Organometallics 1993, *12*, 3575–3585

Thermal Chemistry of $CpMo(NO)(CH_2CMe_3)_2$: Lewis Base Adducts of $CpMo(NO)({=}CHCMe_3)$ and a New Bonding Mode for Nitric Oxide

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Received March 23, 1993®

Treatment of $CpMo(NO)Cl_2$ with $(Me_3CCX_2)_2Mg{\cdot}X(dioxane)$ [X = H, D] in THF at low temperatures provides moderate yields of the bis(neopentyl) complexes, $CpMo(NO)(CH_2CMe_3)_2$ (**1**) and $CpMo(NO)(CD_2CMe_3)_2$ (**1**-d_4). The solid-state molecular structure of **1**-d_4 has been determined at 170 K. Crystals of **1**-d_4 are monoclinic of space group $P2_1/n$; $a = 5.9781(6)$ Å, $b = 20.065(4)$ Å, $c = 13.6355(17)$ Å; $\beta = 95.52(1)°$; $Z = 4$; $R = 0.025$, $R_w = 0.032$ for 2494 reflections with $I \geq 2.5\sigma(I)$. Room-temperature thermolysis of **1** in CH_2Cl_2 solution provides bimetallic $[CpMo(NO)](\mu\text{-}\eta^1{:}\eta^2\text{-}NO)(\mu\text{-}CHCMe_3)[CpMo[{=}CHCMe_3)]$ (**2**) in which the unprecedented μ_2-$\eta^1{:}\eta^2$-NO ligand formally provides five electrons to the two Mo centers. Crystals of **2** are orthorhombic of space group *Pcab*: $a = 17.836(2)$ Å, $b = 18.265(2)$ Å, $c = 13.198(2)$ Å; $Z = 8$; $R = 0.042$, $R_w = 0.037$ for 4081 reflections with $I \geq 3\sigma(I)$. Thermolysis of **1** in the presence of phosphines or pyridine (L) provides the monomeric adducts, $CpMo(NO)({=}CHCMe_3)(L)$ (**3**–**5**, **7**) of which $CpMo(NO)({=}CHCMe_3)(PPh_2Me)$ (**3**) has been crystallographically characterized. Crystals of **3** are monoclinic of space group $P2_1/n$: $a = 9.328(2)$ Å, $b = 15.516(3)$ Å, $c = 15.188(2)$ Å, $\beta = 93.72(1)°$; $Z = 4$; $R = 0.027$, $R_w = 0.026$ for 3406 reflections with $I \geq 3\sigma(I)$. Thermolysis of **1** in the presence of excess PMe_3 in CH_2Cl_2 affords $[(Me_3P)_4Mo(NO)Cl]_2$ (**6**). Displacement of pyridine (py) from $CpMo(NO)({=}CHCMe_3)(py)$ (**7**) with a stoichiometric amount of PMe_3 produces $CpMo(NO)({=}CHCMe_3)(PMe_3)$ (**8**). Reaction of **1** with $CNCMe_3$ yields the η^2-iminoacyl complex, $CpMo(NO)(\eta^2\text{-}C\{NCMe_3\}CH_2CMe_3)(CH_2CMe_3)$ (**9**).

Introduction

In recent years we have been investigating the synthesis and characterization of $Cp'M(NO)R_2$ complexes [Cp′ = Cp or Cp*; M = Mo or W; R = alkyl or aryl].[1] We have also conducted studies of their reactions with H_2,[2,3] CO,[4,5] O_2,[6] and H_2O.[7,8] In general, these 16-valence-electron $Cp'M(NO)R_2$ complexes are thermally stable at room temperature when isolated in an analytically pure form.[9,10] This stability reflects both the nonbonding nature of the metal-centered LUMO[11] of these complexes and their kinetic inertness toward decomposition. However, as the electron deficiency of these complexes increases, so too does their thermal sensitivity.[10] Of the eight possible variants of Cp′, M, and R, only $CpMo(NO)(aryl)_2$ complexes have eluded isolation to date because of their extreme thermal instability.[10] The next most sensitive group of complexes are the $CpMo(NO)(alkyl)_2$ family of which $CpMo(NO)(CH_2CMe_3)_2$ is by far the most thermally sensitive member that we have yet isolated. In this paper, we report the results of our initial investigations into the thermal behavior of this compound. We have discovered that $CpMo(NO)(CH_2CMe_3)_2$ decomposes surprisingly cleanly, in contrast to most other $Cp'M(NO)R_2$ complexes which do not decompose along one pathway, but rather afford a multitude of thermal decomposition products under thermolysis conditions.[12] Portions of this work have been communicated previously.[13]

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere

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® Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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0276-7333/93/2312-3575$04.00/0

of prepurified argon. General procedures routinely employed in our laboratories have been described in detail previously.[10] The flow system for in situ IR spectral monitoring was constructed from a Teflon diaphragm pump (Cole-Parmer 07090-62) and a 0.2-mm NaCl cell (Wilmad 105A10-5).

$CpMo(NO)Cl_2$[14] was recrystallized by Soxhlet extraction with CH_2Cl_2. $(Me_3CCH_2)_2Mg{\cdot}X$(dioxane) [X = 1–2][15] and PMe_3[16] were prepared by their published procedures. $LiAlD_4$ (Aldrich, 98% D), $P(n\text{-}Bu)_3$, $P(p\text{-}tolyl)_3$, PPh_2Me, $CNCMe_3$ (Aldrich), PPh_3 (Strem), and activated Mg dust (Baker) were used as received. $Me_3CC\{O\}Cl$ (Aldrich) was degassed with several freeze–pump–thaw cycles. DMF (BDH) was freshly distilled in vacuo from activated 4-Å molecular sieves, and 1,4-dioxane (BDH) was distilled from Na/benzophenone.[17] The column chromatography material used during this work was alumina (80–200) mesh, Fisher neutral, Brockman activity I). Filtrations were performed through Celite 545 diatomaceous earth (Fisher) that had been oven-dried and cooled in vacuo.

Preparation of $CpMo(NO)(CH_2CMe_3)_2$ (1). Complex 1 is extremely thermally sensitive, and so the following synthetic procedure was used to isolate it in a spectroscopically pure state. THF (3 mL) was vacuum transferred onto $CpMo(NO)Cl_2$ (100 mg, 0.38 mmol) and $(Me_3CCH_2)_2Mg{\cdot}X$(dioxane) (0.75 mmol $Me_3CCH_2^-$) at −196 °C. The reaction mixture was stirred for 1 h as it was warmed to −40 °C, the temperature at which *all* subsequent manipulations were performed. The final red solution (ν_{NO} 1608 cm^{-1}) was taken almost to dryness in vacuo. The oily red residue was suspended in Et_2O (10 mL), and the mixture was filtered through alumina (1 × 2 cm) supported on a medium-porosity glass frit. Solvent was removed from the filtrate under reduced pressure to obtain 1 as a red solid (~70 mg, ~55% yield). Five different estimates of the yield of similar-scale reactions leading to 1 indicated it varied only slightly from 55% (i.e., 50–59%).

IR (THF): ν_{NO} 1608 cm^{-1}. ^1H NMR (C_6D_6): δ 5.04 (s, 5H, C_5H_5), 4.01 (d, 2H, CH_2, $^2J_{HH}$ = 12.1 Hz), 1.31 (s, 18H, $C(CH_3)_3$), 0.27 (d, 2H, CH_2, $^2J_{HH}$ = 12.1 Hz). The thermal instability of $CpMo(NO)(CH_2CMe_3)_2$ as a solid precluded the obtaining of elemental analysis or mass spectral data for the complex.

Preparation of $(Me_3CCD_2)_2Mg{\cdot}X$(dioxane).[18] A large magnetic stirring bar and $LiAlD_4$ (3.50 g, 79.1 mmol) were transferred to a 500-mL round-bottom flask in a drybox. The flask was removed from the drybox and attached to a vacuum line. A 250-mL pressure-equalized addition funnel was attached to the flask and cooled under a flow of argon. Once cool, the addition funnel was charged with $Me_3CC\{O\}Cl$ (19.1 mL, 155 mmol, 0.98 equiv) diluted with Et_2O (100 mL). Et_2O (300 mL) was added to the solid $LiAlD_4$. The flask was cooled to −78 °C, and dropwise addition of the acetyl chloride solution to the $LiAlD_4$ suspension was initiated. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 4 h. No visible change in the reaction mixture was evident. The flask was then cooled to −10 °C, and H_2O (2 mL) was added via a disposable syringe. The contents of the flask were stirred for 5 min, and then NaOH (0.6 g dissolved in 3 mL of water) was added to the flask, thereby causing the contents of the flask to become increasingly viscous. The volatiles were then vacuum transferred from the white solids into a new flask using heating provided by an oil bath. [Attempts to filter the above reaction mixtures proved to be very difficult and decreased yields substantially.] After thawing, the vacuum-transferred solution was dried overnight on $MgSO_4$. The spent $MgSO_4$ was removed by filtration into a tared 500-mL flask. Removal of the solvent in vacuo at −25 °C afforded Me_3CCD_2OH (~10 g, 72% yield) as a waxy, white solid. This solid was used directly in the next step.

Me_3CCD_2OH (~10 g, ~111 mmol) was dissolved in DMF (150 mL) in a flask equipped with two addition funnels and a Liebig condenser connected to a 250-mL, one-necked flask. One addition funnel was charged with $P(n\text{-}Bu)_3$ (42.4 mL, 170 mmol) and the other with Br_2 (8.2 mL, 160 mmol). The $P(n\text{-}Bu)_3$ was added to the DMF solution over a 5-min period at room temperature. The flask was then immersed in an ice bath and the bromine addition commenced. After the bromine had been completely added (30 min), the addition funnels were removed from the reaction flask, and the orange reaction mixture was stirred at room temperature for 30 min. Distillation of the crude reaction mixture under argon (1 atm) at 140–155 °C provided a colorless mixture of DMF and Me_3CCD_2Br. The distillation pot contained a dark red tar which solidified upon cooling.

