Tridentate Ligand Effects on Enthalpies of Protonation of $(L_3)M(CO)_3$ Complexes (M = W, Mo)

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Received May 30, 1997

Titration calorimetry has been used to determine the enthalpies of protonation (ΔH_{HM}) for the reaction of $(L_3)M(CO)_3$ complexes, where M = W and Mo and L_3 = cyclic and noncyclic tridentate ligands of the types $\overline{CH_2-CH_2-X-CH_2CH_2-Y-CH_2CH_2-Z}$ and RX-CH_2CH_2−Y−CH_2CH_2-XR with N, S, and P donor atoms, with CF_3SO_3H in 1,2-dichloroethane solution at 25 °C to give $(L_3)M(CO)_3(H)^+CF_3SO_3^-$. The basicities ($-\Delta H_{HM}$) increase with the ligand donor groups (X, Y, or Z) in the order S ≤ PPh ≪ NR (R = Me, Et) for both cyclic and noncyclic ligand complexes that have the same structure of the protonated product. Although the metal basicity ($-\Delta H_{HM}$) generally increases as the ligand donor group basicities (pK_a's of the conjugate acids) increase, the large difference between the pK_a values of thioethers (−6.8) and phosphines (6.25) suggests that thioether donor groups should be much weaker donors than phosphines. The observation that thioether groups contribute nearly as much as phosphine groups to the basicity of the metal in the $(L_3)M(CO)_3$ complexes may be explained by suggesting that repulsion between the π-symmetry lone electron pair on sulfur and the filled metal d orbitals increases the energies of the d orbitals thereby making the metal more basic than expected from only the σ-donor ability of the sulfur. There is a good correlation ($r = 0.973$) between $-\Delta H_{HM}$ and average ν(CO) values of the eight $(L_3)W(CO)_3$ complexes that have the same structure of their protonated forms. A plot of the average of the three ν(CO) frequencies for the $(L_3)W(CO)_3$ complexes *vs* the average ν(CO) frequencies for the analogous Mo complexes is linear ($r = 0.9996$), and the slope of 1.07 indicates that the tridentate ligands have nearly the same electronic effects on both W and Mo complexes. Noncyclic ligands make the metal more basic by 1.6 ± 0.3 kcal/mol than cyclic ligands with the same donor atoms. The tungsten complexes are 2.8 ± 0.1 kcal/mol more basic than their molybdenum analogs. Determinations of ΔH_{HM} values for both *fac*- and *mer*-(PNP)M(CO)$_3$ complexes (M = W, Mo; PNP = $MeN(C_2H_4PPh_2)_2$) allowed the calculation of enthalpies of *mer*-to-*fac* isomerization for both the tungsten (−2.0 kcal/mol) and molybdenum (−4.8 kcal/mol) complexes. These studies demonstrate that the metal, ligands, and geometry of the protonated products all substantially affect the heats of protonation (ΔH_{HM}) of $(L_3)M(CO)_3$ complexes.

Introduction

Basicities of metal centers[1,2] in transition metal complexes are of particular interest because they can be used as a guide to predict other types of reactivity that depend upon electron richness of the metal center.[3] Properties of transition metal complexes are greatly influenced by their ligands, and several studies[4] of ligand effects on spectroscopic, electrochemical, and kinetic properties of complexes have been reported. In previous studies in our laboratories, excellent correlations between metal basicity ($-\Delta H_{HM}$), as measured by the enthalpies of protonation with CF_3SO_3H in 1,2-dichloroethane (DCE) solution at 25 °C (eq 1), and phosphine basicity ($-\Delta H_{HP}$, eq 2, or pK_a of the conjugate acid) have been reported for the following series of phosphine complexes: $CpIr(CO)(PR_3)$,[5,3d] $Fe(CO)_3(PR_3)_2$,[5] $W(CO)_3(PR_3)_3$,[6] and $CpOs(PR_3)_2Br$.[7a]

$$ML_n + CF_3SO_3H \xrightarrow[25\ °C]{DCE} HML_n^+CF_3SO_3^- \quad \Delta H_{HM} \quad (1)$$

$$PR_3 + CF_3SO_3H \xrightarrow[25\ °C]{DCE} HPR_3^+CF_3SO_3^- \quad \Delta H_{HP} \quad (2)$$

Effects of chelating phosphines on the basicities of metal centers were investigated in several systems;[7] it was established

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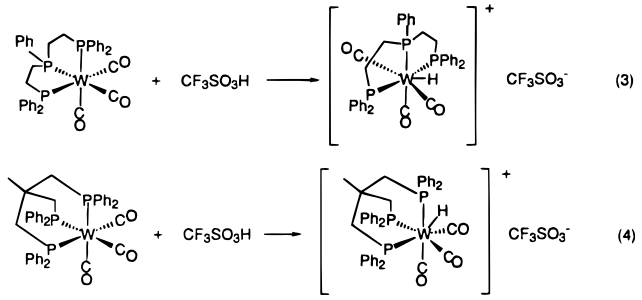
S0020-1669(97)00670-8 CCC: $15.00
Published on Web 01/22/1998

that the metal basicity increases as the size of the chelate ring decreases for *cis*-$M(CO)_2(L\frown L)$ complexes, where M = Mo and W.[7b] Small chelate ring phosphines also increase the basicities of $(L\frown L)Fe(CO)_3$ complexes by distorting their structures from the most stable diaxial P-donor arrangement that is found in the corresponding monodentate phosphine $(L)_2Fe(CO)_3$[7c] complexes. Structural effects of tridentate ligands also influence the $-\Delta H_{HM}$ value of *fac*-$[PhP(C_2H_4PPh_2)_2]W(CO)_3$ (16.7 kcal/mol) (eq 3), which is much more basic than *fac*-$[MeC(CH_2PPh_2)_3]W(CO)_3$ (10.5 kcal/mol) (eq 4).[6,8]



Both complexes have facial structures, but upon protonation, *fac*-$[PhP(C_2H_4PPh_2)_2]W(CO)_3$ rearranges[9] to a structure in which the ligand donor atoms are nearly coplanar with the W atom. The flexibility of the $PhP(C_2H_4PPh_2)_2$ ligand allows the complex to achieve this stable structure, which is also the structure of the complex $(PMePh_2)_3W(CO)_3(H)^+$ with monodentate ligands.[9] On the other hand, the $MeC(CH_2PPh_2)_3$ ligand does not allow the protonated product to achieve this lower energy structure which makes its $-\Delta H_{HM}$ (10.5 kcal/mol) much less favorable for the reaction in eq 4 than that in eq 3.

In order to expand our understanding of tridentate ligand effects on metal basicity, we studied basicities ($-\Delta H_{HM}$, eq 5)

$$fac\text{-}(L_3)M(CO)_3 + CF_3SO_3H \xrightarrow[25\ ^\circ C]{DCE} (L_3)M(CO)_3(H)^+CF_3SO_3^- \quad \Delta H_{HM} \quad (5)$$

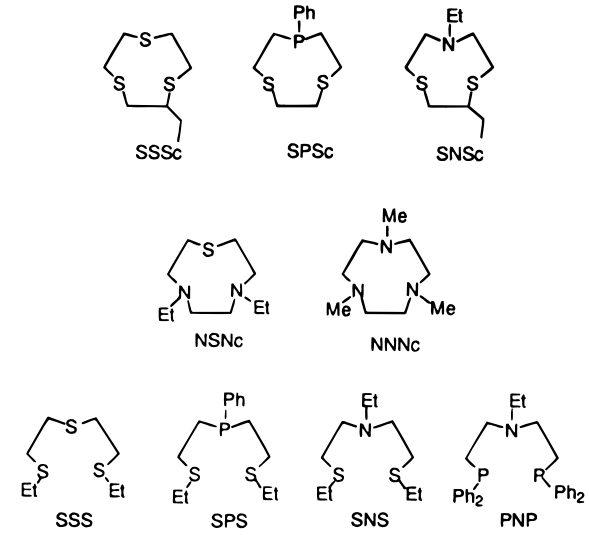
L_3 = SSSc (**1W**, **1Mo**); L_3 = SPSc (**2W**, **2Mo**);
L_3 = SSS (**3W**, **3Mo**); L_3 = SPS (**4W**, **4Mo**);
L_3 = SNSc (**5W**, **5Mo**); L_3 = SNS (**6W**, **6Mo**);
L_3 = NSNc (**7W**, **7Mo**); L_3 = NNNc (**8W**, **8Mo**);
L_3 = PNP (**9W-*fac***, **9Mo-*fac***)

of a series of complexes $(L_3)M(CO)_3$ (M = W, Mo; L_3 = cyclic or noncyclic tridentate ligand with S, N, and/or P donor atoms). The ligands and their abbreviations are shown in Chart 1. The abbreviations are based on the ligand donor atoms, and a small case c distinguishes the cyclic ligands from their noncyclic counterparts. We report here the effects of the donor atoms, the metal, and the structural differences imposed by the ligands on the basicities of these complexes.

Experimental Section

General Procedures. All preparative reactions, chromatography, and manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques,[10] unless otherwise

Chart 1



mentioned. Solvents were purified under nitrogen using standard methods.[11] Hexanes, methylene chloride, and acetonitrile were refluxed over CaH_2 and then distilled. Ethanol (100%) was used as purchased. Tetrahydrofuran (THF), diethyl ether, and dioxane were distilled from sodium benzophenone. CD_2Cl_2 and $CDCl_3$ were stored over molecular sieves under nitrogen. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and again with water. The solvent was then predried over anhydrous $MgSO_4$ and stored in amber bottles over molecular sieves (4 Å). The DCE was distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon prior to use. Neutral alumina (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under vacuum for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under nitrogen. Silica gel (40 μm) used for chromatography was deoxygenated at room temperature under vacuum for 12 h and stored under N_2. 2-Mercaptoethyl sulfide and 1,4,7-trimethyltriazacyclononane (Aldrich) and *N*-ethyldiethanolamine (Acros) were purchased and used as received.

The ^1H NMR spectra were obtained on samples dissolved in $CDCl_3$ or CD_2Cl_2 on a Varian VXR 300-MHz NMR spectrometer using TMS (δ = 0.00 ppm) as the internal reference. The $^{31}P\{H\}$ NMR spectra of samples in CD_2Cl_2 or $CDCl_3$ were recorded on a Bruker AC 200-MHz spectrometer using 85% phosphoric acid (δ = 0.00) as the external reference. Solution spectra were recorded on a Nicolet 710 FT-IR spectrometer using sodium chloride cells with 0.1 mm spacers. Electron ionization mass spectra (EIMS at 70 eV) and chemical ionization mass spectra (CIMS) were run on a Finnigan 4000 spectrometer. Elemental microanalyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

The compounds $M(CO)_3(CH_3CN)_3$, where M = W and Mo, are starting materials for the syntheses of all metal complexes and were prepared according to literature procedures by refluxing $W(CO)_6$ (14 h) or $Mo(CO)_6$(4 h) in CH_3CN.[12,13] The reactions were checked by IR spectroscopy for completeness (ν(CO) (CH_3CN): for $W(CO)_3(CH_3CN)_3$, 1911 (s), 1791 (s, br) cm^{-1}; for $Mo(CO)_3(CH_3CN)_3$, 1920 (s), 1796 (s, br) cm^{-1}). The solutions were then used as such in subsequent reactions.

Preparation of (SSSc)M(CO)$_3$, M = W (1W) and Mo (1Mo). These compounds were prepared by a method described for the synthesis of carbon-substituted 1,4,7 trithiacyclononanes.[14] 1,2-Dibro-

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mobutane (1.12 g, 5.19 mmol) freshly distilled under nitrogen was added dropwise to a suspension of $(NMe_4)_2[W(CO)_3(S(C_2H_4S)_2)]$ (2.82 g, 4.96 mmol), which was prepared exactly as described for the Mo analog,[15] in acetonitrile (20 mL). The resulting brown suspension was stirred for 20 h at room temperature under N_2, and then the solvent was removed under vacuum. The residue was washed with hexanes and then dissolved in CH_2Cl_2 (ca. 30−35 mL). The solution was filtered through a neutral alumina column (2.5 × 3 cm) to remove the Me_4NBr and insoluble decomposition products that formed during the reaction. The filtrate was then concentrated and purified on a neutral alumina column (1.5 × 10 cm) eluting with a 4:1 (v/v) mixture of CH_2Cl_2 and hexanes. The desired product eluted last as a pale yellow band, as determined by checking the fractions by IR spectroscopy. Recrystallization from CH_2Cl_2− ethyl ether gave (SSSc)W(CO)$_3$ (**1W**) (0.732 g, 31%) as a yellow powder. ^{1}H NMR (CD_2Cl_2) for the mixture of isomers: δ [1.12 (t, $^3J_{HH}$ = 6 Hz), 1.19 (t, $^3J_{HH}$ = 7.5 Hz), 3H, CH_3(C−Et)], 1.26−3.59 (m, 13H, CH_2−S). Isomer ratio ∼ 1:2. Anal. Calcd for $C_{11}H_{16}O_3S_3W$: C, 27.74; H, 3.39. Found: C, 27.53; H, 3.38.

The Mo analog, **1Mo**, was obtained in 37% yield (0.731 g) from 1,2-dibromobutane (1.10 g, 5.09 mmol) and $(NMe_4)_2[Mo(CO)_3(S(C_2H_4S)_2)]$[15] (2.45 g, 5.09 mmol) in 15 mL of CH_3CN following the same procedure used for **1W**. ^{1}H NMR (CD_2Cl_2) for the mixture of isomers: δ [1.11 (t, $^3J_{HH}$ = 6 Hz), 1.17 (t, $^3J_{HH}$ = 7.5 Hz), 3H, CH_3(C−Et)], 1.27−3.48 (m, 13H, CH_2−S). Isomer ratio ∼ 1:2. Anal. Calcd for $C_{11}H_{16}O_3S_3Mo$: C, 34.02; H, 4.15. Found: C, 33.82; H, 4.20.

