Synthesis, Characterization, and Reaction Chemistry of (Pentadienyl)molybdenum Carbonyl Complexes

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The reaction of Mo(diglyme)$(CO)_3$ with K(2,4-C_7H_{11}) leads to an exchange of the two organic ligands, yielding K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$. This has been found to be a convenient precursor to other (pentadienyl)molybdenum carbonyl complexes. Thus, reactions with Hg$(CN)_2$, AgI, and I_2 lead respectively to Hg[Mo(2,4-C_7H_{11})$(CO)_3]_2$, [Mo(2,4-C_7H_{11})$(CO)_3]_2$, and Mo(2,4-C_7H_{11})I$(CO)_3$. On the other hand, reactions with CH_3I or C_2H_5I lead to a coupling reaction in which an acyl fragment, generated from a carbonyl ligand and either the CH_3 or C_2H_5 group, has coupled to both ends of the 2,4-C_7H_{11} ligand, leading to a formal trialkylation of the carbonyl group and formation of an alkoxide complex, which thereafter dimerizes. Additionally, reaction of Mo(2,4-C_7H_{11})$(CO)_3^-$ with IC_2H_4I leads to a dimetallic species in which one 2,4-C_7H_{11} ligand has lost two hydrogen atoms, yielding a Mo_2(2,4-C_7H_{11})(2,4-C_7H_9)$(CO)_5$ complex. In this compound, a Mo(2,4-C_7H_9) unit may be formulated as a molybdenabenzene fragment, which is coordinated in η^6 fashion to the other molybdenum center. Single-crystal X-ray diffraction studies have been carried out for K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$, "[Mo(2,4-C_7H_{11})$(CH_3)(CO)_3]_2$", and Mo_2(2,4-C_7H_{11})(2,4-C_7H_9)$(CO)_5$. For the first complex, crystals were found to adopt the orthorhombic space group *Pbca*, with $a = 11.121(3)$, $b = 14.943(4)$, $c = 24.958(5)$ Å; $V = 4148(2)$ Å^3 for $Z = 8$. Final discrepancy indices of $R = 0.049$ and $R_w = 0.063$ were obtained. For the second species, the space group was monoclinic, $P2_1/n$, with $a = 16.782(5)$, $b = 8.461(2)$, $c = 17.523(2)$ Å; $\beta = 110.99(2)°$; and $V = 2323(1)$ Å^3 for $Z = 4$ dimetallic units. Final discrepancy indices of $R = 0.038$ and $R_w = 0.046$ were obtained. For the molybdenabenzene complex, the space group was monoclinic, $P2_1/n$, with $a = 8.039(2)$, $b = 17.873(5)$, $c = 14.019(3)$ Å; $\beta = 98.02(2)°$; and $V = 1995(1)$ Å^3 for $Z = 4$ dimetallic units. Final discrepancy indices of $R = 0.036$ and $R_w = 0.046$ were obtained. A structural determination for Mo(2,4-C_7H_{11})(I)$(CO)_3$ was also carried out, but revealed a solid state disorder. The space group was triclinic, $P\bar{1}$, with $a = 7.620(2)$, $b = 7.928(2)$, $c = 11.347(6)$ Å; $\alpha = 93.45(3)$, $\beta = 93.55(3)$, $\gamma = 105.76(2)°$; and $V = 656.4(4)$ Å^3 for $Z = 2$.

Metal pentadienyl complexes have attracted some interest as a result of the richness of their structural and bonding modes,[1] as well as their versatility in reaction chemistry,[1] including not only synthetic and catalytic applications[2] but also metal film depositions.[3] Historically, some of the earliest examples of applications actually have involved edge-bridged pentadienyl [e.g., cyclo(hexa, hepta, ...)dienyl] ligands, especially in conjunction with carbonyl ligands, and their great utility in the field of organic synthesis has already been well established.[4] In contrast, relatively little reaction chemistry had been developed for the corresponding nonbridged pentadienylmetal carbonyl complexes.[5] It was therefore of interest to investigate the natures and reaction chemistry of such fully open pentadienyl analogues,[6] using the 2,4-C_7H_{11} ligand (C_7H_{11} = dimethylpentadienyl).

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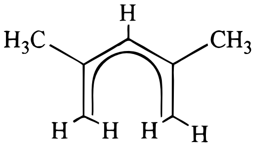

Herein are reported our results on (pentadienyl)molybdenum carbonyl chemistry, to which a convenient entry is provided via the versatile Mo(diglyme)$(CO)_3$ complex.[7] Some related species incorporating the 6,6-dimethylcyclohexadienyl (dmCh) ligand have also been reported.[8]

Experimental Section

All solvents were thoroughly dried and deoxygenated by first storing them over 4 Å molecular sieves followed by distillation over benzophonone ketyl under a nitrogen atmosphere. Deuterated NMR solvents were dried and degassed over potassium and stored in glass ampules fitted with Teflon stopcocks. Dry degassed Nujol, for infrared mulls, was stored over potassium in an inert atmosphere.

A previously published method was used for the synthesis of 2,4-dimethyl-1,3-pentadiene,[9] which was then purified by distillation and dried over magnesium sulfate or 4 Å molecular sieves. Potassium 2,4-dimethylpentadienide was synthesized as reported.[10] Diglyme was purchased commercially and stored over 4 Å molecular sieves. Prior to use, the diglyme was further dried and degassed by distillation over CaH_2 under nitrogen. All phosphines or phosphites were either purchased or synthesized by published procedures.[11]

All the synthetic procedures were performed under an atmosphere of prepurified nitrogen unless specifically stated otherwise. The syntheses were conducted on a double-manifold Schlenk line. All reactions unless otherwise mentioned were carried out in 250 mL, three-neck, round-bottom flasks equipped with a magnetic stir bar. All reactive solutions were added to the flask by a pressure-equalizing addition funnel with Teflon stopcock for dropwise addition or by microsyringe. For the reactions requiring refluxing conditions, the flask was fitted with a water-cooled reflux condenser having a nitrogen inlet. Insoluble particulates were removed from solutions by filtering through a fritted glass apparatus (coarse) with a Celite pad into a flask under a partial vacuum.

Proton NMR spectra were obtained at a frequency of 299.9450 MHz. Samples prepared in benzene-d_6 were referenced to the broad singlet at δ 7.15 resulting from C_6D_5H. Toluene-d_8 samples were referenced to the center line of the quintet at δ 2.09 due to $C_6D_5CD_2H$. Carbon-13 NMR spectra were acquired at a frequency of 75.4295 MHz. Benzene-d_6 samples were referenced to the center line of the triplet at δ 128.0, and samples prepared in toluene-d_8 were referenced to the singlet at δ 137.5. Proton-coupled ^{13}C spectra were obtained using WALTZ-16 inverse-gated proton decoupling with NOE. Proton-decoupled ^{13}C spectra were acquired using WALTZ-16 decoupling with NOE. All phosphorus-31 NMR spectra were proton-decoupled using the WALTZ-16 technique at a frequency of 121.4210 MHz with NOE. The ^{31}P NMR peaks reported are referenced relative to external 85% H_3PO_4 (aqueous).

Infrared spectra were determined using a single-scan Perkin-Elmer 298 infrared spectrophotometer. Solids were prepared as mulls in Nujol and were examined between sodium chloride plates. Solution IR spectra were obtained with matched CaF_2 solution cells using pentane or hexane as the solvent. Gaseous samples were examined by expansion of the gas into an evacuated cell. The cell was fitted with sodium chloride windows and had a path length of 11 cm and a diameter of 2.5 cm. All IR spectra were calibrated with polystyrene, and these and the mass spectral results are provided as supporting information.

Normal- and high-resolution mass spectra were obtained by using a VG Micromass 7070 double-focusing mass analyzer with VG Data System 2000 at 17 eV ionization voltage. FAB spectra were obtained using 3-nitrobenzyl alcohol as the matrix. Except for the parent ion peak, only fragments of relative intensity of at least 10% of the largest peak are reported. Analytical data were obtained from Desert Analytics in Tucson, AZ, or Analytische Laboratorien, Gummersbach/Elbach, West Germany.

Mo(diglyme)$(CO)_3$. The complex (diglyme)Mo$(CO)_3$ can be generated in high yields by modifying a previously presented procedure.[7] This can be accomplished by the addition of dry degassed diglyme (100 mL) and benzene (30 mL) to freshly sublimed Mo$(CO)_6$ (15.0 g, 56.8 mmol) in a 300 mL, three-neck, round-bottom flask. The reaction mixture is allowed to reflux while stirring for 3 days at 128 °C, forming a dark green-yellow solution. The hot solution is immediately filtered through a coarse frit and allowed to cool to ambient temperature. Precipitation of the product is subsequently instigated by the addition of hexane (~200 mL) to the solution, and the supernatant containing any unreacted Mo$(CO)_6$ is then removed by syringe. The reaction product is finally washed with 50 mL of hexane and dried in vacuo. The light yellow-green air-sensitive (diglyme)Mo$(CO)_3$ can be obtained in 90−95% yield. In this procedure, it is important not to have the temperature of the refluxing solution set too high, for this will induce thermal decomposition of the Mo$(CO)_6$. For the highest yields, the temperature should be regulated for minimal boiling conditions while stirring rapidly, such that when the stirring is stopped, the solution does not boil. ^1H NMR (benzene-d_6, ambient): δ 3.45 (m, 4H), 3.32 (m, 4H), 3.10 (s, 6H).

K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$. The complex K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$ may be obtained by the dropwise addition of potassium 2,4-dimethylpentadienide (0.50 g, 3.7 mmol) in THF (50 mL) to a stirred solution of 3.7 mmol of Mo(diglyme)$(CO)_3$ in THF (50 mL) at −78 °C. The solution is allowed to slowly warm to room temperature and stir an additional 1 h, resulting in a dark brown-yellow solution. The solvent is then removed in vacuo, and the product is extracted with two 40 mL portions of an 80% toluene/20% THF mixture, followed by filtration. The resulting solution is bright yellow, and upon total removal of the solvent, yellow platelets of the air-sensitive product are isolated in 80% yield. Single crystals (mp 106−107 °C, dec) may be obtained by slowly cooling the concentrated toluene/THF solution to −20 °C. Anal. Calcd for $C_{16}H_{25}KMoO_6$: C, 42.86; H, 5.62. Found: C, 42.58; H, 5.63. ^1H NMR (benzene-d_6, ambient): δ 5.28 (s, 1H, H-3), 3.25 (m, 8H, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$), 3.15 (s, 6H, $CH_3OCH_2CH_2OCH_2OCH_3$), 3.08 (s, 2H, H_{ex}-1,5), 2.41 (s, 6H, CH_3-2,4), 1.57 (s, 2H, H_{en}-1,5). ^{13}C NMR (benzene-d_6, ambient): δ 233.8 (s, 3C), 119.7 (s, 2C), 85.7 (d, 1C, $J = 159$ Hz), 71.1 (t, 2C, $J = 141$ Hz), 69.6 (t, 2C, $J = 142$ Hz), 59.1 (q, 2C, $J = 141$ Hz), 58.4 (t, 2C, $J = 154$ Hz), 30.7 (q, 2C, $J = 125$ Hz).