The following manipulations were executed in air. Addition of H_2O (80 mL) to the DMF/Me_3CCD_2Br mixture caused the solution to separate into two layers. The lower layer of Me_3CCD_2Br was removed using a separatory funnel and was washed with water (20 mL). At this point, the organic product appeared cloudy. Both fractions of water were combined and extracted with Et_2O (50 mL). The ether wash was combined with the crude Me_3CCD_2Br. The resulting Et_2O solution was dried over $CaCl_2$ for 1 h and then P_2O_5 for several days. The dried ether solution of Me_3CCD_2Br was filtered through Celite (2 × 2 cm) supported on a frit into a new flask. To this filtrate were added dibromoethane (1.0 mL) and Et_2O (50 mL). Meanwhile, in a glovebox, a 500-mL flask was charged with Mg powder (5 g, excess). The flask was removed from the glovebox and attached to a vacuum line, Et_2O (250 mL) was added, and an addition funnel and a reflux condenser were attached to the flask. The contents of the flask were brought to reflux using an oil bath. The $Me_3CCD_2Br/BrCH_2CH_2Br/Et_2O$ solution was transferred to the addition funnel, and dropwise addition of the solution to the refluxing Mg/Et_2O mixture was effected over the course of several hours. The reaction mixture was then refluxed overnight. The resulting yellow mixture was filtered through Celite (3 × 10 cm). The clear yellow filtrate was treated dropwise with 1,4-dioxane (13.0 mL, 153 mmol, excess), and the resulting white slurry was stirred overnight at room temperature. The supernatant solution containing bis(neopentyl)magnesium was isolated by centrifuging aliquots of the slurry for 30 min at 3500 rpm and then removing the clear orange supernatant solutions by cannulation. Rather than isolating the organomagnesium species by crystallization, the combined supernatant solutions were used directly in further reactions, thereby minimizing the losses normally associated with crystallization processes. Hydrolysis of a known volume of sample, then titration against 0.1000 M HCl using phenolphthalein as indicator, established the carbanion concentration of the stock solution to be 0.12 M.

Preparation of $CpMo(NO)(CD_2CMe_3)_2$ (1-d_4). $CpMo(NO)(CD_2CMe_3)_2$ is markedly more thermally stable then its perhydro analogue. Thus, while its synthesis is similar to that described for its nondeuterated analogue, the scale of the reaction can be greatly increased with relative ease. THF (50 mL) was vacuum transferred onto $CpMo(NO)Cl_2$ (1048 mg, 4.00 mmol). The stirred orange dichloride slurry was treated dropwise with $(Me_3CCD_2)_2Mg{\cdot}X$(dioxane) (33.6 mL of a 0.12 M stock solution, 8.1 mmol $Me_3CCD_2^-$) via an addition funnel at −78 °C. The reaction temperature was then slowly raised to 0 °C, and approximately half of the solvent was removed in vacuo. An IR spectrum of the final red solution exhibited a ν_{NO} of 1609 cm^{-1}. Without warming, the reaction mixture was then taken to dryness under reduced pressure. The red residue was suspended in Et_2O (100 mL), and the mixture was filtered through alumina (2 × 5 cm) supported on a medium-porosity glass frit. The alumina column was washed with ether until the red band was completely eluted (~50 mL). The ether was removed in vacuo to leave a red powder which was dissolved in a minimum of pentane and refiltered through a column of Celite (2 × 2 cm). Cooling of the

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pentane solution at −30 °C for several days afforded red needles (526 mg, 39% yield) of the desired complex.

Anal. Calcd for $C_{15}H_{23}D_4NOMo$: C, 53.41; H, 8.07; N, 4.15. Found: C, 53.60; H, 8.00; N, 4.07. IR (THF): ν_{NO} 1609 cm^{-1}. IR (Nujol): ν_{NO} 1623 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.67 (s, 5H, C_5H_5), 1.17 (s, 18H, $C(CH_3)_3$). ^{1}H NMR spectroscopy revealed no detectable methylene proton signals, thus indicating at least 99% D incorporation at C_α. ^{2}H NMR (C_6H_6, 40 MHz): δ 4.00 (s, br, no resolvable couplings), −1.09 (s, br, no resolvable couplings).

Preparation of $[CpMo(NO)(CHCMe_3)]_2$ (2). In a typical experiment, THF (30 mL) was vacuum transferred onto a mixture of $CpMo(NO)Cl_2$ (467 mg, 1.78 mmol) and $(Me_3CCH_2)_2Mg\cdot X$(dioxane) (512 mg, 3.66 mmol $Me_3CCH_2^-$) at −78 °C. The stirred reaction mixture was warmed to −40 °C over 1 h to ensure complete conversion to $CpMo(NO)(CH_2CMe_3)_2$ (1) as judged by IR spectroscopy. The final red solution of 1 was taken almost to dryness in vacuo. The oily red residue was redissolved in CH_2Cl_2/hexanes (1:2, 50 mL), and the red reaction mixture was stirred in the dark at room temperature for 2–3 h during which time it became pale orange. Solvent was removed under reduced pressure, and the brown residue was extracted with Et_2O (2 × 50 mL). Filtration of the combined extracts through alumina (2 × 3 cm) followed by exhaustive washing with Et_2O (200 mL), concentration of the filtrate in vacuo to ~25 mL, and cooling to −30 °C induced the deposition of pale orange crystals of **2** (220 mg, 47% yield) which were collected by filtration.

Anal. Calcd for $C_{20}H_{30}N_2O_2Mo_2$: C, 45.99; H, 5.79; N, 5.36. Found: C, 45.96; H, 5.84; N, 5.34. IR (Nujol): ν_{NO}(terminal) 1595 (vs) cm^{-1}, ν_{NO}(bridging) 1315 (s) cm^{-1}. IR (CH_2Cl_2): ν_{NO}(terminal) 1594 (vs) cm^{-1}, ν_{NO}(bridging) 1328 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 12.42 (s, 1H, $CH_{terminal}$), 9.30 (s, 1H, $CH_{bridging}$), 5.20 (s, 5H, C_5H_5), 5.16 (s, 5H, C_5H_5), 1.28 (s, 9H, $C(CH_3)_3$), 1.23 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 301.12 (s, $=CH_{terminal}$), 243.05 (s, $=CH_{bridging}$), 101.64 (s, C_5H_5), 100.83 (s, C_5H_5), 34.99 (s, $C(CH_3)_3$), 32.23 (s, $C(CH_3)_3$), no resonances for $C(CH_3)_3$ were unambiguously assignable. Low-resolution mass spectrum (probe temperature 120 °C): m/z 522 (P^+).

Preparation of $CpMo(NO)(=CHCMe_3)(L)$ [L = PPh_2Me (3), PPh_3 (4), or $P(p\text{-tolyl})_3$ (5)]. All three phosphine complexes were synthesized in a similar manner. A solution of $CpMo(NO)(CH_2CMe_2)_2$ was generated from $CpMo(NO)Cl_2$ (2.00 mmol) and $(Me_3CCH_2)_2Mg\cdot X$(dioxane) (4.05 mmol $Me_3CCH_2^-$) in THF (30 mL). The solution was taken to dryness in vacuo at −20 °C, extracted with Et_2O (50 mL), and quickly filtered through alumina (2 × 4 cm) into a Schlenk tube containing the appropriate tertiary phosphine (4.0 mmol, ~4 equiv assuming 50% conversion of $CpMo(NO)Cl_2$ to $CpMo(NO)(CH_2CMe_3)_2$). The reaction mixture was then stirred at room temperature for 3 h in the dark. [Dichloromethane or hexanes were also suitable solvents for these reactions, but diethyl ether was the most convenient since the filtration of the dialkyl starting material through alumina *must* be effected using Et_2O as the solvent.] The transformations of $CpMo(NO)(CH_2CMe_3)_2$ to $CpMo(NO)(=CHCMe_3)(L)$ could be conveniently monitored by IR spectroscopy. For example, an IR spectrum of a solution of $CpMo(NO)(CH_2CMe_3)_2$ and PPh_2Me (4.0 equiv) exhibited a ν_{NO} of 1616 cm^{-1} in Et_2O. Monitoring of this solution by in situ flow-cell IR spectroscopy showed loss of the band at 1616 cm^{-1} and appearance of a new band at 1577 cm^{-1}. After 3 h only the 1577 cm^{-1} band remained, and the reaction was deemed to be complete.

After the reaction was complete, the solvent was removed in vacuo leaving a brown powder. The residue was extracted with Et_2O (**3** and **5**) or CH_2Cl_2 (**4**) and filtered through alumina (2 × 2 cm). The column of alumina was washed with the appropriate solvent until the washings were colorless. The filtrate (yellow to amber in color) was taken to dryness and washed with pentane (15 mL) to remove excess phosphine. The remaining residue was crystallized from a minimum of Et_2O. Complexes **3** and **4** were isolated as amber crystals in 57 and 42% yields, respectively, whereas complex **5** was isolated as a yellow powder in 50% yield. Isolated yields are based on $CpMo(NO)Cl_2$ as the limiting reagent.

Complex 3. Anal. Calcd for $C_{23}H_{28}NOPMo$: C, 59.87; H, 6.12; N, 3.04. Found: C, 59.80; H, 5.99; N, 2.94. IR (Nujol): ν_{NO} 1540 (vs) cm^{-1}. ^{1}H NMR (C_6D_6): δ 13.59 (d, 1H, CH, J_{PH} = 3.7 Hz), 7.41 (m, 4H, PPh_2Me), 7.01 (m, 6H, PPh_2Me), 5.26 (s, 5H, C_5H_5), 1.82 (d, 3H, $PPh_2(CH_3)$, J_{PH} = 11.2 Hz), 1.34 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 316.1 (s, $=CH$), 138.9 (d, C_{ipso}, J_{PC} = 42.4 Hz), 137.1 (d, C_{ipso}, J_{PC} = 42.1 Hz), 132.5 (d, C_{ortho}, J_{PC} = 14.1 Hz), 131.3 (d, C_{ortho}, J_{PC} = 14.0 Hz), 130.2 (s, C_{para}), 129.7 (s, C_{para}), 128.6 (d, C_{meta}, J_{PC} = 9.9 Hz), 128.4 (d, C_{meta}, J_{PC} = 9.9 Hz), 98.6 (s, C_5H_5), 52.6 (s, $C(CH_3)_3$), 31.3 (s, $C(CH_3)_3$), 17.6 (d, $PPh_2(CH_3)$, J_{PC} = 21.3 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.9 (s). Low-resolution mass spectrum (probe temperature 120 °C): m/z 393 ($P^+ - CHCMe_3$).

Complex 4. Anal. Calcd for $C_{28}H_{30}NOPMo$: C, 64.25; H, 5.78; N, 2.68. Found: C, 64.15; H, 5.74; N, 2.88. IR (Nujol): ν_{NO} 1540 (vs) cm^{-1}. ^{1}H NMR (C_6D_6): δ 13.80 (d, 1H, CH, J_{PH} = 3.6 Hz), 7.77 (m, 6H, PPh_3), 7.15 (m, 9H, PPh_3), 5.40 (s, 5H, C_5H_5), 1.39 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 319.62 (s, $=CH$), 136.29 (d, C_{ipso}, J_{PC} = 43.2 Hz), 133.70 (d, C_{ortho}, J_{PC} = 12.1 Hz), 130.17 (s, C_{para}), 128.66 (d, C_{meta}, J_{PC} = 9.8 Hz), 98.86 (s, C_5H_5), 53.34 (s, $C(CH_3)_3$), 30.87 (s, $C(CH_3)_3$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.2 (s). Low-resolution mass spectrum (probe temperature 120 °C): m/z 525 (P^+).

