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Steric and Electronic Effects on Ligand Substitution of Cationic Carbonyl Nitrosyl Complexes of Molybdenum(0) Containing Bis(3,5-dimethylpyrazol-1-yl)methane-*N,N′* [1]

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Nitrosylation of either $[M(N,N)(CO)_4]$ or $[Mo(H_2CPz'_2)(CO)_2(NO)I]$, with $NO^+BF_4^-$ in MeOH, afforded readily $[M(N,N)(CO)_2(NO)(MeOH)]BF_4$ (M = Mo, (N,N) = H_2CPz_2 (**1**), $H_2CPz'_2$ (**2**); M = W, (N,N) = H_2CPz_2 (**3**), $H_2CPz'_2$ (**4**); Pz = pyrazol-1-yl; Pz′ = 3,5-dimethylpyrazol-1-yl). **2** reacted with py to form $[Mo(H_2CPz'_2)(CO)_2(NO)(py)]BF_4$ (**5**). Chloride, bromide, iodide, azide, nitrate, thiocyanide, acetate, and cyanide reacted with **2** in MeOH to form $[Mo(H_2CPz'_2)(CO)_2(NO)L]$ (L^- = Cl^- (**6**), Br^- (**7**), I^- (**8**), N_3^- (**9**), NO_3^- (**10**), SCN^- (**11**), $MeCO_2^-$ (**12**), CN^- (**14**)). Alternatively, **7** could also be prepared from reaction of $[Mo(H_2CPz'_2)(CO)_2Br_2]$ with $NaNO_2$, n-Bu_4NNO_2, or $AgNO_2$ in CH_2Cl_2 but with a low yield. In the presence of Cl^-, Br^-, and I^- in MeOH, **5** was transformed back into **6**, **7**, and **8**, respectively. **2** reacted with a 0.5 equiv of KCN or with 1 equiv of **14** in MeOH to form $[\{Mo(H_2CPz'_2)(CO)_2(NO)\}_2(\mu\text{-}CN)]$ (**13**). Both spectral data for **1**−**14** and X-ray crystallographic structures of **9**, **10**, and **12** support that **1**−**4** and **6**−**14** are similar in geometry around the Mo center with the monodentate ligand (MeOH or L^-) *trans* to NO while *cis* to $H_2CPz'_2$ and that **5** may have two conformations with py *cis* to $H_2CPz'_2$ but either *trans* or *cis* to NO. **2** reacted with excess PR_3 in CH_2Cl_2 to form $[Mo(H_2CPz'_2)(CO)(NO)(PR_3)_2]BF_4$ (R = Ph (**15**), OMe (**16**), Me (**17**)). The spectral data for **15**−**17** and the X-ray crystallographic structure of **17** showed that two phosphine ligands in **15**−**17** are *trans* to each other while *cis* to $H_2CPz'_2$. **2** reacted with excess bidentate ligand (L,L) in MeOH to form $[Mo(L,L)_2(CO)(NO)]BF_4$ ((L,L) = bpy (**18**), phen (**19**), Me_2bpy (**20**), dppm (**21**)). However, when the solvent was changed to CH_2Cl_2, several products including **22** were formed. Both ^1H and ^{31}P NMR spectral data showed that **18**−**21** are isostructural with two (L,L) ligands *cis* to each other. **2** reacted with dithiocarbamate anion $(S,S)^-$ in MeCN to form orange-red and yellow products. The orange-red $[Mo(S,S)(CO)_2(NO)]_2$ ($(S,S)^-$ = $Et_2NCS_2^-$ (**22**), $Me_2NCS_2^-$ (**23**), $C_4H_8NCS_2^-$ (**24**)) as a major product was isolated. As supported by the X-ray crystallographic structure of **22**, **22**−**24** are dimeric with the six-electron $(S,S)^-$ ligand bonded in a μ,η^2-fashion. The distance of 3.474(3) Å between two S atoms and that of 3.773(1) Å between two Mo atoms is compatible with no S−S or Mo−Mo bond. The nitrosyl groups are *trans* to the bridging sulfur atoms while *cis* to carbonyls. Structural data: **9**, a = 11.9868(19) Å, b = 10.7998(10) Å, c = 14.723(3) Å, β = 113.995(13)°, $P2_1/c$; **10**, a = 12.993(4) Å, b = 9.497(3) Å, c = 15.090(5) Å, β = 105.49(3)°, $P2_1/c$; **12**, a = 8.854(7) Å, b = 11.904(7) Å, c = 18.238(7) Å, α = 88.06(4)°, β = 97.65(1)°, γ = 80.83(5)°, $P\bar{1}$; **17**, a = 16.637(3) Å, b = 12.379(3) Å, c = 14.6574(20) Å, β = 103.284(14)°, $P2_1/c$; **22**, a = 15.597(4) Å, b = 12.026(3) Å, c = 13.511(3) Å, β = 104.271(19)°, $C2/c$.

Introduction

In order to keep the pyrazolyl ring planar, neutral nitrogen bidentate ligands (N,N) such as dipyrazol-1-ylmethane-*N,N′* (H_2CPz_2) or bis(3,5-dimethylpyrazol-1-yl)diarylmethane-*N,N′* ($Ar_2CPz'_2$) form six-membered-boat metallacycles naturally when chelating a transition-metal atom (Figure 1). The inherent ring strain present in the metallacycle was previously shown in the facile displacement of (N,N) of $[M(N,N)(CO)_4]$ (M = Cr, Mo, W),[3] $[Mo(N,N)(CO)_2(\eta^3\text{-allyl})Br]$,[4−6] and $[Mo(N,N)(CO)_2Br_2]$[5] by MeCN, PR_3 (R = Me, OMe), bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and dithiocarbamate $(S,S)^-$ to afford straightforwardly mononuclear products. However, as described in detail in this paper, reactions of a nitrosyl derivative such as $[Mo(H_2CPz'_2)(CO)_2(NO)(MeOH)]^+$ with a variety of nucleophiles afforded complicated products, which may still contain $H_2CPz'_2$ and are either mono- or dimeric (Scheme 1).

Experimental Section

General Procedures. All manipulations were conducted with standard Schlenk techniques.[7] A blanket of predried dinitrogen was used over each reaction. Solvents were purified by distillation from an appropriate drying agent [ethers, paraffins, and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2; alcohols from the corresponding alkoxide]. ^1H and ^{31}P NMR spectra were recorded on Bruker WP-100 (^1H, 100 MHz), AM-200 (^1H, 200 MHz), AM-300 (^1H, 300 MHz), and AMC-400 (^1H, 400 MHz; ^{31}P, 162 MHz) and Varian Unity Plus-400 (^1H, 400 MHz; ^{31}P, 162 MHz) NMR spectrometers. ^1H chemical shifts (δ in ppm, J in Hz) are defined as positive downfield relative to internal $MeSi_4$ (TMS) or the deuterated solvent, while ^{31}P chemical shifts are defined as positive downfield relative to external 85% H_3PO_4 or internal free

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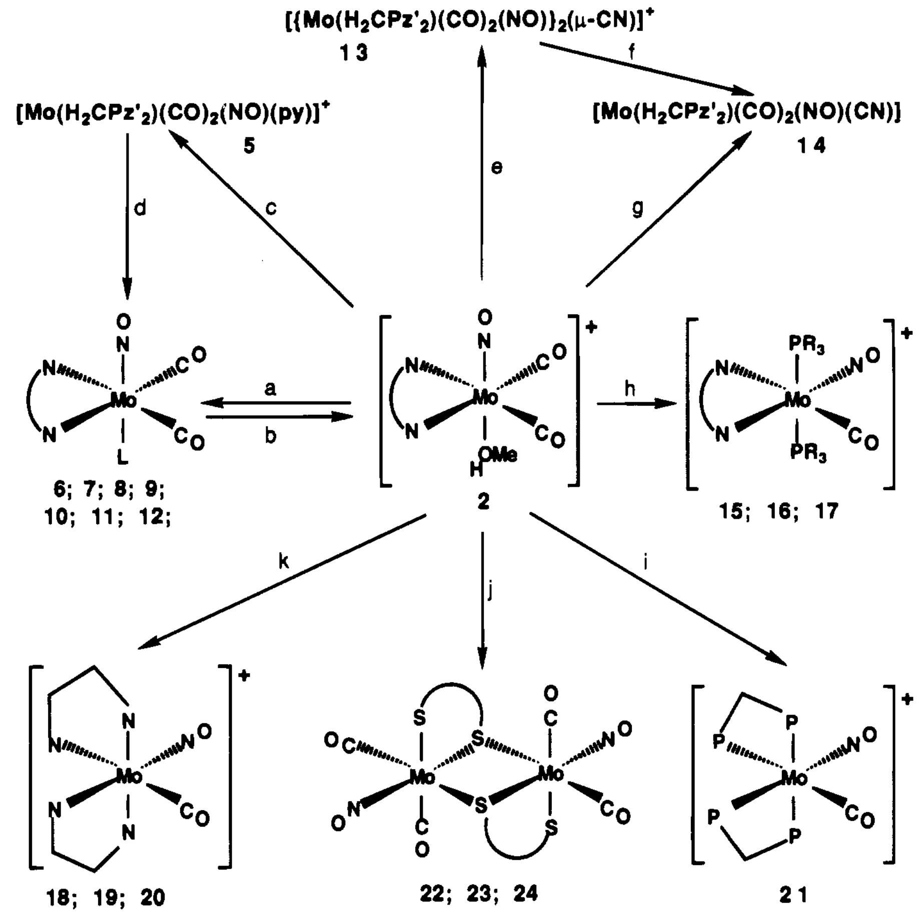
Scheme 1[a]



[a] Key: (a) NaL or KL ($L^- = Cl^-, I^-, N_3^-, NO_3^-, SCN^-, MeCO_2^-$); (b) for $L^- = I^-$, $NO^+BF_4^-$; (c) py; (d) NaCl, NaBr or NaI; (e) **14** or 1/2 KCN; (f) 1/2 KCN; (g) KCN; (h) 2 PR_3; (i) 2 dppm; (j) $Na^+Et_2NCS_2^-$, $Na^+Me_2NCS_2^-$ or $NH_4^+C_4H_8NCS_2^-$; (k) bpy, phen or Me_2bpy.

phosphine ligand with $\delta(^{31}P)$ = 141 for $P(OMe)_3$, −61 for PMe_3,[8a] −6 for PPh_3,[8b] and −23.6 for dppm[8c] (s, singlet; d, doublet; m, multiplet; br, broad). Infrared spectra were recorded by using a Hitachi 260- or 270-30 instrument (vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder). Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University. The complexes $[M(N,N)(CO)_4]$ (M = Mo, W; (N,N) = H_2CPz_2 or $H_2CPz'_2$)[9] and $[Mo(H_2CPz'_2)(CO)_2Br_2]$[10] were prepared according to the literature methods.