Hg[Mo(2,4-C_7H_{11})$(CO)_3]_2$. The stoichiometric reaction of $Hg(CN)_2$ (0.280 g, 1.12 mmol) with K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$ (1.00 g, 2.23 mmol) at room temperature while stirring in THF (50 mL) results in the formation of Hg[Mo(2,4-C_7H_{11})$(CO)_3]_2$. The reaction solution instantly turns red-orange upon addition of the $Hg(CN)_2$, and the reaction is complete within 10 min. The product is immediately isolated at this point because decomposition occurs with longer reaction times. Subsequent removal of the solvent followed by extraction and filtration of the product in hexane results in a fluorescent orange-yellow solution. Bright red crystals of the mercury

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complex may be isolated in 90% yield from concentrated hexane solutions at −20 °C. The solid product (mp 137−138 °C) only shows slight decomposition after 5 days of exposure to air but appears stable indefinitely under nitrogen. Anal. Calcd for $C_{20}H_{22}HgMo_2O_6$: C, 31.99; H, 2.95. Found: C, 32.21; H, 3.12. ^1H NMR (benzene-d_6, ambient): δ 5.47 (s, 2H, H-3), 2.80 (s, 4H, H_{ex}-1,5), 1.70 (s, 12H, CH_3-2,4), 0.85 (s, 4H, H_{en}-1,5). ^{13}C NMR (benzene-d_6, ambient): δ 224.8 (s, 6C), 115.3 (s, 4C), 95.4 (d, 2C, $J = 165$ Hz), 65.0 (t, 4C, $J = 158$ Hz), 29.4 (q, 4C, $J = 128$ Hz).

$Hg[Cr(2,4\text{-}C_7H_{11})(CO)_3]_2$. To a stirred slurry of 0.97 g (3.7 mmol) of $Cr(CH_3CN)_3(CO)_3$[12] in 50 mL of THF at −78° was added 0.50 g (3.7 mmol) of $K(2,4\text{-}C_7H_{11})$ dropwise in a minimum volume of THF. An immediate dark red-brown coloration was observed. Once the addition was finished, the mixture was allowed to warm slowly to room temperature, and stirred for 3 h more. At that point, 0.47 g (1.9 mmol) of $Hg(CN)_2$ was added with stirring. The mixture was allowed to stir an additional 10 min, after which the THF was removed *in vacuo*. The product was then extracted into a minimum volume of toluene, filtered, and crystallized by cooling the solution to −20°. After removal of the supernatant by syringe, the remaining solid was dried by allowing the rest of the supernatant to drain at −20°, after which a nitrogen stream was used for removal of the final traces of solvent. The product was isolated in 45% yield. Anal. Calcd for $C_{20}H_{22}HgO_6Cr_2$: C, 36.26; H, 3.35; O, 14.49; N, 0.00. Found: C, 36.61; H, 3.32; O, 13.46; N, 0.00. ^1H NMR (benzene-d_6, ambient): δ 5.53 (s, 2H, H-3), 2.56 (s, 4H, H_{ex}-1,5), 1.65 (s, 12H, CH_3-2,4), 0.48 (s, 4H, H_{en}-1,5).

$Hg[W(2,4\text{-}C_7H_{11})(CO)_3]_2$. This compound was prepared in the same manner as the corresponding chromium analogue, substituting $W(C_2H_5CN)_3(CO)_3$[13] for $Cr(CH_3CN)_3(CO)_3$, and was isolated as yellow crystals (mp 147−148 °C) from hexane. Anal. Calcd for $C_{20}H_{22}HgO_6W_2$: C, 25.92; H, 2.39. Found: C, 26.40; H, 2.44. ^1H NMR (benzene-d_6, ambient): δ 5.54 (s, 1H, H3), 2.90 (s, 2H, H_{exo}), 1.90 (s, 6H, CH_3), 0.77 (s, 2H, H_{endo}). ^{13}C NMR (benzene-d_6, ambient): δ 214.6 (CO), 112.6, 96.0, 58.9, 29.0.

$Mo(2,4\text{-}C_7H_{11})I(CO)_3$. The complex $Mo(2,4\text{-}C_7H_{11})I(CO)_3$ may be synthesized by the interaction of I_2 with $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$, according to the following procedure. Addition of I_2 (0.570 g, 2.23 mmol) to a solution of **1** (1.00 g, 2.23 mmol) in toluene or THF (50 mL) while stirring at room temperature results in a color change from yellow to orange within a few seconds. After 4 h has elapsed, the solvent is removed in vacuo and the product is extracted in hexanes. Filtration of the extractant renders a bright orange solution and subsequent concentration and cooling to −20 °C affords bright orange, air-stable, crystals. The product $Mo(2,4\text{-}C_7H_{11})I(CO)_3$ (mp 116−118 °C, dec) may be isolated in 60% yield. Anal. Calcd for $C_{10}H_{11}IMoO_3$: C, 29.88; H, 2.76. Found: C, 29.72; H, 2.84. ^1H NMR (benzene-d_6, ambient): δ 4.53 (s, 1H, H-3), 3.67 (dd, 2H, $J = 2.5$ Hz, $J = 1.3$ Hz, H_{ex}-1,5), 1.98 (d, 2H, $J = 2.5$ Hz, H_{en}-1,5), 1.28 (s, 6H, CH_3-2,4). ^{13}C NMR (benzene-d_6, ambient): δ 229.5 (s, 1C), 211.0 (s, 2C), 119.2 (s, 2C), 87.7 (d, 1C, $J = 161$ Hz), 77.8 (t, 2C, $J = 162$ Hz), 26.7 (q, 2C, $J = 129$ Hz).

$[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$. The synthesis of $[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$ may be conducted at room temperature by the reaction of AgI (0.520 g, 2.23 mmol) with $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ (1.00 g, 2.23 mmol) in THF while stirring. The AgI is added as the solid to the solution of the molybdenum salt. The reaction is complete within 4 h, turning the solution dark brown with silver metal precipitated on the bottom of the flask. Occasionally, however, the silver is not visible. After the THF has been removed under reduced pressure, the dimer may be isolated by repeated extractions with hexane. Subsequent to filtration and concentration, the brown-red solution may be easily crystallized at −20 °C. The complex (mp 135−136 °C, dec with gas evolution) is obtained in 45% yield as dark purple crystals and can be handled in air, exhibiting only slight decomposition after 1 day of exposure. Anal. Calcd for $C_{20}H_{22}Mo_2O_6$: C, 43.70; H, 4.03. Found: C, 43.71; H, 4.27.

$[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$ may also be synthesized by the 1:1 reaction of $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ with the following alkyl halides by utilizing the same procedure: carbon tetraiodide, iodoform, methylene iodide, 2-iodopropane, iodocyclohexane, trimethylsilyl iodide, 1,3-diiodopropane, and 1,4-diiodobutane. In all cases the product was isolated in yields up to 35%. ^1H NMR (benzene-d_6, ambient): δ 5.40 (s, 2H, H-3), 2.65 (s, 4H, H_{ex}-1,5), 2.12 (s, 12H, CH_3-2,4), −0.32 (d, 4H, $J = 0.9$ Hz, H_{en}-1,5). ^{13}C NMR (benzene-d_6, ambient): δ 233.0 (s, 3C), 118.1 (s, 2C), 97.0 (d, 1C, $J = 164$ Hz), 58.8 (t, 2C, $J = 158$ Hz), 27.0 (q, 2C, $J = 128$ Hz).

$[Mo(2,4\text{-}C_7H_{11})(CH_3)(CO)_3]_2$. Treatment of $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ (1.00 g, 2.23 mmol) with iodomethane (0.14 mL, 2.2 mmol) while stirring in THF (50 mL) at −78 °C leads to the formation of a dark brown solution upon warming. The reaction is allowed to proceed for 1−2 h after ambient temperature is reached. Following removal of the solvent under vacuum, the crude product is first extracted and filtered in toluene and, after removal of the toluene *in vacuo*, subsequently isolated by extraction of the pure complex in hexanes. (The complex may also be crystallized from toluene solutions; however, oils are occasionally produced which hinder the crystallization process.) The hexane solution is then filtered, concentrated, and cooled to −20 °C to generate dark brown crystals of the pentadienyl complex in an isolated yield of 48%. The complex (mp 134−135 °C, dec) is stable indefinitely under nitrogen and may be handled for short periods of time (1−2 h) in air. Anal. Calcd for $C_{22}H_{28}Mo_2O_6$: C, 45.53; H, 4.86. Found: C, 45.37; H, 5.09. ^1H NMR (benzene-d_6, ambient): δ 2.43 (s, 2H, H-3), 1.92 (s, 12H, CH_3-2,4), 1.72 (d, 4H, $J = 15.0$ Hz, H-1,5), 1.58 (d, $J = 15.0$ Hz, H-1,5), 1.19 (s, 6H, CH_3'). ^{13}C NMR (benzene-d_6, ambient): δ 250.3 (s, 4C), 93.0 (d, 2C, $J = 164$ Hz), 90.5 (s, 4C), 81.1 (s, 2C), 48.8 (t, 4C, $J = 127$ Hz), 27.2 (q, 4C, $J = 126$ Hz), 25.8 (q, 2C, $J = 126$ Hz).

$[Mo(2,4\text{-}C_7H_{11})(C_2H_5)(CO)_3]_2$. Iodoethane (1.00 g, 2.23 mmol) is added to a stirred solution of $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ to afford a coupled pentadienyl complex in 40% yield having the formula $[Mo(C_{10}H_{16}O)(CO)_2]_2$. The cooled solution is permitted to warm to ambient temperature and continued stirring for an additional 1−2 h results in a dark brown solution. The solvent is then removed under vacuum, and the product is isolated by sequential extractions and filtrations with toluene and hexanes similar to that for the methyl compound above. Crystallization may be induced by concentration of the hexane solution and cooling to −20 °C. The product is obtained as dark brown crystals (mp 134−135 °C, dec) and may be handled in air for short periods of time (1−2 h), but extended exposure leads to decomposition. Anal. Calcd for $C_{24}H_{32}Mo_2O_6$: C, 47.38; H, 5.30. Found: C, 47.66; H, 5.06. ^1H NMR (benzene-d_6, ambient): δ 2.47 (s, 2H, H-3), 1.95 (s, 12H, CH_3-2,4), 1.6−1.7 (overlapping m, 12H, CH_2's), 0.72 (t, 6H, $J = 7.5$ Hz, CH_2CH_3'). ^{13}C NMR (benzene-d_6, ambient): δ 250.0 (s, 4C), 93.0 (d, 2C, $J = 154$ Hz), 90.3 (s, 4C), 83.1 (s, 2C), 46.5 (t, 4C, $J = 127$ Hz), 32.0 (t, 2C, $J = 125$ Hz), 27.4 (q, 4C, $J = 126$ Hz), 9.8 (q, 2C, $J = 126$ Hz).

$Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$. To a solution of $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ (1.00 g, 2.23 mmol) in THF (50 mL) at ambient temperature is added 1,2-diiodoethane (0.31 g, 1.1 mmol) while stirring to generate the metallabenzene complex $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$. The clear yellow-brown solution of the potassium molybdenum salt immediately turns a cloudy orange-brown upon addition of the diiodoethane and becomes brown-black over the next few minutes with the liberation of gas. After 1 h, the THF is removed under reduced pressure and the product is extracted with multiple portions of hot hexanes and filtered. The resulting brown-red solution is concentrated to approximately 5 mL whereupon crystals begin to form. Cooling the solution to −20 °C yields dark purple crystals (mp 142−144 °C) of the metallabenzene in 30%

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[12] Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

[13] Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

yield. The complex seems only moderately air-sensitive, showing very slight decomposition after 1 week of exposure to air. Anal. Calcd for $C_{19}H_{20}Mo_2O_5$: C, 43.87; H, 3.87. Found: C, 44.38; H, 4.12. ^1H NMR (toluene-d_8, 80 °C): δ 7.66 (br s, 2H), 5.90 (t, 1H, $J = 1.4$ Hz), 4.90 (s, 1H, H-3), 2.55 (dd, 2H, $J = 3.2$ Hz, $J = 1.6$ Hz, H_{ex}-1,5), 1.89 (s, 6H, CH_3-2,4), 1.41 (s, 6H), 0.66 (dd, 2H, $J = 3.1$ Hz, $J = 0.7$ Hz, H_{en}-1,5). ^1H NMR (toluene-d_8, ambient): δ 7.56 (br s, 2H), 5.85 (t, 1H, $J = 1.5$ Hz), 4.73 (s, 1H, H-3), 2.46 (dd, 2H, $J = 3.2$ Hz, $J = 1.5$ Hz, H_{ex}-1,5), 1.85 (s, 6H, CH_3-2,4), 1.30 (br s, 6H), 0.53 (s, 2H, H_{en}-1,5). ^1H NMR (toluene-d_8, −80 °C): δ 8.31 (s, 1H), 6.91 (s, 1H), 5.74 (s, 1H), 4.11 (s, 1H, H-3), 2.31 (s, 1H, H_{ex}-1 or -5), 2.20 (s, 1H, H_{ex}-1 or -5), 1.84 (s, 3H, CH_3-2 or -4), 1.79 (s, 3H, CH_3-2 or 4), 1.47 (s, 3H), 0.61 (s, 3H), 0.28 (s, 1H, H_{en}-1 or -5), 0.16 (s, 1H, H_{en}-1 or -5). ^{13}C NMR (toluene-d_8, −80 °C): δ 228.1 (s, 1C), 226.2 (br s, 3C), 220.2 (s, 1C), 165.9 (d, 1C, $J = 141$ Hz), 154.5 (d, 1C, $J = 142$ Hz), 117.5 (s, 1C), 111.4 (s, 1C), 110.8 (s, 1C), 108.0 (s, 1C), 103.3 (d, 1C, $J = 160$ Hz), 97.0 (d, 1C, $J = 161$ Hz), 65.9 (t, 1C, $J = 156$ Hz), 55.9 (t, 1C, $J = 159$ Hz), 28.9 (q, 1C, $J = 126$ Hz), 28.4 (q, 1C, $J = 127$ Hz), 28.0 (q, 1C, $J = 127$ Hz), 25.2 (q, 1C, $J = 126$ Hz). $\Delta G^\ddagger$ (coalescence-five proton resonances): 12.6 ± 0.2 kcal/mol. IR (pentane solution): 2037 (s), 1996 (s), 1942 (m), 1928 (s), 1907 (s) cm^{-1}.

Isolation of Ethylene Gas. $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ (1.00 g, 2.23 mmol) and THF (50 mL) were added to a reaction flask, and a solid addition funnel containing 1,2-diiodoethane (0.31 g, 1.1 mmol) was attached. The reaction solution was cooled to −78 °C and connected in series to a flask in a solvent trap at −78 °C and a gas IR cell with its trap immersed in liquid nitrogen. After the entire system had been evacuated, the 1,2-diiodoethane was added to the anionic molybdenum complex. The reaction flask was then allowed to warm to room temperature and react an additional 15 min while changing from yellow-brown to brown-black in color.

During this time, ethylene had been evolved by the reaction and had solidified in the trap of the gas cell. After isolation and warming of the IR cell to ambient temperature, infrared measurements of the gas confirmed the formation of ethylene.

$Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_4P(OCH_3)_3$. The phosphite analogue of $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ may be obtained by the addition of excess $P(OCH_3)_3$ (≥0.11 mL, 0.96 mmol) to a solution of the above metallabenzene complex (0.50 g, 0.96 mmol) in hexane. The hexane solution is then heated to near its normal boiling point in a closed vessel for 5 min, during which time the solution changes from amber to red. The hexane and any excess $P(OCH_3)_3$ are then removed *in vacuo*, and the complex is redissolved in hexane and filtered to give a bright red solution. Upon concentrating and cooling the hexane solution to −20 °C, a crop of red crystals (mp 141−142 °C) is obtained in 85% yield possessing the formula $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_4P(OCH_3)_3$. The phosphite complex is reasonably air-stable for most handling procedures, but should be stored under nitrogen. Anal. Calcd for $C_{21}H_{29}Mo_2O_7P$: C, 40.93; H, 4.74. Found: C, 41.27; H, 5.00. ^1H NMR (benzene-d_6, ambient): δ 9.16 (d, 1H, $J = 26.6$ Hz), 6.87 (s, 1H), 5.98 (s, 1H), 4.54 (s, 1H, H-3), 3.38 (d, 9H, $J_{H-P} = 9.8$ Hz, $P(OCH_3)_3$), 2.71 (br s, 1H, H_{ex}-1 or -5), 2.62 (apparent t, 1H, $J_{H-P} = 2.9$ Hz, H_{ex}-1 or -5), 2.01 (s, 3H, CH_3-2 or -4), 1.86 (s, 6H, CH_3-2 or -4, CH_3'), 1.08 (s, 3H, CH_3'), 0.76 (dd, 1H, $J_{H\text{-}H} = 2.5$ Hz, $J_{H-P} = 9.7$ Hz, H_{en}-1 or -5), 0.44 (apparent t, 1H, $J_{H-P} = 4.7$ Hz, H_{en}-1 or -5). ^{13}C NMR (benzene-d_6, ambient): δ 232.5 (br, CO), 226.9 (s, CO), 182.2 (d, 1C, $J = 143$ Hz), 156.3 (d, 1C, $J = 142$ Hz), 116.5 (s, 1C), 111.0 (s, 1C), 108.8 (s, 1C), 103.8 (d, 1C, $J = 162$ Hz), 102.0 (s, 1C), 97.4 (d, 1C, $J = 160$ Hz), 62.5 (t, 1C, $J = 158$ Hz), 55.3 (t, 1C, $J = 155$ Hz), 52.9 (dq, 3C, $J = 147$ Hz, $J = 9$ Hz), 28.8 (apparent q, 1C, $J = 127$ Hz), 28.1 (apparent q, 1C, $J = 129$ Hz), 27.6 (apparent q, 1C, $J = 128$ Hz), 24.5 (apparent q, 1C, $J = 127$ Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6, ambient): δ 156.5 (s, 1P). IR (hexanes, CaF_2): 1986 (s), 1929 (ms), 1905 (ms), 1893 (ms) cm^{-1}.

$Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_4(dmpe)$. When dmpe (≥0.16 mL, 0.96 mmol) is added to $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ (0.50 g, 0.96 mmol) in hexane at room temperature and subsequently heated in a closed vessel for 5 min, a color change from amber to red results. The solvent and any excess phosphine are then removed under vacuum. The remaining red precipitate, the dmpe metallabenzene complex, is extracted and filtered in hexanes. Concentration and cooling to −20 °C generates a batch of deep red crystals (mp 93−94 °C) in 85% yield having the formula $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_4(dmpe)$. The dmpe complex is similar to the phosphite compound in atmospheric stability, being moderately air-stable; however, extended storage should be in an inert environment. Anal. Calcd for $C_{23}H_{36}Mo_2O_4P_2$: C, 44.87; H, 5.65. Found: C, 45.18; H, 5.83. ^1H NMR (benzene-d_6, ambient): δ 8.67 (d, 1H, $J = 22.4$ Hz), 6.85 (s, 1H), 5.95 (s, 1H), 4.33 (s, 1H, H-3), 2.20 (br m, 1H, H_{ex}-1 or -5), 2.15 (br m, 1H, H_{ex}-1 or -5), 2.00 (s, 3H, CH_3-2 or -4), 1.85 (s, 3H, CH_3-2 or -4), 1.82 (s, 3H, CH_3'), 1.40 (m, 4H, PCH_2CH_2P), 1.12 (d, 3H, $J_{H-P} = 1.4$ Hz, $P(CH_3)_2$), 1.06 (d, 3H, $J_{H-P} = 1.3$ Hz, $P(CH_3)_2$), 0.92 (d, 3H, $J_{H-P} = 2.7$ Hz, $P(CH_3)_2$), 0.90 (d, 3H, $J_{H-P} = 2.9$ Hz), 0.24 (dd, 1H, $J_{H-P} = 8.7$ Hz, $J_{H-P} = 1.8$ Hz, H_{en}-1 or 5), −0.12 (apparent t, 1H, $J_{H-P} = 3.3$ Hz, H_{en}-1 or -5). ^{13}C NMR (benzene-d_6, ambient): 227.3 (s, 1−4C, CO), 185.7 (d, 1C, $J = 142$ Hz), 158.1 (d, 1C, $J = 144$ Hz), 116.4 (s, 1C), 111.5 (s, 1C), 109.9 (s, 1C), 103.7 (d, 1C, $J = 160$ Hz), 100.6 (s, 1C), 97.7 (d, 1C, $J = 160$ Hz), 60.3 (t, 1C, $J = 154$ Hz), 54.5 (t, 1C, $J = 155$ Hz), 28.7 (apparent q, 1C, $J = 124$ Hz), 28.0 (apparent q, 1C, $J = 125$ Hz), 27.8 (apparent q, 1C, $J = 128$ Hz), 24.3 (apparent q, 1C, $J = 128$ Hz), 23.0 (m, 2C, PCH_2CH_2P), 16.1 (m, 1C, $P(CH_3)$, $J_{C-P} = 24$ Hz, coordinated P), 14.0 (m, 1C, $P(CH_3)$, $J_{C-P} = 21$ Hz, coordinated P), 13.7 (m, 1C, $P(CH_3)$, $J_{C-P} = 7$ Hz, uncoordinated P), 13.5 (m, 1C, $P(CH_3)$, $J_{C-P} = 7$ Hz, uncoordinated P). $^{31}P\{^1H\}$ NMR (benzene-d_6, ambient): δ 0.5 (d, 1P, $J_{P-P} = 21$ Hz, coordinated P), −46.3 (d, 1P, $J_{P-P} = 21$ Hz, uncoordinated P). IR (hexanes, CaF_2: 1986 (s), 1928 (s), 1904 (m), 1887 (ms), 1874 (m), 1814 (m) cm^{-1}.