Complex 5. Anal. Calcd for $C_{31}H_{36}NOPMo$: C, 65.84; H, 6.42; N, 2.48. Found: C, 66.11; H, 6.61; N, 2.33. IR (Nujol): ν_{NO} 1553 (vs) cm^{-1}. ^{1}H NMR (C_6D_6): δ 13.70 (d, 1H, CH, J_{PH} = 3.6 Hz), 7.61 (m, 6H, $P(p\text{-tolyl})_3$), 6.90 (m, 6H, $P(p\text{-tolyl})_3$), 5.34 (s, 5H, C_5H_5), 1.98 (s, 9H, $p\text{-}CH_3$), 1.33 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 316.60 (d, $=CH$, J_{PC} = 13.9 Hz), 176.65 (s, C_{para}), 133.71 (d, C_{ortho}, J_{PC} = 12.3 Hz), 129.45 (d, C_{meta}, J_{PC} = 10.3 Hz), 98.85 (d, C_5H_5, J_{PC} = 7.0 Hz), 53.15 (d, $C(CH_3)_3$, J_{PC} = 6.0 Hz), 30.92 (d, $C(CH_3)_3$, J_{PC} = 5.5 Hz), 21.07 (d, $p\text{-}CH_3$, J_{PC} = 6.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.6 (s). Low-resolution mass spectrum (probe temperature 120 °C): m/z 567 (P^+), 497 ($P^+ - CHCMe_3$).

Reaction of $CpMo(NO)(CD_2CMe_3)_2$ with PPh_2Me. The conversion of $CpMo(NO)(CD_2CMe_3)_2$ (1-d_4) to $CpMo(NO)(=CDCMe_3)(PPh_2Me)$ (3-d_1) was moniored by NMR spectroscopy. $CpMo(NO)(CD_2CMe_3)$ (10 mg) and PPh_2Me (10 mg, excess) were dissolved in CD_2Cl_2 (0.6 mL) in an NMR tube and allowed to react overnight. A ^{1}H NMR spectrum of the final reaction mixture revealed $CpMo(NO)(=CDCMe_3)(PPh_2Me)$ to be the only organometallic product. Other resonances were attributable to neopentane-d_3 and residual PPh_2Me.

Preparation of $[(Me_3P)_4Mo(NO)Cl]_2$ (6). A solution of $CpMo(NO)(CH_2CMe_3)_2$ was generated from $CpMo(NO)Cl_2$ (2.00 mmol) and $(Me_3CCH_2)_2Mg\cdot X$(dioxane) (4.05 mmol $Me_3CCH_2^-$) in THF (30 mL). The volume of the red solution was reduced to 5 mL under reduced pressure, and CH_2Cl_2 (50 mL) was added. The solution was cooled to −50 °C, and PMe_3 (1 atm) was vacuum transferred onto the reaction mixture. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 5 h. The resulting orange slurry was taken to dryness in vacuo and washed with pentane (20 mL). The residue was extracted with Et_2O/THF (10:1, 4 × 50 mL), and the combined extracts were filtered through alumina (3 × 3 cm). The orange filtrate was taken to dryness, and the remaining solid was recrystallized from Et_2O. Over time the Et_2O solution darkened[19] and deposited gold flakes of **6** (204 mg, 22% yield).

Anal. Calcd for $C_{12}H_{36}NOP_4ClMo$: C, 30.95: H, 7.79; N, 3.01. Found: C, 31.22; H, 7.77; N, 3.14. IR (Nujol): ν_{NO} 1528 (vs), ν_{PC} 939 (vs) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.30 (br t, $P(CH_3)_3$, J = 2.6 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.29 (br s, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −3.03 (s).

Preparation of $CpMo(NO)(=CHCMe_3)(py)$ (7). A solution of $CpMo(NO)(CH_2CMe_3)_2$ was generated from $CpMo(NO)Cl_2$ (1.80 mmol) and $(Me_3CCH_2)_2Mg\cdot X$(dioxane) (3.62 mmol $Me_3CCH_2^-$) in THF (30 mL). The solution was taken to dryness in vacuo at −20 °C, extracted with Et_2O (40 mL), and quickly filtered

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[19] The darkening of this solution is consistent with the dimerization of CpH to $(CpH)_2$. Additionally, the crystallizing solution had the characteristic odor of dicyclopentadiene.

through alumina (2 × 2 cm) into a reaction vessel containing pyridine (1.0 mL, excess). The contents of the vessel were sealed under vacuum and were stirred overnight in the dark. The amber reaction mixture was then reduced to a brown oil in vacuo. Pentane (50 mL) was added to the oil, the resulting solution was stirred rapidly for 1 h, and the pentane was removed in vacuo. Drying under high vacuum for 4 h afforded a brown powder which was dissolved in Et_2O (20 mL) and filtered through Celite (2 × 2 cm). The filtrate was concentrated in vacuo and placed in a freezer at −30 °C to induce the deposition of crystals. Brown crystals of the pyridine adduct (230 mg, 38% yield) were isolated by cannulation after several days. When crushed, the brown crystals became a bright yellow powder.

Anal. Calcd for $C_{15}H_{20}N_2OMo$: C, 52.95; H, 5.92; N, 8.23. Found: C, 52.56; H, 6.02; N, 8.08. IR (Nujol): ν_{NO} 1532 (vs), 1545 (sh) cm^{-1}. ^1H NMR (C_6D_6): δ 13.56 (s, 1H, C*H*), 8.28 (d, 2H, py protons, J_{HH} = 1.5 Hz), 6.62 (t, 1H, py proton, J_{HH} = 7.8 Hz), 6.20 (t, 2H, py protons, J_{HH} = 5.7 Hz), 5.52 (s, 5H, C_5H_5), 1.56 (s, 9H), $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 303.51 (s, =CH), 155.47, 136.82, 123.93 (s, py carbons), 100.10 (s, C_5H_5), 50.80 (s, $C(CH_3)_3$), 32.33 (s, $C(CH_3)_3$). Low-resolution mass spectrum (probe temperature 150 °C): *m/z* 540 [$(P - CHCMe_3)_2]^+$, 272 ($P^+ - CHCMe_3$).

Preparation of CpMo(NO)(=CHCMe$_3$)(PMe$_3$) (8) by Reaction of 7 with PMe$_3$. An NMR tube was charged with CpMo(NO)(=CHCMe$_3$)(py) (7) and C_6D_6 (0.7 mL). The tube and its contents were frozen at −196 °C, and then PMe_3 (1.1 equiv) was vacuum transferred into the tube. The reaction mixture was then warmed to room temperature. Over the course of 30 min the solution darkened to red-brown from amber. A ^1H NMR spectrum of the sample revealed that the pyridine adduct had been completely converted to the PMe_3 adduct and that 1 equiv of pyridine had been liberated. The CpMo(NO)(=CHCMe$_3$)(PMe$_3$) complex formed was not isolated.

^1H NMR (C_6D_6): δ 13.21 (d, 1H, C*H*, J_{PH} = 3.9 Hz), 5.32 (d, 5H, C_5H_5, J_{PH} = 1.2 Hz), 1.43 (s, 9H, $C(CH_3)_3$), 0.92 (d, 9H, $P(CH_3)_3$, J_{PH} = 9.0 Hz).

Attempted Preparations of CpMo(NO)(=CHCMe$_3$)(L) [L = Acetone, Acetonitrile, Thiophene, PhCCH, P(CMe$_3$)$_3$]. All five of these experiments led to the same result. Typically, a solution of CpMo(NO)(CH_2CMe_3)$_2$ was generated in THF and was then worked up into CH_2Cl_2 or Et_2O. An excess of the appropriate ligand (5–10 equiv) was then introduced into the red solution. Stirring of the mixture overnight in the dark at room temperature resulted in a brown supernatant solution over copious quantities of an intractable, brown powder. Filtration of each reaction mixture through Celite followed by attempts at crystallization provided only more brown powders which were found to consist of many products as judged by ^1H NMR spectroscopy. In some cases resonances attributable to small quantities of 2 were apparent in the NMR spectra.

Preparation of CpMo(NO)(η^2-C{NCMe$_3$}CH$_2$CMe$_3$)(CH$_2$CMe$_3$) (9). A solution of CpMo(NO)(CH_2CMe_3)$_2$ (from 1 mmol of CpMo(NO)Cl_2) in Et_2O (30 mL) was prepared in the usual manner (vide supra). This solution was cannulated into a reaction vessel containing $CNCMe_3$ (~350 μL, ~3 mmol). As the red solution encountered the isocyanide, it immediately became yellow. The yellow solution was taken to dryness in vacuo to remove excess $CNCMe_3$. The resulting yellow powder was crystallized from Et_2O in three fractions to obtain a total of 200 mg (48% yield) of complex 9 as microcrystalline yellow needles.

Anal. Calcd for $C_{20}H_{36}N_2OMo$: C, 57.68; H, 8.71; N, 6.73. Found: C, 57.89; H, 8.71; N, 6.70. IR (Nujol): ν_{NO} 1549 (vs), ν_{NC} 1680 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 5.21 (s, 5H, C_5H_5), 3.17 (d, 1H, CH_2, J_{HH} = 13.5 Hz), 2.68 (d, 1H, CH_2, J_{HH} = 12.0 Hz), 2.25 (d, 1H, CH_2, J_{HH} = 12.0 Hz), 2.20 (d, 1H, CH_2, J_{HH} = 13.5 Hz), 1.51 (s, 9H, $NC(CH_3)_3$), 1.13 (s, 9H, $C(CH_3)_3$), 1.12 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 204.86 (s, CN), 100.49 (s, C_5H_5), 61.25 (s, $NC(CH_3)_3$), 48.30 (s, CH_2), 37.86 (s, $C(CH_3)_3$), 35.20 (s, $NC(CH_3)_3$), 32.80 (s, $C(CH_3)_3$), 31.87 (s, CH_2), 30.30 (s, $C(CH_3)_3$), 30.25 (s, $C(CH_3)_3$). Low-resolution mass spectrum (probe temperature 180 °C): *m/z* 418 (P^+).