Preparation of (SPSc)M(CO)$_3$, M = W (2W) and Mo (2Mo). The synthesis of these compounds uses a molybdenum template reaction previously applied to the preparation of (1,4,7-trithiacyclononane)Mo(CO)$_3$.[15]

$(NMe_4)_2[PhP(C_2H_4S)_2]$. A solution of $PhP(C_2H_4SH)_2$[16] (1.08 g, 4.69 mmol) in 25% methanolic Me_4NOH (3.42 g, 3.95 mL, 9.38 mmol) was prepared under N_2, stirred at room temperature for 5 min, and evaporated to dryness under vacuum. The yellowish-green residue of $(NMe_4)_2[PhP(C_2H_4S)_2]$ was used for subsequent reactions without further purification.

$(NMe_4)_2[W(CO)_3(PhP(C_2H_4S)_2)]$. A solution of $W(CO)_3(CH_3CN)_3$ (1.83 g, 4.68 mmol) in acetonitrile (30 mL) was transferred under N_2 by cannula to a flask containing $(NMe_4)_2[PhP(C_2H_4S)_2]$ (1.76 g, 4.67 mmol) in an inert atmosphere. The reaction mixture was allowed to stir for 8−10 h at room temperature. The resulting suspension containing a yellow precipitate was used as such in subsequent reactions.

(SPSc)W(CO)$_3$ (2W). Freshly distilled 1,2-dibromoethane (0.883 g, 4.70 mmol) that was saturated with N_2 was added dropwise to a suspension of $(NMe_4)_2[W(CO)_3(PhP(C_2H_4S)_2)]$ (3.01 g, 4.67 mmol) in acetonitrile (30 mL). After the reaction mixture was allowed to stir at room temperature for 2 h, the solvent was removed under vacuum and the brown residue was washed with hexanes and dissolved in CH_2Cl_2 (ca. 30 mL). The suspension was filtered through a neutral alumina column (2.5 × 3 cm) to remove Me_4NBr and insoluble decomposition products that formed during the reaction. The filtrate was concentrated and then purified on a neutral alumina column (1.5 × 10 cm) by eluting with a 4:1 (v/v) mixture of CH_2Cl_2 and hexanes. The desired product elutes last, as determined by IR spectroscopy, as a pale yellow band. Recrystallization from CH_2Cl_2−ethyl ether gave (SPSc)W(CO)$_3$ (**2W**) (0.958 g, 39%) as a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 1.80−1.91 (m, 12H, CH_2−S and CH_2−P), 7.50−7.98 (m, 5H, Ph). ^{31}P{H} NMR (CD_2Cl_2): δ 92.32 (s). Anal. Calcd for $C_{15}H_{17}O_3PS_2W$: C, 34.37; H, 3.27. Found: C, 34.44; H, 3.30.

The Mo analog, **2Mo**, was obtained in 43% yield (0.849 g) from 1,2-dibromoethane (0.849 g, 4.52 mmol) and $(NMe_4)_2[Mo(CO)_3(PhP(C_2H_4S)_2)]$ (2.51 g, 4.52 mmol), which was prepared from $Mo(CO)_3(CH_3CN)_3$ (1.37 g, 4.52 mmol) in 25 mL of CH_3CN and $(NMe_4)_2[PhP(C_2H_4S)_2]$ (1.70 g, 4.52 mmol), according to the procedure used for the synthesis of **2W**. ^{1}H NMR (CD_2Cl_2): δ 1.82−2.93 (m, 12H, CH_2−S and CH_2−P), 7.50−7.98 (m, 5H, Ph). ^{31}P{H} NMR (CD_2Cl_2): δ 93.13 (s). Anal. Calcd for $C_{15}H_{17}O_3PS_2Mo$: C, 41.29; H, 3.93. Found: C, 41.13; H, 3.97. Complex **2Mo** was recently prepared by a very similar route.[17a]

Preparation of (SSS)M(CO)$_3$, M = W (3W) and Mo (3Mo). These syntheses are similar to that used for (2,5,8-trithianonane)Mo(CO)$_3$.[17b]

$S(C_2H_4SEt)_2$ (SSS). To a solution of $S(C_2H_4SH)_2$ (1.18 g, 7.66 mmol) in 30 mL of dry THF cooled to −78 °C was added dropwise a solution of *n*-BuLi (2.5 M in hexanes, 6.2 mL, 15.5 mmol). The reaction mixture was allowed to stir for 15 min, and then EtBr (1.69 g, 15.5 mmol) dissolved in 5 mL of THF was added. After 15 more minutes of stirring, the mixture was warmed to room temperature and concentrated to ca. 10 mL on a rotary evaporator. Water (ca. 30 mL) was added, and the product was extracted with ether. After drying of the ether extract over anhydrous Na_2SO_4, the solvent was removed under vacuum to yield the product as a very pale yellow oil (1.42 g, 88%), which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 2.58 (q, $^3J_{HH}$ = 6 Hz, 4 H, CH_2−Me), 2.72−2.79 (m, 8H, S−CH_2−CH_2−S).

(SSS)W(CO)$_3$ (3W). A solution of $W(CO)_3(CH_3CN)_3$ (1.27 g, 3.25 mmol) in CH_3CN (25 mL) was transferred by cannula under N_2 to a flask containing $S(C_2H_4SEt)_2$ (0.684 g, 3.25 mmol) in an inert atmosphere. The reaction mixture was allowed to stir at room temperature for 5 h. The solvent was then removed under vacuum, and the residue was washed with hexanes and then dissolved in a minimum amount of CH_2Cl_2. The CH_2Cl_2 solution was chromatographed on a neutral alumina column (1.5 × 8 cm) using CH_2Cl_2 as the eluent. The yellow band was collected, and the resulting compound was recrystallized from CH_2Cl_2−ether yielding **3W** (0.793 g, 51% based on $W(CO)_6$) as a yellow microcrystalline mass. ^{1}H NMR (CD_2Cl_2): δ 1.37 (t, $^3J_{HH}$ = 7.5 Hz, 6 H, CH_3), 2.32−2.76 (m, 8H, S−CH_2−CH_2−S), 2.83 (q, $^3J_{HH}$ = 7.5 Hz, 4H, CH_2−Me). Anal. Calcd for $C_{11}H_{18}O_3S_3W$: C, 27.62; H, 3.79. Found: C, 27.80; H, 3.80.

The Mo analog, **3Mo**, was obtained in 55% yield (0.751 g) from $Mo(CO)_3(CH_3CN)_3$ (1.06 g, 3.50 mmol) in 25 mL of CH_3CN and $S(C_2H_4SEt)_2$ (0.736 g, 3.50 mmol) according to the above procedure. ^{1}H NMR (CD_2Cl_2): δ 1.40 (t, $^3J_{HH}$ = 7.5 Hz, 6 H, CH_3), 2.34−2.80 (m, 12H, CH_2-S). Anal. Calcd for $C_{11}H_{18}O_3S_3Mo$: C, 33.84; H, 4.65. Found: C, 34.05; H, 4.65.

Preparation of (SPS)M(CO)$_3$, M = W (4W), and Mo (4Mo). $PhP(C_2H_4SEt)_2$ (SPS) was prepared in 81% yield (1.91 g), as described for the synthesis of $S(C_2H_4SEt)_2$, from $PhP(C_2H_4SH)_2$[16] (1.89 g, 8.22 mmol), *n*-BuLi (6.56 mL, 16.4 mmol, 2.5 M in hexanes), and EtBr (1.79 g, 16.4 mmol). ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 2.45−2.61 (m, 4H, CH_2−S), 1.98−2.07 (m, 4H, P−CH_2), 7.35−7.58 (m, 5H, Ph). MS (CI): *m/e* 287 (MH^+).

(SPS)W(CO)$_3$ (4W) was obtained in 56% yield (1.09 g) , as described for the synthesis of (SSS)W(CO)$_3$, from $W(CO)_3(CH_3CN)_3$ (1.38 g, 3.53 mmol) in acetonitrile (25 mL) and $PhP(C_2H_4SEt)_2$ (1.01 g, 3.53 mmol). ^{1}H NMR ($CDCl_3$): δ 1.37 (t, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 1.86−2.90 (m, 12H, CH_2−S and CH_2−P), 7.51−7.99 (m, 5H, Ph). ^{31}P{H} NMR (CD_2Cl_2): δ 80.46 (s). Anal. Calcd for $C_{17}H_{23}O_3PS_2W$: C, 36.84; H, 4.18. Found: C, 37.06; H, 4.10.

The molybdenum analog, **4Mo**, was prepared in 59% yield (1.03 g), from $Mo(CO)_3(CH_3CN)_3$ (1.13 g, 3.73 mmol) in 25 mL of CH_3CN and $PhP(C_2H_4SEt)_2$ (1.07 g, 3.73 mmol). ^{1}H NMR ($CDCl_3$): δ 1.38 (t, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 1.89−2.95 (m, 12H, CH_2−S and CH_2−P), 7.50−8.00 (m, 5H, Ph). ^{31}P{H} NMR (CD_2Cl_2): δ 81.68 (s). Anal. Calcd for $C_{17}H_{23}O_3PS_2Mo$: C, 43.78; H, 4.97. Found: C, 43.80; H, 5.08.

Preparation of (SNSc)M(CO)$_3$, M = W (5W) and Mo (5Mo). The following sequence of reactions for the synthesis of $EtN(C_2H_4SH)_2$ was adapted from a known procedure for the preparation of $TsN(C_2H_4SH)_2$.[18]

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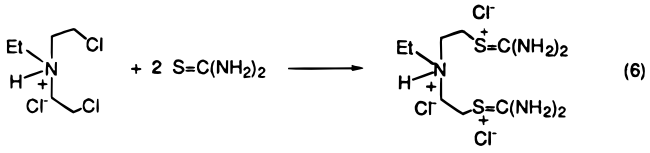
***N*-Ethylbis(2-chloroethyl)ammonium chloride.** To a stirred solution of $SOCl_2$ (14.7 g, 123 mmol) in dry chloroform (10 mL) under N_2 was added dropwise a solution of $EtN(C_2H_4OH)_2$ (7.10 g, 53.3 mmol) in 10 mL of dry chloroform. The reaction mixture was refluxed for 20 min and stirred at room temperature for 1 h. Ethanol (20 mL) was added, and the mixture was refluxed for 2−3 min. Concentrating the solution under vacuum and adding ethyl ether precipitated the product (9.14 g, 83%) as a white solid which was filtered out, washed with ether, and air dried.

Formation of the Thiouronium Salt. *N*-Ethylbis(2-chloroethyl)-ammonium chloride (6.02 g, 29.1 mmol) and thiourea (4.57 g, 60.0 mmol) were refluxed in ethanol (100 mL) under nitrogen for 8−10 h. The fine white precipitate that formed (eq 6) during reflux was filtered



(6)

off, washed with ether and air dried. Concentration of the filtrate and addition of ether yielded more product to give a total yield of 9.53 g (91%). The thiouronium salt was used without further purification.

Hydrolysis of the Thiouronium Salt. A 10% (w/w) aqueous KOH solution (50 mL) was saturated with N_2 for at least 30 min in a 3-necked flask equipped with a condenser. The thiouronium salt (3.02 g, 8.42 mmol) was slowly added in small amounts with stirring while a gentle stream of N_2 was bubbled through the solution. The reaction mixture was then refluxed for 30−40 min under N_2. After cooling, the solution was filtered under N_2 and the filtrate was diluted with 50 mL of deaerated H_2O. Concentrated HCl was then added to the solution until pH ∼ 8 was reached. After the product was extracted with CH_2Cl_2, the resulting solution was dried over anhydrous $MgSO_4$, and the CH_2Cl_2 solvent was removed under vacuum leaving the $EtN(C_2H_4SH)_2$ product as a colorless oil (0.989 g, 71%). ^{1}H NMR ($CDCl_3$): δ 1.03 (t, $^3J_{HH}$ = 6 Hz, 3 H, CH_3), 1.74 (t, $^3J_{HH}$ = 6 Hz, 2H, S−H), 2.51−2.69 (m, 10H, N−CH_2 and S−CH_2). MS (EI): *m/e* 165 (M^+).

$(NMe_4)_2[EtN(C_2H_4S)_2]$ was prepared, as described for $(NMe_4)_2[PhP(C_2H_4S)_2]$, from $EtN(C_2H_4SH)_2$ (0.511 g, 3.09 mmol) and Me_4NOH (2.25 g, 2.60 mL of 25% (w/w) solution in methanol, 6.18 mmol) and used as such in subsequent reactions.

$(NMe_4)_2[W(CO)_3(EtN(C_2H_4S)_2)]$ was prepared, as described for $(NMe_4)_2[W(CO)_3(PhP(C_2H_4S)_2)]$, from $W(CO)_3(CH_3CN)_3$ (1.21 g, 3.09 mmol) in 25 mL of acetonitrile and $(NMe_4)_2[EtN(C_2H_4S)_2]$ (0.963 g, 3.09 mmol); the resulting suspension was used in subsequent reactions.

(SNSc)W(CO)$_3$ (5W) was prepared in 13% yield (0.196 g), as described for the preparation of **1W**, from 1,2-dibromobutane (0.669 g, 3.10 mmol) and $(NMe_4)_2[W(CO)_3(EtN(C_2H_4S)_2)]$ (1.79 g, 3.09 mmol) in 25 mL of acetonitrile. ^{1}H NMR (CD_2Cl_2) for the mixture of isomers: δ [1.12 (t, $^3J_{HH}$ = 7.5Hz), 1.19 (t, $^3J_{HH}$ = 7.5Hz), 3H for both isomers, CH_3(C−Et)],)], [1.28 (t, $^3J_{HH}$ = 7.5 Hz), 1.29 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(N−Et)], 1.60−3.54 (m, 15H, CH_2N and CH_2S). Isomer ratio ∼ 1:8. Anal. Calcd for $C_{13}H_{21}NO_3S_2W$: C, 32.04; H, 4.34; N, 2.87. Found: C, 31.31; H, 4.32; N, 2.88.

