reaction. Labeling studies indicate the reaction proceeds by a 1,2-dehydrogenation mechanism in which the incoming C–O bond is retained in the final product. Kinetic data suggest the reaction with methanol is driven by excess internal excitation in $V(CO)_5^-$.

Acknowledgment is made to Bell Laboratories for an equipment donation.

Registry No. $V(CO)_6$, 14024-00-1; $V(CO)_5^-$, 53221-58-2; CH_3OH, 67-56-1.

Synthesis and Properties of (η^5-6,6-Dimethylcyclohexadienyl)molybdenum ((dmCh)MoL_n) Complexes. X-ray Structure of $[(dmCh)(CO)_2Mo]_2$

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The ancillary character of the 6,6-dimethylcyclohexadienyl ligand (dmCh) was examined via the syntheses of various (dmCh)MoL_n derivatives. Treatment of (diglyme)$Mo(CO)_3$ with K(dmCh) afforded $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1, 85%), which was converted to (dmCh)$Mo(CO)_3I$ (2) by I_2 in low yield. The addition of HgI_2 to 2.0 equiv of 1 produced $[(dmCh)Mo(CO)_3]_2Hg$ (3, 77%); iodination of 3 generated 2 in 65% yield. Photolysis of 3 provided the dimer, $[(dmCh)Mo(CO)_3]_2$ (4), which was most conveniently prepared via $[Cp_2Fe]PF_6$ oxidation of 1 (57%). Thermolysis of 4 yielded a triply bonded dimer, $[(dmCh)Mo(CO)_2]_2$ (5, 80%), that contains a 2.508-Å Mo≡Mo bond and two semibridging carbonyls. Crystal data for 5: Cu Kα, triclinic, $P\bar{1}$, $a = 9.654$ (1) Å, $b = 8.658$ (1) Å, $c = 12.608$ (2) Å, $\alpha = 93.44$ (1)°, $\beta = 104.80$ (1)°, $\gamma = 100.79$ (1)°, $Z = 2$, $T = 23$ °C, $R = 0.049$, $R_w = 0.036$, 2518 reflections ($|F_o| \geq 3\sigma(F_o)$). Anion 1 ($E_a = +0.14$ V) and singly bonded dimer 4 ($E_c = -0.60$ V) were observed to be electrochemically coupled via either an ECE or an ECC process; 5 displayed a reversible reduction at −1.10 V. Diazald reacted with 1 to form (dmCh)$Mo(CO)_2NO$ (6, 46%); exposure of 6 to PPh_3 and PMe_3 resulted in the synthesis of (dmCh)$Mo(PPh_3)(NO)CO$ (7) and (dmCh)$Mo(PMe_3)(NO)CO$ (9) in modest yield, the latter via (η^1-dmCh)$Mo(PMe_3)_2(CO)_2NO$ (8). The characteristics of these complexes, as compared with cyclopentadienyl congeners, are consistent with an assessment of dmCh as a strong-field ligand.

Introduction

The recently explored pentadienyl (pd) ligand[1-4] has drawn substantial interest as an alternative to the ubiquitous cyclopentadienyl (Cp) fragment,[5] primarily due to its ability to stabilize low-valent early metals.[6-8] An investigation into the feasibility of cyclohexadienyl ligation[8] was initiated in an effort to design an ancillary ligand with characteristics similar to pentadienyl. A series of sandwich complexes, $(dmCh)_2M$ (M = Ti, V, Cr, Fe), containing 6,6-dimethylcyclohexadienyl (dmCh = η^5-6,6-$Me_2C_6H_5$) exhibited properties intermediate between related Cp- and pd-containing species.[9] A substantial amount of the strong-field bonding common to the "wrap-around", acyclic, pentadienyl ligand[2] is transposed to the more rigid dmCh, while the combined steric effects of methyl substituents and the six-membered ring inhibit undesirable ligand reactivity. To further examine the ancillary character of dmCh, a series of (dmCh)MoL_n complexes analogous to those derived from $CpMo(CO)_3$ (Mp)[10] were prepared and studied. Reported herein are the results of this investigation.