Preparation of $[Mo(H_2CPz_2)(CO)_2(NO)(MeOH)]BF_4$ (1). To a stirred suspension of $[Mo(H_2CPz_2)(CO)_4]$ (0.358 g, 1.0 mmol) in MeOH (20 mL) was added $[NO]BF_4$ (0.234 g, 2.0 mmol) in portions. Gas evolved briskly, and the suspension soon became a clear orange-yellow solution. When evolution of gas ceased, the volume of the solution was reduced to *ca.* 2 mL and Et_2O (15 mL) was added to give an orange-yellow precipitate, collected on a medium frit. Yield: 0.40 g (89%). IR (CH_2Cl_2): ν_{CO}, 2044 s, 1964 s; ν_{NO}, 1660 s cm^{-1}. ^1H NMR (298 K, CD_3OD, 100 MHz): MeOH, δ 3.36 (3 H, s); CH_2, 6.49 (1 H, d, $^2J_{H,H}$ = 15), 6.97 (1 H, d, $^2J_{H,H}$ = 15); hydrogen atoms on the ring-4 position ($H_{(4)}$) 6.67 (2 H, t); hydrogen atoms on the ring-3 and -5 positions ($H_{(3)}$, $H_{(5)}$), 8.15 (2 H, d, $^3J_{H,H}$ = 2.3), 8.30 (2 H, d, $^3J_{H,H}$ = 2.5). Anal. Calcd for $C_{10}H_{12}BF_4MoN_5O_4$: C, 26.75; H, 2.69; N, 15.60. Found: C, 26.85; H, 2.75; N, 15.55.

Preparation of $[Mo(H_2CPz'_2)(CO)_2(NO)(MeOH)]BF_4$ (2). This orange-yellow compound was prepared similarly from $[Mo(H_2CPz'_2)(CO)_4]$ in 91% yield. IR (CH_2Cl_2): ν_{CO}, 2040 s, 1960 s; ν_{NO}, 1659 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$, 100 MHz): methyl groups on the ring-3 and -5 positions ($Me_{(3)}$, $Me_{(5)}$), δ 2.45 (s), 2.47 (s), 2.50 (s); MeOH, 3.48 (3 H, s), 1.60 (1 H, s); $H_{(4)}$, 6.04 (s), 6.07 (s); CH_2, 6.15 (br), 6.32 (d, $^2J_{H,H}$ = 16), 6.57 (d, $^2J_{H,H}$ = 16). Anal. Calcd for $C_{14}H_{20}BF_4MoN_5O_4$: C, 33.29; H, 3.99; N, 13.87. Found: C, 32.97; H, 4.16; N, 13.65.

Preparation of $[W(H_2CPz_2)(CO)_2(NO)(MeOH)]BF_4$ (3). This orange-yellow compound was obtained by a procedure similar to that of **1** from $[W(H_2CPz_2)(CO)_4]$ in 60% yield. IR (CH_3CN): ν_{CO}, 2010 s, 1902 s; ν_{NO}, 1632 s cm^{-1}. ^1H NMR (298 K, CD_3CN, 100 MHz): MeOH, δ 3.28 (3 H, s), 2.09 (1 H, s); CH_2, 6.39 (1 H, d, $^2J_{H,H}$ = 15), 6.74 (1 H, d, $^2J_{H,H}$ = 15); $H_{(4)}$, 6.61 (2 H, t); $H_{(3)}$, $H_{(5)}$, 8.12 (2 H, d, $^3J_{H,H}$ = 2.1), 8.17 (2 H, d, $^3J_{H,H}$ = 2.7). Anal. Calcd for $C_{10}H_{12}BF_4N_5O_4W$: C, 22.37; H, 2.25; N, 13.05. Found: C, 22.17; H, 2.33; N, 12.96.

Preparation of $[W(H_2CPz'_2)(CO)_2(NO)(MeOH)]BF_4$ (4). This orange-yellow compound was prepared similarly from $[W(H_2CPz'_2)(CO)_4]$ in 72% yield. IR (CH_2Cl_2): ν_{CO}, 2028 s, 1928 s; ν_{NO}, 1644 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$, 200 MHz): $Me_{(3)}$, $Me_{(5)}$, δ 2.43 (6 H, br), 2.47 (6 H, br); MeOH, 3.28 (3 H, s), 1.60 (1 H, s); $H_{(4)}$, 6.25 (2 H, br); CH_2, 6.16 (1 H, d, $^2J_{H,H}$ = 16), 6.28 (1 H, d, $^2J_{H,H}$ = 16). Anal. Calcd for $C_{14}H_{20}BF_4N_5O_4W$: C, 28.35; H, 3.40; N, 11.81. Found: C, 28.50; H, 3.42; N, 11.53.

Preparation of $[Mo(H_2CPz'_2)(CO)_2(NO)(py)]BF_4$ (5). To a stirred solution of **2** (0.253 g, 0.50 mmol) in CH_2Cl_2 (25 mL) was added pyridine (py) (1 mL, *ca.* 12 mmol). The solution was stirred for 10 min, and the solvent was removed under vacuum. Recrystallization from CH_2Cl_2/hexane gave the yellow product (0.25 g, 90%). IR (CH_2Cl_2): ν_{CO}, 2036 s, 1948 s; ν_{NO}, 1680 s, 1657sh cm^{-1}. ^1H NMR (298 K, acetone-d_6, 200 MHz): $Me_{(3)}$, $Me_{(5)}$, δ 2.47 (s), 2.58 (s), 2.62 (s),

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2.67 (s); $\mathrm{H}_{(4)}$ or $\mathrm{CH_2}$, 6.19–6.70 (m); py, 7.57 (2 H, m), 8.16 (2 H, m), 8.74 (1 H, br). Anal. Calcd for $\mathrm{C_{18}H_{21}BF_4MoN_6O_3}$: C, 39.16; H, 3.83; N, 15.22. Found: C, 38.93; H, 3.79; N, 15.15.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)Cl] (6). To a stirred solution of **2** (0.253 g, 0.50 mmol) in MeOH (20 mL) was added NaCl (0.030 g, 0.75 mmol). The solution was stirred for 1.5 h, forming a yellow precipitate. The solvent was removed under vacuum. Recrystallization from $\mathrm{CH_2Cl_2}$/MeOH gave the yellow product (0.19 g, 91%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2032 s, 1944 s; ν_{NO}, 1634 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.52 (6 H, s), 2.58 (6 H, s); $\mathrm{H}_{(4)}$, 6.20 (2 H, br); $\mathrm{CH_2}$, 6.30 (1 H, br), 6.38 (1 H, br). Anal. Calcd for $\mathrm{C_{13}H_{16}ClMoN_5O_3}$: C, 37.03; H, 3.82; N, 16.61. Found: C, 37.06; H, 3.83; N, 16.54.

Compound **6** was also formed as a yellow precipitate from the reaction between **5** and excess NaCl dissolved in MeOH.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)Br] (7). This yellow compound was prepared in 94% yield by a procedure analogous to that of **6**, either from the reaction between **2** and NaBr or that between **5** and this salt. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2032 s, 1944 s; ν_{NO}, 1640 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.55 (6 H, s), 2.60 (6 H, s); $\mathrm{H}_{(4)}$, 6.22 (2 H, br); $\mathrm{CH_2}$, 6.27 (1 H, br), 6.42 (1 H, br). Anal. Calcd for $\mathrm{C_{13}H_{16}BrMoN_5O_3}$: C, 33.50; H, 3.46; N, 15.02. Found: C, 33.53; H, 3.52; N, 14.87.

Compound **7** was also obtained by adding $\mathrm{NaNO_2}$, *n*-$\mathrm{Bu_4NNO_2}$, or $\mathrm{AgNO_2}$ to $[\mathrm{Mo(H_2CPz_2)(CO)_2Br_2}]$ at a yield 33–36%: To a stirred solution of $[\mathrm{Mo(H_2CPz'_2)(CO)_2Br_2}]$ (0.516 g, 1.00 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added $\mathrm{NaNO_2}$, *n*-$\mathrm{Bu_4NNO_2}$, or $\mathrm{AgNO_2}$ (1.00 mmol), dissolved in MeOH (5 mL). The solution was stirred for 10 min. The solvent was then removed under vacuum. Recrystallization from $\mathrm{CH_2Cl_2}$/MeOH gave a yellow product.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)I] (8). This orange-yellow compound was prepared in 94% yield by a procedure analogous to that of **6**, either from the reaction between **2** and NaI or that between **5** and this salt. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2028 s, 1944 s; ν_{NO}, 1642 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.56 (6 H, s), 2.62 (6 H, s); $\mathrm{H}_{(4)}$, 6.24 (2 H, br); $\mathrm{CH_2}$, 6.33 (1 H, br), 6.40 (1 H, br). Anal. Calcd for $\mathrm{C_{13}H_{16}IMoN_5O_3}$: C, 30.37; H, 3.14; N, 13.65. Found: C, 30.43; H, 3.13; N, 13.32.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)(η¹-N₃)] (9). This yellow compound was prepared in 87% yield by a procedure analogous to that of **6**, from **2** and $\mathrm{NaN_3}$. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2024 s, 1938 s; ν_{NNN}, 2076 s; ν_{NO}, 1634 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.48 (6 H, s), 2.58 (6 H, s); $\mathrm{H}_{(4)}$, 6.21 (2 H, br); $\mathrm{CH_2}$, 6.30 (1 H, br), 6.38 (1 H, br). Anal. Calcd for $\mathrm{C_{13}H_{16}MoN_8O_3}$: C, 36.46; H, 3.77; N, 26.16. Found: C, 36.39; H, 3.78; N, 26.15.

Caution! Although we have experienced no explosions, azides must always be treated with great care.

