of pentane was carefully added, and the flask was cooled overnight. The product was isolated by filtration as a dark red crystalline solid (75% yield based on $[(C_2H_5)_4N][Mo(CO)_5I]$). ^{1}H NMR ($CDCl_3$): δ 7.54 (m, 4 H, pyrrole α-H), 6.35 (m, 4 H, pyrrole β-H), 2.87 (m, 4 H, SC_4H_8 α-H), 1.94 (m, 4 H, SC_4H_8 β-H).

$Mo(CO)_2(PR_3)(S_2CNC_4H_4)_2$ (R = Ph, Et, OMe). The following preparative procedure is general for the synthesis of these complexes. $[(C_2H_5)_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ was generated in situ in methylene chloride. PEt_3 (0.9 equiv) was added while the reaction mixture was stirred at 0 °C. After 0.5 h the solution was warmed to room temperature. After 1 h solution IR indicated that the product was the dominant species in solution. The solution was chromatographed on a short alumina column with methylene chloride as eluent. Solvent was reduced in vacuo to 5 mL, and methanol (15 mL) was carefully added before the solution was cooled overnight. The resulting solid was filtered and washed with methanol to give red crystals (69% yield). $Mo(CO)_2[P(OMe)_3](S_2CNC_4H_4)_2$ was isolated by removing the solvent to produce a viscous oil, which was triturated overnight with pentane/ether (90:10).

$Mo(CO)_2(PEt_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.60 (m, 4 H, α-H), 6.30 (m, 4 H, β-H), 1.97 (m, 6 H, CH_2), 1.06 (m, 9 H, CH_3). ^{31}P NMR ($CDCl_3$): δ 41.11 (s).

$Mo(CO)_2(PPh_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 4 H, α-H), 7.35–7.41 (m, 15 H, C_6H_5), 6.27 (m, 4 H, β-H). ^{31}P NMR ($CDCl_3$): δ 60.85 (s).

$Mo(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.63 (m, 4 H, α-H), 6.34 (m, 4 H, β-H), 3.70 (d, $^3J_{HP}$ = 12 Hz, 9 H, Me). ^{31}P NMR ($CDCl_3$): δ −74.72 (s).

$Mo(CO)_2(EPh_3)(S_2CNC_4H_4)_2$ (E = As, Sb). The preparative scheme described below also works for the $SbPh_3$ derivative, but the yield is lower. Molybdenum hexacarbonyl (0.54 g, 2.04 mmol) was converted to $Mo(CO)_4Cl_2$.[6] Methylene chloride (15 mL) was added followed by $AsPh_3$(1.25 g, 4.08 mmol). Carbon monoxide evolved, and the solution turned yellow. A yellow precipitate formed in the bottom of the flask. The solution showed IR bands attributed to $Mo(CO)_3(AsPh_3)_2Cl_2$[11] and $Mo(CO)_2(AsPh_3)_2Cl_2$[12] as well as to unreacted $Mo(CO)_6$. Potassium pyrrole-*N*-carbodithioate (0.88 g, 4.07 mmol) was added to the solution. A gas evolved, and the solution turned dark orange. After the mixture was stirred for 15 min an IR spectrum typical of dicarbonyl species with some hexacarbonyl impurity was observed. The solution was filtered three times to remove KCl and other insoluble impurities. The solution volume was then reduced to 10 mL, and methanol was added before the solution was cooled overnight. An oily dark solid formed and was isolated. This was converted to a dark red-brown solid by trituration for 4 h with a methanol/ether (90:10) mixture. The product was filtered, washed with methanol, and dried. The yield was 70% based on $Mo(CO)_6$. The corresponding stibine derivative was obtained in 24% yield.

$Mo(CO)_2(AsPh_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($C_6D_6$): δ 7.50 (m, 4 H, α-H), 7.45–7.33 (m, 15 H, C_6H_5), 5.92 (m, 4 H, β-H). ^{1}H NMR ($CDCl_3$): δ 7.24–7.36 (m, 19 H, α-H and C_6H_5), 6.30 and 6.23 (m, 4 H, β-H). The β resonances appear in a ratio of 1:2 due to the $AsPh_3$ adduct and dicarbonyl species with the $AsPh_3$ dissociated (see Discussion).

$Mo(CO)_2(SbPh_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($C_6D_6$): δ 7.51 (m, 4 H, α-H), 7.17–7.42 (m, 15 H, C_6H_5), 5.89 (m, 4 H, β-H). ^{1}H NMR ($CDCl_3$): δ (m, 19 H, α-H and C_6H_5), 6.32 and 6.20 (m, 4 H, β-H; these resonances are in the ratio 1:3 presumably due to a $SbPh_3$ adduct and a solvate species in equilibrium with one another).

$W(CO)_2(PR_3)(S_2CNC_4H_4)_2$ (R = Ph, Et). The following preparative procedure works equally well for the PPh_3 derivative. $W(CO)_6$ (2.67g, 7.60 mmol) was converted to $W(CO)_4Cl_2$.[13] Methylene chloride (25 mL) was added to the yellow solid and caused immediate gas evolution with formation of a yellow-orange solution color. PEt_3 (2.24 mL, 1.80 g, 15.2 mmol) was added. Gas evolution was followed by precipitation of a green-yellow solid, which was isolated by filtration and dried. The infrared spectrum (KBr) showed bands attributable to $W(CO)_3(PEt_3)_2Cl_2$[15] (ν(CO) 2002 (s), 1925 (s), 1877 (s) cm^{-1}) and $W(CO)_2(PEt_3)_2Cl_2$ (ν(CO) 1904 (w), 1792 (w) cm^{-1}). Potassium pyrrole-*N*-carbodithioate was added in a stoichiometric amount to the mixture of tungsten complexes in CH_2Cl_2 (25 mL). The solution was stirred for 2 h, the volume of solvent was reduced, and CH_3OH was added. The solution was cooled overnight. Large red crystals of the products were filtered, washed, and dried (78% yield).