Table I. Crystallographic Data for Complexes 1–3[a]

compd	1	2[b]	3[b]
formula	$C_{15}H_{27}MoNO$	$C_{20}H_{30}Mo_2N_2O_2$	$C_{23}H_{28}MoNOP$
fw	333.32	522.35	461.39
color, habit	red, tabular	orange, prism	brown, prism
cryst size, mm	0.24 × 0.33 × 0.40	0.25 × 0.25 × 0.35	0.20 × 0.25 × 0.35
cryst syst	monoclinic	orthorhombic	monoclinic
space gp	$P2_1/n$	*Pcab*	$P2_1/n$
a, Å	5.9781(6)	17.836(2)	9.328(2)
b, Å	20.065(4)	18.265(2)	15.516(3)
c, Å	13.6355(17)	13.198(2)	15.188(2)
β, deg	95.52(1)	90	93.72(1)
V, Å^3	1628.0	4299.4(8)	2193.4(7)
Z	4	8	4
ρ_{calc}, g/cm^3	1.360	1.614	1.397
F(000)	695.75	2112	952
λ(Mo, Kα), Å	0.709 30 (Kα_1)	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	7.8	11.6	6.7
temp, K	170	294	294
trans factors	0.804–0.845	0.91–1.00	0.94–1.00
scan type	ω–2θ	ω–2θ	ω–2θ
scan range, deg in ω	1.00 + 0.35tan θ	1.15 + 0.35tan θ	1.21 + 0.35tan θ
scan rate, deg/min	0.6–5.5	32	16
data collected	±*h*,+*k*,+*l*	+*h*,+*k*,+*l*	+*h*,+*k*,±*l*
$2\theta_{max}$, deg	52	60	65
crystal decay, %	25	negligible	6.3
total no. of reflns	3172	6277	8633
no. of unique reflns	3172	6277	7926
R_{merge}			0.035
no. of reflns with $I \geq 3\sigma(I)$	2494 ($I \geq 2.5\sigma(I)$)	3406	4081
no. of variables	272	235	248
R	0.025	0.027	0.042
R_w	0.032	0.026	0.037
gof	1.45	1.35	2.10
max Δ/σ (final cycle)	0.01	0.07	0.04
residual density, e/Å^3	−0.29(7) to 0.40(7)[c]	−0.45 to 0.48	−1.08 to 1.48

[a] Function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4_{Fo}{}^2/\sigma^2(F_o{}^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for *R*, R_w, and gof are based on those reflections with $I \geq 2.5\sigma(I)$ for complex 1 and $I \geq 3\sigma(I)$ for complexes 2 and 3. For complex 1, $w = [\sigma(F_o)^2 + 0.0002F_o{}^2]^{-1}$. [b] Takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to eight rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/Lp^2$ (*S* = scan rate, *C* = scan count, *B* = normalized background count, *p* = 0.01 for 2, and 0.00 for 3). [c] 1.06 Å from Mo.

X-ray Crystallographic Analysis of CpMo(NO)(CD$_2$CMe$_3$)$_2$ (1-d_4). A crystal of 1-d_4 was mounted in a capillary tube under an argon atmosphere. Data were recorded at 170 K on an Enraf Nonius CAD4F diffractometer equipped with an in-house modified low-temperature system using graphite-monochromatized Mo K_α radiation. Unit cell dimensions were determined from 25 well-centered reflections (42° ≤ 2θ ≤ 50°). Two intensity standards were measured for every hour of exposure time and declined systematically by 25% during the course of the measurements. The data were corrected for absorption by the Gaussian integration method. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

After the non-hydrogen atoms were located and refined, all of the hydrogen atoms were located in an electron-density different map. The final full-matrix least-squares refinement of 272 parameters, using 2494 data ($I_o \geq 2.5\sigma(I_o)$), included an extinction

Table II. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for Complex 1

atom	x/a	y/b	z/c	B_{eq}[a]
Mo	0.24264(4)	0.209158(11)	0.033162(16)	1.661(9)
O	−0.0676(4)	0.22979(12)	0.18741(17)	3.52(10)
N	0.0772(4)	0.22302(12)	0.13175(18)	2.24(9)
C(1)	0.2821(6)	0.18169(17)	−0.13998(22)	2.71(12)
C(2)	0.1598(6)	0.13075(16)	−0.09705(21)	2.73(13)
C(3)	−0.0378(6)	0.15885(18)	−0.06826(22)	2.97(13)
C(4)	−0.0380(5)	0.22716(18)	−0.09232(23)	2.82(13)
C(5)	0.1589(5)	0.24071(17)	−0.13705(23)	2.72(13)
C(6)	0.4403(5)	0.12865(15)	0.09820(22)	2.17(11)
C(7)	0.3834(5)	0.07272(14)	0.16810(21)	2.30(11)
C(8)	0.6018(7)	0.03786(21)	0.2079(3)	3.98(17)
C(9)	0.2694(6)	0.09946(19)	0.25553(25)	3.24(14)
C(10)	0.2267(8)	0.02267(19)	0.1123(3)	3.91(17)
C(16)	0.4250(5)	0.30044(14)	0.0417(3)	2.42(11)
C(17)	0.3597(5)	0.37103(14)	0.07313(21)	2.32(11)
C(18)	0.5722(7)	0.41348(20)	0.0909(4)	4.70(21)
C(19)	0.2427(8)	0.36918(19)	0.1675(3)	3.81(17)
C(20)	0.2056(8)	0.40184(20)	−0.0086(3)	3.88(16)
H(1)	0.411(6)	0.1765(18)	−0.164(3)	3.9(8)
H(2)	0.210(5)	0.0885(17)	−0.0880(23)	2.8(7)
H(3)	−0.141(5)	0.1379(14)	−0.0381(22)	2.1(6)
H(4)	−0.142(5)	0.2571(18)	−0.0842(24)	3.0(7)
H(5)	0.196(5)	0.2785(16)	−0.160(3)	2.6(7)
H(61)	0.551(5)	0.1589(17)	0.1352(24)	3.0(7)
H(62)	0.515(5)	0.1094(15)	0.0491(22)	2.3(6)
H(161)	0.516(7)	0.2797(20)	0.095(3)	5.3(10)
H(162)	0.495(6)	0.3062(15)	−0.012(3)	2.8(7)
H(81)	0.569(7)	−0.0011(21)	0.254(3)	5.8(10)
H(82)	0.713(6)	0.0679(20)	0.248(3)	4.8(9)
H(83)	0.669(7)	0.0214(21)	0.160(3)	5.5(12)
H(91)	0.357(6)	0.1365(18)	0.290(3)	3.6(8)
H(92)	0.115(6)	0.1202(17)	0.2362(25)	3.3(7)
H(93)	0.257(5)	0.0684(17)	0.300(3)	3.0(7)
H(101)	0.283(7)	0.0050(20)	0.067(3)	4.4(10)
H(102)	0.080(6)	0.0444(18)	0.085(3)	3.9(8)
H(103)	0.219(6)	−0.0128(21)	0.154(3)	4.9(9)
H(181)	0.542(6)	0.4611(21)	0.099(3)	5.1(9)
H(182)	0.671(7)	0.3956(20)	0.141(3)	4.8(10)
H(183)	0.654(7)	0.4160(21)	0.025(3)	5.7(11)
H(191)	0.344(7)	0.3446(21)	0.216(3)	5.1(10)
H(192)	0.113(7)	0.3477(22)	0.161(3)	5.3(11)
H(193)	0.227(5)	0.4132(19)	0.192(3)	3.6(8)
H(201)	0.274(7)	0.4055(23)	−0.069(3)	5.9(11)
H(202)	0.068(6)	0.3796(18)	−0.017(3)	3.4(8)
H(203)	0.170(6)	0.4485(20)	0.007(3)	4.5(9)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

parameter,[20] anisotropic thermal parameters for all non-hydrogen atoms, isotropic thermal parameters for all hydrogen atoms, and coordinates for all atoms. An empirical weighting scheme based on counting statistics was applied such that $\omega(|F_o| - |F_c|)^2$ was near constant as a function of both $|F_o|$ and $\sin\theta/\lambda$. The refinement converged at $R = 0.025$.

The programs used for absorption corrections, data reduction, structure solution, refinement, and plot generation were from the *NRCVAX* crystal structure system.[21] Complex scattering factors for neutral atoms[22] were used in the calculation of structure factors. All computations were carried out on a MicroVAX-II computer. Crystallographic data are located in Table I. Fractional atomic coordinates are listed in Table II, and selected bond lengths and angles are provided in Table III. A view of the solid-state molecular structure of 1-d_4 is shown in Figure 1. Anisotropic thermal parameters, complete tables of bond lengths and bond angles (including those involving hydrogen atoms), torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

Table III. Selected Intramolecular Distances (Å) and Angles (deg) for Complex 1-d_4 at 170 K

Mo–N	1.766(3)	O–N	1.213(3)
Mo–Cp[a]	2.051	C(6)–C(7)	1.532(4)
Mo–C(6)	2.143(3)	C(16)–C(17)	111.52(11)
Mo–C(16)	2.129(3)		
N–Mo–C(6)	97.51(11)	Mo–N–O	168.5(3)
N–Mo–C(16)	98.27(11)	Mo–C(6)–C(7)	131.5(2)
C(6)–Mo–C(16)	111.52(11)	Mo–C(16)–C(17)	131.6(2)

[a] Here and elsewhere, Cp denotes the center of mass of the five carbon atoms of the Cp ring.

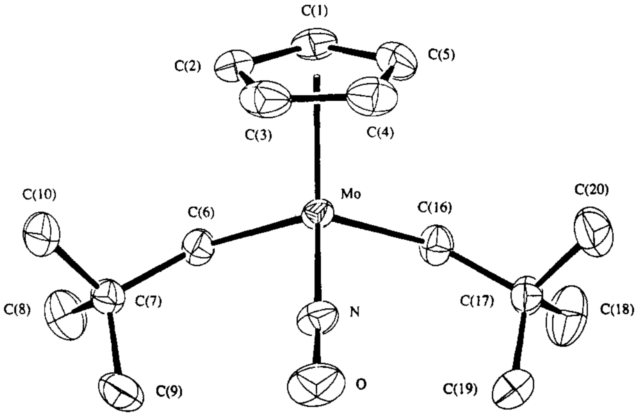

Figure 1. Molecular structure of $CpMo(NO)(CD_2CMe_3)_2$ (1-d_4) at 170 K. The hydrogen atoms have been omitted for clarity.

Table IV. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for Complex 2

atom	x	y	z	B_{eq}[a]
Mo(1)	0.17192(1)	0.04756(1)	0.13728(2)	2.66(1)
Mo(2)	0.22105(2)	0.19993(2)	0.17539(2)	3.50(1)
O(1)	0.2526(2)	0.1338(1)	0.3031(2)	5.0(1)
O(2)	0.1002(2)	0.2863(2)	0.2736(3)	7.5(2)
N(1)	0.2152(2)	0.0909(1)	0.2434(2)	3.5(1)
N(2)	0.1458(2)	0.2460(2)	0.2340(2)	4.8(2)
C(1)	0.1507(2)	−0.0438(2)	0.0080(3)	4.7(2)
C(2)	0.2082(3)	0.0013(2)	−0.0290(3)	5.3(2)
C(3)	0.2694(2)	−0.0047(2)	0.0332(4)	5.7(2)
C(4)	0.2510(3)	−0.0535(2)	0.1109(4)	5.8(2)
C(5)	0.1781(3)	−0.0781(2)	0.0943(3)	5.0(2)
C(6)	0.3146(3)	0.2869(3)	0.1927(4)	6.3(3)
C(7)	0.3525(3)	0.2245(3)	0.1685(4)	6.6(3)
C(8)	0.3323(3)	0.2038(3)	0.0718(5)	7.7(3)
C(9)	0.2822(4)	0.2552(4)	0.0356(4)	8.5(4)
C(10)	0.2715(3)	0.3068(3)	0.1111(5)	7.7(3)
C(11)	0.1533(2)	0.1500(2)	0.0554(2)	2.9(1)
C(12)	0.0789(2)	0.1795(2)	0.0151(3)	4.1(2)
C(13)	0.0156(2)	0.1836(2)	0.0910(3)	5.8(2)
C(14)	0.0531(2)	0.1285(2)	−0.0723(3)	5.6(2)
C(15)	0.0901(3)	0.2562(2)	−0.0308(4)	6.9(3)
C(16)	0.0742(2)	0.0267(2)	0.1948(2)	3.3(2)
C(17)	0.0369(2)	0.0314(2)	0.2986(3)	4.2(2)
C(18)	−0.0481(2)	0.0379(3)	0.2856(4)	7.3(3)
C(19)	0.0547(3)	−0.0410(2)	0.3534(3)	6.8(3)
C(20)	0.0651(3)	0.0943(2)	0.3630(3)	5.5(2)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_i \cdot a_j)$.