The molybdenum analog, **5Mo**, was obtained in 15% yield (0.194 g) from 1,2-dibromoethane (0.702 g, 3.25 mmol) and $(NMe_4)_2[Mo(CO)_3(EtN(C_2H_4S)_2)]$ (1.59 g, 3.24 mmol), which was prepared from $Mo(CO)_3(CH_3CN)_3$ (0.982 g, 3.24 mmol) in 25 mL of CH_3CN and $(NMe_4)_2[EtN(C_2H_4S)_2]$ (1.01 g, 3.24 mmol), according to the procedure used for **5W**. ^{1}H NMR (CD_2Cl_2) for the mixture of isomers: δ [1.11 (t, $^3J_{HH}$ = 7.5 Hz), 1.17 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(C−Et)], [1.29 (t, $^3J_{HH}$ = 7.5 Hz), 1.28 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(N−Et)], 1.60−3.34 (m, 15H, CH_2N and CH_2S). Isomer ratio ∼ 1:1. Anal. Calcd for $C_{13}H_{21}NO_3S_2Mo$: C, 39.10; H, 5.30; N, 3.51. Found: C, 39.30; H, 5.41; N, 3.62.

Preparation of (SNS)M(CO)$_3$, M = W (6W) and Mo (6Mo). The ligand for these complexes was prepared starting with the thiouronium salt that was used in the synthesis of compounds **5W** and **5Mo**.

$EtN(C_2H_4SEt)_2$ (SNS). To a 10% (w/w) ethanolic KOH solution (50 mL) saturated with N_2 for at least 30 min in a 3-necked flask equipped with a condenser was added the thiouronium salt (3.02 g, 8.42 mmol) slowly in small amounts. A gentle stream of N_2 was bubbled through the solution at all times. The reaction mixture was then refluxed for 1 h under a N_2 atmosphere. After the sample was cooled to room temperature, EtBr (1.83 g, 16.8 mmol) was added dropwise, and the reaction mixture was allowed to stir for 30 min at room temperature. The solution was then concentrated to ca. 15 mL on a rotary evaporator, and 40 mL of water was added. The product was extracted from the aqueous solution with ether; the ether extract was dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave $EtN(C_2H_4SEt)_2$ as a pale yellowish oil (1.17 g, 63% based on the thiouronium salt) that was used without further purification for the syntheses of the metal complexes.

(SNS)W(CO)$_3$ (6W) was prepared in 74% yield, based on $W(CO)_6$ (1.52 g), from $W(CO)_3(CH_3CN)_3$ (1.64 g, 4.19 mmol) in 30 mL of acetonitrile and $EtN(C_2H_4SEt)_2$ (0.928 g, 4.19 mmol) as described for the preparation of **3W**. ^{1}H NMR (CD_2Cl_2): δ 1.27 [t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3(N−Et)], 1.36 [t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3(S−Et)], 2.69−3.03 (m, 12H, S−CH_2 and N−CH_2), 3.48 [q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2(N−Et)]. Anal. Calcd for $C_{13}H_{23}NO_3S_2W$: C, 31.91; H, 4.74; N, 2.86. Found: C, 32.17; H, 4.83; N, 2.82.

The molybdenum analog, **6Mo**, was obtained in 78% yield (1.36 g) from $Mo(CO)_3(CH_3CN)_3$ (1.32 g, 4.36 mmol) in 25 mL of CH_3CN and $EtN(C_2H_4SEt)_2$ (0.965 g, 4.36 mmol) following the same procedure described above for the synthesis of **6W**. ^{1}H NMR (CD_2Cl_2): δ 1.27 [t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3(N−Et)], 1.39 [t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3-(S−Et)], 2.53−2.91 (m, 12H, S−CH_2 and N−CH_2), 3.38 [q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2(N−Et)]. Anal. Calcd for $C_{13}H_{23}NO_3S_2Mo$: C, 38.90; H, 5.78; N, 3.49. Found: C, 39.08; H, 5.85; N, 3.51.

Preparation of (NSNc)M(CO)$_3$, M = W (7W) and Mo (7Mo). 4,7-Diethyl-1-thio-4,7-diazacyclononane (NSNc). To an ice-cooled mixture of 1-thia-4,7-diazacyclononane dihydrobromide[19] (2.07 g, 6.72 mmol), methanol (25 mL), and acetaldehyde (1.28 g, 29.1 mmol) was slowly added $NaBH_3CN$ (0.599 g, 9.51 mmol) with continuous stirring. When the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred for 72 h. The solution was then acidified with concentrated HCl to pH = 2, the methanol was removed under vacuum, and 16 mL of H_2O was added to the residue. The solution was brought to pH > 10 with KOH and then saturated with NaCl. After the product was extracted with ether, the ether solution was dried over anhydrous Na_2SO_4 and evaporated to give the product (NSNc) as an oil in 69% yield (0.935 g). ^{1}H NMR ($CDCl_3$): δ 1.03 (t, $^3J_{HH}$ = 6 Hz, 6H, CH_3), 2.54−2.62 (m, 8H), 2.95 (s, 8H). MS (EI): *m/e* 202 (M^+).

(NSNc)W(CO)$_3$ (7W) was prepared in 66% yield (0.808 g) from $W(CO)_3(CH_3CN)_3$ (1.02 g, 2.60 mmol) in 25 mL of acetonitrile and the ligand (NSNc) (0.527 g, 2.60 mmol) as described for the preparation of **3W** but with a longer reaction time, 10 h of stirring at room temperature. ^{1}H NMR (CD_2Cl_2): δ 1.29 [t, $^3J_{HH}$ = 7.5 Hz, 6 H, CH_3-(N−Et)], 2.63−2.85 (m, 8H, S−CH_2−CH_2−N), 3.07−3.14 (m, 4H, N−CH_2−CH_2−N), 3.43−3.55 (m, 4H, CH_2(N−Et)]. Anal. Calcd for $C_{13}H_{22}N_2O_3SW$: C, 33.20; H, 4.72; N, 5.96. Found: C, 33.36; H, 4.77; N, 5.90.

The molybdenum analog, **7Mo**, was obtained in 69% yield (0.760 g) from $Mo(CO)_3(CH_3CN)_3$ (0.873 g, 2.88 mmol) in 25 mL of CH_3CN and the ligand (NSNc) (0.583 g, 2.88 mmol) according to the procedure described above for **7W**. ^{1}H NMR (CD_2Cl_2): δ 1.29 [t, $^3J_{HH}$ = 7.5 Hz, 6 H, CH_3(N−Et)], 2.51−2.81 (m, 8H, S−CH_2−CH_2−N), 2.98−3.10 (m, 4H, N−CH_2−CH_2−N), 3.27−3.45 (m, 4H, CH_2(N−Et)]. Anal. Calcd for $C_{13}H_{22}N_2O_3SMo$: C, 40.84; H, 5.80; N, 7.33. Found: C, 41.09; H, 5.90; N, 7.20.

Preparation of (NNNc)M(CO)$_3$, M = W (8W)[20] and Mo (8Mo),[21] was performed as described in the literature. ^{1}H NMR ($CDCl_3$) for **8W**: δ 2.78−2.87 (m, 6H, N−CH_2), 2.97−3.06 (m, 6H, N−CH_2), 3.16

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Table 1. IR Data for $(L_3)W(CO)_3$ and $(L_3)W(CO)_3(H)^+$ Complexes in CH_2Cl_2 Solution

complex	ν(CO), cm^{-1}			avg ν(CO), cm^{-1}
(SSSc)W(CO)$_3$, **1W**	1929 (s)	1822 (s, br)		1858
(SSSc)W(CO)$_3$H$^+$, **1WH**$^+$	2023 (s)	1950 (s)	1930 (sh)	
(SPSc)W(CO)$_3$, **2W**	1930 (s)	1834 (s)	1819 (s)	1861
(SPSc)W(CO)$_3$H$^+$, **2WH**$^+$	2030 (s)	1952 (s)	1940 (sh)	
(SSS)W(CO)$_3$, **3W**	1923 (s)	1815 (s, br)		1851
(SSS)W(CO)$_3$H$^+$, **3WH**$^+$	2031 (s)	1959 (s)	1942 (sh)	
(SPS)W(CO)$_3$, **4W**	1925 (s)	1829 (s)	1804 (s)	1853
(SPS)W(CO)$_3$H$^+$, **4WH**$^+$	2032 (s)	1961 (s)	1948 (sh)	
(SNSc)W(CO)$_3$, **5W**	1914 (s)	1792 (s, br)		1833
(SNSc)W(CO)$_{3H}^+$, **5WH**$^+$	2025 (s)	1947 (s)	1929 (sh)	
(SNS)W(CO)$_3$, **6W**	1911 (s)	1789 (s, br)		1830
(SNS)W(CO)$_3$H$^+$, **6WH**$^+$	2022 (s)	1942 (s)	1920 (sh)	
(NSNc)W(CO)$_3$, **7W**	1905 (s)	1775 (s, br)		1818
(NSNc)W(CO)$_3$H$^+$, **7WH**$^+$	2015 (s)	1932 (s)	1908 (sh)	
(NNNc)W(CO)$_3$, **8W**	1895 (s)	1758 (s, br)		1804
(NNNc)W(CO)$_3$H$^+$, **8WH**$^+$	2010 (s)	1921 (s)	1902 (sh)	
fac-(PNP)W(CO)$_3$, **9W-fac**	1922 (s)	1823 (s)	1797 (s)	
mer-(PNP)W(CO)$_3$, **9W-mer**	1951 (w)	1839 (vs)	1798 (m)	
(PNP)W(CO)$_3$H$^+$, **9WH**$^+$	2032 (m)	1950 (m)	1919 (vs)	
[MeC(CH$_2$PPh$_2$)$_3$]W(CO)$_3$[a]	1930 (s)	1835 (s, br)		1867
[MeC(CH$_2$PPh$_2$)$_3$]W(CO)$_3$(H)$^+$ [a]	2025 (s)	1954 (s)	1941 (sh)	

[a] Reference 9.

(s, 9H, N−CH$_3$). ^{1}H NMR (CD_2Cl_2) for **8Mo**: δ 2.68−2.79 (m, 6H, N−CH$_2$), 2.91−3.02 (m, 6H, N−CH$_2$), 3.04 (s, 9H, N−CH$_3$).

Preparation of *fac*-(PNP)M(CO)$_3$, M = W (9W-*fac*) and Mo (9Mo-*fac*). Compound **9W** was prepared in 79% yield (4.19 g) from W(CO)$_3$(CH$_3$CN)$_3$ (2.87 g, 7.34 mmol) in 45 mL of CH$_3$CN and MeN(C$_2$H$_4$PPh$_2$)$_2$[22] (PNP) (3.35 g, 7.35 mmol) using a procedure similar to that for the synthesis of **3W**. ^{1}H NMR ($CDCl_3$): δ 2.53−3.10 (m, 8H, P−CH$_2$−CH$_2$−N), 3.06 (s, 3H, CH$_3$−N), 6.84−7.84 (m, 20H, Ph). ^{31}P{H} NMR ($CDCl_3$): δ 33.07 (s).

Compound **9Mo-*fac*** was prepared by following the procedure for the synthesis of **9W-*fac***, in 76% yield (4.13 g) from Mo(CO)$_3$(CH$_3$CN)$_3$ (2.58 g, 8.51 mmol) in 30 mL of CH$_3$CN and MeN(C$_2$H$_4$PPh$_2$)$_2$[22] (PNP) (3.88 g, 8.51 mmol). ^{1}H NMR (CD_2Cl_2): δ 2.48−2.82 (m, 8H, P−CH$_2$−CH$_2$−N), 2.86 (s, 3H, CH$_3$−N), 6.89−7.82 (m, 20H, Ph). ^{31}P{H} NMR (CD_2Cl_2): δ 42.40 (s). Anal. Calcd for $C_{32}H_{31}NO_3P_2Mo$: C, 60.48; H, 4.92; N, 2.20. Found: C, 60.25; H, 5.15; N, 2.13.