$W(CO)_2(PEt_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.55 (m, 4 H, α-H), 6.33 (m, 4 H, β-H), 2.03 (m, 6 H, CH_2), 1.05 (dt, 9 H, CH_3). ^{31}P NMR ($CDCl_3$): δ 11.8 ($^1J_{^{31}P-^{183}W}$ = 215 Hz).

$W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.21–7.49 (m, 19 H, α-H and C_6H_5), 6.27 (m, 4 H, β-H). ^{31}P NMR ($CDCl_3$): δ 34.3 ($^1J_{^{31}P-^{183}W}$ = 220 Hz).

$W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$, ^{13}CO Enriched. PPh_3 (0.28 g, 1.09 mmol) was added to a CH_2Cl_2 solution of $W(^{13}CO)_3(S_2CNC_4H_4)_2$ (0.60 g, 1.09 mmol). After the mixture was stirred for 1 h, the solution IR showed no tricarbonyl reagent. Bands observed were attributed to $W(^{12}CO)_2(PPh_3)(S_2CNC_4H_4)_2$ (ν(CO) 1955 (s), 1871 (s) cm^{-1}) and $W(^{12}CO)(^{13}CO)(PPh_3)(S_2CNC_4H_4)_2$ (ν(CO) 1940 (s), 1846 (m) cm^{-1}). Infrared intensities suggested that approximately 50% of the material contained one ^{13}C carbonyl ligand. The solution was chromatographed on a short alumina column with methylene chloride and reduced in volume before methanol was added. The flask was cooled overnight to precipitate solid product, which was filtered, washed with methanol, and dried. An 80% yield of red crystals resulted.

$W(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$. A solution of $W(CO)_3(S_2CNC_4H_4)_2$ (0.41 g, 0.74 mmol) in CH_2Cl_2 (25 mL) was prepared. Trimethyl phosphite (0.9 equiv, 0.79 mL, 0.83 g, 0.67 mmol) was added dropwise with stirring. Gas evolved over 5 min, and the solution color changed from orange-brown to orange. The solution IR showed the desired dicarbonyl phosphite as the only product. Solvent was removed in vacuo. The oily product was triturated (pentane/ether, 90:10) and produced a bright red solid, which was isolated, washed with pentane, and dried (80% yield). ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 4 H, α-H), 6.29 (m, 4 H, β-H), 3.66 (d, $^3J_{HP}$ = 12 Hz, 9 H, CH_3). ^{31}P NMR ($CDCl_3$): δ −53.10 ($^1J_{^{31}P-^{183}W}$ = 158 Hz).

$Mo(CO)(PR_3)_2(S_2CNC_4H_4)_2$ (R = Et, OMe). The following preparative procedure works equally well for PEt_3, but the reaction is slower. Trimethyl phosphite (6.3 mL, 6.63 g, 53.4 mmol) was added dropwise to a solution of $Mo(CO)_3(S_2CNC_4H_4)_2$ (11.10 g, 23.90 mmol) in CH_2Cl_2 (150 mL). CO evolved rapidly. After 15 min the solution was dark purple, and bands attributable to $Mo(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$ (ν(CO) 1969 (s), 1890 (sh) cm^{-1}) and $Mo(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$ (ν(CO) 1856 (s) cm^{-1}) were observed in the solution IR spectrum. After 1 h excess $P(OMe)_3$ (1 mL) was added to drive the reaction to completion. After an additional 0.5 h only the monocarbonyl band remained. The product was chromatographed on a short alumina column with CH_2Cl_2. Solvent removal left a dark purple crystalline solid, which was

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washed with pentane and dried (52% yield).

$Mo(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.56 (m, 4 H, α-H), 6.24 (m, 4 H, β-H), 3.62 (d, J_{HP} = 11 Hz, 18 H, CH_3). ^{31}P NMR ($CDCl_3$): δ −61.45.

$Mo(CO)(PEt_3)_2(S_2CNC_4H_4)_2$. ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 4 H, α-H), 6.25 (m, 4 H, β-H), 1.99 (m, 6 H, CH_2), 1.12 (dt, 9 H, CH_3). ^{31}P NMR ($CDCl_3$): 38.0 (s).

$Mo(CO)(Ph_2PC_2H_4PPh_2)(S_2CNC_4H_4)_2$. $Mo(CO)_3(Ph_2PC_2H_4PPh_2)I_2$ was prepared by literature methods.[12] Pyrrole-*N*-carbodithioate (0.180 g, 0.827 mmol) was added as the potassium salt to a solution of $Mo(CO)_3(Ph_2PC_2H_4PPh_2)I_2$ (0.344 g, 0.413 mmol) in CH_2Cl_2 (25 mL). After 20 min the homogeneous solution was red-orange, but after 2 h the solution color was purple and a solution IR spectrum showed bands at 1957 (m), 1875 (m), and 1811 (s) cm^{-1}. After 5 h only the 1811-cm^{-1} band remained. The solution was filtered and reduced to 5 mL. Methanol (15 mL) was added, and the flask was cooled. Purple crystals were isolated by filtration, washed, and dried (45% yield). ^{1}H NMR ($CDCl_3$): δ 7.24–7.65 (m, 24 H, C_6H_5 and α-H), 6.11 (m, 4 H, β-H), 2.73 and 2.54 (m, 4 H, CH_2). ^{31}P NMR ($CDCl_3$): δ 82.54 (s).