Preparation of [Mo(H₂CPz₂)(CO)₂(NO)(η¹-NO₃)] (10). This yellow compound was prepared in 82% yield by a procedure analogous to that of **9**, using $\mathrm{NaNO_3}$. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2036 s, 1948 s; ν_{NO}, 1630 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.37 (6 H, s), 2.60 (6 H, s); $\mathrm{H}_{(4)}$, 6.28 (2 H, br); $\mathrm{CH_2}$, 6.30 (1 H, d, J = 16), 6.67 (1 H, d, J = 16). Anal. Calcd for $\mathrm{C_{15}H_{19}MoN_5O_5}$: C, 34.83; H, 3.60; N, 18.75. Found: C, 34.56; H, 3.55; N, 18.38.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)(SCN)] (11). This yellow compound was prepared in 95% yield by a procedure analogous to that of **9**, using KSCN. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2032 s, 1946 s; ν_{SCN}, 2072 s; ν_{NO}, 1646 s cm^{-1}. ^{1}H NMR (acetone-d_6, 300 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.46 (6 H, s), 2.60 (6 H, s); $\mathrm{H}_{(4)}$, 6.23 (2 H, br); $\mathrm{CH_2}$, 6.38 (1 H, br), 6.65 (1 H, d, J = 16) at 298 K and $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.47 (6 H, s), 2.60 (6 H, s); $\mathrm{H}_{(4)}$, 6.21 (2 H, br); $\mathrm{CH_2}$, 6.38 (1 H, d, J = 16), 6.65 (1 H, d, J = 16) at 328 K. Anal. Calcd for $\mathrm{C_{14}H_{16}MoN_6O_3S}$: C, 37.84; H, 3.63; N, 18.91. Found: C, 37.77; H, 3.68; N, 18.85.

Preparation of [Mo(H₂CPz′₂)(CO)₂(NO)(η¹-MeCO₂)] (12). This yellow compound was prepared in 88% yield by a procedure analogous to that of **9**, using sodium acetate, $\mathrm{NaMeCO_2}$. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 2032 s, 1932 s;ν_{NO}, 1630 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.34 (6 H, s), 2.45 (6 H, s); OAC, 2.57 (3 H, s); $\mathrm{H}_{(4)}$, 6.17 (2 H, br); $\mathrm{CH_2}$, 6.34 (1 H, br), 6.41 (1 H, br). Anal. Calcd for $\mathrm{C_{15}H_{19}MoN_5O_5}$: C, 40.46; H, 4.30; N, 15.73. Found: C, 40.39; H, 4.28; N, 15.53.

Preparation of [{Mo(H₂CPz′₂)(CO)₂(NO)}₂(μ-CN)]BF₄ (13) and [Mo(H₂CPz′₂)(CO)₂(NO)(CN)] (14). To a stirred solution of **2** (0.505 g, 1.00 mmol) in MeOH (20 mL) was added a solution of KCN (0.065 g, 1.00 mmol), dissolved in MeOH (10 mL), dropwise. An orange-yellow precipitate was formed first on addition of half the KCN solution, but the solution became clear after complete addition. The precipitate was isolated by filtration after addition of half the KCN solution and characterized as **13**. Yield, 63%. IR ($\mathrm{CH_2Cl_2}$): ν_{CN}, 2140 w; ν_{CO}, 2040 s, 1952 s; ν_{NO}, 1668 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 1.93 (6 H, s), 1.98 (6 H, s), 2.65 (12 H, br); $\mathrm{H}_{(4)}$, 6.19 (2 H, br), 6.22 (2 H, br); $\mathrm{CH_2}$, 6.31 (1 H, br), 6.37 (1 H, br), 6.68 (1 H, br), 6.76 (1 H, br). Anal. Calcd for $\mathrm{C_{27}H_{32}BF_4Mo_2N_{11}O_6}$: C, 36.63; H, 3.64; N, 17.40. Found: C, 36.64; H, 3.70; N, 17.44. In another preparation, after complete addition of the KCN solution, the MeOH was stripped from the clear orange-yellow solution under vacuum. The product, **14**, was recrystallized from $\mathrm{CH_2Cl_2/Et_2O}$ to give 0.30 g (73%). IR ($\mathrm{CH_2Cl_2}$): ν_{CN}, 2116 w; ν_{CO}, 2032 s, 1940 s; ν_{NO}, 1654 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.48 (6 H, s), 2.60 (6 H, s); $\mathrm{H}_{(4)}$, 6.23 (2 H, br); $\mathrm{CH_2}$, 6.39 (1 H, br), 6.46 (1 H, br). Anal. Calcd for $\mathrm{C_{14}H_{16}MoN_6O_3}$: C, 40.79; H, 3.91; N, 20.39. Found: C, 40.69; H, 3.81; N, 20.15. Alternatively, **13** could also be prepared from **2** and 1 equiv of **14**.

Preparation of [Mo(H₂CPz′₂)(CO)(NO)(PPh₃)₂]BF₄ (15). To a stirred solution of **2** (0.258 g, 0.51 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL) was added $\mathrm{PPh_3}$ (0.278 g, 1.06 mmol). The solution was heated under reflux for 2 h, and the solvent was removed under vacuum. The solid residue was then washed with $\mathrm{Et_2O}$ (15 mL) to remove the unreacted $\mathrm{PPh_3}$. Recrystallization from $\mathrm{CH_2Cl_2}$/hexane gave the orange-red product (0.47 g, 95%). The compound is slightly air-sensitive and should be stored under $\mathrm{N_2}$. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 1922 s; ν_{NO}, 1640 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.29 (6 H, m), 2.53 (6 H, m); $\mathrm{H}_{(4)}$, 5.61 (2 H, m); $\mathrm{CH_2}$, 6.23 (m), 6.79 (m). ^{31}P{^{1}H} NMR (298 K, $\mathrm{CH_2Cl_2}$/acetone-d_6 = 1/1, 162 MHz): δ 46.5 (br). Anal. Calcd for $\mathrm{C_{48}H_{46}BF_4MoN_5O_2P_2}$: C, 59.64; H, 4.78; N, 7.22. Found: C, 59.42; H, 4.82; N, 7.24.

Preparation of [Mo(H₂CPz′₂)(CO)(NO){P(OMe)₃}₂]BF₄ (16). To a stirred solution of **2** (0.267 g, 0.53 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL) was added $\mathrm{P(OMe)_3}$ (0.44 mL, 3.7 mmol). The solution was heated under reflux for 44 h, and the solvent was removed under vacuum. Recrystallization from $\mathrm{CH_2Cl_2}$/hexane gave the orange-yellow product (0.32 g, 88%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 1948 s; ν_{NO}, 1660 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.54 (6 H, d, J = 11), 2.58 (6 H, d, J = 11); $\mathrm{P(OMe)_3}$, 3.49 (18 H, J = 6); $\mathrm{H}_{(4)}$, 6.33 (2 H, br); $\mathrm{CH_2}$, 6.27 (1 H, br), 6.36 (1 H, br). ^{31}P{^{1}H} NMR (298 K, $\mathrm{CH_2Cl_2}$/acetone-d_6 = 1/1, 162 MHz): δ 152.2 (br). Anal. Calcd for $\mathrm{C_{18}H_{32}BF_4MoN_5O_8P_2}$: C, 31.19; H, 4.94; N, 10.10. Found: C, 31.15; H, 4.86; N, 10.13.

Preparation of [Mo(H₂CPz′₂)(CO)(NO)(PMe₃)₂]BF₄ (17). This red-brown compound was prepared in 89% yield by a procedure analogous to that of **16**, using excess $\mathrm{PMe_3}$ (1.0 M solution in THF) and **2**. The reaction was completed in 2 h. IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 1914 s; ν_{NO}, 1634 s cm^{-1}. ^{1}H NMR (298 K, acetone-d_6, 200 MHz): $\mathrm{Me}_{(3)}$, $\mathrm{Me}_{(5)}$, δ 2.56 (6 H, d, J = 9), 2.59 (6 H, d, J = 9); $\mathrm{PMe_3}$, 1.24 (18 H, t, J = 3); $\mathrm{H}_{(4)}$, 5.99 (2 H, br); $\mathrm{CH_2}$, 6.31 (1 H, br), 6.38 (1 H, br). ^{31}P{^{1}H} NMR (298 K, $\mathrm{CH_2Cl_2}$/acetone-d_6 = 1/1, 162 MHz): δ −5.9 (br). Anal. Calcd for $\mathrm{C_{18}H_{34}BF_4MoN_5O_2P_2}$: C, 36.20; H, 5.73; N, 10.73. Found: C, 36.11; H, 5.51; N, 11.80.

Preparation of *cis*-[Mo(bpy)₂(CO)(NO)]BF₄ (18). To a stirred solution of **2** (0.253 g, 0.50 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added bpy (0.199 g, 1.28 mmol). Upon addition, the yellow transparent solution changed color almost immediately to dark green and then (ca. 2 h) became cloudy. After 80 h, the volume of the solution was reduced to *ca.* 2 mL and $\mathrm{Et_2O}$ (10 mL) was added to complete precipitation of the dark green compound while dissolving the excess bpy and the extruded $\mathrm{H_2CPz'_2}$. Filtration through a medium frit gave 0.21 g (81%). IR ($\mathrm{CH_2Cl_2}$): ν_{CO}, 1910 s; ν_{NO}, 1614 s cm^{-1}. ^{1}H NMR (25 °C, acetone-d_6, 200 MHz): δ 9.43 (1 H, d, $^3J_{\mathrm{H,H}}$ = 5.7), 9.32 (1 H, d, $^3J_{\mathrm{H,H}}$ = 6.9), 8.87 (1 H, d, $^3J_{\mathrm{H,H}}$ = 8.2), 8.73 (2 H, d, $^3J_{\mathrm{H,H}}$ = 7.7), 8.70 (1 H, d, $^3J_{\mathrm{H,H}}$ = 6.8), 8.51 (1 H, m), 8.21 (3 H, m), 8.01 (1 H, m), 7.77 (3 H, m), 7.52 (2 H, m). Anal. Calcd for $\mathrm{C_{21}H_{16}BF_4MoN_5O_2}$: C, 45.60; H, 2.92; N, 12.66. Found: C, 45.43; H, 3.02; N, 12.67.

Alternatively, this compound was prepared in a shorter period by

Table 1. Crystal Data for Mono- and Dinuclear Nitrosyl Complexes

	9	17	22
formula	$C_{13}H_{16}MoN_8O_3$	$C_{18}H_{34}BF_4MoN_5O_2P_2$	$C_{14}H_{20}Mo_2N_4O_6S_4$
M_r	428.26	597.18	660.44
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	11.9868(19)	16.637(3)	15.597(4)
b, Å	10.7998(10)	12.379(3)	12.026(3)
c, Å	14.723(3)	14.6574(20)	13.511(3)
α, deg	90	90	90
β, deg	113.995(13)	103.284(14)	104.271(19)
γ, deg	90	90	90
V, Å^3	1741.3(5)	2937.9(10)	2456.2(10)
Z	4	4	4
D_{calc}, g cm^{-3}	1.634	1.350	1.786
μ, mm^{-1}	0.7638	0.5881	1.36
no. of reflns collcd	2274	3833	2161
no. of indep reflns	2274	3830	2161
no. of obsd reflns ($>2\sigma$)	1869	2415	1934
R,[a] R_w[a]	0.022, 0.019	0.052, 0.049	0.031, 0.037

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

heating the mixture of **2** (0.260 g, 0.51 mmol) and bpy (0.200 g, 1.28 mmol) in MeOH (20 mL) at 65 °C for 16 h. (The solution changed color from yellow to yellow-brown and then to a dark green suspension within 10 min.) The volume of the suspension was reduced to *ca.* 3 mL, and Et_2O (15 mL) was added. Filtration gave the dark green solid, which was then dried under vacuum. Yield: 0.22 g (79%).