Results and Discussion

Table I. Comparative CO (NO) IR Data (cm^{-1})[a] for (dienyl)MoL_n Complexes (dmCh = η^5-6,6-$Me_2C_6H_5$, Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5)

(dienyl)MoL_n	dmCh	Cp/other
[(dienyl)Mo-$(CO)_3$]K	1:[b] 1890, 1790, 1745	1898, 1790, 1750[c,12]
(dienyl)$Mo(CO)_3I$	2:[b] 2015, 1959, 1948	2040, 1970, 1955[d,13]
[(dienyl)Mo-$(CO)_3]_2Hg$	3:[e] 1990, 1968, 1914, 1880	1998, 1971, 1917, 1908, 1890[f,12]
[(dienyl)$Mo(CO)_3]_2$	4:[d] 1950, 1900	1960, 1915[g,14] Cp*: 1940, 1907[g,14] indenyl: 2020 (vw), 1958, 1910[h,15]
[(dienyl)$Mo(CO)_2]_2$	5:[d] 1945, 1886	1889, 1859[g,14] Cp*: 1874, 1846[d,14] indenyl: 1893, 1858[h,15]
(dienyl)Mo-$(CO)_2NO$	6:[d] 2017, 1957, (1678)	2016, 1936, (1674)[e,16]
(dienyl)$Mo(PPh_3)$-(NO)(CO)	7:[e] 1930, (1616)	1906, (1617)[e,16]
(dienyl)$Mo(PMe_3)$-(NO)(CO)	9:[d] 1933, (1625)	1901, (1610)[c,17]

[a] Bands are medium to strong. Solvents/media: [b] Nujol; [c] THF; [d] cyclohexane; [e] benzene; [f] toluene; [g] octane; [h] CH_2Cl_2.

Synthesis and Characterization. All members of the (dmCh)MoL_n class of half-sandwich complexes were ultimately derived from $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1), prepared from treatment of (diglyme)$Mo(CO)_3$[11] with K(dmCh)[9] at −78 °C in THF according to eq 1. Precip-

$$(diglyme)Mo(CO)_3 + K(dmCh) \xrightarrow[-78\ ^\circ C]{THF} \underset{1}{[K(diglyme)_n][(dmCh)Mo(CO)_3]} \quad (1)$$

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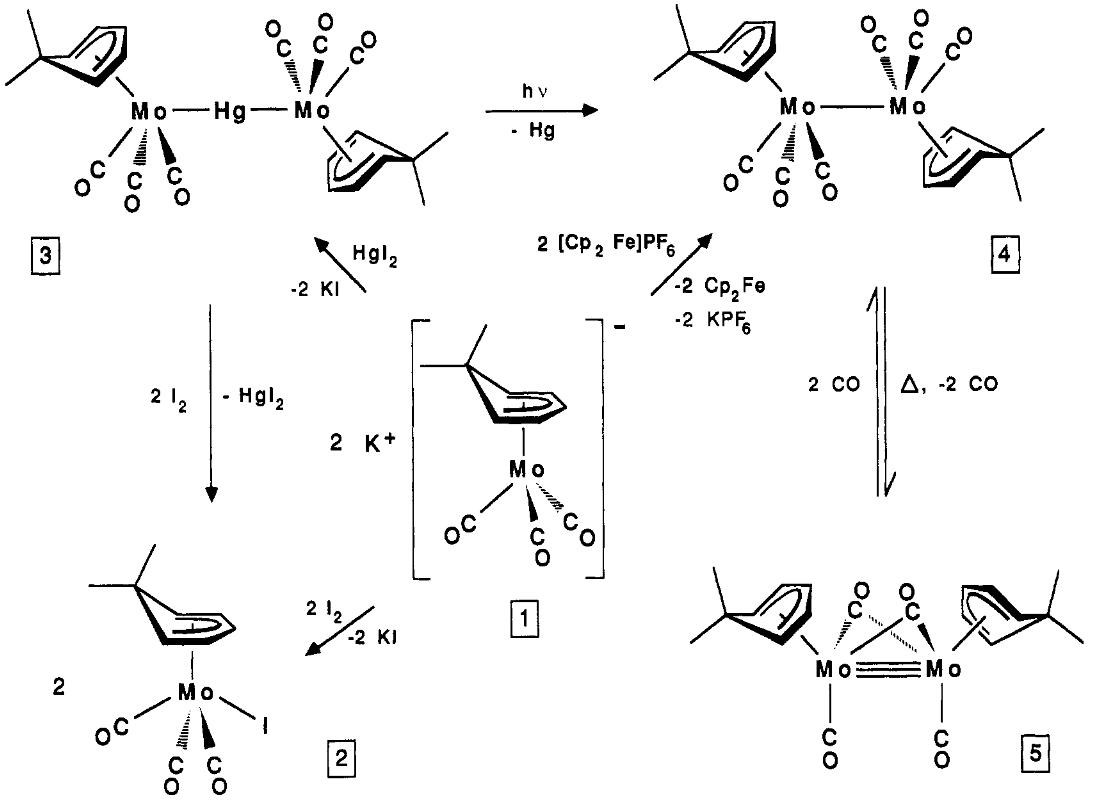
Table II. ^{1}H NMR Data (δ (J, Hz)) for (dmCh)MoL$_n$ Complexes (dmCh = η^5-H$_a\overline{\text{C(CH}_b\text{)(CH}_c\text{)(CMe}_2\text{)(CH}_{c'}\text{)(C}H_{b'}$))^a