Crystallographic Structural Determinations. All crystals were mounted under a nitrogen atmosphere in capillaries. Important crystallographic data are collected in Table 1. The crystal systems were determined photographically, and space groups were uniquely defined by systematic absences. Empirical corrections for absorption were applied to the data. The Mo atom positions were located from a Patterson map for "$Mo(2,4\text{-}C_7H_{11})(CH_3)(CO)_3$," but by direct methods for the other two structures. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions, except for $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$, for which the hydrogen atom positions were refined. All computations used SHELX-76 or SHELXDL programs (version 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

The previously reported $Mo(diglyme)(CO)_3$ complex,[7] which we have found can be prepared in ∼90−95% yield, was found to provide a convenient entry into (pentadienyl)molybdenum carbonyl complexes (eq 1), by

$$Mo(diglyme)(CO)_3 + K(2,4\text{-}C_7H_{11}) \rightarrow K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^- \quad (1)$$

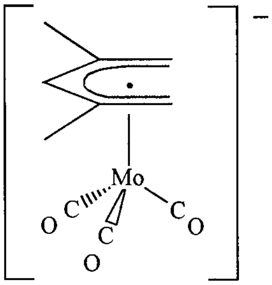
exchanging its diglyme ligand for the $2,4\text{-}C_7H_{11}$ anion. The isolated salt, $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$, is soluble in toluene, from which it may readily be isolated by crystallization at low temperatures. Characterization has been achieved analytically, through ^1H and ^{13}C NMR spectroscopies, and by an X-ray diffraction study (*vide infra*). The IR spectrum of this salt as a Nujol mull showed C−O stretching frequencies of 1893, 1802, and 1742 cm^{-1}, significantly lower than those observed for $Mo(diglyme)(CO)_3$, 1905 and 1835 cm^{-1}, and reasonably comparable to those of $K^+Mo(C_5H_5)(CO)_3^-$ (1898,

Table 1. Crystallographic Data for K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$, "Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$", and Mo_2(2,4-C_7H_{11})(2,4-C_7H_9)$(CO)_3$

	(a) Crystal Parameters		
formula	$C_{16}H_{24}KMoO_6$	$C_{22}H_{28}O_6Mo_2$	$C_{19}H_{20}O_5Mo_2$
formula weight	447.40	580.4	424.30
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$
a, Å	11.121(3)	16.782(5)	8.039(2)
b, Å	14.943(4)	8.461(2)	17.873(5)
c, Å	24.958(5)	17.523(2)	14.019(3)
β, deg		110.99(2)	98.02(2)
V, Å^3	4148(2)	2323(1)	1995(1)
Z	8	4	4
cryst color	yellow-orange	brown	black
D(calc), g cm^{-3}	1.433	1.659	1.732
μ(Mo Kα), cm^{-1}	8.6	10.9	12.5
temp, K	294	293	294
T(max)/T(min)	1.11	1.18	1.14
	(b) Data Collection		
diffractometer	Siemens P4	Nicolet Siemens P$\bar{1}$	Siemens P4
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
2θ scan range, deg	4−48	3−50	4−50
no. of rflns collected	3164	4769	3799
no. of indpt rflns	3059	4067	3513
no. of indpt obsd rflns $F_o \geq n\sigma(F_o)$	1837 (n = 4)	2942 (n = 2.5)	2827 (n = 3)
std/rfln	3/197	5/95	3/197
var in stds, %	<1	11	<1
	(c) Refinement[a]		
$R(F)$, %	4.90	3.77	3.64
$R(wF)$, %	6.34	4.57	4.59
$\Delta\sigma$(max)	0.01	0.08	0.07
$\Delta(\varrho)$, eÅ^{-3}	0.42	0.88	0.61
N_o/N_v	8.4	10.9	9.0

[a] Quantity minimized, $= \Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R(w) = \Sigma\Delta w^{1/2}/\Sigma(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

1790, and 1750 cm^{-1}) in THF or those of Mo(dmCh)-$(CO)_3^-$ (1890, 1790, and 1745 cm^{-1} as a Nujol mull, dmCh = 6,6-dimethylcyclohexadienyl).[8] Together with the NMR spectra, these data are consistent with the expected structure **1** for the anionic portion of the salt, having the three carbonyls positioned opposite to the formally charged (C[1,3,5]) positions of the pentadienyl ligand.



1

This anion has proven to be a useful starting material for the preparations of other (pentadienyl)molybdenum carbonyl complexes. Reactions with $Hg(CN)_2$, AgI, and I_2 were found to lead to the expected products, Hg[Mo-(2,4-C_7H_{11})$(CO)_3]_2$, [Mo(2,4-C_7H_{11})$(CO)_3]_2$, and Mo(2,4-C_7H_{11})(I)$(CO)_3$, respectively. The middle compound also was found to result from 1:1 reactions of **1** with CI_4, CHI_3, CH_2I_2, CH_3CHICH_3, c-$C_6H_{11}I$, $(CH_3)_3SiI$, IC_3H_6I, and IC_4H_8I. Analytical and spectroscopic data for these complexes are consistent with the respective structures **2**−**4** (Scheme 1). Thus, the C−O stretching frequencies are significantly higher than for **1** but are reasonably similar to those reported for the dmCh[8] and cyclopentadienyl analogues.[14]

The ^{1}H and ^{13}C NMR spectra for **1-4** all reveal four line patterns for the 2,4-C_7H_{11} ligands, reflecting formal mirror plane symmetry for these ligands. However, one peculiar difference is displayed by **4**.[15] While the respective chemical shifts for the H(1,5$_{exo}$) and H(1,5$_{endo}$) resonances for **1**−**3** are not unusual (3.08, 2.80, and 2.65 ppm) and (1.57, 0.85, and −0.32 ppm), the two corresponding resonances for **4** are found at 3.67 and 1.98 ppm. The latter value of 1.98 ppm is particularly unusual for H-1,5$_{endo}$ resonances (although not that much higher than that for **2**) and suggests that the H-1,5 atoms are in close proximity to the iodine atom, consistent with **4**.[15] In contrast, the H-3 resonance for **4** (4.53 ppm) is shifted significantly upfield of those for **1-3** (5.28, 5.47, and 5.40 ppm, respectively).

Notably, $Cr(CH_3CN)_3(CO)_3$ and $W(C_2H_5CN)_3(CO)_3$ also react with K(2,4-C_7H_{11}), apparently leading to the analogous M(2,4-C_7H_{11})$(CO)_3^-$ species (M = Cr, W). While these species were not isolated, their *in situ* reactions with $Hg(CN)_2$ led cleanly to the expected Hg-[M(2,4-C_7H_{11})$(CO)_3]_2$ complexes, which were readily isolated as solid compounds. Spectroscopic data were essentially identical to those of the molybdenum complex.

A partial view of the solid state structure of K(diglyme)Mo(2,4-C_7H_{11})$(CO)_3$ is presented in Figure 1, while pertinent bonding parameters are given in Tables

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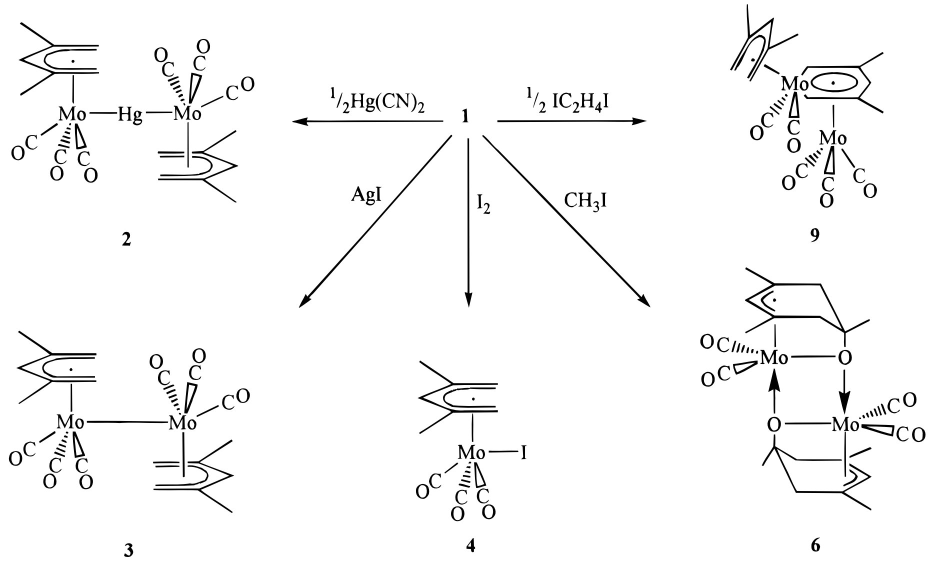
(14) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (b) Fischer, R. D.; Noack, K. *J. Organomet. Chem.* **1969**, *16*, 125. (c) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. *Inorg. Chim. Acta* **1977**, *21*, 191. (d) White, C.; Mawby, R. J. *J. Chem. Soc. A* **1971**, 940. (e) Parker, D. J. *J. Chem. Soc. A* **1970**, 480. (f) Parker, D. J.; Stiddard, M. H. B. *J. Chem. Soc. A* **1970**, 480.

(15) This assignment was confirmed by a single-crystal X-ray diffraction study for the complex. Unfortunately, the structure appeared to suffer from disorder. Pertinent details of the structure are included in the supporting information.

Scheme 1



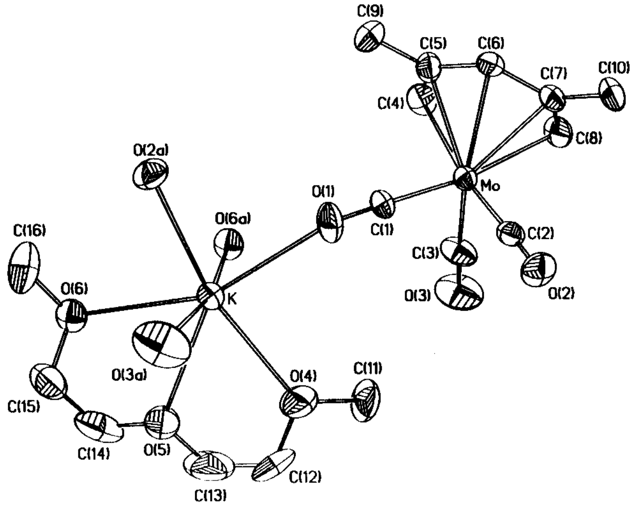


Figure 1. Perspective view and numbering scheme for K(diglyme)$^+$Mo(2,4-C$_7$H$_{11}$)(CO)$_3$$^-$.