Preparation of *cis*-[Mo(phen)$_2$(CO)(NO)]BF$_4$ (19). This dark green compound was obtained by a procedure similar to that of **18**. A typical yield of 0.27 g (89%) was obtained from **2** (0.26 g, 0.51 mmol) and phen (0.28 g, 1.55 mmol) in CH_2Cl_2 (20 mL) for 30 h. IR (CH_2Cl_2): ν_{CO}, 1914 s, 1934 sh; ν_{NO}, 1625 br cm^{-1}. ^1H NMR (25 °C, acetone-d_6, 200 MHz): δ 9.92 (1 H, m), 9.82 (1 H, m), 9.16 (1 H, m), 8.77 (3 H, m), 8.40 (3 H, m), 8.25 (3 H, m), 8.02 (2 H, m), 7.64 (2 H, m). Anal. Calcd for $C_{25}H_{16}BF_4MoN_5O_2$: C, 49.95; H, 2.68; N, 11.65. Found: C, 49.62; H, 2.42; N, 11.57.

Preparation of *cis*-[Mo(Me$_2$bpy)$_2$(CO)(NO)]BF$_4$ (20). This dark green compound was obtained by a procedure similar to that of **18**, by heating the mixture of **2** (0.27 g, 0.53 mmol) and Me_2bpy (0.22 g, 1.17 mmol) in MeOH (20 mL) at 65 °C for 56 h. A typical yield of 0.24 g (75%) was obtained. IR (CH_2Cl_2): ν_{CO}, 1904 s; ν_{NO}, 1600 m cm^{-1}. ^1H NMR (25 °C, acetone-d_6, 200 MHz): δ 9.11 (1 H, d, J = 5.8), 9.08 (1 H, d, J = 5.8), 8.43 (1 H, br), 8.28 (1 H, br), 8.20 (1 H, br), 8.13 (1 H, br), 7.26 (1 H, d, J = 5.8), 7.30 (1 H, d, J = 5.8), 7.14 (4 H, m), 2.71 (3 H, s), 2.65 (3 H, s), 2.44 (3 H, s), 2.43 (3 H, s). Anal. Calcd for $C_{25}H_{24}BF_4MoN_5O_2$: C, 49.28; H, 3.98; N, 11.50. Found: C, 48.90; H, 3.92; N, 11.47.

Preparation of *cis*-[Mo(dppm)$_2$(CO)(NO)]BF$_4$ (21). This orange-red compound was obtained as precipitate by a procedure similar to that of **18**, by heating the mixture of **2** (0.23 g, 0.45 mmol) and dppm (0.38 g, 1.00 mmol) in 20 mL of MeOH at 65 °C for 2 h. A typical yield of 0.39 g (86%) was obtained. IR (CH_2Cl_2): ν_{CO}, 1964 s; ν_{NO}, 1650 m cm^{-1}. ^1H {^{31}P} NMR (25 °C, $CH_2Cl_2/CDCl_3$ = 1/1, 400 MHz): δ 7.85−6.34 (40 H, m), 4.71 (1 H, d, J = 15), 4.44 (1 H, d, J = 15), 4.35 (1 H, d, J = 15), 3.82 (1 H, d, J = 15). $^{31}P\{^1H\}$ NMR (298 K, CH_2Cl_2/acetone-d_6 = 1/1, 162 MHz): δ 9.54 (1 P, ddd, J = 21, 27, 88), 4.63 (1 P, ddd, J = 16, 27, 88), −7.25 (1 P, dt, J = 16, 27), −17.75 (1 P, dt, J = 21, 27). Anal. Calcd for $C_{51}H_{44}BF_4MoNO_2P_4$: C, 60.68; H, 4.39; N, 1.39. Found: C, 60.61; H, 4.42; N, 1.34.

Preparation of [Mo(Et$_2$NCS$_2$)(CO)$_2$(NO)]$_2$ (22). A solution of **2** (3 mmol) in MeCN (10 mL) was added dropwise with a solution of $Na^+Et_2NCS_2^-$ (3 mmol) in MeCN (30 mL). After addition, the solution was stirred for 30 min and the solvent was removed under vacuum to give an off-yellow solid residue. The residue was first washed with Et_2O (3 × 20 mL) to remove $H_2CPz'_2$ and then dissolved in CH_2Cl_2 (20 mL). Hexane (60 mL) was carefully poured down the side of the tube onto the solution. After 24 h, many orange-red microcrystals of **22** and some yellow precipitate appeared on the bottom of the flask. The clear solution was removed into another flask through a cannula, and the crystals were washed gently with CH_2Cl_2 (1−2 mL) to dissolve any deposited yellow solid. The resulting yellow solution was also removed by the cannula. Collection of the crystals gave 0.99 g. Yield: 65%. IR: ν_{CO}, 2028 (sh), 2024 (s), 1952 (s), 1936 (s); ν_{NO}, 1662 (s) and ν_{CN}, 1512 (s) cm^{-1} in CH_2Cl_2; ν_{CO}, 2024 (s), 1936 (s) and ν_{NO}, 1652 (s) cm^{-1} in CH_3CN. ^1H NMR (296 K, 200 MHz): δ 3.86 (8 H, m), 1.35 (12 H, m) in $CDCl_3$ and δ 3.86 (8 H, q, J = 7), 1.25 (t, 12 H) in acetone-d_6. Anal. Calcd for $C_{14}H_{20}Mo_2N_4O_6S_4$: C, 25.26; H, 3.05; N, 8.48. Found: C, 25.44; H, 3.02; N, 8.38.

Preparation of [Mo(Me$_2$NCS$_2$)(CO)$_2$(NO)]$_2$ (23). This orange-red compound was prepared by a procedure similar to that of **22**, using $Na^+Me_2NCS_2^-$. Yield: 58%. IR (CH_2Cl_2): ν_{CO}, 2026 (sh), 2024 (s), 1936 (s), 1916 (s); ν_{NO}, 1662 (s) and ν_{CN}, 1538 (s) cm^{-1}. ^1H NMR (acetone-d_6, 296 K, 200 MHz): δ 3.36 (6 H, s). Anal. Calcd for $C_{10}H_{14}Mo_2N_4O_6S_4$: C, 19.88; H, 1.99; N, 9.27. Found: C, 19.82; H, 2.10; N, 9.25.

Preparation of [Mo(C$_4$H$_8$NCS$_2$)(CO)$_2$(NO)]$_2$ (24). This orange-red compound was prepared by a procedure similar to that of **22**, using ammonium pyrrolidinedithiocarbamate (NH_4^+ $Me_2NCS_2^-$). Yield: 62%. IR (CH_2Cl_2): ν_{CO}, 2024 (s), 2014 (sh), 1932 (s); ν_{NO}, 1652 (s) and ν_{CN}, 1508 (s) cm^{-1}. ^1H NMR (acetone-d_6, 296 K, 200 MHz): δ 3.70 (16 H, m). Anal. Calcd for $C_{14}H_{16}Mo_2N_4O_6S_4$: C, 25.62; H, 2.46; N, 8.53. Found: C, 25.64; H, 2.49; N, 8.51.

X-ray Diffraction Measurements. Single crystals were grown by the liquid diffusion method from CH_2Cl_2/hexane, MeOH/Et_2O, or MeCN/Et_2O. Diffraction data for **9**, **10**, **12**, **17**, and **22** were collected on a Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.709 30 Å).

The metal atom in any structure was first solved by the heavy-atom method. The remaining non-hydrogen atoms were subsequently located from the Fourier difference maps, and all atoms except the disordered atom were then refined anisotropically. (C(5) (occupancy = 0.75) and C(5*) (occupancy = 0.25) in structure **22** were found to be disordered.) The ambiguities of locating NO and CO positions, if there are any, were solved according to the chemical and crystallographic meaningfulness of thermal displacement coefficients. A more restricted N atomic peak with a lower thermal parameter, U, than the neighboring O atomic peak confirmed the successful assignment of the NO positions.[11] Accordingly, only one nitrosyl position was found for any of the five structures described here. The positions of all hydrogen atoms were calculated and refined isotropically to give residual R and R_w values shown in Table 1 with other crystallographic information. All calculations were performed by use of the NRCVAX system of computer programs.[12]

There are two independent molecules, **12A** and **12B**, of **12** found in the asymmetric unit of the crystal used. Since **9**, **10**, and **12A** (or **12B**)- are isostructural with η^1-azide, -nitrate, and -acetate *trans* to NO, respectively, only the ORTEP plots for **9** (Figure 2), **17** (Figure 3), and **22** (Figure 4) containing 50% probability thermal ellipsoids are