compound	Me(exo)	Me(endo)	H$_c$,H$_c'$	H$_b$,H$_b'$	H$_a$	others
[(dmCh)Mo(CO)$_3$]K (**1**)^b	0.50 (s, 3 H)	1.18 (s, 3 H)	2.73 (dd, *J* = 7.2, 1.3, 2 H)	4.83 (dd, *J* = 7.2, 5.5, 2 H)	5.21 (tt, *J* = 5.4, 1.5, 1 H)	
(dmCh)Mo(CO)$_3$I (**2**)	0.24 (s, 3 H)	1.09 (s, 3 H)	3.52 (dd, *J* = 6.2, 1.8, 2 H)	3.93 (dd, *J* = 6.2, 5.0, 2 H)	5.04 (t, *J* = 5.0, 1.7, 1 H)	
[(dmCh)Mo(CO)$_3$]$_2$Hg (**3**)	0.37 (s, 6 H)	1.06 (s, 6 H)	2.95 (dd, *J* = 5.8, 1.6, 4 H)	4.23 (dd, *J* = 6.0, 5.0, 4 H)	5.98 (tt, *J* = 5.0, 1.2, 2 H)	
[(dmCh)Mo(CO)$_3$]$_2$ (**4**)	0.23 (s, 6 H)	1.12 (s, 6 H)	3.25 (dd, *J* = 7.0, 1.8, 4 H)	4.64 (dd, *J* = 6.9, 5.4, 4 H)	5.18 (tt, *J* = 5.4, 1.7, 2 H)	
[(dmCh)Mo(CO)$_2$]$_2$ (**5**)	0.06 (s, 6 H)	0.83 (s, 6 H)	2.84 (dd, *J* = 7.4, 1.4, 4 H)	4.82 (dd, *J* = 7.4, 5.5, 4 H)	5.55 (tt, *J* = 5.5, 1.6, 2 H)	
(dmCh)Mo(CO)$_2$NO (**6**)	0.35 (s, 3 H)	0.82 (s, 3 H)	2.19 (dd, *J* = 7.5, 1.2, 2 H)	4.56 (dd, *J* = 7.4, 5.8, 2 H)	5.16 (tt, *J* = 5.5, 1.5, 1 H)	
(dmCh)Mo(PPh$_3$)(NO)-(CO) (**7**)	0.49 (s, 3 H)	1.05 (s, 3 H)	1.72 (d"t", *J* = 8, 2, 1 H), 3.88 (d"q", *J* = 7, 1, 1 H)	4.38 ("q"d, *J* = 5, 2, 1 H), 4.65 ("tt", *J* = 5.5, 1.8, 1 H)	5.61 ("tt", *J* = 5, 1.5, 1 H)	6.9–7.8 (m, 15 H), PPh$_3$
(dmCh)Mo(PMe$_3$)(NO)-(CO) (**3**)^c	0.58 (s, 3 H)	1.01 (s, 3 H)	2.39 (d"t"d, *J* = 7.9, 2.2, 0.7, 1 H), 3.98 (ddd, *J* = 7.5, 2.7, 1.6, 1 H)	4.77 ("t"d, *J* = 6.6, 1.6, 1 H), 5.07 (m, 1 H)	5.81 (tdd, *J* = 5.5, 3.4, 1.4, 1 H)	1.38 (d, (*J* = 8.4, 9 H), PMe$_3$