Preparation of *mer*-(PNP)M(CO)$_3$, M = W (9W-*mer*) and Mo (9Mo-*mer*). When the protonated complexes **9WH**$^+$**CF$_3$SO$_3$**$^-$ and **9MoH**$^+$**CF$_3$SO$_3$**$^-$ are deprotonated with 1 equiv of 1,3-diphenylguanidine base (DPG) in CH_2Cl_2 or DCE solvent, the reactions are rapid and quantitative, but they yield in both cases the meridional isomers, which are orange compounds as compared with the yellow facial isomers. Attempts to isolate the pure *mer* isomers from these solutions by chromatography on alumina eluting with CH_2Cl_2 yielded only mixtures of facial and meridional isomers; the amounts of the facial isomers increased the longer time the solution was on the column. Chromatography on silica gel afforded almost exclusively the facial isomer. In order to obtain mixtures as rich as possible in the meridional isomers, the solutions of **9WH**$^+$**CF$_3$SO$_3$**$^-$ (4.55 g, 5.21 mmol) and **9MoH**$^+$**CF$_3$SO$_3$**$^-$ (4.20 g, 5.35 mmol) in 20 mL of CH_2Cl_2 were deprotonated with 1 equiv of DPG (1.10 g, 5.21 mmol, for **9WH**$^+$**CF$_3$SO$_3$**$^-$ and 1.13 g, 5.35 mmol, for **9MoH**$^+$**CF$_3$SO$_3$**$^-$) and then chromatographed under N_2 on neutral alumina columns (1.5 × 5 cm) that had been previously rinsed with a dilute solution of NMe_3 in CH_2Cl_2. Solutions of the complexes eluting from the columns were concentrated under vacuum; addition of ether gave orange precipitates that were filtered out and dried under vacuum. Yield = 81% (3.05g) for the **9W-*mer*** + **9W-*fac*** mixture, and yield = 85% (2.89 g) for the **9Mo-*mer*** + **9Mo-*fac*** mixture. Spectroscopic data for **9W-*mer*** are as follows: ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 3H, CH$_3$−N), 2.63−3.40 (m, 8H, P−CH$_2$−CH$_2$−N), 7.27−7.79 (m, 20H, Ph). ^{31}P{H} ($CDCl_3$): δ 41.46 (s). Spectroscopic data for **9Mo-*mer*** are as follows: ^{1}H NMR (CD_2Cl_2): δ 2.48 (s, 3H, CH$_3$−N), 2,68−3.31 (m, 8H, P−CH$_2$−CH$_2$−N), 7.14−7.79 (m, 20H, Ph). ^{31}P{H} (CD_2Cl_2): δ 59.51 (s). The compositions (mole percent) of these mixtures (**9W-*fac*** = 1−3%, **9W-*mer*** = 99−97% for the W system and **9Mo-*fac*** = 8−12%, **9Mo-*mer*** = 92−88% for the Mo system) were determined using Beer plots for pure **9W-*fac*** and **9Mo-*fac*** and absorbances of the ν(CO) peaks in DCE at 1922 cm^{-1} (for **9W-*fac***) and 1929 cm^{-1} (for **9Mo-*fac***) of the mixtures.

Protonation Reactions. Compounds **7W**, **7Mo**, **8W**, **8Mo**, **9W-*fac***, **9Mo-*fac***, **9W-*mer***, and **9Mo-*mer*** were protonated for spectroscopic characterization by dissolving approximatively 5 mg of the complex in 0.7 mL of either CD_2Cl_2 or $CDCl_3$ (for NMR) or in CH_2Cl_2 (for IR) in an NMR tube under nitrogen. To the solution was added 1 equiv of CF_3SO_3H using a gastight microliter syringe. The solutions immediately changed color from yellow to pale yellow with the exception of **9W-*mer*** and **9Mo-*mer***, which were orange and turned pale yellow. The facial isomers (**9W-*fac*** and **9Mo-*fac***) and the meridional isomers (**9W-*mer*** and **9Mo-*mer***) gave the same protonated complex (**9WH**$^+$ and **9MoH**$^+$) upon addition of 1 equiv of CF_3SO_3H. Yields of the protonated products were determined to be quantitative by IR and ^{1}H NMR or ^{31}P{H} NMR spectroscopy. No precipitates formed, and no unidentified bands were present in the ^{1}H NMR spectra which indicates that no other products were formed. Attempts to isolate any of the $(L_3)M(CO)_3(H)^+$ complexes were unsuccessful due to their air-sensitivity. To our knowledge, the only previously reported $(L_3)M(CO)_3(H)^+$ complexes in addition to those in eqs 3 and 4 are (1,4,7-triazacyclononane)M(CO)$_3$(H)$^+$ (M = W, Mo), which were characterized by their elemental analyses and infrared spectra.[23] ^{1}H NMR and ^{31}P{H} NMR data for the protonated complexes at room temperature except where indicated otherwise are given below. IR data are presented in Table 1 for the W complexes and in Table 2 for the Mo complexes.

[(NSNc)W(CO)$_3$(H)](CF$_3$SO$_3$) (7WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.45 (s, 1H,W−H), 1.36 [t, $^3J_{HH}$ = 7.5 Hz, 6H, CH$_3$ (N−Et)], 2.82−2.92 (m, 2H), 3.16−3.25 (m, 6H), 3.38−3.52 (m, 4H), 3.58−3.81 (m, 4H).

[(NSNc)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (7MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −5.12 (s, 1H, Mo−H), 1.37 [t, $^3J_{HH}$ = 7.5 Hz, 6H, CH$_3$ (N−Et)], 2.51−2.81 (m, 8H), 2.98−3.10 (m, 4H), 3.27−3.45 (m, 4H).

[(NNNc)W(CO)$_3$(H)](CF$_3$SO$_3$) (8WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR ($CDCl_3$): δ −4.10 (s, 1H, W−H), 3.06−3.16 (m, 6H, CH$_2$−N), 3.21−3.31 (m, 6H, CH$_2$−N), 3.39 (s, 9H, CH$_3$N).

[(NNNc)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (8MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.87 (s, 1H, Mo-H), 2.99−3.09 (m, 6H, CH$_2$−N), 3.17−3.27 (m, 15H, CH$_2$−N and CH$_3$−N).

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Table 2. IR Data for $(L_3)Mo(CO)_3$ and $(L_3)Mo(CO)_3(H)^+$ Complexes in CH_2Cl_2 Solution

complex	ν(CO), cm^{-1}			avg ν(CO), cm^{-1}
(SSSc)Mo(CO)$_3$, **1Mo**	1936 (s)	1827 (s, br)		1863
(SSSc)Mo(CO)$_3$H$^+$, **1MoH**$^+$	2040 (s)	1963 (s)	1936 (sh)	
(SPSc)Mo(CO)$_3$, **2Mo**	1937 (s, br)	1839 (s)	1824 (s)	1867
(SPSc)Mo(CO)$_3$H$^+$, **2MoH**$^+$	2040 (s)	1989 (s)	1952 (sh)	
(SSS)Mo(CO)$_3$, **3Mo**	1930 (s)	1820 (s, br)		1857
(SSS)Mo(CO)$_3$H$^+$, **3MoH**$^+$	2037 (s)	1967 (s)	1951 (sh)	
(SPS)Mo(CO)$_3$, **4Mo**	1932 (s)	1836 (s)	1810 (s)	1859
(SPS)Mo(CO)$_3$H$^+$, **4MoH**$^+$	2038 (s)	1970 (s)	1955 (sh)	
(SNSc)Mo(CO)$_3$, **5Mo**	1924 (s)	1800 (s, br)		1841
(SNSc)Mo(CO)$_3$H$^+$, **5MoH**$^+$	2030 (s)	1954 (s)	1938 (sh)	
(SNS)Mo(CO)$_3$, **6Mo**	1920 (s)	1796 (s, br)		1837
(SNS)Mo(CO)$_3$H$^+$, **6MoH**$^+$	2028 (s)	1952 (s)	1936 (sh)	
(NSNc)Mo(CO)$_3$, **7Mo**	1914 (s)	1784 (s, br)		1827
(NSNc)Mo(CO)$_3$H$^+$, **7MoH**$^+$	2022 (s)	1941 (s)	1921 (sh)	
(NNNc)Mo(CO)$_3$, **8Mo**	1905 (s)	1765 (s, br)		1812
(NNNc)Mo(CO)$_3$H$^+$, **8MoH**$^+$	2018 (s)	1930 (s)	1911 (sh)	
fac-(PNP)Mo(CO)$_3$, **9Mo-*fac***	1929 (s)	1828 (s)	1804 (s)	
mer-(PNP)Mo(CO)$_3$, **9Mo-*mer***	1958 (w)	1849 (vs)	1803 (m)	
(PNP)Mo(CO)$_3$H$^+$, **9MoH**$^+$	2039 (m)	1939 (vs)		

[(PNP)W(CO)$_3$(H)](CF$_3$SO$_3$) (9WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR ($CDCl_3$): δ −4.71 (dd, $^2J_{HP1}$ = 20 Hz, $^2J_{HP2}$ = 47 Hz, 1H, W-H), 3.04−4.11 (m, 8H, P−CH_2−CH_2−N), 7.45−7.76 (m, 20H, Ph). ^{31}P{H} ($CDCl_3$): δ 41.81 (d, $^2J_{P1P2}$ = 76 Hz), 31.40 (d, $^2J_{P2P1}$ = 76 Hz).

[(PNP)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (9MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2) (−80 °C) : δ −5.3 (dd, $^2J_{HP1}$ = 20 Hz, $^2J_{HP2}$ = 40 Hz, 1H, Mo-H), 2.82−3.79 (m, 8H, P−CH_2−CH_2−N), 7.45−7.83 (m, 20H, Ph). ^{31}P{H} (CD_2Cl_2): δ 58.73 (d, $^2J_{P1P2}$ = 80 Hz), 46.68 (d, $^2J_{P2P1}$ = 80 Hz).

Compounds **1W**−**6W** and **1Mo**−**6Mo** were protonated similarly, but as indicated by the spectroscopic data, the protonations were not complete with 1 equiv of CF_3SO_3H. However, 3 equiv of CF_3SO_3H gave complete protonation in all cases. ^{1}H NMR and ^{31}P{H} NMR data of **1WH**$^+$−**6WH**$^+$ and **1MoH**$^+$−**6MoH**$^+$ are listed below; IR data are presented in Table 1 for the W complexes and in Table 2 for the Mo complexes.

[(SSSc)W(CO)$_3$(H)](CF$_3$SO$_3$) (1WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ [−4.16 (s), −4.15 (s), 1H for both isomers, W−H], [1.20 (t, $^3J_{HH}$ = 7.5 Hz), 1.23 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(C−Et)], 1.78−4.11 (m, 13H, CH_2−S). Isomer ratio ∼ 1:2.

[(SSSc)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (1MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ [−4.33(s), −4.32 (s), 1H for both isomers, Mo−H], [1.18 (t, $^3J_{HH}$ = 7.5 Hz), 1.21 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3-(C−Et)], 1.79−3.93 (m, 13H, CH_2−S). Isomer ratio ∼ 1:2.

[(SPSc)W(CO)$_3$(H)](CF$_3$SO$_3$) (2WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.67 (d, $^2J_{HP}$ = 20 Hz, 1H, W−H), 2.25−3.30 (m, 12H, CH_2S and CH_2P), 7.61−7.81 (m, 5H, Ph). ^{31}P{H} (CD_2Cl_2): δ 88.61 (s).

[(SPSc)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (2MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.67 (d, $^2J_{HP}$ = 20 Hz, 1H, W−H), 2.30−3.26 (m, 12H, CH_2S and CH_2P), 7.59−7.79 (m, 5H, Ph). ^{31}P{H} (CD_2Cl_2): δ 95.26 (s).

[(SSS)W(CO)$_3$(H)](CF$_3$SO$_3$) (3WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.75 (s, 1H, W−H), 1.50 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3), 2.89−3.30 (m, 12H, S−CH_2).

[(SSS)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (3MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.77 (s, 1H, Mo−H), 1.51 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3), 2.95−3.23 (m, 12H, S−CH_2).

[**(SPS)W(CO)$_3$(H)](CF$_3$SO$_3$) (4WH$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ −5.07 (d, $^2J_{HP}$ = 22 Hz, 1H, W-H), 1.49 (t, $^3J_{HH}$ = 8 Hz, 6H, CH_3), 2.17−3.22 (m, 12H, CH_2S and CH_2P), 7.63−7.91 (m, 5H, Ph). ^{31}P{H} (CD_2Cl_2): δ 78.88 (s).

[**(SPS)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (4MoH$^+$CF$_3$SO$_3^-$).** ^{1}H NMR (CD_2Cl_2): δ −5.14 (d, $^2J_{HP}$ = 26 Hz, 1H, W−H), 1.50 (t, $^3J_{HH}$ = 8 Hz, 6H, CH_3), 2.19−3.20 (m, 12H, CH_2S and CH_2P), 7.64−7.89 (m, 5H, Ph). ^{31}P{H} (CD_2Cl_2): δ 85.13 (s).

[(SNSc)W(CO)$_3$(H)](CF$_3$SO$_3$) (5WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ [−4.66 (s), −4.56 (s), 1H for both isomers, W−H], [1.15 (t, $^3J_{HH}$ = 7.5 Hz), 1.19 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3-(C−Et)], [1.35 (t, $^3J_{HH}$ = 7.5 Hz), 1.39 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(N−Et)], 1.86−3.82 (m, 15H, CH_2−S and CH_2−N). Isomer ratio ∼ 1:8.

[(SNSc)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (5MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ [−5.16 (s), −5.09 (s), 1H for both isomers, Mo−H], [1.14 (t, $^3J_{HH}$ = 7.5 Hz), 1.17(t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3-(C−Et)], [1.34 (t, $^3J_{HH}$ = 7.5 Hz), 1.35 (t, $^3J_{HH}$ = 7.5 Hz), 3H for both isomers, CH_3(N−Et)], 1.58−3.58 (m, 15H, CH_2−S and CH_2−N). Isomer ratio ∼ 1:1.

[(SNS)W(CO)$_3$(H)](CF$_3$SO$_3$) (6WH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.47 (s, 1H, W−H), 1.37 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3-(N−Et)), 1.48 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3(S−Et)), 3.01−3.41 (m, 12H, S−CH_2 and N−CH_2), 3.76 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2(N−Et).

[(SNS)Mo(CO)$_3$(H)](CF$_3$SO$_3$) (6MoH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ −4.89 (s, 1H, Mo−H), 1.37 (t, $^3J_{HH}$ = 6 Hz, 3H, CH_3-(N−Et)), 1.49 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3(S−Et)), 2.93−3.35 (m, 12H, S−CH_2 and N−CH_2), 3.66 (q, $^3J_{HH}$ = 6 Hz, 2H, CH_2(N−Et).

Calorimetric Studies. Heats of protonation (ΔH_{HM}) for complexes **7W**, **7Mo**, **8W**, **8Mo**, **9W-*fac***, and **9Mo-*fac***, which were protonated by 1 equiv of acid, were determined under an argon atmosphere by titration with CF_3SO_3H in DCE solution at 25.0 °C, using a Tronac model 458 isoperibol calorimeter as originally described[24] and then modified.[25] A typical calorimetric run consisted of three sections:[26] initial heat capacity calibration, titration, and final heat capacity calibration. Each section was preceded by a baseline acquisition period. During the titration, about 1.2 mL of an approximately 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of a 2.6 mM solution of the complex (5−10% excess) in DCE at 25.0 °C.