$W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$. $W(CO)_2\{P(OMe)_3\}_2Cl_2$ was prepared by addition of slightly more than 2 equiv of $P(OMe)_3$ to $W(CO)_4Cl_2$ dissolved in CH_2Cl_2. Solvent removal produced a red-orange oil. Ether was used to triturate the oil to produce a yellow-green solid, which was filtered and dried in vacuo (73% yield). The product turns blue-green under vacuum. The IR (KBr) spectrum indicates that $W(CO)_2\{P(OMe)_3\}_2Cl_2$ is the only species present in the pellet (ν(CO) 1958 (s), 1869 (s) cm^{-1}). The potassium pyrrole-*N*-carbodithioate salt (0.35 g, 1.60 mmol) was added to a solution of $W(CO)_2\{P(OMe)_3\}_2Cl_2$ (0.47 g, 0.80 mmol) in CH_2Cl_2 and produced an orange-red solution. A solid was isolated after 1 h and showed infrared bands attributable to both the dicarbonyl and the monocarbonyl complexes. This solid was dissolved in THF, and the resulting solution was heated to reflux for 7 h. Only $W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$ was observed in the solution infrared spectrum. The solvent volume was reduced, methanol was added, and the solution was cooled. The dark purple solid that formed was isolated by filtration and dried (35% yield). ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 4 H, α-H), 6.29 (m, 4 H, β-H), 3.66 (d, 18 H, $^3J_{HP}$ = 11 Hz). ^{31}P NMR ($CDCl_3$): δ −51.61 ($^1J_{^{31}P-^{183}W}$ = 184 Hz).

Results

Syntheses. The parent $M(CO)_3(S_2CNC_4H_4)_2$ (M = Mo, W) complexes were prepared directly from $M(CO)_4Cl_2$ (M = Mo, W). The product-containing solutions were rapidly passed through a short alumina column to remove byproducts, all of which adhered to the column. Rapid elution is important since the products slowly decompose on chromatographic supports. $Mo(CO)_3(S_2CNC_4H_4)_2$ must be chromatographed under a carbon monoxide atmosphere to inhibit CO dissociation, and crystallization of $Mo(CO)_3(S_2CNC_4H_4)_2$ required the use of noncoordinating solvents to avoid displacement of a CO ligand.

The 16-electron $Mo(CO)_2(S_2CNC_4H_4)$ complex can be isolated as a tractable green solid by removing all solvent from a methylene chloride solution of $Mo(CO)_3(S_2CNC_4H_4)_2$ and rigorously drying the green oil under dynamic vacuum. Placement of a carbon monoxide blanket over the oil in methylene chloride regenerated the tricarbonyl derivative, which precipitated as large red crystals.

Anionic dicarbonyl halide derivatives were prepared from a slight excess of the tricarbonyl reagents (eq 1 and 2, respectively).

$$Mo(CO)_3(S_2CNC_4H_4)_2 + [Et_4N]X \xrightarrow{CH_2Cl_2} [Et_4N][Mo(CO)_2X(S_2CNC_4H_4)_2] \quad (1)$$

$$W(CO)_3(S_2CNC_4H_4)_2 + [Et_4N]F \xrightarrow{CH_2Cl_2} [Et_4N][W(CO)_2F(S_2CNC_4H_4)_2] \quad (2)$$

The molybdenum iodide analogue, $[Mo(CO)_2I(S_2CNC_4H_4)_2]^-$, was isolated as either the tetraethylammonium or the tetra-*n*-butylammonium salt (Scheme I). The pentacarbonyl iodide anion[8] provided a convenient starting point for the one-pot synthesis of $[R_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ via $[R_4N][Mo(CO)_4I_3]$. Treatment of dissolved $[Mo(CO)_4I_3]^-$ with the dithiocarbamate salt yields a mixture of $Mo(CO)_3(S_2CNC_4H_4)_2$ and $[Mo(CO)_2I(S_2CNC_4H_4)_2]^-$, and passage of nitrogen through the flask promoted CO loss and completely converted the tricarbonyl to the iodo complex. Grinding the solid tetraethylammonium salt of the iodo complex caused a brown to green color change, and the resulting dicarbonyl IR pattern indicated that $Mo(CO)_2(S_2CNC_4H_4)_2$ had formed. Unlike the other halide derivatives, the iodide complexes readily dissociate halide in coordinating solvents as judged by electronic spectra.

Scheme I

$$Mo(CO)_6 + [R_4N]I \xrightarrow[1h]{THF,\ 67\ ^\circ C} [R_4N][Mo(CO)_5I] + CO(g)$$

$$[R_4N][Mo(CO)_5I] + I_2 \xrightarrow[15\ min]{CH_2Cl_2} [R_4N][Mo(CO)_4I_3] + CO(g)$$

$$[R_4N][Mo(CO)_4I_3] + 2K[S_2CNC_4H_4] \xrightarrow[1\ h,\ N_2\ sparge]{CH_2Cl_2} [R_4N][Mo(CO)_2I(S_2CNC_4H_4)_2] + 2CO(g) + 2KI$$

$$R = Et,\ t\text{-}Bu$$

Molybdenum monophosphine complexes $[Mo(CO)_2(PR_3)(S_2CNC_4H_4)_2$ (R = Ph, Et, OMe) were conveniently prepared by using slightly less than 1 equiv of the free phosphine reagent (eq 3). Analogous tungsten complexes $[W(CO)_2(PR_3)(S_2CNC_4H_4)_2$ (R = Ph, Et)] were prepared from $W(CO)_3(PR_3)_2Cl_2$[13] (eq 4). These tungsten products show no inclination to react with free phosphine at room temperature. Trimethyl phosphite, however, readily substitutes for a second carbonyl, so an alternate route (eq 5) was used to prepare $W(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$; slightly less than 1 equiv of phosphite was used to prevent disubstitution. Monocarbonyl $Mo(CO)(PR_3)_2(S_2CNC_4H_4)_2$ products (R = OMe, Et) were prepared from $Mo(CO)_3(S_2CNC_4H_4)_2$ (eq 6). $Mo(CO)(dppe)(S_2CNC_4H_4)_2$ was prepared directly from $Mo(CO)_3(dppe)I_2$ by substitution of pyrrole-*N*-carbodithioate for iodide and carbonyl. The initial product of this reaction is orange and displays a dicarbonyl pattern in the IR spectrum, but after 5 h only the monocarbonyl derivative is detectable in solution.