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Table 2. Fractional Atomic Coordinates

	x	*y*	*z*	B_{eq}[a]		*x*	*y*	*z*	B_{eq}[a]
(a) $[Mo(H_2CPz'_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (**9**)									
Mo	0.168615(24)	0.99928(3)	0.246872(19)	2.538(14)	C(2)	−0.0109(3)	0.9884(4)	0.16177(24)	3.59(19)
N(1)	0.37251(23)	1.02054(24)	0.33196(18)	2.66(14)	C(3)	0.4576(5)	0.8328(4)	0.2874(4)	4.2(3)
N(2)	0.42049(24)	1.12594(24)	0.38647(19)	2.78(15)	C(4)	0.4696(3)	0.9548(3)	0.33750(24)	2.94(18)
N(3)	0.26674(23)	1.27443(25)	0.30055(20)	2.82(14)	C(5)	0.5761(3)	1.0171(4)	0.39477(25)	3.55(20)
N(4)	0.18132(24)	1.20373(25)	0.22742(20)	2.77(14)	C(6)	0.5444(3)	1.1249(3)	0.42476(24)	3.16(18)
N(5)	0.13378(21)	1.0074(3)	0.35387(19)	3.20(14)	C(7)	0.6202(5)	1.2277(5)	0.4862(4)	4.8(3)
N(6)	0.2098(3)	0.9800(3)	0.11737(19)	3.47(15)	C(8)	0.3381(4)	1.2177(4)	0.3951(3)	3.14(19)
N(7)	0.2816(3)	1.0375(3)	0.09768(20)	3.38(16)	C(9)	0.3511(4)	1.4882(5)	0.3353(4)	4.5(3)
N(8)	0.3499(3)	1.0902(4)	0.07512(25)	5.82(22)	C(10)	0.2670(3)	1.3924(3)	0.2706(3)	3.14(20)
O(1)	0.1386(3)	0.7121(3)	0.2494(3)	7.09(21)	C(11)	0.1792(3)	1.3985(4)	0.1758(3)	3.50(21)
O(2)	−0.11197(23)	0.9752(3)	0.11697(18)	6.04(18)	C(12)	0.1286(3)	1.2816(3)	0.1509(3)	3.18(18)
O(3)	0.11261(21)	1.0124(3)	0.42665(17)	5.19(15)	C(13)	0.0297(6)	1.2412(6)	0.0550(4)	4.9(3)
C(1)	0.1561(3)	0.8162(4)	0.2508(3)	4.03(21)					
(b) $[Mo(H_2CPz'_2)(CO)(NO)(PMe_3)_2]BF_4$ (**17**)									
Mo	0.17908(4)	0.99795(7)	0.22662(5)	4.11(3)	O(8)	0.0312(4)	0.9019(6)	0.0920(5)	8.3(4)
P(1)	0.25701(15)	0.82234(19)	0.23852(18)	5.15(14)	C(11)	0.2534(6)	0.9963(10)	0.4862(6)	8.4(7)
P(2)	0.11155(15)	1.17912(21)	0.21297(21)	6.25(16)	C(12)	0.3099(5)	1.0428(7)	0.4326(5)	5.2(5)
N(1)	0.2874(4)	1.0594(5)	0.3408(4)	4.1(3)	C(13)	0.3916(5)	1.0749(7)	0.4673(5)	5.3(5)
N(2)	0.3561(4)	1.1033(5)	0.3168(4)	3.9(3)	C(14)	0.4191(5)	1.1143(6)	0.3934(5)	4.5(4)
N(3)	0.2532(4)	1.0467(5)	0.1210(4)	4.2(3)	C(15)	0.4990(5)	1.1634(8)	0.3896(6)	6.2(5)
N(4)	0.3291(4)	1.0940(5)	0.1480(4)	4.1(3)	C(16)	0.1721(6)	0.9647(9)	−0.0265(6)	7.9(7)
C	0.3461(5)	1.1609(6)	0.2308(6)	4.4(4)	C(17)	0.2464(5)	1.0195(7)	0.0308(5)	5.5(5)
C(1)	0.3091(16)	0.7771(14)	0.3419(11)	33.6(24)	C(18)	0.3174(6)	1.0484(8)	0.0026(6)	6.4(6)
C(2)	0.2012(8)	0.7092(10)	0.2021(16)	23.3(18)	C(19)	0.3683(5)	1.0973(7)	0.0766(6)	5.3(5)
C(3)	0.3363(11)	0.8102(12)	0.1883(17)	26.7(20)	C(20)	0.4511(6)	1.1462(9)	0.0871(7)	7.6(6)
C(4)	0.0032(6)	1.1679(9)	0.2059(11)	13.4(11)	B	0.3892(9)	0.4454(10)	0.2571(9)	7.9(8)
C(5)	0.1433(7)	1.2733(9)	0.3069(8)	9.8(8)	F(1)	0.4082(6)	0.3989(7)	0.3328(4)	18.2(7)
C(6)	0.1161(7)	1.2619(9)	0.1142(9)	10.5(8)	F(2)	0.3114(5)	0.4100(7)	0.2199(9)	22.5(9)
N(7)	0.1170(5)	0.9571(6)	0.3082(6)	8.1(5)	F(3)	0.4270(6)	0.4042(7)	0.1998(5)	17.8(7)
O(7)	0.0694(5)	0.9300(7)	0.3554(6)	11.2(5)	F(4)	0.3791(4)	0.5482(4)	0.2524(5)	12.1(5)
C(8)	0.0908(5)	0.9411(6)	0.1398(6)	4.7(4)					
(c) $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (**22**)									
Mo	0.47046(3)	0.23606(3)	0.10595(3)	3.163(18)	C(5)[b]	0.2637(6)	0.6172(8)	0.1250(7)	6.83(23)
S(1)	0.38757(8)	0.26866(10)	0.24458(9)	3.14(5)	C(5*)[c]	0.4056(20)	0.6717(25)	0.2778(23)	8.1(8)
S(2)	0.42991(9)	0.43926(11)	0.11200(10)	3.52(6)	C(6)	0.5412(3)	0.2410(4)	0.0066(4)	3.99(24)
C(1)	0.3822(3)	0.4102(4)	0.2092(3)	2.99(21)	O(6)	0.5836(3)	0.2423(4)	−0.0530(3)	7.5(3)
N(1)	0.34219(25)	0.4840(3)	0.2540(3)	3.54(19)	C(7)	0.4983(3)	0.0753(4)	0.1247(4)	3.74(24)
C(2)	0.3082(4)	0.4576(5)	0.3441(4)	5.0(3)	O(7)	0.5127(3)	−0.0184(3)	0.1311(3)	6.22(23)
C(3)	0.2115(4)	0.4624(7)	0.3229(5)	8.2(5)	N(2)	0.3729(3)	0.1974(4)	0.0038(3)	5.21(25)
C(4)	0.3358(4)	0.6021(5)	0.2181(4)	4.9(3)	O(2)	0.3120(3)	0.1702(4)	−0.0620(3)	8.4(3)

[a] B_{eq}, equivalent isotropic thermal parameter, is the mean of the principal axes of the thermal ellipsoid. [b] Mean atoms with occupancy = 0.75. [c] Mean atoms with occupancy = 0.25.

shown. The numbering schemes in the figures correspond to the atomic positions (Table 2). Some selected bond lengths and angles are also collected in Table 3. ORTEP plots for **10** (Figure S1) and **12A** (Figure S2), atomic positions for **10** and **12**, more detailed crystal data, a complete table of bond lengths and angles, a table of anisotropic thermal displacement coefficients, and that of hydrogen coordinates of **9**, **10**, **12**, **17**, and **22** are deposited as supplementary material.

Results and Discussion

Synthesis of $[M(N,N)(CO)_2(NO)(MeOH)]BF_4$ (M = Mo, (N,N) = H_2CPz_2 (1), $H_2CPz'_2$ (2); M = W, (N,N) = H_2CPz_2 (3), $H_2CPz'_2$ (4)). Complexes **1**–**4** are readily formed by nitrosylation of $[M(N,N)(CO)_4]$ with $NO^+BF_4^-$ in MeOH. The structures are believed to be similar to each other, as reflected in the similarity of the IR spectra of the four complexes. From the $^{31}P\{^1H\}$ NMR evidence for the reactions between **2** and phosphine ligands and the solid-state structures of **9**, **10**, and **12**, described below, the structure for **1**–**4** may have the nitrosyl group *cis* to the bidentate ligand, $H_2CPz'_2$, but *trans* to MeOH (i.e., L_1 = NO and L_2 = MeOH in Figure 1).

Ligand Substitution of $[Mo(H_2CPz'_2)(CO)_2(NO)(MeOH)]BF_4$ (2). The substitution reaction first appeared straightforward, when the weakly coordinated MeOH of **2** was replaced readily with pyridine (py) to afford $[Mo(H_2CPz'_2)(CO)_2(NO)(py)]BF_4$ (**5**). The reactions soon behaved complicated when some other nucleophiles were used. A detailed study on the reactions of **2** with many different nucleophiles was hence carried out, and a total of four types of products was observed (Scheme 1). In types **1** and **2**, the reaction products contain $H_2CPz'_2$, whereas, in types **3** and **4**, the products do not have the $H_2CPz'_2$ ligation.

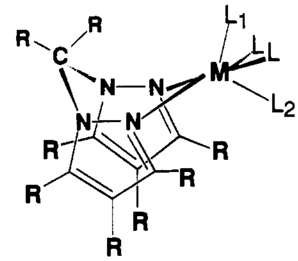

Figure 1. Structural plot of six-coordinate M(N,N) complexes ((N,N) = pyrazole-derived bidentate ligands).

Type 1. Addition of a nitrogen monodentate ligand such as py, oxygen donors such as nitrate and acetate, halides (Cl^-, Br^-, I^-), and pseudohalides (azide, thiocyanide, cyanide) to a solution of **2** in MeOH afforded **5** and $[Mo(H_2CPz'_2)(CO)_2(NO)(L)]$ (L^- = Cl^- (**6**), Br^- (**7**), I^- (**8**), N_3^- (**9**), NO_3^- (**10**), SCN^- (**11**), $MeCO_2^-$ (**12**), CN^- (**14**)), respectively. Compound **8** could also be prepared by using Gladfelter's approach[13] (i.e., by treating the 16-electron compound $[Mo(H_2CPz'_2)(CO)_2Br_2]$ with

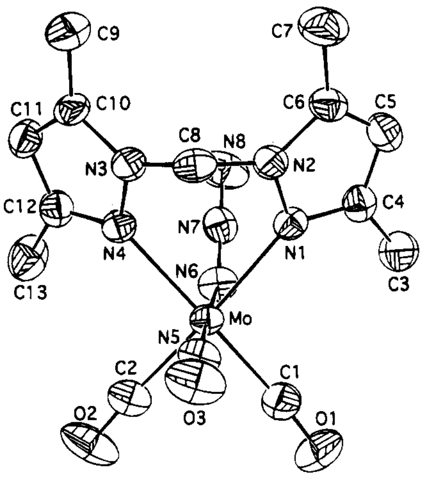

Figure 2. ORTEP plot of $[Mo(H_2CPz'_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (**9**).