Two separate standardized acid solutions were used for the determination of the ΔH_{HM} of each complex. The reported values are the average of at least four titrations and as many as five. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (−0.2 kcal/mol).[25] The reported error in ΔH_{HM} is the average deviation from the mean of all determinations. Titrations of 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (−36.9 ± 0.3 kcal/mol; lit.[24] −37.2 ± 0.4 kcal/mol) were used to monitor the performance of the calorimeter before each set of determinations.

Heats of protonation for complexes **1W**−**6W** were determined by a modified titration procedure which involved adding excess acid (3 equiv) to the complex solution during the 3-min titration period to ensure complete protonation. A typical calorimetric run consisted of the same three sections: initial heat capacity calibration, titration, and

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(25) Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537.
(26) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University: Provo, UT, 1974.

final heat capacity calibration, each section being preceded by a baseline acquisition period. During the titration, about 1.2 mL of an approximately 0.3 M CF_3SO_3H solution (standardized to a precision of ±0.001 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of an approximately 2.4 mM solution of the complex in DCE at 25.0 °C. Because the voltage/time data for the titration period were, as expected, not linear for these complexes, only the initial and the final titration points were used for calculation of the total reaction heat. The reaction enthalpies (ΔH_{exp}), obtained as averages of at least four titrations with two separately standardized acid solutions, were corrected for the heat of dilution of the acid and the heat of hydrogen bonding (see below) between the triflate anion of the protonated complex and the excess triflic acid (eq 9). The magnitude of the correction for dilution and hydrogen bonding was determined by titrating **9Mo-*fac*** with 3 equiv of acid using the same conditions as for complexes **1W**−**6W** and then by subtracting the previously determined ΔH_{HM}(**9Mo-*fac***) from the average value [ΔH_{exp}(**9Mo-*fac***)] of four titrations with two different excess acid solutions (eqs 7 and 8). The error in

$$\Delta H_{\text{Hbond+dil}} = \Delta H_{\text{exp}}(\textbf{9Mo-}\textit{fac}) - \Delta H_{\text{HM}}(\textbf{9Mo-}\textit{fac}) \quad (7)$$

$$\Delta H_{\text{Hbond+dil}} = -32.4(2) - [-19.2(3)] = -13.2(5)\ \text{kcal/mol} \quad (8)$$

$$\Delta H_{\text{HM}}(\textbf{1W}-\textbf{6W}) = \Delta H_{\text{exp}}(\textbf{1W}-\textbf{6W}) - \Delta H_{\text{Hbond+dil}} \quad (9)$$

$\Delta H_{Hbond+dil}$ is the sum of the errors in ΔH_{exp}(**9Mo-*fac***) and ΔH_{HM}(**9Mo-*fac***). The values of ΔH_{exp} (kcal/mol) for complexes **1W**−**6W** are given in brackets: **1W** [−23.8(3)], **2W** [−24.7(3)], **3W** [−25.7(3)], **4W** [−26.5(1)], **5W** [−27.4(3)], **6W** [−28.6(4)]. The reported error in ΔH_{HM} for complexes **1W**−**6W** is the sum of the average deviation from the mean of all the determinations of ΔH_{exp} and the calculated error in $\Delta H_{Hbond+dil}$.

As noted above, the titration of **9Mo-*fac*** which requires only 1 equiv of CF_3SO_3H for complete protonation continues to liberate heat when one and two more equivalents of CF_3SO_3H are added. We attribute this additional heat to the heat of dilution of the acid and to the heat of hydrogen bonding between the $CF_3SO_3^-$ anion generated when **9Mo-*fac*** was protonated and the free CF_3SO_3H acid ($\Delta H_{Hbond+dil} = -13.2$ kcal/mol). There is evidence in the literature that $[CF_3SO_3H\cdots O_3SCF_3]^-$ hydrogen bonding occurs in nonpolar solvents. Bullock and coworkers[27] observed two CF_3SO_3H resonances in the ^{1}H NMR spectra of mixtures of $[Cp^*Os(CO)_2(H)_2]^+CF_3SO_3^-$ and of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+ CF_3SO_3^-$ in the presence of excess acid in CD_2Cl_2 solvent and assigned them to CF_3SO_3H hydrogen bonded to itself and to $CF_3SO_3^-$ as $[CF_3SO_3H\cdots O_3SCF_3]^-$. A CD_2Cl_2 solution of equimolar CF_3SO_3H and $[(Ph_3P)_2N]^+CF_3SO_3^-$ also shows ^{1}NMR evidence for the $[CF_3SO_3H\cdots O_3SCF_3]^-$ species.[27]

Because **9W-*mer*** and **9Mo-*mer*** could not be completely separated from their *fac*-isomers, their heats of protonation were determined by calorimetric titration of three-component mixtures with known compositions of **9W-*mer*** + **9W-*fac*** + DPG and **9Mo-*mer*** + **9Mo-*fac*** + DPG, respectively. During the 3-min titration period, about 1.2 mL of an approximately 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of a 1.8 mM solution of the mixture in DCE. A small excess of acid (20−25%) was used in order to ensure complete protonation of all the species. The compositions (mole percent) of the mixtures varied from run to run but were approximately as follows: **9W-*mer***, = 85−92%; **9W-*fac***, = 3−1%; DPG, 12−7% for the W system; **9Mo-*mer***, 70−80%; **9Mo-*fac***, 15−8%; DPG, 15−12% for the Mo system. The exact composition of each mixture was determined by IR intensities (ν(CO) for *fac*) and weight (*mer* + *fac* and DPG). The extinction coefficients in DCE for **9W-*fac*** and **9Mo-*fac*** were 428 M^{-1} mm^{-1} (at 1922 cm^{-1}) and 480 M^{-1} mm^{-1} (at 1929 cm^{-1}), respectively. During the titration, there is a clear change in slope in the voltage/time data after complete protonation of the complexes and DPG. The heat that is given off beyond that point is attributed to hydrogen bonding between the triflate anion of the protonated complex and the excess acid. The heat of protonation (ΔH_{exp}) of the three-component mixture was determined using the value at the point where the change of slope occurred, i.e., when the complexes and DPG were completely protonated. This heat of reaction was then corrected for acid dilution ($\Delta H_{dil} = -0.2$ kcal/mol) to give ΔH_{total} (eq 10).

$$\Delta H_{\text{total}} = \Delta H_{\text{exp}} - \Delta H_{\text{dil}} = \Delta H_{\text{exp}} - (-0.2\ \text{kcal/mol}) \quad (10)$$

$$\Delta H_{\text{total}} = (\%\ \text{mol}_{fac})\Delta H_{fac} + (\%\ \text{mol}_{mer})\Delta H_{mer} + (\%\ \text{mol}_{\text{DPG}})\Delta H_{\text{DPG}} \quad (11)$$

$$\Delta H_{mer} = \{\Delta H_{\text{total}} - [(\%\ \text{mol}_{fac})\Delta H_{fac} + (\%\ \text{mol}_{\text{DPG}})\Delta H_{\text{DPG}}]\}/\%\ \text{mol}_{mer} \quad (12)$$

Subtraction of the contributions of the DPG ($\Delta H = -36.9$ kcal/mol) and the **9W-*fac*** ($\Delta H_{HM} = -22.1$ kcal/mol) or **9Mo-*fac*** ($\Delta H_{HM} = -19.2$ kcal/mol) from the overall heat of reaction yielded $\Delta H_{H\textbf{9W}-\textit{mer}}$ and $\Delta H_{H\textbf{9Mo}-\textit{mer}}$, respectively (eq 12). The experimental values (ΔH_{exp}) varied from run to run due to the differences in the compositions of the mixtures but were in the range 24.9−25.7 kcal/mol for the W complexes and 24.5−25.6 kcal/mol for the Mo compounds. The reported values are the average of at least four titration runs with two separately standardized acid solutions. The reported error is the average deviation from the mean of all determinations.

Results

Syntheses of the $(L_3)M(CO)_3$ Complexes. Both the molybdenum and tungsten complexes were prepared by following the same procedures. All the complexes with noncyclic ligands were synthesized by the reaction of the ligand L_3 and $M(CO)_3(CH_3CN)_3$ (M = Mo, W) in acetonitrile at room temperature (eq 13).

$$\underset{\text{M = W, Mo}}{M(CO)_3(CH_3CN)_3} + L_3 \xrightarrow[\text{rt}]{CH_3CN} (L_3)M(CO)_3 \quad (13)$$

In the series of complexes with cyclic ligands, compounds **8W**[20] and **8Mo**[21] were prepared as described in the literature by refluxing $W(CO)_6$ or $Mo(CO)_6$ with the ligand in decalin solvent. The syntheses of complexes **7W** and **7Mo** were based on that used for (1-thia-4,7-diazacyclononane)$Mo(CO)_3$[19b] which proved to be extremely insoluble in either CH_2Cl_2 or DCE and therefore not suitable for calorimetric titrations. In order to increase the solubility, complexes of alkylated 1-thia-4,7-diazacyclononane were prepared. Methylation of the diamine with a mixture of formic acid and formaldehyde, as described for the preparation of tetramethylcyclam from cyclam,[28] led to the formation of the still insoluble (4,7-dimethyl-thia-4,7-diazacyclononane)$Mo(CO)_3$. However, compounds **7W** and **7Mo**, obtained by ethylation of 1-thia-4,7-diazacyclononane with acetaldehyde in the presence of $NaBH_3CN$ followed by reaction of the ligand with $M(CO)_3(CH_3CN)_3$ (M = Mo, W), proved to have satisfactory solubilities for the calorimetric studies.

The other members of the series of complexes with cyclic ligands were prepared by a method that was initially used for the synthesis of (1,4,7-trithiacyclononane)$Mo(CO)_3$.[15] The ligand precursor, a dithiolate, is attached as a dianion to the metal−tricarbonyl fragment, and the macrocycle is then closed with a 1,2-dibromoalkane, using the metal−tricarbonyl as a

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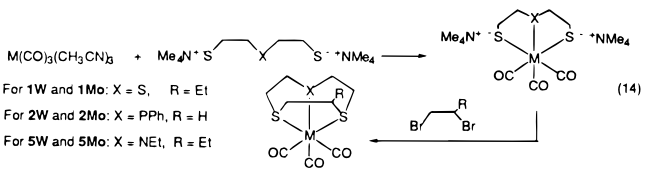
template (eq 14). The synthesis of $(SPSc)M(CO)_3$ (**2W**, **2Mo**)



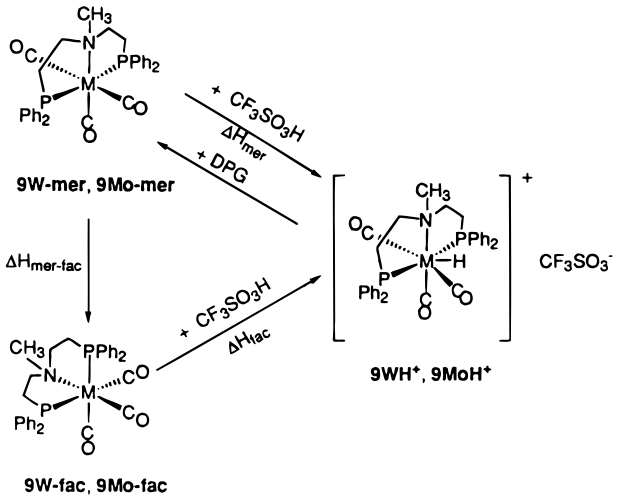
was based on this approach.[29] Complexes (1,4,7-trithiacyclononane)$Mo(CO)_3$[15] and its readily synthesized W analog were not sufficiently soluble in DCE to be studied calorimetrically. In order to increase the solubility, complexes **1W** and **1Mo** were prepared, each as a mixture of isomers, by the method described in the literature for the preparation of carbon-substituted 1,4,7-trithiacyclononanes[14] that uses 1,2-dibromobutane instead of 1,2-dibromoethane to close the ligand cycle. The two isomers differ by the orientation of the ethyl group, which points toward or away from the metal. Their ratio is approximately 1:2 for both the W and Mo complexes, as indicated by ^{1}H NMR data, but the predominant isomer was not determined. The ν(CO) values were the same for the two isomers, which suggests that the orientation of the Et group does not significantly affect the electron-richness of the metal.

Although the preparation of 7-aza-1,4-dithiacyclononane[18] has been reported, it was not chosen as a ligand in these studies because of the difficulty in detosylating 1-tosyl-1-aza-4,7-dithiacyclononane and the expected low solubility in CH_2Cl_2 or DCE of its molybdenum and tungsten tricarbonyl complexes. The related compounds (7-ethyl-7-aza-1,4-dithiacyclononane)$M(CO)_3$ (M = Mo,W) were prepared by following the above-described template synthesis (eq 14) using 1,2-dibromoethane for the ring closure, but their solubilities were still too low. In order to achieve a higher solubility, the cycle was closed with 1,2-dibromobutane, yielding compounds **5W** and **5Mo**, again as a mixture of isomers. The preparation of the ligand precursor $EtN(C_2H_4SH)_2$ was adapted from the synthesis of $TsN(C_2H_4SH)_2$.[18] The ratio of the two isomers, as indicated by NMR data, is approximately 1:8 for **5W** and 1:1 for **5Mo**, but ^{1}H NMR signals were not assigned to specific isomers. Infrared data for the mixture of isomers show only one set of ν(CO) values.