X-ray Crystallographic Analyses of Complexes 2 and 3. Data for these two complexes were recorded on a Rigaku AFC6S diffractometer. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 25.3° $\leq 2\theta \leq$ 42.2° for 2 and 28.4° $\leq 2\theta \leq$ 39.6° for 3. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for 2 and decreased uniformly by 6.3% for 3. The data were processed[23]

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[20] Larson, A. C. In *Crystallographic Computing*; Munksgaard: Copenhagen, 1970; p 291.

[21] Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* **1989**, *22*, 384.

[22] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, p 99.

[23] TEXSAN/TEXRAY structure analysis package, Molecular Structure Corporation, 1985.

Table V. Selected Intramolecular Distances (Å) and Angles (deg) for Complex 2

Mo(1)–Mo(2)	2.9607(5)	Mo(2)–O(1)	2.149(2)
Mo(1)–N(1)	1.784(3)	Mo(1)–C(16)	1.940(3)
Mo(2)–N(2)	1.763(3)	Mo(1)–C(11)	2.186(3)
N(1)–O(1)	1.296(3)	Mo(2)–C(11)	2.192(3)
N(2)–O(2)	1.216(4)	Mo(1)–Cp(1)	2.085(2)
Mo(2)–N(1)	2.187(3)	Mo(2)–Cp(2)	2.049(3)
Mo(1)–N(1)–O(1)	165.5(2)	Mo(1)–C(16)–C(17)	137.1(2)
Mo(2)–N(2)–O(2)	171.0(3)	Mo(1)–N(1)–Mo(2)	95.9(1)
Mo(2)–N(1)–O(1)	71.0(2)	Mo(1)–C(11)–C(12)	127.4(2)
Mo(1)–C(11)–Mo(2)	85.1(1)	Mo(2)–C(11)–C(12)	125.7(2)

Table VI. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2) for Complex 3

atom	x	y	z	B_{eq}[a]
Mo(1)	0.40636(3)	0.21251(2)	0.23795(2)	3.03(1)
P(1)	0.6606(1)	0.17577(6)	0.26718(5)	3.07(4)
O(1)	0.3349(3)	0.0435(2)	0.1521(2)	4.6(1)
N(1)	0.3641(3)	0.1106(2)	0.1929(2)	3.3(1)
C(1)	0.2499(4)	0.3082(3)	0.1581(3)	5.4(2)
C(2)	0.3757(5)	0.3077(2)	0.1121(2)	4.6(2)
C(3)	0.4844(4)	0.3425(2)	0.1666(3)	4.8(2)
C(4)	0.4282(5)	0.3664(3)	0.2451(3)	5.6(2)
C(5)	0.2847(6)	0.3477(3)	0.2401(3)	6.1(3)
C(6)	0.3585(4)	0.1955(2)	0.3598(2)	3.7(2)
C(7)	0.2957(4)	0.1281(2)	0.4190(2)	3.8(2)
C(8)	0.3774(5)	0.1297(3)	0.5088(3)	6.2(2)
C(9)	0.1405(5)	0.1518(3)	0.4297(3)	6.0(2)
C(10)	0.3009(5)	0.0376(3)	0.3801(3)	6.4(2)
C(11)	0.7601(3)	0.2666(2)	0.3166(2)	3.2(1)
C(12)	0.7329(4)	0.2910(3)	0.4024(2)	4.4(2)
C(13)	0.7980(5)	0.3638(3)	0.4404(3)	5.1(2)
C(14)	0.8897(4)	0.4121(2)	0.3945(3)	5.0(2)
C(15)	0.9163(4)	0.3898(2)	0.3095(3)	4.7(2)
C(16)	0.8513(4)	0.3180(2)	0.2705(2)	3.9(2)
C(17)	0.7580(3)	0.1456(2)	0.1713(2)	3.3(1)
C(18)	0.6850(4)	0.1384(2)	0.0891(2)	3.4(1)
C(19)	0.7571(4)	0.1129(2)	0.0160(2)	4.0(2)
C(20)	0.9007(4)	0.0943(3)	0.0246(3)	4.7(2)
C(21)	0.9744(4)	0.1006(3)	0.1056(3)	5.3(2)
C(22)	0.9037(4)	0.1265(3)	0.1789(2)	4.7(2)
C(23)	0.7044(4)	0.0870(2)	0.3427(2)	4.5(2)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_i \cdot a_j)$.

and corrected for Lorentz and polarization effects, linear decay (for 3), and absorption (empirical, based on azimuthal scans for three reflections for 2 and 3).

The structures were solved by heavy-atom methods, the coordinates of the molybdenum atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$, methyl group orientations based on difference map positions) with the exception of the Mo=CHR hydrogen in 3 (H(6)) which was refined with an isotropic thermal parameter. No corrections for secondary extinction were applied. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography*.[24] Crystallographic data for both complexes are located in Table I. Fractional atomic coordinates for 2 (3) are listed in Table IV (Table VI), and selected bond lengths and angles for 2 (3) are provided in Table V (Table VII). Views of the solid-state molecular structures of 2 and 3 are shown in Figures 2 and 3, respectively. Hydrogen-atom parameters, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

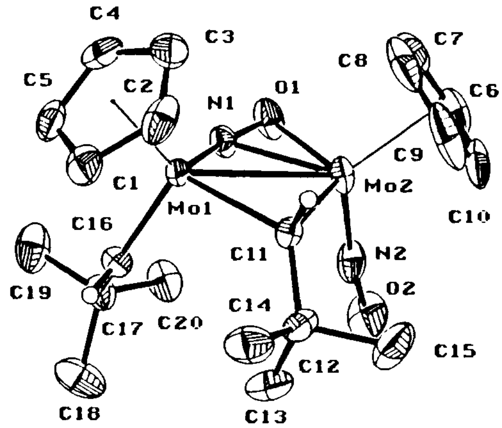

Figure 2. View of the solid-state structure of complex 2.

Table VII. Selected Intramolecular Distances (Å) and Angles (deg) for Complex 3

Mo(1)–P(1)	2.451(1)	Mo(1)–Cp	2.087
Mo(1)–N(1)	1.757(3)	O(1)–N(1)	1.233(3)
Mo(1)–C(6)	1.950(3)	C(6)–C(7)	1.521(5)
P(1)–Mo(1)–N(1)	92.94(8)	Mo(1)–N(1)–O(1)	172.7(2)
P(1)–Mo(1)–C(6)	94.3(1)	Mo(1)–C(6)–C(7)	140.8(3)
N(1)–Mo(1)–C(6)	100.8(1)	C(6)–H(6)	1.01(4)

Results and Discussion

Since the first alkylidene complex with no α-carbon-heteroatom bond, $(Me_3CCH_2)_3Ta(=CHCMe_3)$, was reported in 1974 by Schrock,[25] a plethora of complexes containing transition-metal-carbon double bonds have been prepared and studied.[26] Typically, Schrock-type alkylidene complexes are derived via alkane loss from precursors containing *cis*-dialkyl ligands.[27] In this paper, we report the thermal behavior of $CpMo(NO)(CH_2CMe_3)_2$, a thermally unstable, 16-valence electron *cis*-dialkyl complex which spontaneously decomposes to the low-valent 16-electron neopentylidene complex, $CpMo(NO)(=CHCMe_3)$.

Synthesis and Characterization of CpMo(NO)(neopentyl)$_2$ (1 and 1-d_4). $CpMo(NO)(CH_2CMe_3)_2$ and its per-α-deuterated analogue $CpMo(NO)(CD_2CMe_3)_2$ are preparable by methodology similar to that which we developed for the preparation of $Cp^*M(NO)(aryl)_2$ complexes,[10] i.e.

$$CpMo(NO)Cl_2 \xrightarrow[\text{THF},-40\ °C]{(Me_3CCX_2)Mg\cdot X(\text{dioxane})} CpMo(NO)(CX_2CMe_3)_2 \quad (1)$$
$$X = H\ (1),\ D\ (1\text{-}d_4)$$

Complex 1 must be prepared at low temperatures (yield ca. 55%) and used immediately in further derivatization reactions. On the other hand, 1-d_4 can be crystallized from pentane in about 40% yield, but must be stored at −30 °C. Both complexes are exceptionally temperature- and air-sensitive, but they are not particularly sensitive to deaerated water.[7]

The spectral properties of both complexes are consistent with their formulation as monomeric species. The ^1H NMR spectrum of 1-d_4 shows no signals attributable to methylene protons, thus implying nearly 100% deuteration

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(24) Reference 22 (Vol. IV, pp 99–102 and 149).

(25) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.

(26) For a comprehensive list of structurally characterized species of this type, see: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John-Wiley and Sons Ltd.: New York, 1988; Table 5.4.