$$[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2] + PR_3 \xrightarrow[0\ ^\circ C,\ 0.5\ h]{CH_2Cl_2} Mo(CO)_2PR_3(S_2CNC_4H_4)_2 + [Et_4N]I \quad (3)$$

$$W(CO)_3(PR_3)_2Cl_2 + 2K[S_2CNC_4H_4] \xrightarrow{CH_2Cl_2} W(CO)_2(PR_3)(S_2CNC_4H_4)_2 + PR_3 + CO(g) + 2KCl \quad (4)$$

$$W(CO)_3(S_2CNC_4H_4)_2 + P(OMe)_3 \xrightarrow{CH_2Cl_2} W(CO)_2\{P(OMe)_3\}(S_2CNC_4N_4)_2 + CO(g) \quad (5)$$

$$Mo(CO)_3(S_2CNC_4H_4)_2 + 2PR_3 \rightarrow Mo(CO)(PR_3)_2(S_2CNC_4H_4)_2 \quad (6)$$

The only monocarbonyl tungsten derivative we isolated was prepared according to eq 7. We synthesized $W(CO)_2[P(OMe)_3]_2Cl_2$, previously unreported, via a route analogous to that utilized for $W(CO)_3(PR_3)_2Cl_2$ (R = Ph, Et).[9] Some yellow $W(CO)_3\{P(OMe)_3\}_2Cl_2$ forms, but it readily loses CO to form the blue $W(CO)_2\{P(OMe)_3\}_2Cl_2$ product. Addition of pyrrole-*N*-carbodithioate followed by heating promotes CO loss and drives the reaction to $W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$.

$$W(CO)_2\{P(OMe)_3\}_2Cl_2 + 2K[S_2CNC_4H_4] \xrightarrow[67\ ^\circ C,\ 7\ h]{THF} W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2 + 2KCl + CO(g) \quad (7)$$

Several heptacoordinate molybdenum complexes containing a weakly bound seventh ligand ($Mo(CO)_2L(S_2CNC_4H_4)_2$, L = CO, I^-, SC_4H_8, $AsPh_3$, $SbPh_3$) were prepared as red solids. When these were dissolved in coordinating solvents (e.g. THF), $Mo(CO)_2(S)(S_2CNC_4H_4)_2$ species formed, where S is a solvent molecule. The resulting solutions were dark purple in color and IR and UV–vis solution spectra were independent of the identity of the weakly bound ligand L. Addition of THF to solid $Mo(CO)_2(S_2CNC_4H_4)_2$ produced the same solvento complex in solution with spectral properties identical with those of $Mo(CO)_2L(S_2CNC_4H_4)_2$ compounds with weakly bound L ligands (as listed above) in THF. In noncoordinating solvents (e.g. CH_2Cl_2) these

Table I. Infrared Carbonyl Stretching Frequencies for $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ Complexes (n = 0–2)

complex	ν(CO), cm^{-1} solution spectral [solvent]	ν(CO), cm^{-1} solid-state spectra[a]
$Mo(CO)_3(S_2CNC_4H_4)_2$	2042, 1966, 1943 [CH_2Cl_2]	2036, 1946, 1924 (sh)
$W(CO)_3(S_2CNC_4H_4)_2$	2034, 1948, 1928 [CH_2Cl_2]	2028, 1954, 1937, 1912
$Mo(CO)_2(S_2CNC_4H_4)_2$[b]		1956, 1879[b]
$Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$	1949, 1856 [CH_2Cl_2]	1948, 1878
$Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$	1947, 1878 [CH_2Cl_2]	1947, 1878
$Mo(CO)_2(PPh_3)(S_2CNC_4H_4)_2$	1946, 1860 [CH_2Cl_2]	1959, 1892, 1883
$W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$	1941, 1861 [THF]	1953, 1882, 1872
$Mo(CO)_2(AsPh_3)(S_2CNC_4H_4)_2$	1953, 1877 [CH_2Cl_2]	1957, 1893, 1883
$Mo(CO)_2(SbPh_3)(S_2CNC_4H_4)_2$	1947, 1880 [THF]	1954, 1891, 1882
$Mo(CO)_2(PEt_3)(S_2CNC_4H_4)_2$	1955, 1870 [CH_2Cl_2]	1943, 1862
$W(CO)_2(PEt_3)(S_2CNC_4H_4)_2$		1935, 1841
$Mo(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$	1971, 1892 [CH_2Cl_2]	1978, 1895
$W(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$	1960, 1877 [CH_2Cl_2]	1954, 1871
$Mo(CO)(dppe)(S_2CNC_4H_4)_2$	1812 [CH_2Cl_2]	1819
$Mo(CO)(PEt_3)_2(S_2CNC_4H_4)_2$	1804 [THF]	1808
$Mo(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$	1854 [THF]	1849, 1831, 1821
$W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$	1843 [THF]	1839, 1825, 1811
$[Et_4N][Mo(CO)_2F(S_2CNC_4H_4)_2]$	1936, 1855 [CH_2Cl_2]	1924, 1914, 1828
$[Et_4N][W(CO)_2F(S_2CNC_4H_4)_2]$	1904, 1811 [CH_2Cl_2]	1913, 1816
$[Et_4N][Mo(CO)_2Cl(S_2CNC_4H_4)_2]$	1940, 1860 [CH_2Cl_2]	1927, 1832
$[Et_4N][Mo(CO)_2Br(S_2CNC_4H_4)_2]$	1938, 1854 [CH_2Cl_2]	1930, 1833
$[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$	1941, 1855 [THF]	1918, 1836
$[n\text{-}Bu_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$	1935, 1853 [CH_2Cl_2]	1924, 1848

[a] Spectra were recorded with the sample in a compressed KBr pellet unless otherwise indicated. [b] Nujol mull.