2 and 3. It can first be observed that the potassium ions have a coordination number of 7, achieved through attachments to a first diglyme molecule [O(4), O(5), O(6)] and three isocarbonyls from two different molybdenum centers [O(1), O(2a), O(3a)], and from a single attachment to another (diglyme)K$^+$ unit [through O(6a)]. Because of these intermolecular interactions, a complex polymeric structure results in the solid state. The local coordination about the potassium ion is naturally greatly dictated by the chelating nature of the diglyme molecule and perhaps by three-dimensional packing constraints. As a result, the coordination geometry is not very regular; nevertheless, it could be described as roughly pentagonal bipyramidal, with O(3a) and O(6a) serving as the axial ligands. Overall, the K−isocarbonyl bond lengths are shortest, ranging from 2.639(11) to 2.809(8) Å, while the K−diglyme bond lengths range from 2.780(11) to 2.944(8) Å. Interestingly, the bridging oxygen donor site in the diglyme ligand [O(6)] forms a shorter interaction with the potassium ion *not* being chelated with the diglyme molecule [cf. 2.818(8) vs 2.944(8) Å].

The Mo(2,4-C$_7$H$_{11}$)(CO)$_3$$^-$ unit displays the expected piano stool geometry, as in **1**. The Mo−C[1,5], −C[2,4], −C[3],[16] and −CO bond lengths average 2.447(8), 2.365(7), 2.320(10), and 1.925(6) Å, respectively, compared to average Mo−C(C$_5$H$_5$) and Mo−CO distances of 2.371(4) and 1.909(5) Å in the Mo(C$_5$H$_5$)(CO)$_3$ anion.[17] The five skeletal dienyl carbon atoms are nearly planar, with the methyl groups tilting below the plane by an average of 0.168 Å (6.4°). As is generally observed, the unique carbonyl ligand [(C(3)] is tilted up toward the open dienyl edge by some 16° relative to the other two, the actual tilts below the molybdenum position being 41.1°, 40.9°, and 25.0°, respectively. There is a very pronounced short−long−long−short pattern of C−C bond lengths in the dienyl skeleton, attributable to a contribution of resonance form **5**, with the short and long bond lengths averaging 1.363(12) and 1.444(10) Å. The apparent significant contribution of this form may be responsible for the shortness of the Mo−C(6) bond. As is usual, the presence of a methyl group on a skeletal

Table 2. Positional Parameters for the Non-Hydrogen Atoms of K(diglyme)$^+$Mo(2,4-C$_7$H$_{11}$)(CO)$_3$$^-$

atom	*x*	*y*	*z*
Mo	0.45012(6)	0.60973(5)	0.13514(3)
K	0.3662(2)	0.8978(1)	−0.0065(1)
O(1)	0.3385(7)	0.7655(5)	0.0693(3)
O(2)	0.2786(7)	0.4905(5)	0.0672(3)
O(3)	0.6557(9)	0.5858(8)	0.0544(4)
O(4)	0.4530(11)	0.7587(7)	−0.0696(4)
O(5)	0.4491(8)	0.9309(7)	−0.1111(4)
O(6)	0.4115(7)	1.0803(5)	−0.0461(3)
C(1)	0.3826(8)	0.7072(6)	0.0951(4)
C(2)	0.3444(8)	0.5342(6)	0.0931(3)
C(3)	0.5772(10)	0.5980(9)	0.0838(4)
C(4)	0.5621(12)	0.6974(8)	0.2008(4)
C(5)	0.4436(11)	0.6923(6)	0.2161(4)
C(6)	0.3805(11)	0.6096(6)	0.2227(4)
C(7)	0.4216(11)	0.5189(7)	0.2115(4)
C(8)	0.5360(10)	0.4996(7)	0.1972(5)
C(9)	0.3713(14)	0.7753(8)	0.2225(5)
C(10)	0.3290(12)	0.4458(7)	0.2149(4)
C(11)	0.5003(14)	0.6744(8)	−0.0556(7)
C(12)	0.4710(27)	0.7729(14)	−0.1232(7)
C(13)	0.5088(23)	0.8616(15)	−0.1366(7)
C(14)	0.4768(18)	1.0176(16)	−0.1267(5)
C(15)	0.3985(19)	1.0855(11)	−0.1008(6)
C(16)	0.3314(13)	1.1421(8)	−0.0197(8)

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[16] The use of brackets designates the positions of the dienyl ligand rather than the assigned atom numbering scheme.

[17] Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920.

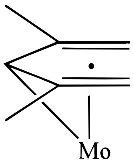
Table 3. Selected Bond Distances and Angles for K(diglyme)$^+$Mo(2,4-C_7H_{11})$(CO)_3^-$

Bond Distances, Å

Mo−C(1)	1.919(9)	K−O(4)	2.780(11)	O(1)−C(1)	1.190(11)	C(4)−C(5)	1.374(18)
Mo−C(2)	1.939(9)	K−O(5)	2.813(9)	O(2)−C(2)	1.174(11)	C(5)−C(6)	1.431(14)
Mo−C(3)	1.916(11)	K−O(6)	2.944(8)	O(3)−C(3)	1.154(16)	C(5)−C(9)	1.488(17)
Mo−C(4)	2.440(12)	K−O(2a)	2.809(8)	O(4)−C(11)	1.409(17)	C(6)−C(7)	1.457(14)
Mo−C(5)	2.369(10)	K−O(3a)	2.639(11)	O(4)−C(12)	1.370(21)	C(7)−C(8)	1.352(16)
Mo−C(6)	2.320(10)	K−O(6a)	2.818(8)	O(5)−C(13)	1.383(24)	C(7)−C(10)	1.504(16)
Mo−C(7)	2.361(9)	K(a)−O(6)	2.818(8)	O(5)−C(14)	1.388(25)	C(12)−C(13)	1.431(31)
Mo−C(8)	2.454(11)	K(b)−O(2)	2.810(8)	O(6)−C(15)	1.376(17)	C(14)−C(15)	1.485(27)
K−O(1)	2.754(8)	K(c)−O(3)	2.639(11)	O(6)−C(16)	1.441(17)		

Bond Angles, deg

Mo−C(1)−O(1)	177.7(7)	C(2)−Mo−C(7)	91.2(4)	K−O(6)−C(16)	109.5(7)	O(6)−K−O(6a)	84.2(2)
Mo−C(2)−O(2)	178.2(8)	C(2)−Mo−C(8)	100.8(4)	O(1)−K−O(4)	83.7(3)	O(2a)−K−O(3a)	75.1(3)
Mo−C(3)−O(3)	175.6(12)	C(3)−Mo−C(4)	97.0(5)	O(1)−K−O(5)	143.1(3)	O(2a)−K−O(6a)	98.1(2)
Mo−C(5)−C(4)	76.3(6)	C(3)−Mo−C(5)	129.9(5)	O(1)−K−O(6)	156.2(2)	O(3a)−K−O(6a)	168.0(3)
Mo−C(5)−C(6)	70.4(5)	C(3)−Mo−C(6)	151.3(4)	O(1)−K−O(2a)	80.8(2)	O(4)−C(12)−C(13)	114.4(16)
Mo−C(5)−C(9)	122.8(8)	C(3)−Mo−C(7)	125.9(5)	O(1)−K−O(3a)	106.2(3)	O(5)−C(13)−C(12)	116.5(19)
Mo−C(7)−C(6)	70.3(5)	C(3)−Mo−C(8)	94.2(4)	O(1)−K−O(6a)	82.0(2)	O(5)−C(14)−C(15)	112.7(14)
Mo−C(7)−C(8)	77.5(6)	C(4)−Mo−C(8)	74.8(4)	O(4)−K−O(5)	59.5(3)	O(6)−C(15)−C(14)	109.4(14)
Mo−C(7)−C(10)	123.7(7)	C(5)−Mo−C(7)	66.8(3)	O(4)−K−O(6)	116.3(3)	C(11)−O(4)−C(12)	108.9(14)
C(1)−Mo−C(2)	85.6(4)	K−O(6)−K	95.8(2)	O(4)−K−O(2a)	159.7(3)	C(13)−O(5)−C(14)	117.6(13)
C(1)−Mo−C(3)	90.6(5)	K−O(1)−C(1)	148.4(7)	O(4)−K−O(3a)	96.9(4)	C(15)−O(6)−C(16)	110.7(12)
C(1)−Mo−C(4)	98.2(4)	K(b)−O(2)−C(2)	172.4(7)	O(4)−K−O(6a)	92.6(3)	C(4)−C(5)−C(6)	123.4(10)
C(1)−Mo−C(5)	92.1(4)	K(c)−O(3)−C(3)	160.7(10)	O(5)−K−O(6)	58.0(3)	C(4)−C(5)−C(9)	120.1(10)
C(1)−Mo−C(6)	111.2(4)	K−O(4)−C(11)	131.2(9)	O(5)−K−O(2a)	135.2(3)	C(5)−C(6)−C(7)	128.8(10)
C(1)−Mo−C(8)	171.9(4)	K−O(4)−C(12)	119.3(11)	O(5)−K−O(3a)	81.6(3)	C(6)−C(5)−C(9)	116.3(11)
C(2)−Mo−C(3)	91.8(4)	K−O(5)−C(13)	116.9(9)	O(5)−K−O(6a)	97.1(2)	C(6)−C(7)−C(8)	123.0(10)
C(2)−Mo−C(4)	170.3(4)	K−O(5)−C(14)	119.8(8)	O(6)−K−O(2a)	82.0(2)	C(6)−C(7)−C(10)	116.7(10)
C(2)−Mo−C(6)	107.9(4)	K−O(6)−C(15)	111.6(8)	O(6)−K−O(3a)	85.1(3)	C(8)−C(7)−C(10)	120.2(10)



5

dienyl carbon atom leads to contraction of the delocalized C−C−C bond angle about that atom, cf. 128.8(10)° about C(6) vs an average of 123.2(7)° about C(5) and C(7).