(27) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

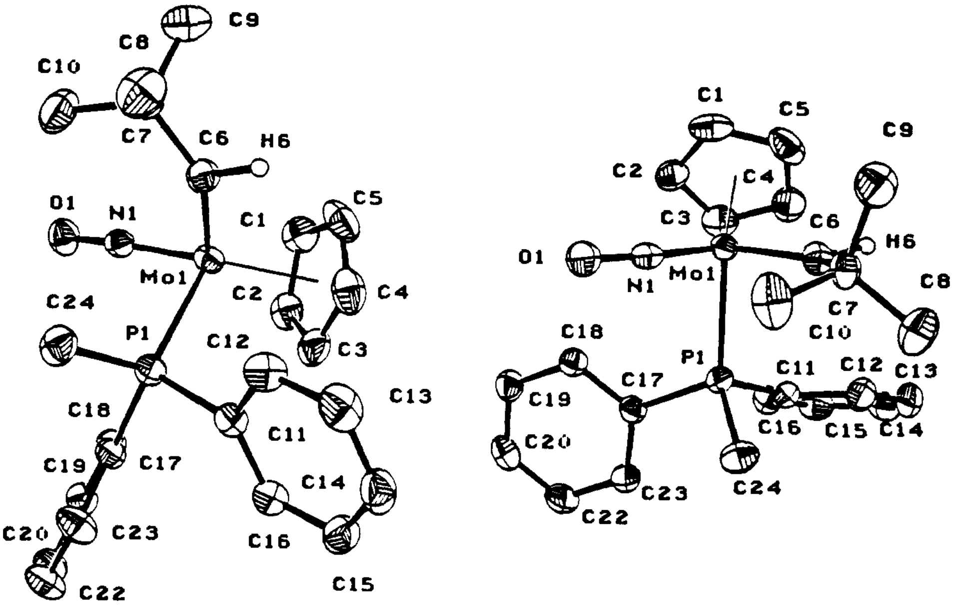

Figure 3. Views of the solid-state structure of CpMo(NO)(=CHCMe$_3$)(PPh$_2$Me) (3): (a) view perpendicular to alkylidene plane; (b) view parallel to alkylidene plane.

at C$_\alpha$. A possible explanation for this observation is that any α-protio-containing complexes decompose, and are removed, under the conditions in which 1-d_4 is handled during workup. While this seems reasonable, we are unable to attempt to quantify this "isotopomer purification". The ^{2}H NMR spectrum of 1-d_4 exhibits two broad singlets at approximately the same chemical shifts as the two doublets ($^2J_{HH}$ = 12.1 Hz) in the ^{1}H NMR spectrum of 1 attributed to the methylene protons of the complex; however, no D–D coupling constants could be extracted from the ^{2}H NMR spectrum.

Solid-State Molecular Structure of CpMo(NO)(CD$_2$CMe$_3$)$_2$. Maintaining a saturated pentane solution of 1-d_4 at −30 °C for several days results in the formation of high quality red crystals suitable for an X-ray crystallographic analysis. This analysis was performed at low temperature (170 K) since the complex, even in highly crystalline form, decomposes completely in under 12 h in the solid state at room temperature.[28] The solid-state molecular structure of the complex is shown in Figure 1. No anomalously close contacts exist either between the alkyl residues or between the metal and the CD$_2$ groups. The refined positions of the methylene deuterons do not suggest any significant agostic-type C–D–Mo interactions.[29] The intramolecular dimensions about Mo (Table III) are as expected and consistent with this species being a potent Lewis acid; most importantly, the large C(6)–Mo–C(16) angle of 111.52(11)° is characteristic of all structurally characterized Cp′M(NO)R$_2$ complexes.[1,10] While the Mo–C$_\alpha$–C$_{butyl}$ angles are somewhat obtuse (Mo–C(6)–C(7) = 131.5(2)° and Mo–C(16)–C(17) = 131.6(2)°), related H–C–C and H–C–H angles do not significantly deviate from 109°. The only intermolecular separations significantly less than the sums of the appropriate pairs of van der Waals radii are O--C(1)′ (3.148 (4) Å) and O--C(5)′ (3.083) (4) Å) where the primes indicate the operation $-1/2 + x$, $1/2 - y$, $1/2 + z$ (space group: $P2_1/n$).

Synthesis and Characterization of [CpMo(NO)(CHCMe$_3$)]$_2$. Stirring of a deep red solution of CpMo(NO)(CH$_2$CMe$_3$)$_2$ in dichloromethane (ν_{NO} 1609 cm^{-1}) at room temperature for several hours results in the color of the solution fading with time such that the final solution is pale orange (ν_{NO} 1594 (br) cm^{-1}). Removal of the solvent, followed by exhaustive extraction with Et$_2$O, affords an amber solution. Attempts to crystallize the product complex from this solution yield an impure brown powder. Additionally, the color of the solution continues to darken with time, thereby implying that chemical reactions are still occurring. Fortunately, chromatography permits the isolation of a pure product. Filtration of the above-mentioned amber solution through neutral alumina I and crystallization of the eluted complex from Et$_2$O yields pale orange crystals of 2. To date, the highest isolated yield of the complex is 47%. ^{1}H NMR spectroscopic monitoring of the thermolysis of 1 shows that the yield of 2 is quite variable (30–60%).

At first glance, complex 2 exhibits very unusual spectral properties which are not easily interpretable. For example, its IR spectrum (Nujol mull) exhibits two strong bands at 1595 and 1315 cm^{-1}, and its ^{1}H (Figure 4) and ^{13}C NMR spectra exhibit two sets of equal intensity C$_5$H$_5$, CH, and CMe$_3$ resonances, but no resonances characteristic of methylene-type protons. By elemental analysis, the empirical formula of the isolated compound is CpMo(NO)(CHCMe$_3$), but a mass-spectral parent ion having m/z 526 implies that the complex is dimeric (eq 2). Nevertheless,

$$\underset{\mathbf{1}}{2\,\mathrm{CpMo(NO)(CH_2CMe_3)_2}} \xrightarrow{\Delta} \underset{\mathbf{2}}{[\mathrm{CpMo(NO)(CHCMe_3)}]_2} \quad (2)$$

the spectroscopic properties indicate that the two halves of the dimer are inequivalent. Consequently, to resolve any ambiguity as to the molecular structure of complex

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[28] The red solid turns brown and exhibits two nitrosyl-stretching frequencies at 1597 and 1578 cm^{-1} in its Nujol mull IR spectrum. A ^{1}H NMR spectrum of the solid in C$_6$D$_6$ displays two major Cp resonances at δ 5.43 and 5.34 ppm in a 1:2 ratio as well as two CMe$_3$ peaks at δ 1.35 and 1.29 ppm in a 2:1 ratio. Numerous other smaller resonances are also observed. As more spectra are recorded signals due to numerous products appear and/or disappear. There is no evidence for the presence of complex 2 in these spectra.

[29] The shortest Mo–H$_\alpha$ separation is Mo–H(161) = 2.26 (5) Å. The other Mo–H$_\alpha$ separations are 2.42 (4), 2.58 (4), and 2.58 (4) Å.

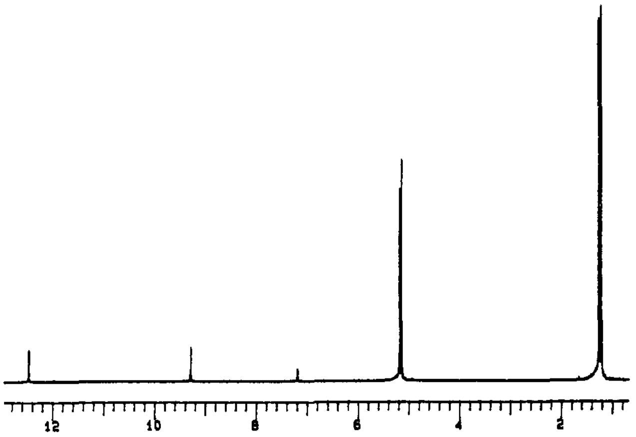
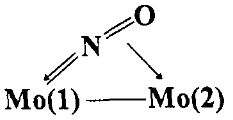


Figure 4. 300 MHz ^1H NMR spectrum of complex **2** in C_6D_6.

2, an X-ray crystallographic analysis was performed on a suitable crystal of the complex.

X-ray Crystallographic Analysis of [CpMo(NO)(CHCMe$_3$)]$_2$. A crystallographic analysis of **2** establishes that the molecular unit is indeed a dimer of CpMo(NO)(CHCMe$_3$) whose structure is unique for two significant reasons: (1) the CpMo(NO)(CHCMe$_3$) units are associated very asymmetrically through bridging nitrosyl and alkylidene groups even through there are no apparent factors prohibiting symmetric association[30] and (2) a μ-η^1:η^2-NO group has never before been observed.[31] An ORTEP diagram of the solid-state molecular structure of **2** is shown in Figure 2.

The bonding of the bridging nitrosyl group in **2** is clearly η^1 to Mo(1) and η^2 to Mo(2) and is best described in terms of the bridging NO ligand acting as a typical 3-electron donor to Mo(1) and a rather atypical 2-electron donor to Mo(2) as depicted below.



Thus, the intramolecular dimensions (Table V) of the Mo(μ-η^1:η^2-NO)Mo entity involve an elongated N–O linkage (1.296(3) Å)[32] which is essentially linear with respect to Mo(1) [Mo(1)–N(1)–O(1) = 165.5 (2)°] and is symmetrically disposed with respect to Mo(2) [Mo(2)–N(1) = 2.187(3) and Mo(2)–O(1) = 2.149(2) Å]. The Mo–Mo separation of 2.9607(5) Å in complex **2** is consistent with the existence of a single metal–metal bond which may be invoked to account for the compound's diamagnetism and to provide each metal center with an 18-valence-electron configuration.[33] The spectroscopic properties of **2** (vide supra) thus confirm that the solid-state molecular structure persists in solution. We have not observed any fluxional processes for complex **2** by NMR spectroscopy; thus, thermolysis of the complex in C_6D_6 at 80 °C leads only to slow decomposition.

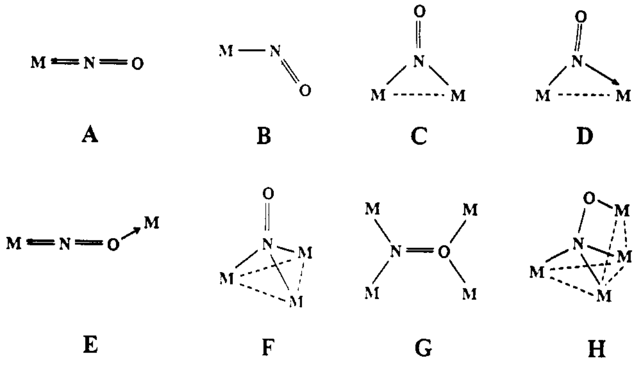


Figure 5. Known nitrosyl bonding modes (dashed lines indicate that a bonding interaction may or may not be present).

Known Nitrosyl Bonding Modes. At the inception of this work there were eight known bonding modes for coordinated nitric oxide reported in the literature (Figure 5).[31] Monomeric complexes can have linear (**A**) or bent (**B**) terminal nitrosyl ligands, although structurally characterized bent nitrosyl groups are relatively rare.[34] Three types of bridging nitrosyl ligands have been found for bimetallic complexes. Two of these are η^1 bound through nitrogen and can be symmetrically (**C**) or asymmetrically (**D**) bound to the two metal centers. On the other hand, isonitrosyl complexes (**E**) are bound through nitrogen to one metal and oxygen to another metal. Three cluster complexes fill out the eight known bonding modes of NO. These complexes contain NO ligands that are μ_3-η^1 bound (**F**) and two variants on μ_4-η^2 coordination (**G**, **H**).