Table II. Visible Absorption Data for $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ Complexes (n = 0–2)[a]

complex	λ_{max}, nm
$W(CO)_3(S_2CNC_4H_4)_2$	755, 577, 460 (sh) [755,574,430(sh)]
$Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$	452 [547]
$Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$	[547]
$Mo(CO)_2(PPh_3)(S_2CNC_4H_4)_2$	482, 434 (sh) [489,434(sh)]
$W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$	509, 433 (sh)
$Mo(CO)_2(AsPh_3)(S_2CNC_4H_4)_2$	633, 515, 450 [547]
$Mo(CO)_2(SbPh_3)(S_2CNC_4H_4)_2$	620, 490, 445 [546]
$Mo(CO)_2(PEt_3)(S_2CNC_4H_4)_2$	495, 432 (sh)
$W(CO)_2(PEt_3)(S_2CNC_4H_4)_2$	513, 433 (sh)
$Mo(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$	481, 409 (sh)
$W(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$	740, 573, 497
$Mo(CO)(dppe)(S_2CNC_4H_4)_2$	544
$Mo(CO)(PEt_3)_2(S_2CNC_4H_4)_2$	568
$Mo(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$	506, 420 (sh, w)
$W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$	527
$[Et_4N][Mo(CO)_2F(S_2CNC_4H_4)_2]$	568, 425 (sh, w)
$[Et_4N][W(CO)_2F(S_2CNC_4H_4)_2]$	530
$[Et_4N][Mo(CO)_2Cl(S_2CNC_4H_4)_2]$	536, 445 (sh)
$[Et_4N][Mo(CO)_2Br(S_2CNC_4H_4)_2]$	518, 450 (sh)
$[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$	440 [549]

[a] Spectra were recorded in CH_2Cl_2 solution, except values in brackets, which were recorded in THF solution.

$Mo(CO)_2L(S_2CNC_4H_4)_2$ complexes yielded orange solutions.

Infrared Data. A tabulation of carbonyl stretching frequencies is reported in Table I. Solution spectra exhibited patterns expected for the various complexes: tricarbonyls display bands reminiscent of a (in-phase, higher energy) and e (nearly degenerate, lower energy, broad with some splitting) normal modes, while dicarbonyls show two bands (in-phase and out-of-phase) and monocarbonyls exhibit only one band. Solid-state splittings were particularly evident in spectra of $Mo(CO)_2(EPh_3)(S_2CNC_4H_4)_2$, $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$, $M(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$ (M = Mo, W), and $W(CO)_3(S_2CNC_4H_4)_2$. Carbonyl stretching frequencies for pyrrole-*N*-carbodithioate complexes are generally 20–40 cm^{-1} higher in energy than those of analogous dialkyldithiocarbamate complexes.

Electronic Spectra. Visible absorption data for new seven-coordinate complexes are organized in Table II. Dicarbonyl halide derivatives, $[Et_4N][Mo(CO)_2X(S_2CNC_4H_4)_2]$, have a characteristic absorption, which is halide-dependent: λ_{max} decreases in the order $X = F^- > Cl^- > Br^- > I^-$. The observed λ_{max} for $[Et_4N][W(CO)_2F(S_2CNC_4H_4)_2]$ is less than that of $[Et_4N][Mo(CO)_2F(S_2CNC_4H_4)_2]$. Moncarbonyl bis(phosphine) derivatives show one broad band with λ_{max} between 506 and 568 nm. Molybdenum compounds with a labile seventh ligand ($AsPh_3$, $SbPh_3$, I^-, SC_4H_8, CO) show complex visible spectra with multiple absorptions in methylene chloride, but in THF solution each displays only one broad band (λ_{max} = 547 nm), which we attribute to $Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$. $Mo(CO)_2(S_2CNC_4H_4)_2$ also produces this same absorption with λ_{max} at 547 nm in THF. The visible spectrum of $Mo(CO)_2(S_2CNC_4H_4)_2$ could not be obtained in noncoordinating solvents due to rapid decomposition.

NMR Properties. ^1H, ^{13}C, and ^{31}P NMR data are listed in the Experimental Section. All seven-coordinate compounds appear to be stereochemically nonrigid on the NMR time scale, with room-temperature spectra showing one multiplet each for the α (near 7.5 ppm) and β (near 6.3 ppm) pyrrole protons. The $Mo(CO)_2L(S_2CNC_4H_4)_2$ derivatives with L = $AsPh_3$ or $SbPh_3$ each show two nonintegral pyrrole proton resonances for β protons in $CDCl_3$ (the α protons are masked by phenyl protons), which presumably reflect some dissociation of L. In C_6D_6 only one resonance is observed for the β protons.

Fluxionality of two representative seven-coordinate complexes was probed by variable-temperature ^{13}C NMR studies of ^{13}CO enriched $W(CO)_3(S_2CNC_4H_4)_2$ (Figure 1) and $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$. Experiments performed in $CD_2Cl_2/CDCl_3/CCl_4$ (60:30:10) with $W(CO)_3(S_2CNC_4H_4)_2$ at 0 °C exhibited only one carbonyl resonance (a singlet at 228.8 ppm surrounded by a low-intensity doublet attributed to tungsten–carbon coupling: $^1J_{CW}$ = 120 Hz). Cooling the sample caused this resonance to split into two broad resonances (coalescence at −60 °C) with an intensity ratio of 1:2. Further cooling causes the less intense downfield peak to sharpen to a singlet (244.9 ppm, $^1J_{CW}$ = 126 Hz at −100 °C) while the upfield resonance broadens and splits into two resonances (229.4 and 215.6 ppm), each of the same intensity as the distinct downfield peak. The coalescence temperature for this process was −103 °C.