Table 3. Selected Bond Lengths (Å) and Angles (deg)

(a) $[Mo(H_2CPz'_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (**9**)			
Mo−N(1)	2.260(3)	N(5)−O(3)	1.199(3)
Mo−N(4)	2.240(3)	N(6)−N(7)	1.190(5)
Mo−N(5)	1.789(3)	N(7)−N(8)	1.151(5)
Mo−N(6)	2.165(3)	O(1)−C(1)	1.141(5)
Mo−C(1)	1.986(4)	O(2)−C(2)	1.129(4)
Mo−C(2)	2.005(4)		
N(1)−Mo−N(4)	81.73(10)	Mo−N(5)−O(3)	178.81(22)
N(1)−Mo−C(2)	175.06(11)	Mo−N(6)−N(7)	127.66(22)
N(6)−N(7)−N(8)	177.1(3)	Mo−C(1)−O(1)	174.3(3)
N(4)−Mo−C(1)	174.48(13)	Mo−C(2)−O(2)	175.4(3)
N(4)−Mo−C(2)	95.11(14)	N(5)−Mo−N(6)	177.27(13)
C(1)−Mo−C(2)	83.42(16)		
(b) $[Mo(H_2CPz'_2)(CO)(NO)(PMe_3)_2]BF_4$ (**17**)			
Mo−P(1)	2.517(3)	C(8)−O(8)	1.180(10)
Mo−P(2)	2.496(3)	P(1)−C(2)	1.696(14)
Mo−N(3)	2.271(6)	P(1)−C(3)	1.659(12)
Mo−N(7)	1.823(8)	P(2)−C(4)	1.787(10)
Mo−C(8)	1.847(8)	P(2)−C(5)	1.788(10)
P(1)−C(1)	1.660(14)	P(2)−C(6)	1.789(12)
N(7)−O(7)	1.211(10)	Mo−N(1)	2.290(6)
P(1)−Mo−P(2)	175.61(9)	N(3)−Mo−C(8)	95.9(3)
N(3)−Mo−N(7)	178.1(3)	N(7)−Mo−C(8)	82.3(4)
Mo−N(7)−O(7)	173.9(7)	Mo−C(8)−O(8)	173.2(8)
N(1)−Mo−N(3)	87.16(21)	N(1)−Mo−N(7)	94.73(29)
(c) $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (**22**)			
Mo−S(1′)	2.5549(14)	Mo−C(6)	1.937(5)
Mo−S(1)	2.6326(14)	Mo−C(7)	1.984(5)
Mo−S(2)	2.5306(15)	Mo−N(2)	1.844(4)
N(2)−O(2)	1.176(6)	C(6)−O(6)	1.161(6)
C(7)−O(7)	1.148(6)		
S(1)−Mo−S(1′)	84.07(4)	S(1′)−Mo−C(7)	86.02(14)
S(1)−Mo−S(2)	69.66(4)	S(1′)−Mo−N(2)	173.96(16)
S(1)−Mo−C(6)	168.76(15)	S(2)−Mo−C(6)	100.50(15)
S(1)−Mo−C(7)	100.98(14)	S(2)−Mo−C(7)	170.22(14)
S(1)−Mo−N(2)	96.54(15)	S(2)−Mo−N(2)	95.79(15)
S(1′)−Mo−S(2)	90.06(4)	C(6)−Mo−C(7)	88.52(20)
S(1′)−Mo−C(6)	90.68(16)	Mo−S(1)−Mo′	93.31(4)
C(6)−Mo−N(2)	89.73(21)	Mo−C(6)−O(6)	179.0(4)
C(7)−Mo−N(2)	87.96(21)	Mo−C(7)−O(7)	177.0(4)
Mo−N(2)−O(2)	178.1(4)		

$M'^+NO_2^-$ ($M'^+ = Na^+, Ag^+, n\text{-}Bu_4N^+$)) but with a lower yield. Although compounds **6**−**12** and **14** display one NO and two CO stretching bands, compound **5** shows two NO and two CO bands in the IR spectra, measured in CH_2Cl_2. With the solid-state structures of **9** (Figure 2), **10** (Figure S1), and **12** (Figure S2), determined by X-ray crystallography, we believe that **6**−**12** and **14** all are isostructural with L^- *cis* to $H_2CPz'_2$ but *trans* to NO. However, in structure **5**, there are two different conformations with py *cis* to $H_2CPz'_2$ but either *trans* or *cis* to NO, reflecting the higher π-acidity of py, compared with L^-. In addition, the monohapticity of azide in **9**, nitrate in **10**, and acetate in **12** was also confirmed. The Mo−N distances of 2.224(23)−2.271(24) Å found in **9**, **10**, and **12** are significantly smaller than those of 2.286(2) and 2.288(2) Å found in $[Mo(H_2CPz'_2)(CO)_4]$.[14] Apparently, a better π-acid such as NO, compared with CO, can tighten the $H_2CPz'_2$ ligation. However, the $Mo-N_3$ distance 2.165(3) Å, the central and terminal N−N distances within the MoN_3 unit at 1.190(5) and 1.151(5) Å, respectively, the Mo−N−N angle 127.66(22)°, and the N(6)−N(7)−N(8) angle 177.1(3)° are found comparable to the reported values.[15] Apparently, the expected shortening in the $Mo-N_3$ bond by the electronic tightening effect of the *trans*-nitrosyl group in **9** is counterbalanced by the increased steric repulsion between the bulky $H_2CPz'_2$ and azide groups.

Interestingly, although reaction of **2** with **14** formed an adduct, probably with a cyanide bridge, $[\{Mo(H_2CPz'_2)(CO)_2(NO)\}_2(\mu\text{-}CN)]BF_4$ (**13**), a similar reaction of **2** with **9** or **11** gave no adduct. Obviously, the nucleophilicity of a coordinated azide or thiocyanide ligand decreases appreciably. Although one may deduce from this failure something about the structure of **11**, having a Mo−SCN or Mo−NCS bond, an unambiguous assignment should be subjected to a single-crystal structure analysis or the integrated intensity measurements at ν_{CN}.[16a] The pyridine ligand in **5** was readily replaced by Cl^-, Br^-, and I^- in MeOH to give back **6**, **7**, and **8**, respectively. However, among these three compounds, only **8** reacted with $NO^+BF_4^-$ in MeOH to reproduce **2**. A comparison among the nitrosyl stretching frequencies, displayed by **5**−**8** in CH_2Cl_2, shows that ν_{NO} decreases in the order **5** (1680 and 1657 cm^{-1}) > **8** (1642 cm^{-1}) > **7** (1640 cm^{-1}) > **6** (1634 cm^{-1}). This order indicates probably that the bonding strength increases as Mo−py < Mo−I < Mo−Br < Mo−Cl in the series of compounds, which may explain the reactivity of **5** toward halides and the result of reaction of **6**−**8** with NO^+. The reaction between **8** and NO^+ to give **2** is reminiscent of that between $Et_4N[Mo(CO)_5I]$ and dppe in the presence of Et_3OBF_4 to give $[Mo(\eta^1\text{-}dppe)(CO)_5]$.[17] The bonding-strength order appears contradictory to what can be expected, since the iodo ligand is usually regarded as the best or nearly the best σ-donor. However, it looks reasonable in consideration of the steric effect of the bulky $H_2CPz'_2$ ligand, which may inhibit the σ-donicity by forming a long, weak bond between the sizable σ-donor and the central metal atom.

Type 2. Although complexes $[Mo(H_2CPz'_2)(CO)_2(\eta^3\text{-}allyl)Br]$ and $[Mo(H_2CPz'_2)(CO)_2Br_2]$ were found previously to react with some soft phosphorous monodentate ligands with cone angles less than or equal to 125° to yield the products without coordination of $H_2CPz'_2$,[5] **2** was found to react with any phosphine ligand we tried, including PPh_3 (cone angle 145°),[18] to afford products $[Mo(H_2CPz'_2)(CO)(NO)(PR_3)_2]BF_4$ (R = Ph (**15**), OMe (**16**), Me (**17**)). As shown in the crystal structure of **17** (Figure 3), the two phosphine ligands are *cis* to $H_2CPz'_2$ but *trans* to each other. Although structure **17** contains

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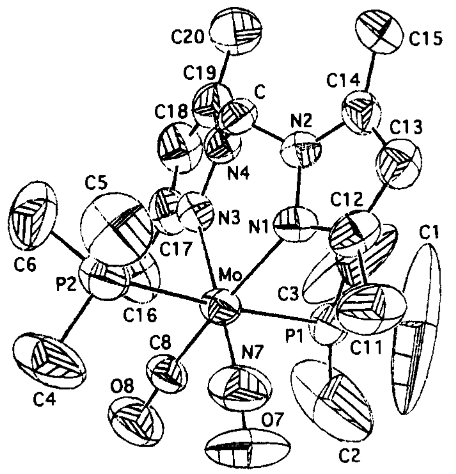


Figure 3. ORTEP plot of the cation, $[Mo(H_2CPz'_2)(CO)(NO)(PMe_3)_2]^+$ (17^+).

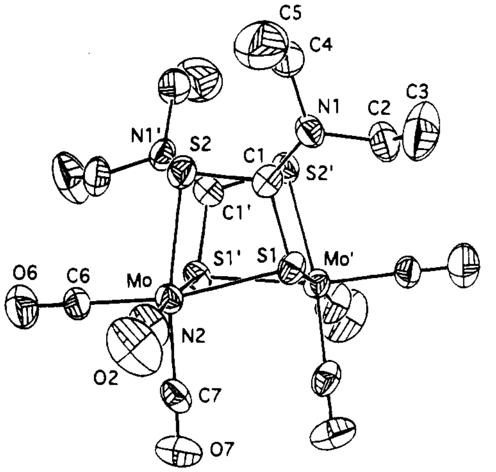
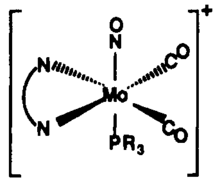


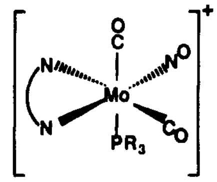
Figure 4. ORTEP plot of $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (**22**).

a bulky boat metallacycle, the Mo−P distances 2.517(3) and 2.496(3) Å fall within the reported range 2.369−2.598 Å.[19] The two significantly different Mo−P distances and the angles ∠P−Mo−P = 175.61(9)°, deviating from 180°, indicate that a strong Mo−P bond was achieved via bending the P−Mo−P linkage.