In contrast to the above results, reactions of **1** with several organic halides proceeded along unexpected pathways. Thus, the reaction of **1** with CH_3I or C_2H_5I, which had been expected to lead to Mo(2,4-C_7H_{11})(R)$(CO)_3$ (R = CH_3, C_2H_5), led to compounds for which NMR spectroscopic data clearly indicated a more complex constitution. In the ^{1}H NMR spectrum, for example, the “H-3” resonance was observed at 2.43 ppm, too far upfield of what would be expected (*vide supra*). The “H-1,5$_{exo}$” and “H-1,5$_{endo}$” resonances were extraordinarily close together, appearing as an AB pair near 1.65 ppm. The ^{13}C NMR spectrum revealed an extra peak for a quaternary carbon center at 81.1 ppm, while the triplet resonance for the “terminal” CH_2 groups appeared at 48.8 ppm, with $J_{^{13}C-H} = 127$ Hz, clearly indicative of formal sp^3 hybridization. These data demonstrated that a coupling reaction had taken place, involving *both* terminal CH_2 groups, rather than a single end, as might have been expected based upon precedent for butadiene complexes.[18] A single-crystal X-ray diffraction study (*vide infra*) revealed that the isolated complex was dimeric (**6**, Scheme 1) and that both CH_2 groups had indeed undergone a coupling reaction, essentially a rare example of a 5 + 1 ring construction.[19]

The likely method of formation of this complex is provided in Scheme 2. The expected 18-electron product, Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$, should be in equilibrium with an acyl complex, which could have either a 16- or an 18-electron configuration, depending on whether one has η^1- or η^2-acyl coordination. Stepwise couplings of the acyl carbon atom to the two ends of the 2,4-dimethylpentadienyl ligand would follow, so that the acyl ligand then becomes an alkoxide; thus, what had been a carbonyl ligand has been trialkylated in this reaction. Simultaneously, the pentadienyl fragment has become an allyl ligand. The putative monomeric complex could have a 16-electron configuration by virtue of a π-alkoxide interaction. Conceivably, the alkoxide ligand could serve as a five-electron donor, giving an 18-electron configuration, were it possible for the C−O−Mo unit to be nearly linear. Such an arrangement is clearly not possible for the complex, requiring dimerization for the 18-electron configuration to be attained (*vide infra*).

The structure of “Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$” is provided in Figure 2, and pertinent bonding parameters are given in Tables 4 and 5. As can be seen, the molecule is indeed much more complex, having undergone a series of coupling reactions leading to a dimeric compound. The bonding patterns in each half of the dimer seem to differ slightly, which might be due to small variations in ligand orientations (Figure 2, Table 5). However, their magnitudes are such that they appear relatively insignificant. While two of each molybdenum center's carbonyl groups have been retained as such, the third has coupled to the methyl group and both ends of the 2,4-C_7H_{11} fragment, leading to a bifunctional allyl/alkoxide ligand. Interestingly, essentially the inverse conversions of alkoxide (or even methyl) ligands to carbonyls have also been observed.[20]

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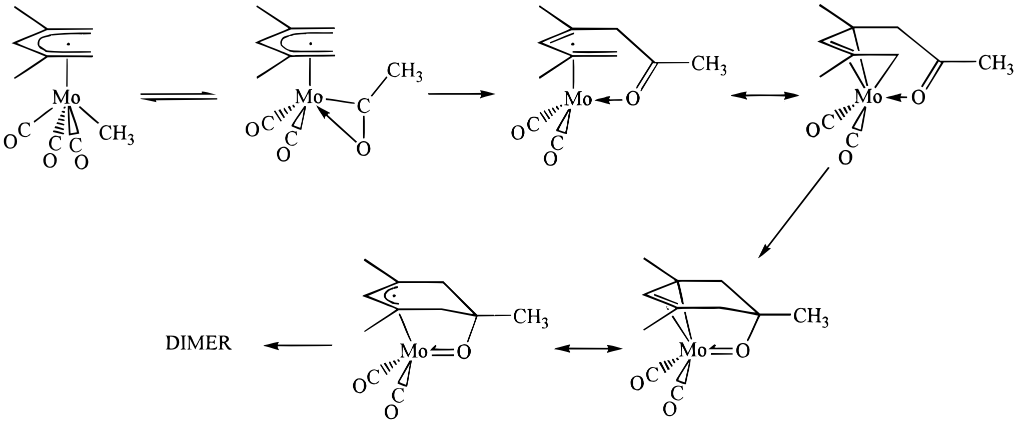
[19] (a) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5478. (b) Posner, G. H. *Chem. Rev.* **1986**, *86*, 831.

[20] (a) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (b) Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. *Inorg. Chem.* **1992**, *31*, 3699.

Scheme 2



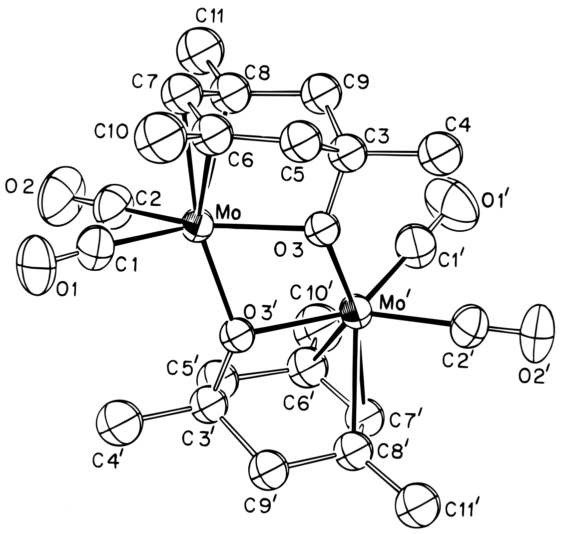
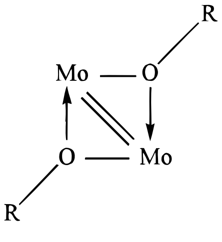
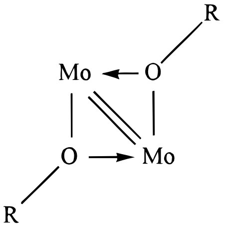


Figure 2. Perspective view and numbering scheme for "Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$" dimer.

Considering a separate monometallic half-dimer, there would be a 14 electron configuration at the metal center, counting the alkoxide group as a one electron donor. Upon dimerization, an extra two electrons can be donated through a lone pair of a bridging oxygen center, bringing the electron count to 16. One can propose two other interactions that could lead to the expected 18-electron count. First, there could be a Mo–Mo double bond, as in **7**. However, the Mo–Mo separation of 3.215(1) Å is comparable to that of 3.235(1) Å in $[Mo(C_5H_5)(CO)_3]_2$[21] but much longer than the value of 2.448(1) Å in $[Mo(C_5H_5)(CO)_2]_2$.[22] Additionally, the large Mo–O–Mo and small O–Mo–O angles [102.0(2)° vs 71.6(1)°] do not suggest any attempt to bring the molybdenum centers into closer proximity; rather, they lead to an extremely short O–O separation of 2.424(5) Å. Hence, there is no evidence of multiple bonding between the molybdenum centers. On the other hand, the three bond angles about the alkoxide oxygen atoms average 116.3°, suggesting sp^2 hybridization. Futhermore, the Mo–O bond distances are not unlike those in similar compounds for which π-bonding interactions have been invoked.[23] It therefore appears that the 18-electron configuration is reached for the molybdenum centers through π-alkoxide interactions, as in **8**. The Mo_2O_2 unit, however, is not symmetric, but alternates between short and long bond distances, suggesting a greater contribution from one form than the other. The Mo–allyl bonding is symmetric, with respective average Mo–C[1,3], Mo–C[2], and C–C bond lengths of 2.349-



7a



7b

Table 4. Positional Parameters for the Non-Hydrogen Atoms of the "Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$" Dimer

atom	*x*	*y*	*z*
Mo	0.01150(3)	0.53250(6)	0.69993(3)
O(1)	0.0905(5)	0.2333(7)	0.6558(4)
O(2)	0.1371(4)	0.6452(8)	0.6194(4)
O(3)	−0.0680(2)	0.6086(5)	0.7613(2)
C(1)	0.0592(5)	0.3460(10)	0.6705(4)
C(2)	0.0891(4)	0.6038(9)	0.6499(4)
C(3)	−0.1528(4)	0.6240(9)	0.7025(4)
C(4)	−0.2137(4)	0.6787(11)	0.7452(4)
C(5)	−0.1738(4)	0.4632(9)	0.6648(4)
C(6)	−0.1181(4)	0.4150(9)	0.6173(4)
C(7)	−0.0955(4)	0.5291(9)	0.5710(4)
C(8)	−0.0868(4)	0.6852(9)	0.5986(4)
C(9)	−0.1442(4)	0.7429(9)	0.6404(4)
C(10)	−0.1267(6)	0.2438(9)	0.5896(6)
C(11)	−0.0592(5)	0.8121(10)	0.5519(5)
Mo′	0.01596(3)	0.73339(6)	0.85716(3)
O(1)′	−0.0546(4)	1.0714(7)	0.8145(4)
O(2)′	−0.0954(4)	0.8080(7)	0.9588(4)
O(3)′	0.0844(2)	0.5619(5)	0.8202(2)
C(1)′	−0.0274(5)	0.9481(9)	0.8311(4)
C(2)′	−0.0531(5)	0.7795(8)	0.9221(4)
C(3)′	0.1744(4)	0.5769(7)	0.8717(4)
C(4)′	0.2270(5)	0.4559(8)	0.8469(5)
C(5)′	0.1979(4)	0.7465(7)	0.8630(5)
C(6)′	0.1480(4)	0.8638(8)	0.8922(4)
C(7)′	0.1325(4)	0.8300(8)	0.9625(4)
C(8)′	0.1232(4)	0.6733(8)	0.9834(4)
C(9)′	0.1718(4)	0.5473(8)	0.9572(4)
C(10)′	0.1580(5)	1.0353(8)	0.8693(6)
C(11)′	0.1037(5)	0.6327(9)	1.0587(4)

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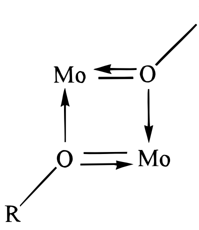
Table 5. Selected Bond Distances and Angles for the “Mo(2,4-C_7H_{11})(CH_3)$(CO)_3$” Dimer

Bond Distances, Å

Mo−Mo′	3.215(1)	O−O′	2.424	C(3)−C(4)	1.537(11)	C(3)′−C(4)′	1.514(11)
Mo−C(1)	1.922(8)	Mo′−C(1)′	1.949(7)	C(3)−C(5)	1.499(10)	C(3)′−C(5)′	1.511(9)
Mo−C(2)	1.911(8)	Mo′−C(2)′	1.932(9)	C(3)−C(9)	1.527(11)	C(3)′−C(9)′	1.533(10)
Mo−C(6)	2.358(6)	Mo′−C(6)′	2.351(7)	C(5)−C(6)	1.513(12)	C(5)′−C(9)′	1.502(11)
Mo−C(7)	2.329(6)	Mo′−C(7)′	2.305(6)	C(6)−C(7)	1.397(11)	C(6)′−C(7)′	1.376(11)
Mo−C(8)	2.333(6)	Mo′−C(8)′	2.353(5)	C(7)−C(8)	1.396(10)	C(7)′−C(8)′	1.399(9)
Mo−O(3)	2.093(4)	Mo′−O(3)	2.056(3)	C(8)−C(9)	1.486(11)	C(8)′−C(9)′	1.512(10)
Mo−O(3)′	2.037(3)	Mo′−O(3)′	2.092(4)	C(6)−C(10)	1.517(11)	C(6)′−C(10)′	1.531(10)
C(1)−O(1)	1.161(11)	C(1)′−O(1)′	1.134(9)	C(8)−C(11)	1.519(12)	C(8)′−C(11)′	1.508(11)
C(2)−O(2)	1.168(11)	C(2)′−O(2)′	1.142(11)	C(3)−O(3)	1.433(6)	C(3)′−O(3)′	1.462(6)