The ^{13}C NMR of $W(CO)_2(PPh)_3(S_2CNC_4H_4)_2$ displays one carbonyl resonance at 20 °C (245.92 ppm, d, $^2J_{CP}$ = 17 Hz, $^1J_{CW}$

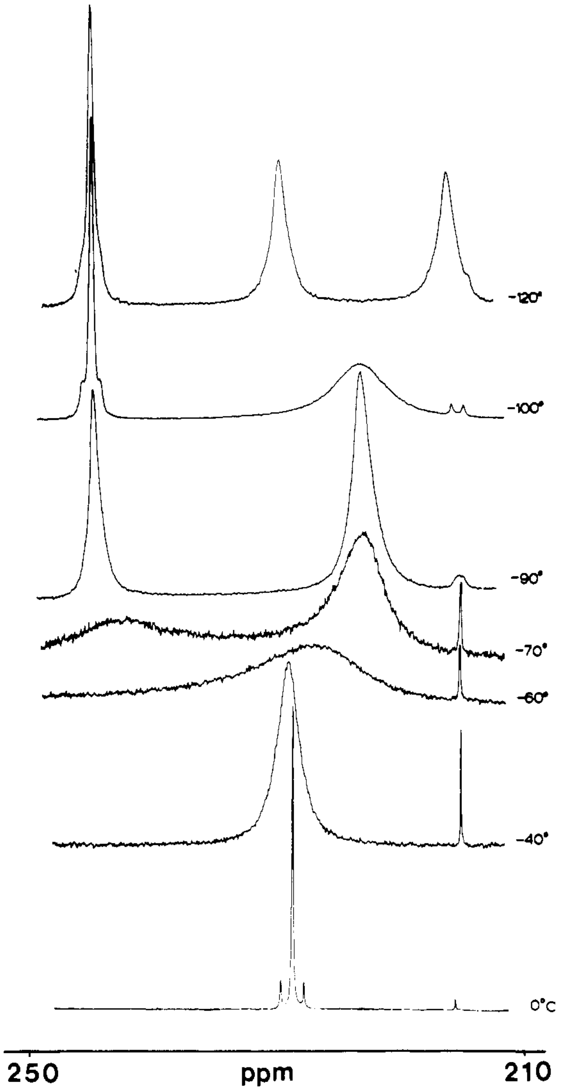

Figure 1. ^{13}C NMR spectra of ^{13}CO-enriched $W(CO)_3(S_2CNC_4H_4)_2$ as a function of temperature. The small high-field signal is due to the central S_2CN carbons.

= 127 Hz). At −90 °C two peaks of equal intensity are observed at 263.2 (d, $^2J_{CP}$ = 32 Hz, $^1J_{CW}$ = 104 Hz) and 227.83 ppm (s, $^2J_{CP} \approx 0$ Hz, $^1J_{CW}$ = 142 Hz). A coalescence temperature of −42 °C was measured for this pairwise exchange of carbonyl carbons.

Discussion

Chemical Reactivity Patterns. Seven-coordinate *N*,*N*-dialkyldithiocarbamate compounds, $M(CO)_3(S_2CNR_2)_2$ (M = Mo,[13] W[14]) and carbonyl substitution products obtained under ambient[15] and forcing[16] conditions have been studied. Carmona and coworkers have recently reported reaction conditions for interconverting $M(CO)_2(PMe_3)(S_2CNR_2)_2$ and $M(CO)(PMe_3)_2(S_2CNR_2)_2$.[17] We report here reactivity and spectral differences observed when the electronically unique pyrrole-*N*-carbodithioate ligand ($^-S_2CNC_4H_4$) is used in place of dialkyldithiocarbamate ligands.

Decreased electron delocalization from nitrogen into the CS_2 fragment makes the pyrrole-*N*-carbodithioate ligand a poor electron donor relative to dialkyl analogues. The reactivity differences observed between heptacoordinate pyrrole-*N*-carbodithioate and dialkyldithiocarbamate complexes confirm the hypothesis that the former have relatively electron-poor metal centers.[12] Major chemical differences observed for the pyrrole-*N*-carbodithioate derivatives include enhanced carbonyl lability and stronger adduct formation with Lewis base donor ligands. Since less metal dπ electron density is available, back-donation to the carbonyls is decreased and this lowers the activation energy for metal–carbonyl bond cleavage. Once a metal–carbonyl bond is broken, the electron-poor pyrrole-*N*-carbodithioate species appears to be more electrophilic than its dialkyldithiocarbamate analogue.

The ease with which $M(CO)_3(S_2CNC_4H_4)_2$ loses carbon monoxide dictates that (1) its synthesis be performed in methylene chloride instead of methanol to prevent solvent coordination and (2) that workup be performed under a CO atmosphere to inhibit CO loss.

Identification of $Mo(CO)_2(S_2CNC_4H_4)_2$ as a green solid rests on infrared spectra (two bands of appropriate energy and relative intensity) and on reactivity properties. The solid reacts rapidly with donor ligands, including CO, to form $Mo(CO)_2L(S_2CNC_4H_4)_2$ adducts; oxygen induces rapid decomposition. The possibility that the green solid was a weakly bound nitrogen adduct, $Mo(CO)_2(N_2)(S_2CNC_4H_4)_2$, was eliminated by use of an argon atmosphere in place of nitrogen during a successful synthesis. This compound was not suitable for use as a reagent due to facile decomposition.

Numerous $M(CO)_nL_{3-n}(S_2CNC_4H_4)_2$ (n = 1, 2) derivatives were accessible from the parent molybdenum or tungsten tricarbonyl bis(pyrrole-*N*-carbodithioate) reagent. Due to the effort required to prepare crystalline $M(CO)_3(S_2CNC_4H_4)_2$, other reagents were often used as vehicles to substituted derivatives as discussed below.