The introduction of ethyl groups on the C-bridge in the cyclic ligands **1W**, **1Mo**, **5W**, and **5Mo** or replacement of the methyl group with an ethyl group on the N in **5W**, **5Mo**, **7W**, **7Mo**, **8W**, and **8Mo** in order to increase the solubility of the metal complexes in DCE is expected to have a minor effect on the donor ability of the ligand. This is supported by the observation that such substitutions do not measurably affect ν(CO) values for the complexes. It has also been shown that complexes of iron, cobalt, nickel, copper, and silver with 1,4,7-trithiacyclononane or 2-methyl-1,4,7-trithiacyclononane ligands have stoichiometries, electronic spectra, and electrochemistries that are not significantly affected by the presence of the methyl group in the ring.[14]

Characterization of the $(L_3)M(CO)_3$ Complexes. The identity and purity of the **1W**−**8W**, and **1Mo**−**8Mo** complexes were established by elemental analysis, IR, ^{1}H NMR, and ^{31}P{H} NMR spectroscopy. The complexes are pale yellow to yellow solids that are air-stable in the solid state for several days, but upon longer exposure to air they show signs of decomposition as indicated by a greenish coloration. All

Scheme 1



complexes have an octahedral geometry with the carbonyl ligands occupying mutually *cis* positions. The *fac* geometry is supported by the IR spectra (Tables 1 and 2) which show a strong, sharp ν(CO) A_1 band at 1895−1937 cm^{-1} and a broad E band at 1758−1839 cm^{-1}. The latter band becomes extremely broad or even splits into two bands when the symmetry of the complex is lowered, especially in the case of tridentate ligands with mixed donor atoms. These spectra are very similar to those of the closely related complexes (1,4,7-trithiacyclononane)$Mo(CO)_3$,[30] (1-thia-4,7-diazacyclononane)$Mo(CO)_3$,[19b] and (2,5,8-trithianonane)$Mo(CO)_3$,[17] whose structures have been established as being octahedral with facially coordinated L_3 ligands by X-ray diffraction studies. The only complexes of the series that exist both as the *fac*- and *mer*- isomers are those with the PNP ligand. Compounds **9W-*mer*** and **9Mo-*mer*** are thermodynamically unstable and isomerize to the *fac* isomers when refluxed in DCE or when traces of acid are present in their solutions. The isomerization of related complexes of the type *fac*-[(η^2−dppm)(PR_3) $M(CO)_3$] and *fac*-[(η^2−dppm)(η^1-dppm-)$M(CO)_3$] (M = W, Mo; dppm = $PPh_2CH_2PPh_2$, PR_3 = PEt_2-Ph, PEt_3) to their *mer* isomers have been reported[31] to be catalyzed by acid; a cationic seven-coordinate hydride complex is proposed as an intermediate. The *mer* isomers **9W-*mer*** and **9Mo-*mer*** could be isolated only as mixtures that contained small amounts of the *fac*-isomers. The *mer* geometry of **9W-*mer*** and **9Mo-*mer*** was assigned on the basis of their weak (∼1955 cm^{-1}), very strong (∼1844 cm^{-1}), and medium (∼1800 cm^{-1}) pattern of ν(CO) bands. The same pattern was reported for other related *mer*-compounds, *mer*-[(η^2-dppm)(η^1-dppm)$W(CO)_3$][32] [1958 (w), 1856 (s), 1833 (m) cm^{-1}] and *mer*-[(η^2−dppm)-(PEt_3)$W(CO)_3$][31] [1954 (w), 1852 (vs), 1832 (m) cm^{-1}].

Characterization of the Protonated Complexes $(L_3)M(CO)_3(H)^+$. The hydride resonances observed in the ^{1}H NMR spectra of the complexes **1WH**$^+$−**9WH**$^+$ and **1MoH**$^+$−**9MoH**$^+$ indicate that the protonation occurs quantitatively at the metal center with 1 equiv of CF_3SO_3H for compounds **7W**, **7Mo**, **8W**, **8Mo**, **9W-*fac***, **9Mo-*fac***, **9W-*mer***, and **9Mo-*mer*** and with 2−3 equiv for compounds **1W**−**6W** and **1Mo**−**6Mo**. Protonation of the *mer* compounds, **9W-*mer*** and **9Mo-*mer***, gives the same protonated forms, **9WH**$^+$ and **9MoH**$^+$, that are obtained by protonation of the *fac*-isomers, **9W-*fac*** and **9Mo-*fac*** (Scheme 1).

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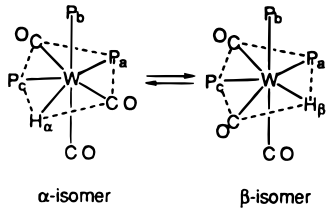
Scheme 2



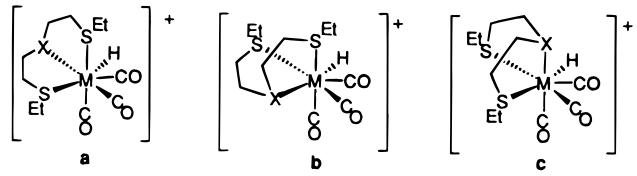
The ν(CO) pattern of compounds **9WH**$^+$ and **9MoH**$^+$, medium (∼2035 cm^{-1}), medium (∼1950 cm^{-1}), and very strong (∼1920 cm^{-1}), is the same as that observed for other protonated complexes of the type $(L)_3W(CO)_3(H)^+$, where L = PR_3, such as $(PEt_3)_3W(CO)_3(H)^+$ [2022 (m), 1943 (m), 1908 (vs) cm^{-1}][9] and $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ [2038 (m), 1976 (m), 1918 (vs) cm^{-1}].[9] These phosphine-containing complexes were proposed to have the pentagonal bipyramidal structure shown in eq 3. The variable-temperature ^{1}H NMR of $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ was investigated extensively.[9] At low temperature (−35 °C) the hydride resonance (−3.78 ppm) was a doublet of doublets which was attributed to α- and β-isomers (Scheme 2), where $J_{PaH\alpha} = J_{PcH\beta} = 46$ Hz and $J_{PcH\alpha} = J_{PaH\beta} = 18$ Hz. At higher temperatures (37 °C), hydride migration is fast and the hydride resonance appears as a triplet as P_a and P_c become equivalent on the NMR time scale.

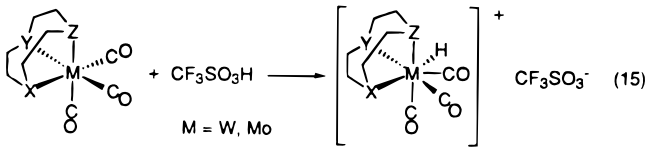
Coupling of the hydride ligand with the axial phosphorus P_b is not observed as P_b is perpendicular to the equatorial plane that contains the hydride and $J_{PbH} \sim 0$.[9] The ^{1}H NMR spectrum of **9WH**$^+$ is very similar to that of $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$, but the hydride migration is slow at room temperature and the hydride resonance (−4.71 ppm) appears as a doublet of doublets with $J_{PaH\alpha} = J_{PcH\beta} = 47$ Hz and $J_{PcH\alpha} = J_{PaH\beta} = 20$ Hz. In the case of **9MoH**$^+$, the ^{1}H NMR spectrum in the hydride region at room temperature was poorly resolved. However, at low temperature (−80 °C), the hydride resonance (−5.3 ppm) appears as a doublet of doublets with $J_{PaH\alpha} = J_{PcH\beta} = 40$ Hz and $J_{PcH\alpha} = J_{PaH\beta} = 20$ Hz. The similarities in their infrared and ^{1}H NMR spectra lead to the conclusion that the protonated complexes **9WH**$^+$ and **9MoH**$^+$ and $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ share the same structure, a pentagonal bipyramid with the ligand having a nearly coplanar disposition of the donor atoms.

In contrast to the structure for **9WH**$^+$ and **9MoH**$^+$, the protonated complexes **1WH**$^+$−**8WH**$^+$ and **1MoH**$^+$−**8MoH**$^+$ have a different disposition of donor atoms in the trigonal bipyramidal structure. The pattern of ν(CO) bands in their IR spectra (Tables 1 and 2), a strong band at 2010−2040 cm^{-1}, a strong band at 1921−1989 cm^{-1}, and a shoulder at 1902−1955 cm^{-1}, is characteristic of three mutually *cis* CO ligands. The positions of the ν(CO) bands in the protonated complexes are 100−150 cm^{-1} higher than those of the $(L_3)M(CO)_3$ compounds, and this shift is consistent with an increase in the positive charge on the metal in these formally divalent seven-coordinate species.

Complexes **1W**, **2W**, **5W**, **7W**, **8W**, **1Mo**, **2Mo**, **5Mo, 7Mo**, and **8Mo** with cyclic ligands have protonated forms that can be compared with $[CH_3C(CH_2PPh_2)_3]W(CO)_3(H)^+$.[9] All of these complexes have rigid tridentate ligands that force the donor atoms to be mutually *cis*. Compound $[CH_3C(CH_2PPh_2)_3]W(CO)_3(H)^+$ was proposed[9] to have the pentagonal structure shown in eq 4. The IR spectra of $[CH_3C(CH_2PPh_2)_3]W(CO)_3(H)^+$ [2025 (s), 1954 (s), 1941 (sh) cm^{-1}][9] and of the protonated complexes with cyclic ligands [∼2025 (s), ∼1940 (s), ∼1930 (sh) cm^{-1}] have the same pattern. The ^{1}H NMR (CD_2Cl_2) spectrum[9] of $[CH_3C(CH_2PPh_2)_3]W(CO)_3(H)^+$ at room temperature in the hydride region consists of a quartet at −4.62 ppm due to equal coupling ($J_{PH} = 21$ Hz) to the three P atoms. The equivalence of the three P atoms suggests that the hydride is fluxional. The phosphorus-containing compounds **2W** and **2Mo** both have hydride signals at −4.67 with $J_{PH} = 20$ Hz. The similarities of the IR and ^{1}H NMR spectra of $[CH_3C(CH_2PPh_2)_3]W(CO)_3(H)^+$ and the protonated complexes with cyclic ligands suggest that they have the same structure (eq 15), a

Chart 2



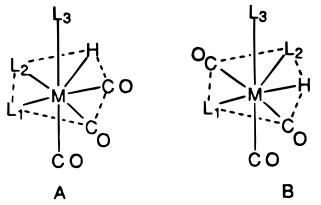


pentagonal bipyramid with mutually *cis* CO ligands. Complexes **1W**, **1Mo**, **5W**, and **5Mo** each exist as mixtures of two isomers resulting from the ethyl group being on the same or opposite side of the ring from the metal. Upon protonation, each isomer yields a separate protonated complex, as indicated by the two hydride peaks in their ^{1}H NMR spectra.

While the structures of the $(L_3)M(CO)_3(H)^+$ complexes are proposed to be based on a trigonal bipyramidal geometry, it is possible that they have a 4:3 piano stool structure as was established for the related cation $[(L_3)Mo(CO)_3Br]^+$ (L_3 = 1,4,7-triazacyclononane).[23] The exact disposition of the ligand donor atoms in these complexes is not known. Assuming a pentagonal bipyramidal structure as in eq 15, it is possible to assign a specific location to the X, Y, and Z atoms for complexes with ligands that contain a P donor atom. This occurs only for (SPSc)W(CO)$_3$(H)$^+$ (**2WH**$^+$) and (SPSc)Mo(CO)$_3$(H)$^+$ (**2MoH**$^+$), for which the coupling constant between the P donor and hydride ligand is $J_{PH} = 20$ Hz. This is very similar to that (18 Hz) for the P-donor *cis* to the hydride in $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ (Scheme 2),[9] which suggests that the P atom in **2WH**$^+$ and **2MoH**$^+$ occupies the Y position (eq 15) *cis* to the hydride in the pentagonal plane.

The protonated complexes **3WH**$^+$, **3MoH**$^+$, **4WH**$^+$, **4MoH**$^+$, **6WH**$^+$ and **6MoH**$^+$, which have noncyclic ligands, have the same ν(CO) pattern as the protonated complexes with cyclic ligands. Thus, they are assigned the same pentagonal bipyramidal structure (eq 15) with mutually *cis* CO ligands. There are three possible structures of this type (Chart 2) that might be considered for **3WH**$^+$, **3MoH**$^+$, **4WH**$^+$, **4MoH**$^+$, **6WH**$^+$, and **6MoH**$^+$. In structure **a** (Chart 2), the hydride ligand is *cis* to the central donor atom X; in structure **b**, these ligands are approximately *trans*. In structure **c**, the bond is perpendicular to the plane that contains the hydride ligand. Complexes **4WH**$^+$ and **4MoH**$^+$, that have X = PPh, are the only compounds for which the structure can be assigned on the basis of the coupling constants $J_{PH} = 22$ Hz (**4WH**$^+$) and $J_{PH} = 26$ Hz (**4MoH**$^+$). As discussed previously (Scheme 2), $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ has a structure in which the hydride lies in the pentagonal plane *cis* to one P atom ($J_{PH} = 18$ Hz) and approximatively *trans* to the other ($J_{PH} = 46$ Hz); J_{PH} coupling to the phosphine that is perpendicular to the pentagonal plane that contains the hydride in $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ is unobservably small

Chart 3



(<2 Hz). On the basis of these coupling constants and the 22 and 26 Hz J_{PH} coupling constants for compounds **4WH**$^+$ and **4MoH**$^+$, we assign structure **a** (Chart 2), in which the hydride and P donor groups are *cis* to each other, to complexes **4WH**$^+$ and **4MoH**$^+$. It is not possible to assign a specific structure **a**, **b**, or **c** to **3WH**$^+$, **3MoH**$^+$, **6WH**$^+$, or **6MoH**$^+$.