Bond Angles, deg

C(1)−Mo−O(3)	142.6(3)	C(1)′−Mo′−O(3)′	140.7(3)	O(3)−C(3)−C(9)	104.4(5)	O(3)′−C(3)′−C(9)′	101.8(5)
C(1)−Mo−O(3)′	102.9(2)	C(1)′−Mo′−O(3)	101.4(2)	C(4)−C(3)−C(5)	113.3(6)	C(4)′−C(3)′−C(5)′	114.4(6)
C(1)−Mo−C(2)	73.6(4)	C(1)′−Mo′−C(2)′	72.4(3)	C(4)−C(3)−C(9)	113.4(6)	C(4)′−C(3)′−C(9)′	113.2(5)
C(2)−Mo−O(3)	143.5(3)	C(2)′−Mo′−O(3)′	146.5(2)	C(5)−C(3)−C(9)	110.5(6)	C(5)′−C(3)′−C(9)′	110.7(6)
C(2)−Mo−O(3)′	100.4(2)	C(2)′−Mo′−O(3)	101.8(2)	C(3)−C(5)−C(6)	113.2(6)	C(3)′−C(5)′−C(6)′	113.3(7)
O(3)−Mo−O(3)′	71.8(2)	O(3)−Mo′−O(3)′	71.5(1)	C(5)−C(6)−C(7)	118.9(7)	C(5)′−C(6)′−C(7)′	118.3(6)
Mo−C(1)−O(1)	177.4(6)	Mo′−C(1)′−O(1)′	178.1(6)	C(5)−C(6)−C(10)	115.2(7)	C(5)′−C(6)′−C(10)′	114.2(7)
Mo−C(2)−O(2)	179.0(7)	Mo′−C(2)′−O(2)′	178.3(6)	C(7)−C(6)−C(10)	119.2(7)	C(7)′−C(6)′−C(10)′	120.4(7)
Mo−O(3)−Mo′	101.6(2)	Mo−O(3)′−Mo′	102.3(2)	C(6)−C(7)−C(8)	118.0(7)	C(6)′−C(7)′−C(8)′	120.4(6)
Mo−O(3)−C(3)	108.1(4)	Mo′−O(3)′−C(3)′	108.0(3)	C(7)−C(8)−C(9)	118.4(7)	C(7)′−C(8)′−C(9)′	117.7(7)
Mo′−O(3)−C(3)	138.9(4)	Mo−O(3)′−C(3)′	139.0(4)	C(7)−C(8)−C(11)	119.8(7)	C(7)′−C(8)′−C(11)′	121.7(6)
O(3)−C(3)−C(4)	109.9(5)	O(3)′−C(3)′−C(4)′	110.1(5)	C(9)−C(8)−C(11)	114.2(6)	C(9)′−C(8)′−C(11)′	114.5(6)
O(3)−C(3)−C(5)	104.5(5)	O(3)′−C(3)′−C(5)′	105.6(4)	C(8)−C(9)−C(3)	112.3(6)	C(8)′−C(9)′−C(3)′	112.9(5)



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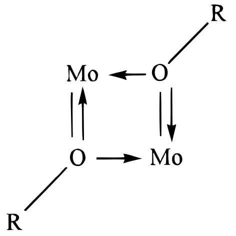

8b

(3), 2.317(4), and 1.392(5) Å. The substituents on the terminal carbon atoms show reasonable deviations from the C[1−3] planes, averaging 1.1° toward the metal center by the methyl groups and 27.7° away from the metal by the other two substituents. The Mo−CO bonding is mostly reasonable, with average Mo−C and C−O distances of 1.929(4) and 1.151(5) Å, and average Mo−C−O and C−Mo−C angles of 178.2(3)° and 73.0-(3)°, respectively. The value of the OC−Mo−CO angle appears small but is probably not too unusual compared to various Mo(C_5H_5)(X)$(CO)_3$ structures.[24]

The reaction of Mo(2,4-C_7H_{11})$(CO)_3^-$ with IC_2H_4I also took an unexpected pathway. In this case, ^1H NMR data revealed the presence of at least two organic fragments, although some expected resonances were not observed. An isopiestic molecular weight determination suggested a dimeric formulation in THF, and IR spectroscopy indicated that there were no bridging carbonyl ligands. To determine the nature of this complex, resort was made to a diffraction study (*vide infra*), which revealed the complex to have the formulation Mo_2(2,4-C_7H_{11})(2,4-C_7H_9)$(CO)_5$ (**9**, Scheme 1). It can be seen that one of the original 2,4-C_7H_{11} ligands has lost two hydrogen atoms, thus leading to a metallabenzene unit coordinated to the second molybdenum atom. The 2,4-C_7H_{11} ligand has adopted an unsymmetric orientation, resulting in an absence of any symmetry in the molecule. As a result, some broad resonances are observed in the room-temperature ^1H NMR spectrum (300 MHz), but on cooling to −50 °C, one observes the 1:1:1:1:1:1:3:3:3:3:1:1 pattern expected for such an environment, while on heating to 80 °C, rotation (or oscillation) of the 2,4-C_7H_{11} ligand occurs, leading to effective mirror plane symmetry for the molecule, and a 2:1:1:2:6:6:2 pattern. From the coalescence temperatures, the value of $\Delta G^\ddagger$ for the dienyl ligand oscillation can be determined to be 12.6 ± 0.2 kcal/mol, consistent with values observed in a variety of other metal pentadienyl complexes.[1,25]

The positioning of some of the resonances for the 2,4-C_7H_9 ligand provides further support for the formulation of the Mo(2,4-C_7H_9) unit as a metallabenzene. In particular, while H(3) resonances for pentadienyl ligands tend to be shifted furthest downfield, in this complex the spectrum at 80 °C reveals a resonance at 7.66 ppm due to the two hydrogen atoms located on the terminal carbon atoms of the 2,4-C_7H_9 group. At −80 °C, this signal has decoalesced, leading to separate peaks at 8.31 and 6.91 ppm. The significant downfield shifts for these resonances can be ascribed to π delocalization in the molybdenabenzene fragment. Such shifts are typically observed in other metallabenzene complexes.[26]

The structure of Mo_2(2,4-C_7H_{11})(2,4-C_7H_9)$(CO)_5$ may be seen in Figure 3, while important bonding parameters are given in Tables 6 and 7. The two metal centers can be seen to have distinctly different coordination environments. Ignoring the Mo(1)−Mo(2) interaction, the coordination geometry about Mo(2) is reasonably similar to those displayed by various M(Pdl)$(L)_4$ (Pdl = C_5H_7 or substituted pentadienyl ligand) complexes,[1] i.e., **10**. Thus, Mo(2) is coordinated by a 2,4-dimethylpentadienyl ligand and two carbonyl groups and also engages in bonding interactions with C(4), C(8), and Mo-(1). Should these last three interactions be considered as single bonds, one would obtain an 18-electron configuration for Mo(2). The bonding between Mo(2) and the 2,4-C_7H_{11} ligand is not unusual, with average Mo−C[1,5], −C[2,4], and −C[3] bond lengths of 2.346(4), 2.334(4), and 2.319(5) Å, respectively. The C(13)−C(17)

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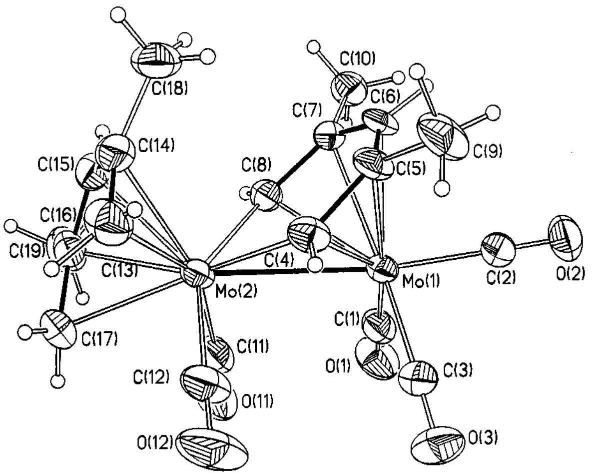
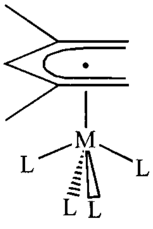


Figure 3. Perspective view and numbering scheme for $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$. The hydrogen atom positions were located and refined.

Table 6. Positional Parameters for the Non-Hydrogen Atoms of $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$

atom	*x*	*y*	*z*
Mo(1)	0.17558(4)	0.21845(2)	0.12471(3)
Mo(2)	0.18257(4)	0.08434(2)	0.25253(3)
O(1)	−0.0493(5)	0.3307(2)	0.2212(3)
O(2)	0.2220(5)	0.3550(3)	0.0090(3)
O(3)	−0.1387(5)	0.1687(3)	−0.0184(3)
O(11)	−0.1021(5)	0.1841(3)	0.3201(3)
O(12)	−0.1067(6)	0.0005(3)	0.1170(3)
C(1)	0.0348(6)	0.2905(3)	0.1871(4)
C(2)	0.2035(6)	0.3039(3)	0.0402(4)
C(3)	−0.0232(6)	0.1878(4)	0.0334(4)
C(4)	0.2629(5)	0.0968(3)	0.1134(3)
C(5)	0.3892(5)	0.1400(3)	0.0783(3)
C(6)	0.4645(5)	0.2018(3)	0.1321(4)
C(7)	0.4379(5)	0.2246(2)	0.2250(3)
C(8)	0.3200(5)	0.1883(3)	0.2739(3)
C(9)	0.4393(8)	0.1249(4)	−0.0206(4)
C(10)	0.5324(7)	0.2927(3)	0.2686(5)
C(11)	0.0009(6)	0.1525(3)	0.2900(4)
C(12)	−0.0048(7)	0.0306(3)	0.1664(4)
C(13)	0.2992(7)	−0.0348(3)	0.2441(4)
C(14)	0.4177(6)	0.0100(3)	0.2990(4)
C(15)	0.3792(6)	0.0490(3)	0.3817(4)
C(16)	0.2221(7)	0.0544(3)	0.4166(4)
C(17)	0.0785(6)	0.0151(3)	0.3743(4)
C(18)	0.5856(7)	0.0250(3)	0.2675(5)
C(19)	0.2080(9)	0.1100(4)	0.4965(4)