The anionic halide complexes, $[Et_4N][M(CO)_2X(S_2CNC_4H_4)_2]$, are stable, crystalline solids for X = F, Cl, and Br. In contrast, the only dialkyldithiocarbamate halide congener that has been isolated as a solid is $[Et_4N][Mo(CO)_2F(S_2CNEt_2)_2]$,[18] and it readily eliminates $[Et_4N]F$ in solution to regenerate $Mo(CO)_2(S_2CNEt_2)_2$. Carbonyl fluoride complexes are rare across the periodic chart.[19] Except for the synthesis of $Mn(CO)_3F_3$ from $Mn(CO)_5Br$ and AgF,[20] preparative routes to date have been based on exotic starting materials and reaction apparatus. In contrast the fluoride complexes reported here are accessible by simple displacement of a carbonyl ligand by fluoride ion. These carbonyl halide salts are the only anionic molybdenum(II) and tungsten(II) dithiocarbamate complexes of which we are aware.

The isolated iodide adduct, $[R_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$ (R = Et, *n*-Bu), is not very stable and slowly decomposes even under nitrogen. The weakly bound iodide ligand is easily displaced by other nucleophiles, and this feature allows a convenient one-pot synthesis of $Mo(CO)_nL_{3-n}(S_2CNC_4H_4)_2$ phosphine adducts from $[Et_4N][Mo(CO)_4I_3]$. An unusual feature of the solid iodide adduct is that grinding the $[Et_4N]^+$ salt produces a solid-state chemical change, apparently forming the dicarbonyl (eq 8). A

$$[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2] \xrightarrow{\text{grinding}} Mo(CO)_2(S_2CNC_4H_4)_2 + [Et_4N]I \quad (8)$$

similar elimination reaction does not occur for the tetra-*n*-butylammonium derivative. The differences in the solid-state stabilities of these derivatives are subtle and may hinge on lattice energy variations.

Access to $Mo(CO)L_2(S_2CNC_4H_4)_2$ bis(phosphine) derivatives by facile replacement of two carbonyls contrasts with the chemistry of $Mo(CO)_3(S_2CNR_2)_2$ complexes. Consider the synthesis of $Mo(CO)(PR_3)_2(S_2CNEt_2)_2$ (PR_3 = PMe_2Ph, $PMePh_2$), which

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requires boiling in methanol,[16] while $Mo(CO)(PR_3)_2(S_2CNC_4H_4)_2$ (R = OMe, Et) can be prepared in several hours at room temperature. The first carbon monoxide substitution by phosphine is rapid with the second substitution much slower.

A seven-coordinate monocarbonyl complex could also be obtained with the chelating phosphine dppe. Treatment of $Mo(CO)_3(dppe)I_2$ with $^-S_2CNC_4H_4$ immediately produced a dicarbonyl species, ostensibly the monodentate phosphine complex. Chelation of dppe then provides the driving force[21] for formation of $Mo(CO)(dppe)(S_2CNC_4H_4)_2$. The smaller steric bulk of the chelating phosphine compared to two triphenylphosphines probably accounts for the ease of formation of $Mo(CO)(dppe)(S_2CNC_4H_4)_2$ while we were unable to convert $Mo(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ to the bis(triphenylphosphine) derivative.

Formation of the only monocarbonyl tungsten derivative we synthesized, $W(CO)[P(OMe)_3]_2(S_2CNC_4H_4)_2$, required several hours in refluxing THF. The relative inertness of carbonyls bound to tungsten compared to molybdenum is well documented. Enhanced M–C multiple bonding in tungsten carbonyl complexes is reflected in infrared data where tungsten carbonyl complexes have slightly lower carbonyl stretching frequencies than analogous molybdenum complexes.[17]

For several molybdenum dicarbonyl complexes, solution NMR studies show, vide infra, that the donor ligand dissociates in solution with the degree of dissociation dependent on the polarity of the solvent. A tetrahydrothiophene adduct of $Mo(CO)_2(S_2CNEt_2)_2$ that is only stable in the presence of tetrahydrothiophene has been isolated previously.[22] In contrast, $Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$ can be isolated and dried under vacuum without decomposition, although sulfide displacement by solvent does occur in donor solvents. This comparative behavior is reminiscent of the pyrrole-*N*-carbodithioate and dialkyldithiocarbamate dicarbonyl halide complexes discussed above. The stronger adducts formed with pyrrole-*N*-carbodithioate derivatives are a manifestation of increased transition-metal electrophilicity.

Electronic Spectral Data. Visible absorption spectra proved particularly useful for studying complexes with dissociable ligands. $Mo(CO)_3(S_2CNC_4H_4)_2$, $Mo(CO)_2(S_2CNC_4H_4)_2$, and $Mo(CO)_2L(S_2CNC_4H_4)_2$ (L = SC_4H_8, $AsPh_3$, $SbPh_3$, I^-) each have a broad absorption with a λ_{max} of 547 ± 1 nm (Table II) when dissolved in THF; in CH_2Cl_2 the spectra are much more complex. A dicarbonyl infrared pattern is observed for all of these purple THF solutions; recall that the 16-electron $Mo(CO)_2(S_2CNC_4H_4)_2$ complex is green. We believe the only species present in these THF solutions is $Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$. Unlike $Mo(CO)_3(S_2CNC_4H_4)_2$, visible spectra of $W(CO)_3(S_2CNC_4H_4)_2$ in different solvents are in accord with retention of all three carbonyl ligands in solution.