In order to understand a possible reaction pathway for replacing two ligands, MeOH and CO, of **2** with two PR_3 to form **15**−**17**, $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **2** and excess PR_3 were measured sequentially in the mixed solvents of CH_2Cl_2 and acetone-d_6 in a ratio of 1/1. Addition of CH_2Cl_2 was necessary to help dissolution of **2** and reaction products to form a homogeneous solution, and the deuterated solvent was used for the deuterium lock. After **2** was added to a solution of excess PMe_3, three highly intense ^{31}P singlets at −61.0, −26.9, and −13.0 ppm and one weak broad singlet at −5.9 ppm were observed. This observation indicates that ligand exchange is not rapid enough to cause chemical shift averaging of complexed and free ligand. The free PMe_3 is responsible for the singlet with the greatest intensity at −61.0 ppm,[8a] and to the isolated product **17** belongs the broad peak at −5.9 ppm. According to the theory of Letcher and Van Wazer,[20] we believe that **2** and PMe_3 first give $[Mo(H_2CPz'_2)(CO)_2(NO)(PMe_3)]BF_4$ (**17-I**) with NO *trans* to PMe_3 ($\delta(^{31}P) = -26.9$), and isomerization of this complex soon produces a new structure (**17-II**) with CO *trans* to the phosphine ligand ($\delta(^{31}P) = -13.0$). After 40 min, the signal at −5.9 ppm became much more intense than the signal at −61.0 ppm, whereas the other two shrank to small signals. This finding is compatible with the brief duration of preparation of **17**, monitored by IR measurements, reflecting the strong donating ability of PMe_3. However, upon dissolving **2** and excess PPh_3 in the solvents, only three singlets appeared at 26.2, 34.7, and −6.0 ppm. After 70 min, the signal at 34.7 ppm increased appreciably but the signal at 26.2 remained almost constant relative to the signal at −6.0 ppm. The singlet at 34.7 ppm was later confirmed to be due to **15** by comparison with the ^{31}P chemical shift of the isolated product **15** in the solvents. As the singlet at −6 ppm is due to the free ligand, PPh_3,[8b] the singlet at 26.2 ppm is assigned to either **15-I** or **15-II**. On the basis of the rapid conversion from **2** to **15** (ca. 2 h) and the almost constant intensity observed for this singlet relative to the PPh_3 peak, we assign the singlet to **15-I**. Probably the bulky PPh_3 may help induce decarbonylation sterically so that **15-II** reacted with PPh_3 with loss of one CO as soon as it was formed from **15-I** to give **15**. Unlike the reaction between **2** and PPh_3, that between **2** and $P(OMe)_3$ gave four singlets at δ 152.2 (for **16**), 29.9 (for **16-I**), 54.5 (for **16-II**), and 141 ppm (for free $P(OMe)_3$).[8a]



15-, 16- or 17-I



15-, 16- or 17-II

Type 3. Soft neutral bidentate ligands (L,L) were found to convert **2** into *cis*-$[Mo(L,L)_2(CO)(NO)]BF_4$ ((L,L) = bpy (**18**), phen (**19**), Me_2bpy (**20**), dppm (**21**)). The reaction products of **2** with dppm depend on the solvent used. Upon mixing **2** and dppm in a mixed solvent system of CH_2Cl_2 and acetone-d_6 in a ratio of 1/1, one singlet at −22.3 ppm (for free dppm),[8c] four clear doublets, and two apparent triplets appeared (Figure 5a). The doublets at 22.1 and −26.0 ppm with J = 110 Hz are assigned to coordinated and free phosphorus atoms of η^1-dppm, respectively, in **21-I** and those at 30.2 and −28.9 ppm with J = 52 Hz are assigned to **21-II.** After spectrum expansion, the triplets were decomposed into four doublets at 29.1 and −27.1 ppm with J = 26.3 Hz and 29.3 and −27.3 ppm with J = 26.0 Hz. These four doublets are assigned to $[Mo(H_2CPz'_2)(\eta^1\text{-dppm})_2(CO)(NO)]BF_4$ (**21-III**) with one dppm *trans* to another dppm, which is expected to have a structure similar to that of **17** (Figure 3). The ring-flip motion of the six-membered-boat metallacycle does not occur in solution for **15**, **16**, **17**, or **21-III** to average the phosphorus chemcial shifts; hence two closed doublets at the high fields and two at the low fields are observed for **21-III** whereas two closed singlets overlap as a unresolved broad peak found for **15**, **16**, and **17**. After 90 min,

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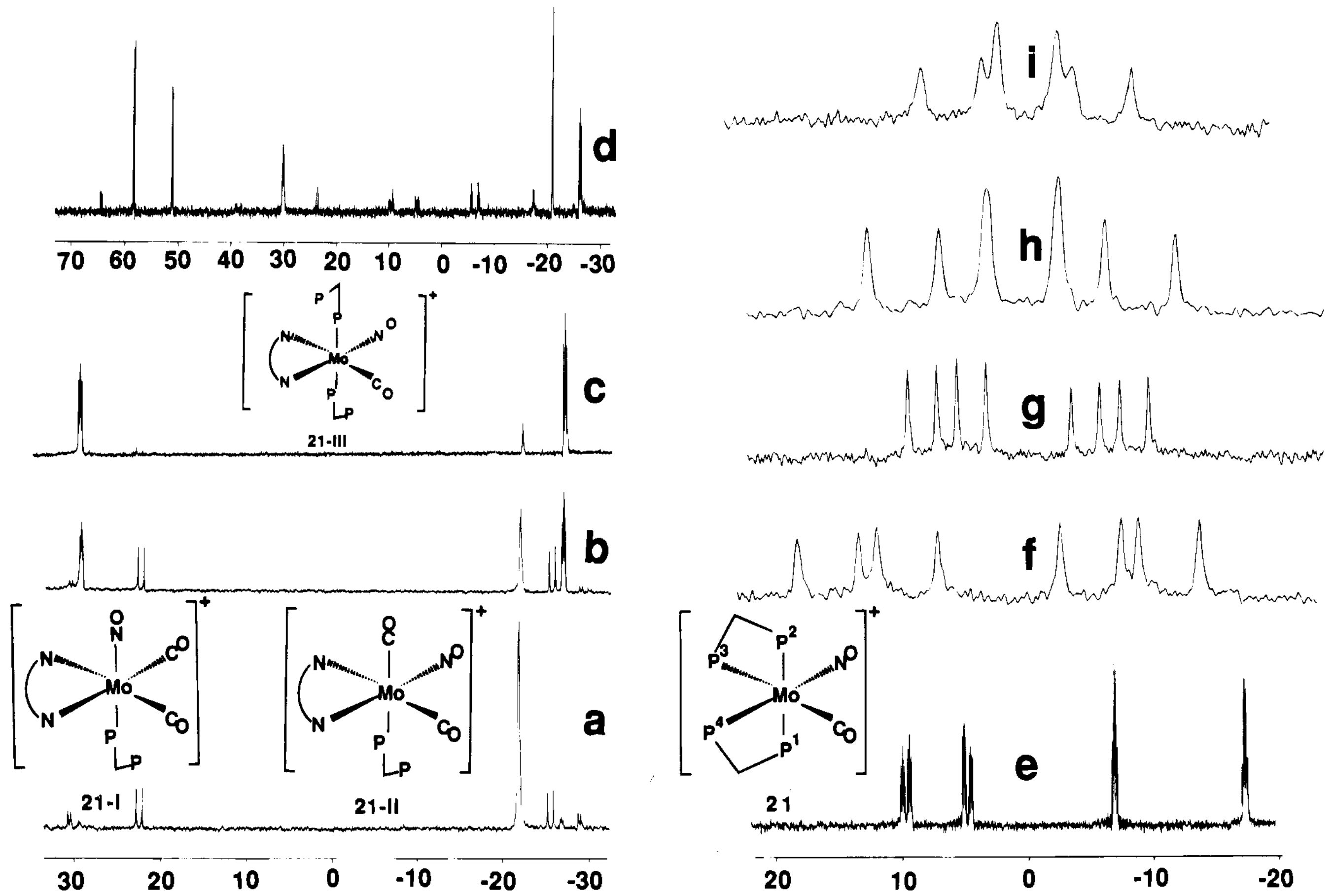

Figure 5. The 162-MHz $^{31}P\{^1H\}$ NMR spectra recorded for (a) [Mo($H_2CPz'_2$)$(CO)_2$(NO)(MeOH)]BF_4 (**2**) and dppm at $t = 0$; (b) at $t = 90$ min; (c) **2** and excess dppm at $t = 60$ min; (d) **2** and excess dppm at $t = 70$ h and (e) *cis*-[Mo$(dppm)_2$(CO)(NO)]BF_4 (**21**). The expanded $^{31}P\{^1H\}$ spectrum of **21** at (f) $\delta\ ^{31}P = 9.54$; (g) $\delta\ ^{31}P = 4.63$; (h) $\delta\ ^{31}P = -7.25$ and (i) $\delta\ ^{31}P = -17.75$.

the triplets (of **21-III**) increased appreciably (Figure 5b). Adding further dppm brought the complete conversion of **2** into **21-III** (Figure 5c). Alternatively, we added in about 1 h a solution of **2** (1.0 mmol) in CH_2Cl_2 (25 mL) dropwise to another solution of dppm (3.0 mmol) in CH_2Cl_2 (25 mL) to form a solution of **21-III** with excess dppm, giving a $^{31}P\{^1H\}$ NMR spectrum similar to Figure 5c. However, the color of this solution gradually altered from orange-red into dark brown after 23 h. After 70 h, an IR solution spectrum showed "completion" of the reaction; it contains two ν_{CO} bands at 1944 m and 1917 s cm^{-1} and two ν_{NO} bands at 1617 s and 1597 sh cm^{-1}. A $^{31}P\{^1H\}$ NMR spectrum was recorded for this solution and consisted of many lines, located at the range +64 to −27 ppm (Figure 5d). Although we could not separate various products from this reaction on a column chromatograph, we noticed that at least one product did not dissolve in MeOH. Accordingly, a mixture of **2** (0.45 mmol) and dppm (1.00 mmol) in MeOH (20 mL) was heated at 65 °C for 2 h. A pure compound (**21**) was obtained as precipitate in satisfactory yield. The $^{31}P\{^1H\}$ NMR spectrum of **21** contains four multiplets (Figure 5e), and the $^1H\{^{31}P\}$ NMR spectrum of this compound has four doublets at 4.71, 4.44, 4.35, and 3.82 ppm with $J = 15$ Hz, consistent with a *cis* disposition of two η^2-dppm ligands in **21**. When the $^{31}P\{^1H\}$ NMR spectrum was recorded without NOE, the four multiplets were found in an integration ratio 1.00:1.05:1.04: 1.01. These multiplets are assigned to the four P atoms shown in Figure 5e, based on various coupling parameters and the theory of Letcher and Van Wazer.[20] The doublet of doublet of doublet at 9.54 ppm ($J = 21, 27, 88$ Hz) is assigned to P^1 (Figure 5f), and another doublet of doublet of doublet at 4.63 ppm ($J = 16, 27, 88$ Hz) is assigned to P^2 (Figure 5g); the doublet of triplet at −7.25 ppm ($J = 16, 27$ Hz) is assigned to P^3 (Figure 5h), and another doublet of triplet at −17.75 ppm ($J = 21, 27$ Hz) is assigned to P^4 (Figure 5i). Hence, $J(P^1, P^2) = 88$, $J(P^1, P^3) = J(P^2, P^4) = J(P^3, P^4) = 27$, $J(P^1, P^4) = 21$, and $J(P^2, P^3) = 16$ Hz. The signals due to P^4, *trans* to NO, are broadened, corroborating the assignment of that particular atom.[21] According to detailed reports about metal complexes of dppm,[22] the lines at positions greater than 40 ppm, shown in Figure 5d, are possibly due to formation of multinuclear complexes containing μ-dppm linkages, such as $\{Mo_2(\mu\text{-dppm})_2\}^{2+}$ complexes.