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skeleton seems to show the expected short–long–long–short pattern in its bond lengths, with average C–C distances of 1.400(5) and 1.422(6) Å. The presence of methyl groups on C(14) and C(16) leads to the usual contraction in C–C–C bond angles, which average 122.0(4)° vs 128.2(5)° around C(15).[1] While the C(13)–C(17) skeleton is planar to within $\sim$0.02 Å, the substituents display more significant deviations, as is generally observed. Thus, the H(1,5-exo), CH_3, and H-3 substituents all tilt toward Mo(2), by averages of 15.6°, 8.0°, and 5.2°, respectively, while the H(1,5-endo) substituents tilt in the other direction by an average of 40.4°. Perhaps most peculiar are the Mo(2)–C(4,8) bond lengths, which average 2.156(3) Å, compared to $\sim$2.34–2.35 Å for various $Mo(C_5H_5)(R)(CO)_3$ complexes.[27] This shortening must be considered dramatic, as the average Mo(2)–C bond lengths for the 2,4-C_7H_{11} and CO ligands are not greatly different from the Mo–C bond lengths for the C_5H_5 and CO ligands in the $Mo(C_5H_5)(R)(CO)_3$ complexes,[27] [2.335(3) vs 2.339(4) and 2.030(4) vs 1.993(3) Å, respectively]. Together with the NMR spectral data (*vide supra*) and some metrical parameters describing the Mo(1) coordination sphere (*vide infra*), one can conclude that some degree of multiple Mo–C bonding is present, leading to the formulation of this compound as an (η^6-metallabenzene)metal complex **9**.

Notably, both complexed and uncomplexed metallabenzene compounds are somewhat uncommon. Uncomplexed examples have been found for osmium, iridium, and tantalum[26] and could be involved as possible reaction intermediates for iron and tungsten.[28] Aside from the present species, only two other complexed metallabenzenes have been reported.[29] Interestingly, evidence has been presented that metal-complexed arenes may be more "aromatic" than the free arenes.[30]

The coordination sphere about Mo(1) could also be looked upon as a M(Pdl)L_4 variant, i.e., **10**, with the four L's being Mo(2) and the carbonyls, while the Pdl would be an edge-bridged [by Mo(2)] pentadienyl ligand, analogous to cyclohexadienyl, for example. While one could also consider it as a M(Pdl)L_3 variant, in all such species to date one has the three ligands located opposite to the formally charged carbon atoms in the 1, 3, and 5 positions, cf. **1**, unlike that observed here (**11**).[1] However, as already noted, the Mo(2)–C(4,8) bond lengths are too short to be regarded as single bonds. Further, the positioning of the substituents on atoms C(4–8) is not consistent with what would be expected for a pentadienyl ligand. Thus, the average tilts for the C(4,8), C(5,7), and C(6) substituents are only 2.3°, 0.8°, and 9.6° toward Mo(1), respectively, with the tilt for the central carbon atom substituent being greatest instead of least. Additionally, Mo(2) is tilted only 8.8° away from Mo(1) (cf. 40.4° for the endo substituents on C(13,-17), *vide supra*). Hence, the metrical parameters suggest a different formulation, and together with the Mo(2)–C(4,8) bond lengths and the NMR spectral data

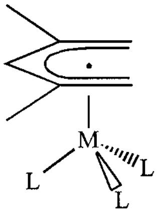

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Table 7. Selected Bond Distances and Angles for $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$

Bond Distances, Å

Mo(1)−Mo(2)	2.989(1)	Mo(2)−C(4)	2.150(5)	O(1)−C(1)	1.136(7)	C(7)−C(8)	1.404(6)
Mo(1)−C(1)	1.996(5)	Mo(2)−C(8)	2.161(4)	O(2)−C(2)	1.166(7)	C(7)−C(10)	1.517(7)
Mo(1)−C(2)	1.965(5)	Mo(2)−C(11)	2.026(5)	O(3)−C(3)	1.148(6)	C(13)−C(14)	1.391(7)
Mo(1)−C(3)	1.980(5)	Mo(2)−C(12)	2.034(5)	O(11)−C(11)	1.132(7)	C(14)−C(15)	1.423(8)
Mo(1)−C(4)	2.297(5)	Mo(2)−C(13)	2.336(6)	O(12)−C(12)	1.133(7)	C(14)−C(18)	1.502(8)
Mo(1)−C(5)	2.377(5)	Mo(2)−C(14)	2.328(5)	C(4)−C(5)	1.418(7)	C(15)−C(16)	1.420(8)
Mo(1)−C(6)	2.329(4)	Mo(2)−C(15)	2.319(5)	C(5)−C(6)	1.424(6)	C(16)−C(17)	1.409(7)
Mo(1)−C(7)	2.369(4)	Mo(2)−C(16)	2.339(5)	C(5)−C(9)	1.521(8)	C(16)−C(19)	1.514(8)
Mo(1)−C(8)	2.310(4)	Mo(2)−C(17)	2.355(6)	C(6)−C(7)	1.410(7)		

Bond Angles, deg

Mo(1)−Mo(2)−C(4)	49.9(1)	Mo(2)−C(4)−C(5)	133.8(3)	C(4)−C(5)−C(6)	120.7(4)	C(13)−C(14)−C(15)	121.5(5)
Mo(1)−Mo(2)−C(8)	50.2(1)	Mo(2)−C(8)−C(7)	134.2(3)	C(4)−C(5)−C(9)	120.9(5)	C(13)−C(14)−C(18)	120.9(5)
Mo(1)−Mo(2)−C(11)	73.7(2)	C(1)−Mo(1)−C(2)	83.2(2)	C(5)−C(6)−C(7)	127.4(4)	C(14)−C(15)−C(16)	128.2(5)
Mo(1)−Mo(2)−C(12)	94.2(2)	C(1)−Mo(1)−C(3)	90.3(2)	C(6)−C(5)−C(9)	118.3(5)	C(15)−C(14)−C(18)	117.3(5)
Mo(2)−Mo(1)−C(1)	102.7(2)	C(2)−Mo(1)−C(3)	88.6(2)	C(6)−C(7)−C(8)	121.1(4)	C(15)−C(16)−C(17)	122.5(5)
Mo(2)−Mo(1)−C(2)	172.2(1)	C(4)−Mo(2)−C(8)	79.9(2)	C(6)−C(7)−C(10)	118.2(4)	C(15)−C(16)−C(19)	117.5(5)
Mo(2)−Mo(1)−C(3)	96.4(2)	C(11)−Mo(2)−C(12)	86.4(2)	C(8)−C(7)−C(10)	120.6(4)	C(17)−C(16)−C(19)	119.8(5)
Mo(1)−C(1)−O(1)	178.1(4)	Mo(1)−C(2)−O(2)	179.1(4)	Mo(1)−C(3)−O(3)	178.6(5)	Mo(2)−C(11)−O(11)	171.2(5)
Mo(2)−C(12)−O(12)	178.4(5)						

(*vide supra*), it is clear that the $Mo(2)C_5H_3(CH_3)_2$ unit is best considered to be an aromatic molybdenabenzene, η^6 coordinated to Mo(1). Interestingly, the Mo(1)−CO bond lengths average 1.980(3) Å, significantly shorter than those for Mo(2), 2.030(4) Å. This could be in accord with the presumed weaker Mo(2)−CO bonding, as a result of the formally higher oxidation state of Mo(2), as evidenced also by the facile substitution of one of its carbonyl ligands (*vide infra*).

The solution phase IR spectrum of the molybdenabenzene complex shows five C−O stretching modes, two of which are somewhat higher than the others (1996 and 2037 cm^{-1} vs 1907, 1928, and 1942 cm^{-1}). This suggested that the two carbonyl ligands on Mo(2) might be relatively weakly attached, perhaps because Mo(2) would seem to be in a higher formal oxidation state than Mo(1). In accord with this notion, the molybdenabenzene complex reacts fairly readily with either $P(OMe)_3$ or dmpe ($(CH_3)_2PC_2H_4P(CH_3)_2$), leading to incorporation of one ligand in each case eq 2). The IR spectra for these

$$Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5 + L \rightarrow Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_4(L) \quad (2)$$

$$L = P(OCH_3)_3,\ \text{dmpe}$$

complexes now reveal only one C−O stretching mode at higher frequency, suggesting that substitution of a CO ligand on Mo(2) has occurred. Notably, the retention of four CO ligands in the dmpe complex, as well as NMR spectroscopic data, demonstrates that the dmpe ligand has bound in only an η^1 fashion, leaving one phosphorus center uncoordinated. In the absence of X-ray structural data, it cannot be unambiguously determined whether the new complexes have the phosphorus center formally replacing CO(11) or CO(12) (Figure 3). However, in other $M(Pdl)(CO)_x(PR_3)_y$ complexes, the phosphine ligands have displayed a preference for binding at the open dienyl edge.[31] This would suggest that the phosphorus centers have formally replaced CO(12). Indeed, the ^1H NMR spectra provide further support for this expectation. Thus, in both complexes one sees significant coupling not only between the coordinated phosphorus centers and *one* of the metallabenzene's terminal CH groups [i.e., C(4) or C(8) in Figure 3] but also between the phosphorus centers and some of the H-1,5(endo) and H-1,5(exo) resonances. These latter couplings have been observed in other complexes having phosphine ligands situated by an open pentadienyl edge and would not be expected were these ligands attached to Mo(1) (Figure 3).[32]

Conclusions

$Mo(diglyme)(CO)_3$ has been found to provide a convenient entry into (pentadienyl)molybdenum carbonyl chemistry. A number of simple species could be prepared such as $Mo(2,4\text{-}C_7H_{11})(CO)_3^-$, $[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$, $Mo(2,4\text{-}C_7H_{11})(I)(CO)_3$, and $Hg[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$, which have well-known C_5H_5 counterparts. On the other hand, reactions of $Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ with CH_3I or $0.5(1,2\text{-}C_2H_4I_2)$ took unexpected courses, in which the open dienyl ligand underwent dramatic changes, in one case leading to a potentially useful 5 + 1 ring construction via acyl−pentadienyl coupling, while in the other case dehydrogenation ensued, leading to a coordinated molybdenabenzene complex. It is clear that the pentadienyl ligands are characterized by much greater reactivity than their cyclopentadienyl analogues, and this can bring about some unusual transformations.

Acknowledgment. R.D.E. expresses his gratitude to the National Science Foundation for generous support of this work.

Supporting Information Available: A listing of infrared and mass spectral data, tables of hydrogen atom parameters, anisotropic thermal parameters, and selected structural parameters for $Mo(2,4\text{-}C_7H_{11})(I)(CO)_3$ (21 pages). The material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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