NMR Properties. Both $Mo(CO)_2(AsPh_3)(S_2CNC_4H_4)_2$ and $Mo(CO)_2(SbPh_3)(S_2CNC_4H_4)_2$ give a normal ^1H NMR spectrum in C_6D_6, but two unequal sets of β pyrrole protons are observed in the more polar solvent $CDCl_3$. Apparently dissociation of the tenuously held donor ligand can occur (eq 9). In benzene the

$$Mo(CO)_2L(S_2CNC_4H_4)_2 \rightleftharpoons Mo(CO)_2(S_2CNC_4H_4)_2 + L \quad (9)$$

equilibrium lies completely to the left, in THF it lies completely to the right (as demonstrated by electronic spectra), and in chloroform both compounds are present in detectable amounts.

The sterochemical nonrigidity of $W(CO)_3(S_2CNC_4H_4)_2$ and $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ was probed for comparison with analogous dialkyldithiocarbamate systems. Retention of tungsten–carbon coupling information in the one carbonyl signal observed at room temperature indicates that interconversions of carbonyl ligands are intramolecular.

Table III. Activation Barriers from Variable-Temperature Carbon-13 NMR Data

complex	T, °C	$\Delta G^{\ddagger}$, kcal/mol
$W(CO)_3(S_2CNC_4H_4)_2$	−60	8.9
	−80	9.0
	−80	9.0
		9.0 ± 0.1 (av)
	−103	7.2
	−110	7.1
		7.2 ± 0.1 (av)
$W(CO)_2PPh_3(S_2CNC_4H_4)_2$	−42	9.5
$W(CO)_3(S_2CNEt_2)_2$		8.5 ± 0.1[a]
		7.5 ± 0.1[a]
$W(CO)_2(PPh_3)(S_2CNEt_2)_2$		9.9 ± 0.1[b]

[a] From ref 23. [b] From ref 24.

Two fluxional processes were observed for the carbonyls in $W(CO)_3(S_2CNC_4H_4)_2$. The low-temperature process exchanges two of the three carbonyl ligands. The high-temperature process exchanges these two average carbonyls with the one remaining carbonyl. A simple two-site carbonyl exchange process was evident for $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$. Experimental values of $\Delta G^{\ddagger}$ for these processes at various temperatures are listed in Table III. These energy barriers parallel those previously reported for seven-coordinate dialkyldithiocarbamates.[23] In addition the downfield carbonyl resonance for $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$ has a smaller tungsten–carbon coupling constant ($^1J_{CW}$ = 104 Hz) than the upfield carbon ($^1J_{CW}$ = 142 Hz), an empirical trend evident in other dicarbonyl phosphine complexes. Furthermore the downfield carbonyl resonance couples more strongly to phosphorus than does the upfield carbonyl, presumably reflecting P–W–C angle variations similar to those observed previously.[24] Detection of two independent $S_2CNC_4H_4$ ^{13}C environments is consistent with NMR and X-ray structural results for related compounds.[24] The similarity of temperature-dependent NMR data for pyrrole-*N*-carbodithioate and dialkylidithiocarbamate derivatives suggests that each set of compounds adopts the same gross geometry in solution and undergoes analogous rearrangement processes. We conclude that the electronic character of dithiocarbamates may alter the activation barriers of heptacoordinate complexes slightly, but the overall coordination geometry and seven-coordinate rearrangement schemes are unaffected. Possible rearrangement processes have been presented in detail.[24]

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Registry No. $Mo(CO)_3(S_2CNC_4H_4)_2$, 100993-32-6; $W(CO)_3(S_2CNC_4H_4)_2$, 95069-52-6; $Mo(CO)_2(S_2CNC_4H_4)_2$, 101009-35-2; $Mo(CO)_2(SC_4H_8)(S_2CNC_4H_4)_2$, 100993-33-7; $Mo(CO)_2(OC_4H_8)(S_2CNC_4H_4)_2$, 101009-36-3; $Mo(CO)_2(PPh_3)(S_2CNC_4H_4)_2$, 100993-34-8; $W(CO)_2(PPh_3)(S_2CNC_4H_4)_2$, 101009-37-4; $Mo(CO)_2(AsPh_3)(S_2CNC_4H_4)_2$, 100993-35-9; $Mo(CO)_2(SbPh_3)(S_2CNC_4H_4)_2$, 100993-36-0; $Mo(CO)_2(PEt_3)(S_2CNC_4H_4)_2$, 100993-37-1; $W(CO)_2(PEt_3)(S_2CNC_4H_4)_2$, 101009-38-5; $Mo(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$, 100993-38-2; $W(CO)_2\{P(OMe)_3\}(S_2CNC_4H_4)_2$, 101009-39-6; $Mo(CO)(dppe)(S_2CNC_4H_4)_2$, 100993-39-3; $Mo(CO)(PEt_3)_2(S_2CNC_4H_4)_2$, 100993-40-6; $Mo(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$, 100993-41-7; $W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_4)_2$, 101009-40-9; $[Et_4N][Mo(CO)_2F(S_2CNC_4H_4)_2]$, 100993-43-9; $[Et_4N][W(CO)_2F(S_2CNC_4H_4)_2]$, 101009-42-1; $[Et_4N][Mo(CO)_2Cl(S_2CNC_4H_4)_2]$, 100993-45-1; $[Et_4N][Mo(CO)_2Br(S_2CNC_4H_4)_2]$, 100993-47-3; $[Et_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$, 100993-49-5; $[n\text{-}Bu_4N][Mo(CO)_2I(S_2CNC_4H_4)_2]$, 100993-50-8; $Mo(CO)_4Cl_2$, 15712-13-7; $W(CO)_4Cl_2$, 22172-29-8; $[Et_4N][Mo(CO)_4I_3]$, 85543-14-2; $Mo(CO)_3(Ph_2PC_2H_4PPh_2)I_2$, 17192-23-3; $W(CO)_2\{P(OMe)_3\}_2Cl_2$, 100993-51-9.

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