To summarize the structures of the $(L_3)M(CO)_3(H)^+$ complexes, the protonated forms **1WH**$^+$−**8WH**$^+$ and **1MoH**$^+$−**8MoH**$^+$ are assigned a pentagonal bipyramidal structure with mutually *cis* ligand donor atoms and mutually *cis* CO ligands (structure A, Chart 3) and complexes **9WH**$^+$ and **9MoH**$^+$ a pentagonal bipyramidal structure with the ligand donor atoms approximately coplanar with the metal and the CO ligands also approximately coplanar with the metal (structure B, Chart 3).

Complexes **1H**$^+$−**8H**$^+$ and **1MoH**$^+$−**8MoH**$^+$ are deprotonated rapidly (< 5 s) by 1,3-diphenylguanidine base (DPG) in CH_2Cl_2 or DCE solvent. This deprotonation gives back complexes **1W**−**8W** and **1Mo**−**8Mo** as their *fac* isomers, which are recovered by chromatography on an alumina column (1.5 × 8 cm) by elution with CH_2Cl_2 and recrystallization of the chromatographed product from CH_2Cl_2/ether. In the cases of **9WH**$^+$ and **9MoH**$^+$, deprotonation with DPG yields isomers that are different than the starting **9W-*fac*** and **9Mo-*fac*** (Scheme 1). Addition of 1 equiv of DPG to a solution of **9WH**$^+$ or **9MoH**$^+$ in DCE or CH_2Cl_2 generates immediately the deep orange color of **9W-*mer*** and **9Mo-*mer***, as opposed to the yellow color of **9W-*fac*** or **9Mo-*fac*** solutions. Chromatography on alumina eluting with CH_2Cl_2 yields a mixture of the two isomers, but when silica gel is used, the final mixture contains almost exclusively the *fac* isomer. The *mer* complexes proved to be stable at room temperature in the solid state; however, in solution, heat (refluxing in DCE) or even traces of acid trigger the *mer*-to-*fac* isomerization. However, in the presence of small amounts (1−2%) of basic DPG, which presumably scavenges any acidic species, the *mer* isomers are stable in solution at room temperature for several hours.

Calorimetry Studies. Heats of protonation (ΔH_{HM}) determined by calorimetric titration of the complexes, **1W**−**8W**, **9W-*fac***, **9W-*mer***, and **7Mo**, **8Mo**, **9Mo-*fac***, and **9Mo-*mer***, with CF_3SO_3H in DCE solvent at 25.0 °C are presented in Tables 3 and 4. For the compounds that protonated completely with 1 equiv of acid (**7W**, **8W**, **9W-*fac***, **7Mo**, **8Mo**, and **9Mo-*fac***) the plots of temperature *vs* amount of acid added were linear. There was no decomposition of either the neutral or protonated complexes during the titration experiment, as evidenced by normal pre-and post-titration baseline slopes. For the complexes that required excess acid (3 equiv) for complete protonation, plots of temperature vs amount of acid added were not linear, as expected for equilibrium protonations, but the normal pre- and post-titration baseline slopes indicated that there was no decomposition during the experiment. However, this was not the case with the molybdenum complexes **1Mo**−**6Mo**, and we were unable to obtain reproducible ΔH_{HM} values for these compounds.

Table 3. Heats of Protonation (ΔH_{HM}) for the $(L_3)W(CO)_3$ Complexes

compd	$-\Delta H_{HM}$, kcal/mol
(SSSc)W(CO)$_3$, **1W**	10.6(8)[a]
(SPSc)W(CO)$_3$, **2W**	11.5(8)[a]
(SSS)W(CO)$_3$, **3W**	12.5(8)[a]
(SPS)W(CO)$_3$, **4W**	13.3(6)[a]
(SNSc)W(CO)$_3$, **5W**	14.2(8)[a]
(SNS)W(CO)$_3$, **6W**	15.4(9)[a]
(NSNc)W(CO)$_3$, **7W**	17.4(1)[b]
(NNNc)W(CO)$_3$, **8W**	20.9(3)[b]
fac-(PNP)W(CO)$_3$, **9W-fac**	22.1(1)[b]
mer-(PNP)W(CO)$_3$, **9W-mer**	24.1(2)[b]
fac-[PhP($C_2H_4PPh_2$)$_2$]W(CO)$_3$	16.7(1)[c]
[MeC(CH_2PPh_2)$_3$]W(CO)$_3$	10.5(1)[c]

[a] Protonation with excess (3 equiv) of CF_3SO_3H in DCE solvent at 25.0 °C. Numbers in parentheses are average deviations of at least 4 determinations, as described in the text. [b] Protonation with 1 equiv of CF_3SO_3H in DCE solvent at 25.0 °C. Numbers in parentheses are average deviations from the mean of at least four titrations. [c] Reference 8.

Table 4. Heats of Protonation (ΔH_{HM}) for the $(L_3)Mo(CO)_3$ Complexes

compd	$-\Delta H_{HM}$,[a] kcal/mol
(NSNc)Mo(CO)$_3$, **7Mo**	14.6(3)
(NNNc)Mo(CO)$_3$, **8Mo**	18.3(3)
fac-(PNP)Mo(CO)$_3$, **9Mo-*fac***	19.2(3)
mer-(PNP)Mo(CO)$_3$, **9Mo-*mer***	24.0(3)

[a] Protonation with 1 equiv of CF_3SO_3H in DCE solvent at 25.0 °C. Numbers in parentheses are average deviations from the mean of at least four titrations.

Discussion

Thioether and Tertiary Amine Ligand Effects on Metal Basicity ($-\Delta H_{HM}$). The heats of protonation of the series of $(L_3)W(CO)_3$ complexes with tridentate cyclic ligands containing S and N donor atoms (Table 3) increase with the ligand in the following order ($-\Delta H_{HM}$, kcal/mol, in parentheses): SSSc (10.6) < SNSc (14.2) < NSNc (17.4) < NNNc (20.9). In an effort to understand this trend, one might consider the relative electron-donating abilities of the S and NR (R = Me or Et) groups. As discussed in the Introduction, the basicities ($-\Delta H_{HM}$) of metal complexes increase linearly with the basicities (as measured by $-\Delta H_{HP}$ or pK_a) of their phosphine ligands. Thus one might expect the pK_a's of the conjugate acids of thioethers (Et_2S) and amines (Et_2N-R) to be a guide to the donor abilities of the S and NR groups in the cyclic ligands and to the $-\Delta H_{HM}$ values of their complexes. The pK_a of the conjugate acid of Et_3N is 10.80[33] while that of Et_2S[34] is only −6.8. Therefore, we expect the basicities ($-\Delta H_{HM}$) of the complexes to increase as S donors are replaced by NR, as observed. Replacement of each S by a NR group (R = Me or Et) increases the basicity by 3.4 ± 0.2 kcal/mol; this value is the same within experimental error whether it is for the first S atom, the second, or the third. The same trend is observed in the molybdenum series (Table 4), although only two ΔH_{HM} values are available for comparison. Thus, the increase in basicity ($-\Delta H_{HM}$) for replacement of a S by NR in (NSNc)Mo(CO)$_3$ (**7Mo**) (14.6 kcal/mol) to give (NNNc)Mo(CO)$_3$ (**8Mo**) (18.3 kcal/mol) is 3.7 kcal/mol, which is the same within experimental error as for the W series (3.4 kcal/mol). That replacement of ligand donor groups affects the

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(34) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

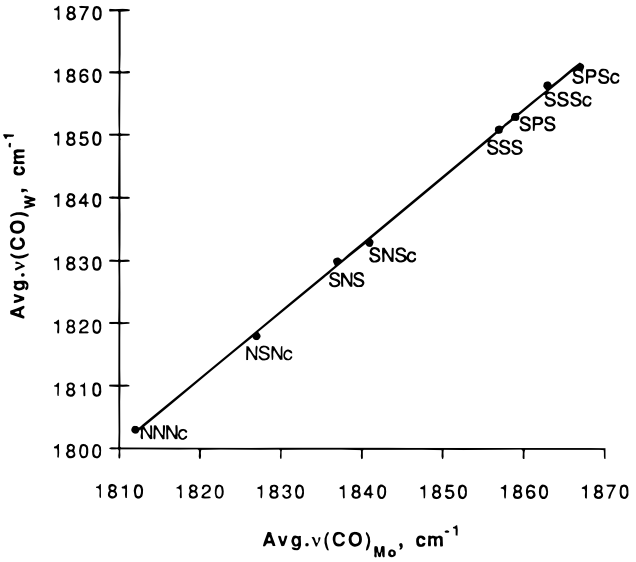

Figure 1. Correlation (eq 16) of the average value of the ν(CO) bands of $(L_3)W(CO)_3$ complexes (Table 1) with the average value of the ν(CO) bands of $(L_3)Mo(CO)_3$ complexes (Table 2).

electron richness of both tungsten and molybdenum complexes to the same extent is also supported by a plot of the average of the three ν(CO) frequencies (Table 1) for the $(L_3)W(CO)_3$ complexes vs the average ν(CO) frequencies (Table 2) for the analogous Mo complexes (Figure 1). The correlation (r = 0.9996) is expressed in eq 16, and the slope of approximately 1 indicates that the ligands have nearly the same effect on both W and Mo complexes.

$$\text{avg } \nu(\text{CO})_{\text{W}} = -139.8 + 1.072[\text{avg } \nu(\text{CO})_{\text{Mo}}] \quad (16)$$

For complexes with noncyclic tridentate ligands containing S and N donor atoms, replacement of the central S by NEt increases the basicity by 2.9 kcal/mol from (SSS)W(CO)$_3$ (**3W**) (12.5 kcal/mol) to (SNS)W(CO)$_3$ (**6W**) (15.4 kcal/mol). Although this replacement seems to have a somewhat smaller effect on the basicity of the metal, the overall trend is the same as in the case of the cyclic ligand complexes.

Phosphine and Amine Ligand Effects on Metal Basicity ($-\Delta H_{\text{HM}}$). As expected from the pK_a values of the conjugate acids of Et_3N (pK_a = 10.8)[33] and Et_2PhP (pK_a = 6.25)[35] and from their enthalpies of protonation ($-\Delta H_{\text{HN}}$ = 39.3 kcal/mol[7b] and $-\Delta H_{\text{HP}}$ = 27.8 kcal/mol,[6] respectively), the NEt group is a better donor than the PPh group. This is reflected in the higher basicity of (SNSc)W(CO)$_3$ (**5W**) (14.2 kcal/mol) as compared with that of (SPSc)W(CO)$_3$ (**2W**) (11.5 kcal/mol). Thus in the cyclic ligand complexes, replacement of PPh by NEt results in a 2.7 kcal/mol increase in the basicity of the metal.

For complexes with noncyclic ligands, the basicity of the metal in (SPS)W(CO)$_3$ (**4W**) (13.3 kcal/mol) increases by 2.1 kcal/mol when the central PPh group is substituted by NEt to give (SNS)W(CO)$_3$ (**6W**) (15.4 kcal/mol). Thus the complexes with noncyclic ligands follow the same trend as those with cyclic ligands when their protonated complexes have the same structure (structure A, Chart 3).

Complex *fac*-(PNP)W(CO)$_3$ (**9W-*fac***) (22.1 kcal/mol), which also has a noncyclic ligand, is 5.4 kcal/mol more basic than the previously studied *fac*-[PhP($C_2H_4PPh_2)_2$]W(CO)$_3$ (16.7 kcal/mol).[6,8] However, both protonated forms **9WH**$^+$ and [PhP(C_2H_4-PPh_2)]W(CO)$_3$(H)$^+$ have structure B (Schemes 1 and Chart 3). Thus, for reasons that are not known at this time, the replacement of PPh by NEt increases the basicity by 5.4 kcal/mol when the protonated products have structure B (Scheme 1 and Chart 3) but only 2.7 or 2.1 kcal/mol when the products have structure A (Chart 3).

Phosphine and Thioether Ligand Effects on Metal Basicity ($-\Delta H_{\text{HM}}$). Replacement of a S donor atom by a PPh in (SSSc)W(CO)$_3$ (**1W**) (10.6 kcal/mol) to give (SPSc)W(CO)$_3$ (**2W**) (11.5 kcal/mol) increases the basicity of the metal only very slightly (by 0.9 kcal/mol). A comparison of $-\Delta H_{\text{HM}}$ for **1W** with that of the related *fac*-[MeC($CH_2PPh_2)_3$]W(CO)$_3$ (10.5 kcal/mol),[6,8] which has a ligand that also requires the three donor atoms to be *fac*-coordinated in the reactant and protonated product, shows that they have the same $-\Delta H_{\text{HM}}$ values within experimental error. Thus, in this latter comparison, the thioether and PPh_2 donor groups have about the same effect on the basicity of the metal assuming the different structures of the SSSc and MeC($CH_2PPh_2)_3$ ligands do not affect the $-\Delta H_{\text{HM}}$ values significantly.