Clearly, the μ-η^1:η^2-NO ligand in complex **2** constitutes the ninth type of nitrosyl ligand to be structurally characterized. It may be noted that a few examples of similar μ-η^1:η^2-CO ligands can be found in the literature.[35] A theoretical study of μ-η^1:η^2-CO bonding has been presented by Hall and Simpson.[36] Their conclusion was that such CO ligands are a consequence of steric crowding.

Trapping Reactions: Synthesis and Characterization of CpMo(NO)(=CHCMe$_3$)(L) Complexes [L = Lewis Base]. While the transformation of **1** into **2** is interesting and unusual, it also appears to be quite complex. As evidenced by NMR spectroscopic monitoring, compound **2** is the major product of several resulting from the thermolysis of **1** (conversion 2). In order to gain some chemical evidence for the transient formation of CpMo(NO)(=CHCMe$_3$) from **1**, the dialkyl complex was allowed to decompose thermally in the presence of potential trapping ligands such as phosphines. Stirring a solution of **1** in the presence of excess tertiary phosphines or pyridine, L, produces the adducts CpMo(NO)(=CHCMe$_3$)(L) [**3**, L = PPh$_2$Me; **4**, L = PPh$_3$; **5**, L = P(p-tolyl)$_3$; **7**, L = py] in moderate yields in a matter of hours at room temperature (eq 3). The moderate yields of the phosphine adducts (~50% based on CpMo(NO)Cl$_2$)

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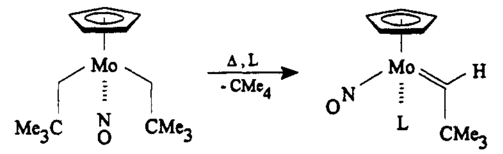
(30) Examples of complexes being associated symmetrically via two bridging alkylidene ligands,[30a] two conventionally bridging nitrosyl ligands,[30b] or multiple metal–metal bonds[30c] are well known. For instance, see: (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (b) Calderón, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W.; Iske, S. D. *J. Organomet. Chem.* **1974**, *64*, C10 and C16. (c) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610 and references cited therein.

(31) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyl*; Oxford University Press: New York, 1992; Chapter 2 and references cited therein.

(32) For comparison, other long N–O bonds are as follows: (a) 1.247(5) Å for the μ_3-NO of $Cp_3Mn_3(NO)_4$ (Elder, R. C. *Inorg. Chem.* **1974**, *13*, 1037); (b) 1.271(7) Å for the μ_4-η^2-NO of a mixed Co/Mo cluster (Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Mountzouris, J. A.; Davis, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 905); and (c) 1.47 (1) Å for CpRe(PPh$_3$)(SiMe$_2$Cl)(NOBCl$_3$) (Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 2885).

(33) Other long Mo–Mo single bonds have been reported: (a) 3.056 (1) Å for [CpMo(CO)$_2$]$_2$ (μ-NCNMe$_2$) (Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807) and (b) 3.117 (1) Å for [CpMo(CO)$_2$]$_2$ (μ-allene) (Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 802).



(3)

are more a function of the $CpMo(NO)Cl_2$ to $CpMo(NO)(CH_2CMe_3)_2$ step (~55% yield) rather than the trapping step, the quantitative nature of which can be demonstrated by NMR spectroscopy. For example, an NMR-tube experiment in CD_2Cl_2 of the reaction of **1**-d_4 with an excess of PPh_2Me affords $CpMo(NO)({=}CDCMe_3)(PPh_2Me)$ (**3**-d_1) as the sole organometallic product. Furthermore, since the nitrosyl-stretching frequencies (in Et_2O) of the starting material (1616 cm^{-1}) and product (1577 cm^{-1}) are so different, the progress of this trapping reaction can also be easily monitored by IR spectroscopy. An isosbestic point occurs at 1602 cm^{-1} and implies that the lifetime of the undetectable transient alkylidene intermediate is brief.[37]

The alkylidene adduct complexes formed during reaction 3 are generally thermally stable, 18-valence-electron species that can be handled as solids in air for short periods of time. They are markedly less soluble in common organic solvents than is their dialkyl precursor (**1**). So, while **1** is soluble in pentane, the adducts **3**, **4**, **5**, and **7** are only moderately soluble in Et_2O, but considerably more so in benzene or CH_2Cl_2. The $CpMo(NO)({=}CHCMe_3)(L)$ complexes exhibit classic neopentylidene resonances in their NMR spectra.[38] For example, compound **4** exhibits a very low-field doublet (δ 13.80 ppm, $^3J_{PH}$ = 3.6 Hz) in its ^1H NMR spectrum assignable to the alkylidene proton of the complex. Interestingly, the cyclopentadienyl, $C(CH_3)_3$, and $C(CH_3)_3$ carbons of complex **5** all show coupling (5–7 Hz) to the ^{31}P nucleus of the molecule. As expected, all three alkylidene phosphine complexes exhibit singlets (δ 36–57 ppm) in their $^{31}P\{^1H\}$ NMR spectra in C_6D_6. The ^1H NMR spectrum of the pyridine adduct (**7**) shows only three sets of clearly resolved resonances for the pyridine ring protons, thereby implying that the pyridine ring rotates quickly about the Mo–N axis on the NMR time scale at 25 °C.

Not only are the 18-electron adduct complexes (**3**–**5**, **7**) formally Mo(II) species and thus rare examples of low-valent alkylidene complexes,[39] they are the first Group 6 mononitrosyl Schrock-type alkylidene compounds to have been isolated.[40] A few related Fischer-type carbene complexes are known. These are (i) the diphenyl[41] carbene complex, $CpCr(NO)(CO)({=}CPh_2)$,[42] (ii) $CpM(NO)(CO)({=}C(OMe)(Ph))$ [M = Cr, Mo, W],[43] (iii) $CpMo(NO)(CO)({=}CN(R)(CH_2)_nNR)$ [R = Me, *p*-tolyl (*n* = 2); R = Me (*n* = 3)],[44] and (iv) $[(RNC)_4Mo(NO)({=}C(NHR)(NHR'))]I$ [R, R′ = Me, Et, *i*-Pr, CMe_3].[45] All of these carbene complexes originate from carbonyl nitrosyl precursors.

X-ray Crystallographic Analysis of $CpMo(NO)({=}CHCMe_3)(PPh_2Me)$ (3). The solid-state molecular structure of $CpMo(NO)({=}CHCMe_3)(PPh_2Me)$ (Figure 3) additionally confirms the monomeric nature of this and related neopentylidene nitrosyl complexes prepared in this work. As established by X-ray diffraction, the intramolecular dimensions of **3** (Table VII) resemble those exhibited by the related $[CpRe(NO)({=}CHPh)(PPh_3)]^+$ cation.[46] Typically, high-valent alkylidene complexes exhibit M–C_α\{H\}–C bond angle distortions, and complex **3** is no exception.[47] However, the distortion from idealized sp^2 geometry for complex **3** is not severe. In general, an M=C_α–C bond angle of 150° implies a significant M=C–H agostic interaction.[27,48] $CpMo(NO)({=}CHCMe_3)(PPh_2Me)$, formally a Mo(II) species, exhibits a smaller angle at C_α of 140.8(3) Å. In addition, M=C_α bond lengths vary from 1.83 to 2.14 Å, with the shorter bond lengths being found in increasingly electron-deficient complexes. Structurally characterized Mo alkylidene complexes show very little variance of Mo=C_α bond length even though many "oxidation states" have been characterized.[49] The Mo=C_α bond length of 1.950(3) Å in **3** is in the middle of the known range (1.917–1.989 Å).[50] Finally, it may be noted that in **3** the plane defined by the alkylidene group [Mo(1)/C(6)/C(7)/H(6)][51] forms a dihedral angle of 16.5° with one of the phenyl rings of the PPh_2Me ligand and is virtually coplanar with the nitrosyl ligand, since the torsion angle N(1)–Mo(1)–C(6)–C(7) is only 3.5(4)°. Similar torsion angles in $[CpRe(NO)({=}CHPh)(PPh_3)]PF_6$[46] and $CpCr(NO)({=}CPh_2)$[42] are 4.0 ± 0.7° and 2.0°, respectively.

Attempted Preparation of $CpMo(NO)({=}CHCMe_3)(PMe_3)$. When a dichloromethane solution of **1** is treated with PMe_3, the expected $CoMo(NO)({=}CHCMe_3)(PMe_3)$ complex is not obtained. Instead, $[(Me_3P)_4Mo(NO)Cl]_2$ (**6**) is the only isolable product. Evidently the Cp ligand can be removed from the coordination sphere of **1** by the potent base PMe_3, whereas weaker and bulkier nucleophiles cannot access the Mo center until the thermally induced loss of neopentane has occurred. The chloride ligand in the ultimate product must arise from the solvent. The dimeric nature of $[(Me_3P)_4Mo(NO)Cl]_2$ has been established by a partial X-ray crystallographic analysis of the complex, but the structure could not be refined due to severe disorder among the ligands. ^1H, ^{13}C, and ^{31}P NMR spectra of complex **7** exhibit only broad singlets at room temperature, thereby implying that fast

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(34) Reference 31, p 64.

(35) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219 and references cited therein. (b) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.

(36) Simpson, C. Q.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 1641.

(37) Ebsworth, E. A. V.; Rankin, D. W. H.; Cradock, S. *Structural Methods in Inorganic Chemistry*; Blackwell Scientific, Oxford, U.K., 1987; p 276.

(38) Reference 26, Chapter 4.

(39) Typically, Schrock-type alkylidene complexes of the Group 6 metals are formally in M (IV) or M (VI) oxidation states.

(40) Dinitrosyl alkylidene complexes, $(AlCl_2)_2(\mu\text{-}OR)_2Mo(NO)_2({=}CHMe)$ [R = Me, Et, *i*-Pr], have been cursorily characterized; see: Keller, A. *J. Organomet. Chem.* **1991**, *407*, 237.

(41) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 126. It is stated here that CPh_2 groups are electrophilic and thus best considered as Fischer carbenes.

(42) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978.

(43) Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407.

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(49) For the purposes of this comparison formal oxidation state is determined by assuming alkylidene ligands to be CHR^{2-} groups and not neutral dative donor ligands.

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(51) Mean deviation from this plane is 0.0508 Å.