Unlike the reaction of **2** with dppm, those of **2** with bpy, phen, and Me_2bpy are straightforward. In either CH_2Cl_2 or MeOH, only one product was obtained to give **18**, **19**, and **20**, respectively. As no further substituted product such as [Mo($H_2CPz'_2$)$(py)_2$(CO)(NO)]BF_4 was formed from the reaction of **5** with excess pyridine in MeCN under forcing conditions, the reaction pathway from **2** to **18**−**20** may involve two successive intermediates such as [Mo($H_2CPz'_2$)(η^1-bpy)$(CO)_2$(NO)]BF_4 and

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Table 4. Angles α, β, γ, and θ for (N,N)-Ligated Complexes

complex[a]	α	β	γ	θ	ref
$[W(H_2CPz'_2)(CO)_4]$	111.8(3)	146.6(3)	128.4(7)	167.7(3)	9b
$[W(H_2CPz''_2)(CO)_4]$	120.8(3)	152.1(2)	125.0(5)	170.8(2)	9b
$[Mo(H_2CPz'_2)(CO)_4]$	111.9(2)	147.2(2)	126.7(2)	167.3(1)	14
$[Mo(PhHCPz'_2)(CO)_4]$	127.6(4)	159.7(4)	128.7(4)	166.0(2)	27
$[Mo\{H_2C(Pz^*)(Pz^{*\prime})\}(CO)_4]$[b]	111.4(3)	148.4(3)	127.1(6)	165.7(3)	27
	105.2(3)	146.3(3)	127.4(6)	164.6(3)	
$[Mo\{H_2C(Pz^{\ddagger})_2\}(CO)_4]$	130.1(3)	150.5(2)	123.9(6)	165.9(3)	27
$[Mo(H_2CPz'_2)(CO)_2(NO)(N_3)]$	119.4(2)	150.6(1)	124.6(4)	177.3(1)	this work
$[Mo(H_2CPz'_2)(CO)_2(NO)(MeCO_2)]BF_4$[b]	121.6(1)	150.9(1)	127(3)	177.6(1)	this work
	120.8(1)	152.9(1)	129(3)	176.4(1)	
$[Mo(H_2CPz'_2)(CO)_2(NO)(NO_3)]$	122.3(2)	155.5(2)	123.6(3)	177.3(1)	this work
$[Mo(H_2CPz'_2)(CO)(NO)(PMe_3)_2]BF_4$	153.9(4)	179.1(3)	119.9(8)	175.6(9)	this work

[a] Pz″ = 3,4,5-trimethylpyrazol-1-yl; Pz* = 3-phenylpyrazol-1-yl; Pz* ′ = 5-phenylpyrazol-1-yl; Pz‡ = 3,5-dimethyl-4-benzylpyrazol-1-yl. [b] Two different molecules in the asymmetric unit of the crystal used.

$[Mo(\eta^2\text{-bpy})(\eta^1\text{-bpy})(CO)_2(NO)]BF_4$,[23] the latter of which then formed the final product **18**. The *cis* arrangement of two nitrogen bidentate ligands is clearly supported by observation of four methyl singlets for **20** in a ^1H NMR spectrum. The compound of *cis*-$[Mo(bpy)_2(CO)(NO)]PF_6$ was reported in 1984, from the reaction of *cis*-$[Mo(CO)_2(bpy)_2]$ with $NO^+PF_6^-$.[24] Spectral data of this compound and **18** are similar. However, caution in using an appropriate proportion of $NO^+PF_6^-$ to react with *cis*-$[Mo(CO)_2(bpy)_2]$ was described for preparation of *cis*-$[Mo(bpy)_2(CO)(NO)]PF_6$, because excess nitrosylating agent produced only an intractable oily material. The influence of strongly donating N−N ligands (N−N = bpy and phen), permitting access of *cis*-$[M(N{-}N)_2(CO)_2]$ to *cis*-$[M(N{-}N)_2(CO)_2]^{2+}$ and *cis*-$[M(N{-}N)_2(CO)_2(\text{solvent})]^{2+}$, was also described.[24] Coincidentally, Bond and co-workers found previously that *cis*-$[M(dppm)_2(CO)_2]$ compounds are oxidized and isomerized easily.[25] This propensity would make preparation of **21** difficult via nitrosylation of *cis*-$[M(dppm)_2(CO)_2]$ with $NO^+PF_6^-$. The reactions of **2** (and **4**) with either nitrogen or phosphorus bidentate ligands (L,L) to give *cis*-$[M(L,L)_2(CO)(NO)]BF_4$ such as **18**, **19**, **20**, or **21** may represent a more convenient synthetic method.

Type 4. The reaction of **2** with dithiocarbamate anion, $(S,S)^-$, proceeded smoothly according to the solution IR spectra. However, after removal of solvent, there appeared one orange-red compound $[Mo(S,S)(CO)_2(NO)]_2$ ($(S,S)^- = Et_2NCS_2^-$ (**22**), $Me_2NCS_2^-$ (**23**), $C_4H_8NCS_2^-$ (**24**)) as major product and one yellow compound as minor product. Only the orange-red compound was cleanly separated and characterized. Dinuclearity of compounds associated with the six-electron dithiocarbamato ligand in a μ,η^2-fashion is confirmed by the structural determination of **22** (Figure 4), which contains a crystallographically imposed inversion center. The distance of 3.474(3) Å between two S atoms and that of 3.773(1) Å between two Mo atoms is compatible with no S−S or Mo−Mo bond. The nitrosyl groups are *trans* to the bridging sulfur atoms while *cis* to carbonyls. The failure to isolate and to characterize the yellow product causes ambiguity about the possible pathway to form $[Mo(S,S)(CO)_2(NO)]_2$ from **2**. However, on the basis of the bridging propensity of organic sulfur compounds,[26] the pathway may involve an intermediate like $[Mo(H_2CPz'_2)(\eta^1\text{-}(S,S))(CO)_2(NO)]$, which loses $H_2CPz'_2$ and forms the 16-electron compound $[Mo(\eta^2\text{-}(S,S))(CO)_2(NO)]$. Dimerization of this intermediate then affords the product $[Mo(S,S)(CO)_2(NO)]_2$.

Conformational Difference in the Six-Membered Boat Metallacycles. Previously, we reported that the conformation of the six-membered metallacycle, formed by a (N,N) ligand and a metal atom, is flexible, depending on the substituents on the pyrazolyl skeleton.[9b] We now wish to add that different ligands in the coordination sphere of a metal atom can also cause a different conformation of the metallacycle. Though the crystallographic data refer to a molecule in a crystal field and undergoing vibrational motion, various metallacycle conformations present in M(N,N) solid-state structures reflect that the complexes may retain the metallacycle flexibility in solution or during a reaction course.[28] In order to gain a better understanding about this flexible metallacycle, we calculated four angles α, β, γ, and θ of all M(N,N) structures, including **9**, **10**, **12**, and **17** (Table 4). Angle α is defined by the two azolyl planes, angle β by the MNN and the NNNN planes, angle γ by the NNNN and the CNN planes, and angle θ is formed by the two ligands, *trans* to each other but *cis* to $H_2CPz'_2$ (i.e., $\angle L_1{-}M{-}L_2 = \theta$; cf. Figure 1). To make a consistent set of α, β, and γ values, we should also calculate angle ω, defined by the MNN and the CNN planes, and two vertical distances from the boat-end atom, Mo (or C), to each azolyl plane. Simple geometry indicates that the angles β, γ, and ω should follow $\beta + \gamma - 180° = \omega$; if one distance is positive, the other value should be negative.

By comparison of the four angles of M(N,N) complexes (Table 4), it is quite clear that the metallacyles in nitrosyl complexes are more distorted than those in $[M(N,N)(CO)_4]$ complexes. The range of angles found for α, β, or γ is larger in the nitrosyl-ligated complexes ($\Delta\alpha = \alpha_{max} - \alpha_{min} = 34.5°$; $\Delta\beta = 28.5°$; $\Delta\gamma = 9.1°$) than that in $[M(N,N)(CO)_4]$ complexes ($\Delta\alpha = 24.9°$; $\Delta\beta = 13.4°$; $\Delta\gamma = 4.8°$). The θ values found in $[M(N,N)(CO)_4]$ complexes are 164.6−170.8°, much smaller than those of 175.6−177.6° in the nitrosyl complexes. In either complex, the feature of $\beta > \gamma$ may reflect the much greater congestion near the metal center.

As already mentioned above, the fact that the Mo−N distances 2.224(23)−2.271(24) Å found in the nitrosyl complexes **9**, **10**, and **12** are significantly shorter than those of 2.286(2) and 2.288(2) Å found in $[Mo(H_2CPz'_2)(CO)_4]$[14] reflects the presence of the electronic tightening effect of a nitrosyl group. It thus appears obvious that this effect can induce a more distorted structure in the nitrosyl-ligated complexes by shortening the Mo−N bonds.

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Conclusions

The present study demonstrates that the presence of a nitrosyl group in a complex such as **2** can help to tighten the $H_2CPz'_2$ ligation during some nucleophilic substitution reactions in spite of the inherent ring strain present in the six-membered-boat metallacycle, formed between $H_2CPz'_2$ and the central metal atom (Figure 1). Flexibility of the metallacycle is still present even with this electronic tightening in all the $H_2CPz'_2$-ligated metal nitrosyl products (Table 4). It appears that the steric effect of $H_2CPz'_2$, the inherent ring strain and flexibility of the metallacyle, and the electronic effect of NO contribute to allow formation of four types of products from the reactions of **2** (Scheme 1). Clearly, the results of this study establish benchmarks for future studies on the stereochemical effect of (N,N) in the related M(N,N) complexes.

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Supplementary Material Available: ORTEP plots of **10** (Figure S1) and **12** (Figure S2), atomic positions for **10** and **12** (Table S1), complete crystal data (Table S2), bond lengths and angles (Table S3), anisotropic thermal displacement coefficients of non-hydrogen atoms (Table S4), and fractional atomic coordinates for hydrogen atoms in **9**, **10**, **12**, **17**, and **22** (Table S5) (18 pages). Ordering information is given on any current masthead page.

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