^{a} All spectra recorded in C$_6$D$_6$ (Me$_4$Si, δ 0.0) at 25 °C, unless otherwise noted. ^{b} CD$_3$CN. ^{c} CD$_2$Cl$_2$.

Scheme I



itation from THF afforded air-sensitive 1 ($n \sim 0.7$) in 85% yield as a tan solid, which could be freed from residual diglyme after careful washing with cold THF/pentane (1:5). Prior to its use in ensuing reactions, the diglyme

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content of each batch of 1 was analyzed by ^{1}H NMR. Insoluble in ether and hydrocarbons, 1 dissolved readily in THF or CH_3CN, resulting in dark brown solutions. The IR spectrum (Table I)[12-17] showed the requisite CO stretches (1890, 1790, 1745 cm^{-1}, Nujol) indicative of terminal carbonyls that constitute the legs of a three-legged "piano stool" of C_s symmetry, and the ^{1}H NMR spectrum (Table II) revealed a typical dmCh pattern.

An attempt to substitute for CO in $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1) with PMe_3 (1.0 equiv, CD_3CN) resulted in no reaction over 2 days at 100 °C. Electrophilic attack of 1 by CH_3I or $HBF_4{\cdot}Et_2O$ at −78 °C in THF offered no tractable organometallic products[7] besides $Mo(CO)_6$. Anion 1 failed to undergo metalation with $ZnCl_2$ in THF and was recovered unchanged when subjected to H_2O or CH_3OH, consistent with the weak basicity inherent to a carbonylate. Treatment with Me_3SiI in THF produced a colorless oil that possessed resonances (^{1}H NMR) characteristic of a substituted 1,3-cyclohexadiene,[18] suggesting that electrophilic attack at dmCh preceded decomposition. Ample precedent for attack at the dienyl fragment has been established by Semmelhack et. al., who, for example, have described the electrophilic functionalization of the cyclohexadienyl group in $(\eta^6\text{-}C_6H_7)Cr(CO)_3^-$.[8]

As indicated in Scheme I, oxidation of $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1) in THF at −78 °C by I_2 produced $(dmCh)Mo(CO)_3I$ (2) in low yield (~10–15%). Red-orange crystals of 2 were isolated only after exhaustive hexane extraction of the dark solid remaining upon removal of THF at 25 °C. Repeated attempts at optimizing the yield through varied reaction times, with use of CH_2Cl_2 as the solvent, or with $[I(pyridine)_2][BF_4]$[19] as the I^+ source were unsuccessful. Iodide 2 was soluble in aromatics and polar solvents and slightly soluble in hexane from which an insoluble orange solid deposited with time. The IR spectrum of 2 reflects the Mo(II) oxidation state, exhibiting CO stretches at 2015, 1959, and 1948 cm^{-1}. Phosphine substitution reactions (e.g., PPh_3, $P(OMe)_3$, in C_6H_6) involving 2 were uncontrollable, giving a myriad of products, along with an immediate, copious evolution of CO. Similar phenomena have been observed in the analogous Cp system.[20]