In the noncyclic ligand series, replacement of the central S (structure **a**, Chart 2) in (SSS)W(CO)$_3$ (**3W**) (12.5 kcal/mol) by a PPh donor group to give (SPS)W(CO)$_3$ (**4W**) (13.3 kcal/mol) results again in a very small increase of the basicity of the metal center (0.8 kcal/mol), which leads to the conclusion that the donor ability of PPh is slightly larger than that of S for complexes that give protonated complexes of type A structure (Chart 3). The relative donor abilities of these groups toward H^+ can be evaluated by comparing the pK_a values of the protonated forms of Et_2S (−6.8)[34] and Et_2PPh (6.25).[35] On this basis, S is expected to be a *much* weaker donor than PPh. In order to understand why the basicity of **3W** is nearly as large as that of **4W**, one might consider that, besides the σ-donor electrons on S, there is also a lone electron pair that can raise the energy of the metal dπ orbitals by repulsive interactions, which would make the S atom a stronger overall donor than expected from σ-donation alone. Effects of lone electron pairs on properties of sulfur ligands have been noted in other systems.[36]

A comparison of $-\Delta H_{\text{HM}}$ values for noncyclic ligand complexes (SNS)W(CO)$_3$ (**6W**) (15.4 kcal/mol) and *fac*-(PNP)W(CO)$_3$ (**9W-*fac***) (22.1 kcal/mol) would indicate at first glance that replacement of two SEt donor groups with two PPh_2 donor groups enhances the basicity of the metal center by 6.7 kcal/mol. However, the two complexes give protonated forms that have different structures; in **6WH**$^+$ the donor atoms occupy mutually *cis* positions (structure A, Chart 3), while in **9WH**$^+$ the donor atoms are approximately coplanar with the metal (structure B, Chart 3). Considering that the thioether and PPh_2 donor groups make essentially the same contribution to the basicity of the metal (see two paragraphs above), the 6.7 kcal/mol difference can be attributed primarily to steric repulsion between the PPh_2 groups which is relieved by rearrangement to structure B in the **9WH**$^+$ product. The 6.7 kcal/mol difference between ΔH_{HM} values for **9W-*fac*** and **6W** is similar to that (6.2 kcal/mol) between *fac*-[MeC($CH_2PPh_2)_3$]W(CO)$_3$ (ΔH_{HM} = −10.5 kcal/mol)[6,8] and *fac*-[PhP($C_2H_4PPh_2)_2$]W(CO)$_3$ (ΔH_{HM} = −16.7 kcal/mol),[6,8] whose protonated forms have structures (A and B, Chart 3) that differ in the same way as **9WH**$^+$ and **6WH**$^+$ (eqs 3 and 4). The more exothermic value for *fac*-[PhP($C_2H_4PPh_2)_2$]W(CO)$_3$ is also presumably due to relief of steric repulsion between the PPh_2 groups upon protonation to give a product with structure B (eq 3).

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(36) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

Enthalpy for the Isomerization of *mer*-(PNP)M(CO)$_3$ to *fac*-(PNP)M(CO)$_3$. The $(PNP)M(CO)_3$ (M = W, Mo) complexes were the only ones that could be prepared as both the *fac* and *mer* isomers. They both protonate to give the same product, **9WH**$^+$ or **9MoH**$^+$ (Scheme 2). Using ΔH_{HM} values for both isomers allows one to calculate the heat of reaction ($\Delta H_{mer-fac}$) for the isomerization of the *mer* complex to the thermodynamically more stable *fac* isomer using the thermodynamic cycle given in eqs 17−19 and represented in Scheme

$$\Delta H_{mer-fac} = \Delta H_{mer} - \Delta H_{fac} \quad (17)$$

$$\text{W system:} \quad \Delta H_{mer-fac}(W) = -24.1(2) - [-22.1(1)] = -2.0(3) \text{ kcal/mol} \quad (18)$$

$$\text{Mo system:} \quad \Delta H_{mer-fac}(Mo) = -24.0(3) - [-19.2(3)] = -4.8(6) \text{ kcal/mol} \quad (19)$$

1. In order to understand the less exothermic *mer*-to-*fac* rearrangement for **9W-*mer*** as compared with that for **9Mo-*mer***, one can consider that tungsten behaves as a more electron rich metal center than Mo as suggested by pK_a,[37] enthalpy of protonation,[7b] and redox potential[38] studies of their complexes. This greater electron richness allows W to π-back-bond to a larger degree to the CO groups that are *trans* to each other in the *mer* isomer, thereby stabilizing this isomer more in the tungsten complex than the molybdenum. The greater stabilization of **9W-*mer*** as compared to **9Mo-*mer*** results in a less exothermic $\Delta H_{mer-fac}$ for the tungsten complex rearrangement.

Cyclic and Noncyclic Tridentate Ligand Effects on Metal Basicity ($-\Delta H_{HM}$). A comparison of ΔH_{HM} values for complexes with cyclic and noncyclic ligands that have the same donor groups, (SNSc)W(CO)$_3$ (**5W**) (14.2 kcal/mol) and (SNS)W(CO)$_3$ (**6W**) (15.4 kcal/mol), (SSSc)W(CO)$_3$ (**1W**) (10.6 kcal/mol) and (SSS)W(CO)$_3$ (**3W**) (12.5 kcal/mol), and (SPSc)W(CO)$_3$ (**2W**) (11.5 kcal/mol) and (SPS)W(CO)$_3$ (**4W**) (13.3 kcal/mol), shows that, in each pair, the complex with the noncyclic ligand is the more basic (by 1.2 kcal/mol for the pair **5W** and **6W**, by 1.9 kcal/mol for the pair **1W** and **3W**, and by 1.8 kcal/mol for the pair **2W** and **4W**). The greater exothermicity of the noncyclic ligand complex protonations may be due to the greater flexibility of the noncyclic ligands which allows the protonated products (structure A, Chart 3) to adopt more stable structures than can be achieved with the less flexible cyclic ligands. That this is likely has been shown for (1,4,7-trithiacyclononane)Mo(CO)$_3$ and the analogous complex with the noncyclic ligand (2,5,8-trithianonane)Mo(CO)$_3$.[17] Crystallographically-determined structures of these complexes suggest that the flexibility of the 2,5,8-trithianonane ligand allows for better overlap between the orbitals of the sulfur donor atoms and the orbitals of the metal than is possible for the 1,4,7-trithiacyclononane ligand. This greater overlap puts more electron density on the metal in the 2,5,8-trithianonane complex whose ν(CO) bands therefore occur at lower frequencies than those of (1,4,7-trithiacyclononane)Mo(CO)$_3$.

It is interesting to note that of all the $(L_3)M(CO)_3(H)^+$ complexes discussed in this paper only **9WH**$^+$, **9MoH**$^+$, and $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ have structure B (Chart 3), while all of the others have structure A. In order to understand this result, opposing steric and electronic factors must be considered. Stabilization of the π-bonding CO groups would be greater in structure A in which all of the CO groups are *trans* to S, P, or N donor groups in the coordination sphere. This π-back-bonding to the CO groups may be particularly important in these cationic complexes. On the other hand, the steric bulkiness of the terminal PPh_2 groups in **9WH**$^+$, **9MoH**$^+$, and $[PhP(C_2H_4PPh_2)_2]W(CO)_3(H)^+$ may force these complexes out of structure A to give B. Thus, all of the $(L_3)M(CO)_3(H)^+$ complexes with relatively small SEt groups adopt structure A, while complexes with bulky PPh_2 groups in the terminal positions favor the less crowded structure B.

Effect of the Metal on the Basicity of $(L_3)M(CO)_3$ Complexes. Enthalpies of protonation for W−Mo pairs of complexes with the same ligands may be compared as follows: (NNNc)W(CO)$_3$ (**8W**) (20.9 kcal/mol) and (NNNc)Mo(CO)$_3$ (**8Mo**) (18.3 kcal/mol), (NSNc)W(CO)$_3$ (**7W**) (17.4 kcal/mol) and (NSNc)Mo(CO)$_3$ (**7Mo**) (14.6 kcal/mol), *fac*-(PNP)W(CO)$_3$ (**9W-*fac***) (22.1 kcal/mol) and *fac*-(PNP)Mo(CO)$_3$ (**9Mo-fac**) (19.2 kcal/mol). These results demonstrate that the W complexes are more basic than their Mo analogs by an average of 2.8 kcal/mol (2.6 kcal/mol for **8W** and **8Mo**, 2.8 kcal/mol for **7W** and **7Mo** and 2.9 kcal/mol for **9W-*fac*** and **9Mo-*fac***). Previously it was found[7b] that the $-\Delta H_{HM}$ values for the protonation of the *cis*-$M(CO)_2(Ph_2PCH_2PPh_2)_2$ complexes are 1.8 kcal/mol higher for the W complex (31.5 kcal/mol) than the Mo analog (29.7 kcal/mol). The same trend was observed in pK_a values of the conjugate acids of $[CpM(CO)_3]^-$ complexes determined in CH_3CN solvent: Mo (13.9) < W (16.1).[37] The trend that complexes of third-row metals are more basic than their second-row analogs[1,38] is also noted in other transition metal groups. In previous ΔH_{HM} studies,[7a] it was shown that Os complexes of the type $CpM(PR_3)_2X$ were more basic than their Ru analogs by an average of 7.4 kcal/mol.

Conclusions

Comparisons of basicities of tungsten complexes (**1W**, **2W**, and **5W**) with cyclic ligands establish that the trend in donor ability relative to S is as follows: S (0 kcal/mol) ≤ PPh (0.9 kcal/mol) ≪ NR (R = Me, Et) (3.6 kcal/mol). While ΔH_{HM} values serve as a measure of the relative donor abilities of the S, PPh, and NR groups, Lever[4d] has described E_L as another parameter for ligand donor ability. It is an electrochemical parameter defined as $^1/_6$ of the Ru(III)/Ru(II) potential for RuL_6 complexes in CH_3CN, assuming that all ligand contributions are additive. This definition means that the most strongly donating ligands have the lowest E_L values. The E_L[4d] values for ligands similar to the S, P, and N donor groups in complexes **1W**, **2W**, and **5W** are as follows: Et_2S (0.35 V) > Me_2PPh (0.34 V) ≫ NH_3 (0.07 V). Although there are no data for Et_2PPh and Et_3N, it is to be expected that the E_L values for Et_2PPh and Me_2PPh are very similar, and E_L for Et_3N is likely to be nearly the same as that (0.07 V) for NH_3 since E_L values for saturated amines all fall in a very narrow range between 0 and 0.1 V. Thus, the trend in donor ability as measured by E_L parallels the one found from our calorimetry studies. Both ΔH_{HM} and E_L parameters suggest that the donor abilities of the R_2PPh group is only slightly higher than that of R_2S. If one uses pK_a values of the conjugate acids as a measure of ligand donor ability, one finds the same trend, Et_2S (pK_a = −6.8)[34] < Et_2PPh (pK_a = 6.25[35]) < Et_3N (pK_a = 10.80[33]), but the very large difference in pK_a values between Et_2S and Et_2PPh indicates that thioethers are much weaker donors than phosphines. That thioethers behave as donors that are nearly as strong as phosphines in their metal complexes suggests that the lone electron pairs on sulfur, which are not present in phosphines or amines, are able to increase the electron density on the metal by π-donation[17] or repulsion with filled metal d orbitals.[36]

(37) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.
(38) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711.

In the series of metal complexes (**3W**, **4W**, and **6W**) with noncyclic ligands, where the structures of the protonated products are the same (structure A, Chart 3) as those of the complexes with cyclic ligands, a similar trend in donor ability relative to S is observed: S (0 kcal/mol) ≤ PPh (0.8 kcal/mol) ≪ NR (R = Me, Et) (2.9 kcal/mol). With the goal of correlating this trend with another measure of electron density on the metal, we plot (Figure 2) $-\Delta H_{HM}$ *vs* average ν(CO) values of complexes **1W**−**8W** and *fac*-[$MeC(CH_2PPh_2)_3$]$W(CO)_3$ that have the same reactant and product structures. This correlation (r = 0.973) is expressed in eq 20 and shows that as the basicity

$$-\Delta H_{HM} = 300.1 - 0.1553[\nu(CO)] \text{ (kcal/mol)} \quad (20)$$

($-\Delta H_{HM}$) of a complex increases, its average ν(CO) decreases. Equation 20 may be useful for estimating basicities of other $(L_3)W(CO)_3$ complexes with S, P, and N donor ligands.

In contrast to this correlation with ν(CO), an attempt to plot $-\Delta H_{HM}$ for complexes **1W**−**8W** *vs* the ^{1}H NMR chemical shift of the hydride signal in the **1WH**$^+$−**8WH**$^+$ complexes resulted in a very poor correlation ($r = 0.415$).

Several other factors besides the donor groups affect the basicities of the $(L_3)M(CO)_3$ complexes. Noncyclic ligands make the metal more basic, by 1.6 ± 0.3 kcal/mol, than cyclic ligands with the same donor atoms. The tungsten complexes are 2.8 ± 0.1 kcal/mol more basic than their molybdenum analogs. And the isomeric form of the $(PNP)M(CO)_3$ (M = W, Mo) complexes influences the $-\Delta H_{HM}$ of their protonation. For both the W and Mo complexes the *mer* isomer is more basic than the *fac*. These protonations also show that the *fac* isomer is more stable than the *mer* by 2.0 kcal/mol for $(PNP)W(CO)_3$ and by 4.8 kcal/mol for $(PNP)Mo(CO)_3$.

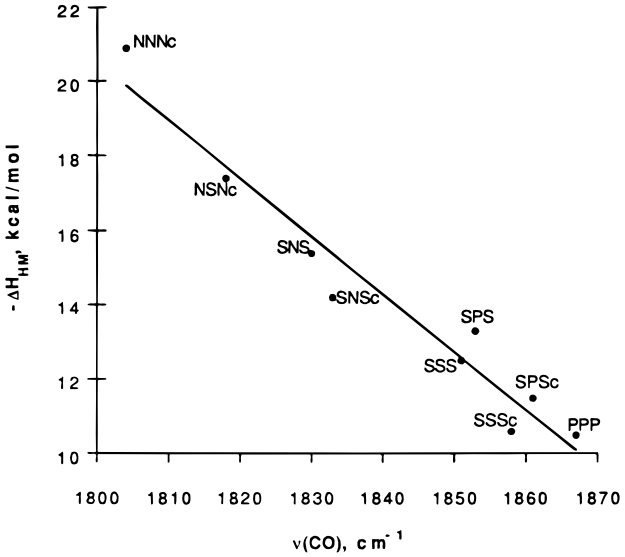

Figure 2. Correlation (eq 20) of $(L_3)W(CO)_3$ basicity ($-\Delta H_{HM}$) (Table 3) with average ν(CO) values of the $(L_3)W(CO)_3$ complexes (Table 1). PPP = $MeC(CH_2PPh_2)_3$.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9414242) for support of this work

IC970670E