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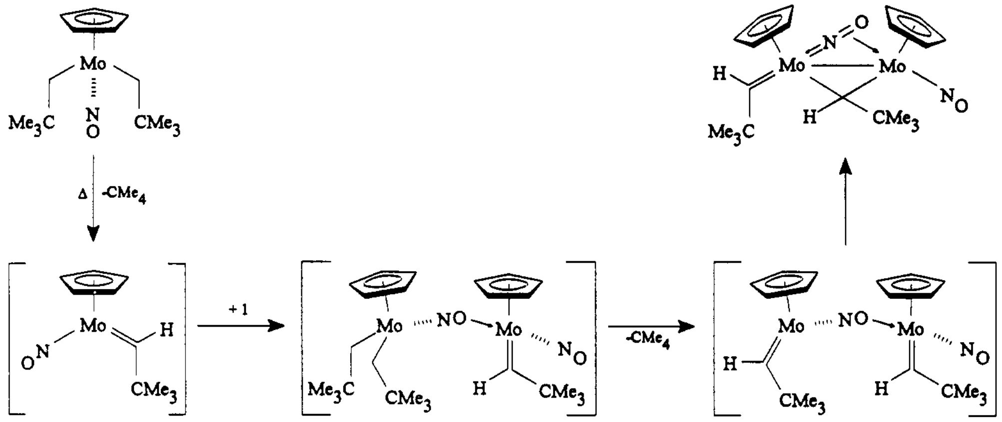
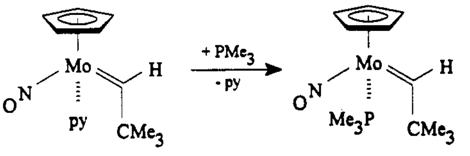
Scheme I



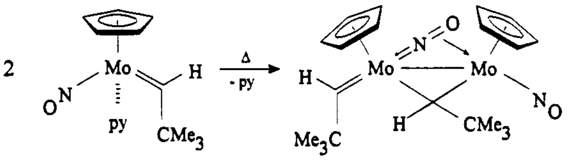
chemical exchange of the PMe$_3$ ligands occurs in solution. The low ν_{NO} value of complex **6** as a Nujol mull (1528 cm^{-1}) is reflective of the very electron-rich metal center in this complex. The related iodide complexes, [(Me$_3$P)$_4$M(NO)I]$_x$ [M = Mo, W; x is unknown], can be prepared by treating CpM(NO)I$_2$ with excess PMe$_3$.[52] The related complexes [(dppe)$_2$Mo(NO)Cl]$_x$ and [(Ph$_2$HP)$_4$Mo(NO)Cl]$_x$ have also been prepared.[53]

Preparation of CpMo(NO)(=CHCMe$_3$)(PMe$_3$). While the reaction of CpMo(NO)(CH$_2$CMe$_3$)$_2$ with PMe$_3$ does not afford the PMe$_3$ adduct of CpMo(NO)(=CHCMe$_3$), the complex can be prepared by a different route. Treatment of the pyridine complex (**7**) with 1 equiv of PMe$_3$ in benzene cleanly forms the desired PMe$_3$ complex at ambient conditions (eq 4). CpMo(NO)(=CHCMe$_3$)(PMe$_3$) (**8**) exhibits spectroscopic properties similar to complexes **3**–**5**. Most notably the ^{1}H NMR (C$_6$D$_6$) spectrum of **8** exhibits a signal attributable to the alkylidene hydrogen at δ 13.21 (d, $^3J_{PH}$ = 3.9 Hz). Interestingly, the cyclopentadienyl protons of **8** are weakly coupled to phosphorus ($^3J_{PH}$ = 1.2 Hz). The success of reaction 4 establishes that the pyridine ligand in complex **7** is very labile. We thus anticipate that we shall be able to utilize CpMo(NO)(=CHCMe$_3$)(py) as a stable (storable) source of CpMo(NO)(=CHCMe$_3$) in further reactivity studies.



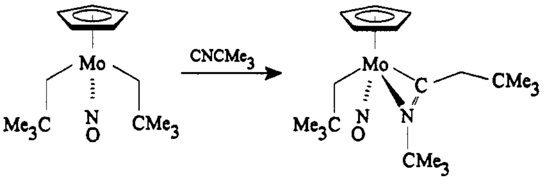
(4)

Thermal Stability of Adduct Complexes. The three isolated phosphine adducts (**3**–**5**) are thermally robust species that are unreactive with other Lewis bases. For example, thermolysis of **4** in C$_6$D$_6$ at 150 °C for 12 h in the presence of 10 equiv of acetone or PhN=C(H)Ph does not result in any reaction. In other words, oxo and imido complexes such as CpMo(NO)(=O)(L) and CpMo(NO)(=NPh)(L), isoelectronic with CpMo(NO)(=CHCMe$_3$)(L), are not synthesizable via simple alkylidene interchange reactions.[54] Thermolysis of the alkylidene phosphine complexes in C$_6$D$_6$ at 180 °C for 24 h results only in equilibration of the two possible alkylidene rotamers.[55] The pyridine adduct, **7**, however, is quite thermally sensitive due to the lability of the pyridine ligand in solution.[56] Over the course of several months at room temperature in C$_6$D$_6$ the pyridine complex decomposes to yield (~80%) the asymmetric dimer **2** (eq 5).



(5)

Attempted Preparation of CpMo(NO)(=CHCMe$_3$)(CNCMe$_3$): Synthesis of an Insertion Product. CNCMe$_3$ is exceptionally reactive toward CpMo(NO)(CH$_2$CMe$_3$)$_2$. Unlike other trapping ligands which cannot access the Mo center of this complex, *tert*-butyl isocyanide reacts instantly at room temperature to give an air-stable iminoacyl complex, CpMo(NO)(η^2-C{NCMe$_3$}CH$_2$CMe$_3$)(CH$_2$CMe$_3$) (**9**) (eq 6). CpMo(NO)(CH$_2$CMe$_3$)$_2$ is a potent 16-electron Lewis acid (ν_{NO} 1623 cm^{-1}), and insertion of CNCMe$_3$ into one of the Mo-neopentyl bonds causes a dramatic drop in ν_{NO} by 74 cm^{-1} to that observed for **9** (ν_{NO} 1549 cm^{-1}). The η^2 nature of the iminoacyl group is best established by a ν_{CN} band at 1680 cm^{-1} in the IR spectrum of the product. This low-energy stretch is typical of other η^2-iminoacyl ligands.[57]



(6)

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[53] Both of these complexes exhibit ν_{NO} bands at 1542 cm^{-1} in their respective Nujol mull IR spectra. No attempts to characterize these complexes by X-ray crystallography were made; see: King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* 1977, 429.

[54] Such Wittig-type metathesis reactions have been demonstrated; see ref 26 (section 3.2.6). For the reaction of an alkylidene complex with acetone, see: Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. For the reaction of an alkylidene complex with *N*-benzylideneaniline, see: Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.

[55] This interconversion, while not studied in any detail, is very clean spectroscopically. Additionally, a sample of an adduct complex can be thermolyzed to a mixture of rotational isomers and then recrystallized at low temperature to yield only the kinetic isomer. The ^{1}H NMR spectra of the second isomers are very similar to that of their kinetic isomers. For example, the minor isomer of complex **4** exhibits the following ^{1}H NMR spectral shifts in C$_6$D$_6$, which are nearly identical to those shifts reported for the major isomer: δ 14.88 (d, 1H, C*H*, J_{PH} = 3.9 Hz), 7.8 (m, 6H, PPh$_3$), 7.2 (m, 9H, PPh$_3$), 5.60 (s, 5H, C$_5$*H*$_5$), 1.03 (s, 9H, C(C*H*$_3$)$_3$).

The ^1H NMR spectrum of complex **9** displays four distinct resonances due to the four diastereotopic methylene protons of the complex. Signals due to the three inequivalent tertiary butyl groups are also apparent at δ 1.51, 1.13, and 1.12 ppm.

Since $CNCMe_3$ can access the Mo atom in $CpMo(NO)(CH_2CMe_3)_2$, no attempts to trap $CpMo(NO)(=CHCMe_3)$ with smaller Lewis bases such as CO or H_2 were essayed since it was obvious that they would preferentially react with the starting material. Previous studies have also shown that CO[4,5] and H_2[2,3] are generally very reactive with a wide variety of $Cp'M(NO)R_2$ complexes.

Many trapping reactions are not successful. For example, acetone, acetonitrile, thiophene, PhCCH, and $P(CMe_3)_3$ are not appropriate ligands for the formation of $CpMo(NO)(=CHCMe_3)(L)$ species. Thus, when complex **1** is allowed to decompose thermally in the presence of these ligands, total decomposition of the organometallic species in the reaction mixture occurs.

Mechanistic Implications on the Formation of $[CpMo(NO)(CHCMe_3)]_2$. With substantial chemical evidence for the transient formation of $CpMo(NO)(=CHCMe_3)$ (vide supra), a kinetic investigation of the trapping reactions **3** seemed in order. Consequently, we have conducted a preliminary analysis of the reactions of $CpMo(NO)(CD_2CMe_2)_2$ with phosphines.[13] While complete details of the fully elaborated kinetic studies will be reported in a future paper, the major conclusion to emanate from this work is that **1**-d_4 decomposes via a rate-determining α-D abstraction step that is independent of the nature or concentration of added ligand. Thus, the generation of the transient alkylidene complex, $CpMo(NO)(=CDCMe_3)$, is first-order in its dialkyl precursor. This conclusion is additionally substantiated by the observation of an isosbestic point in both IR and UV–vis spectral monitoring of these thermolysis reactions.[37]

Since the formation of $CpMo(NO)(=CHCMe_3)$ is rate-determining, simple coupling of two molecules of $CpMo(NO)(=CHCMe_3)$ is not a mechanistic path to the asymmetric dimer **2**. Instead, the transient neopentylidene monomer in all likelihood forms an isonitrosyl adduct[58] with a second molecule of **1** which then eliminates neopentane and rearranges to produce **2**. Just why the dimer adopts such an asymmetric structure remains to be ascertained. A proposal for the mechanistic sequence of events from **1** to **2** is outlined in Scheme I. Finally, it is interesting that $CpMo(NO)(=CHCMe_3)(py)$ (**7**) thermally decomposes to complex **2**, albeit at a much slower rate than does complex **1**. It is likely that the mechanistic pathways to the dimer **2** from **1** and **7** are similar, but they clearly cannot be the same.

Epilogue

Interest in transition-metal alkylidene complexes continues unabated. Recent experimental studies have focused on high-valent alkylidene species and their roles in olefin metathesis processes such as ring-opening metathesis polymerization (ROMP)[59] and ring-closing metathesis.[60] Continuing studies in our laboratories are focusing attention on the characteristic chemistry of $CpMo(NO)(=CHCMe_3)(py)$ (**7**) especially in regard to its reactivity with various organic substrates in connection with the above-mentioned metathesis chemistry.[61] It will be interesting to determine whether this low-valent molybdenum (II) alkylidene complex will mirror known reactivity or display previously unobserved chemical transformations.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes for complexes **1**-d_4, **2** and **3** (37 pages). Ordering information is given on any current masthead page.

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[56] In the solid state, complex **6** appears to be indefinitely stable at room temperature.

[57] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

[58] $CpW(NO)(CH_2SiMe_3)_2$ has been shown to form such adducts with Lewis acids such as $AlMe_3$ and MgI_2, see reference 9.

[59] For a recent review, see: Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

[60] Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426.

[61] For reactivity of an alkylidene complex with various unsaturated organic substrates, see: Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383 and references cited therein.