It was necessary to develop an alternate, higher yield synthesis of 2 to exploit its iodo functionality. Using methodology applied to Mp,[21] $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1) was cleanly metalated with 0.5 equiv of HgI_2 (THF, 0 °C) to form light- and heat-sensitive $[(dmCh)Mo(CO)_3]_2Hg$ (3), isolated as a yellow powder in 77% yield. Fortunately, further handling of 3 proved unnecessary, as both IR (ν(CO) = 1990, 1968, 1914, 1880 cm^{-1}) and NMR data indicated a sufficient purity (>95%) to proceed with derivatization studies. Exposure of 3 to 2.0 equiv of I_2 in CH_2Cl_2 (25 °C, 12 h) provided 2 in good quantity upon crystallization from hexane (65%). Alternatively, 3 could be generated in THF and reacted in situ with I_2 to give comparable yields of 2.

As expected, the photosensitivity of 3 could be traced to the cleavage of its Hg–Mo single bonds. When thin-walled, Pyrex NMR tubes containing dilute C_6D_6 solutions of 3 (0.03 M) were exposed to standard fluorescent room light at 25 °C, wisps of green color were immediately detected and the entire solution rapidly (10 min) became deep green. The formation of $[(dmCh)Mo(CO)_3]_2$ (4), with concomitant Hg droplets, was complete within 12 h of irradiation according to ^{1}H NMR (Scheme I). A scale-up of this reaction using a simple laboratory apparatus failed to near completion. Apparently the rapid buildup of intensely colored 4 inhibits its photosynthesis because the product preferentially absorbs the available light. Since reaction of the dilute sample monitored by NMR appeared quantitative, utilization of a flow system during photolysis would probably solve the scale-up problem. Dimer 4 was most efficiently prepared (57%) via oxidation of $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (1) with $[Cp_2Fe]PF_6$ (THF, −78 to 0 °C, ~30 min), followed by rapid workup. Ferricinium, either the PF_6 or BPh_4 salt, proved best in numerous trials, although various oxidants produced some amount of 4.

Crystallization of $[(dmCh)Mo(CO)_3]_2$ (4) from deep green solutions in toluene/hexane provided analytically pure purple needles, which appeared green when pulverized. The reflectance responsible for the purple hue in large crystals is characteristic of a complex possessing intense absorptions in the blue and red regions of the spectrum. In cyclohexane solution, 4 exhibits bands at $\lambda = 424$ nm ($\epsilon > 5 \times 10^4$ M^{-1} cm^{-1}), and $\lambda = 622$ nm ($\epsilon \sim 1 \times 10^4$ M^{-1} cm^{-1}). The energy and intensity of these absorptions suggest that the former is the $\sigma \rightarrow \sigma^*$ transition of the Mo–Mo bond, while the latter may be assigned as the $d\pi \rightarrow \sigma^*$ transition, analogous to ones in similar d^5 $[(dienyl)M(CO)_3]_2$ dimers.[22] The bands are at lower energies than those of Mp_2 (λ = 382, 508 nm).[14] Two sharp terminal carbonyl bands in the IR spectrum (ν(CO) = 1950, 1900 cm^{-1}) are suggestive of an antidienyl geometry (C_{2h}). In this case the dmCh ligand appears to function as a somewhat better π-donor than Cp, since the CO stretches characterizing Mp_2 (ν = 1960, 1915 cm^{-1})[14] are slightly higher. The ^{1}H and ^{13}C NMR spectra were normal for η^5-dmCh (Table II), and the CO resonance (25 °C) was detected at δ 223.7. No EPR absorptions were observed for dilute benzene solutions of 4. EPR signals centered at $\langle g \rangle$ = 2.044 and 2.0455 have been observed for solutions of $[pdFe(CO)_2]_2$ (pd = pentadienyl) and $[ChFe(CO)_2]_2$ (Ch = cyclohexadienyl), respectively.[23] Presumably the weakened Fe–Fe linkages in these complexes lead to small

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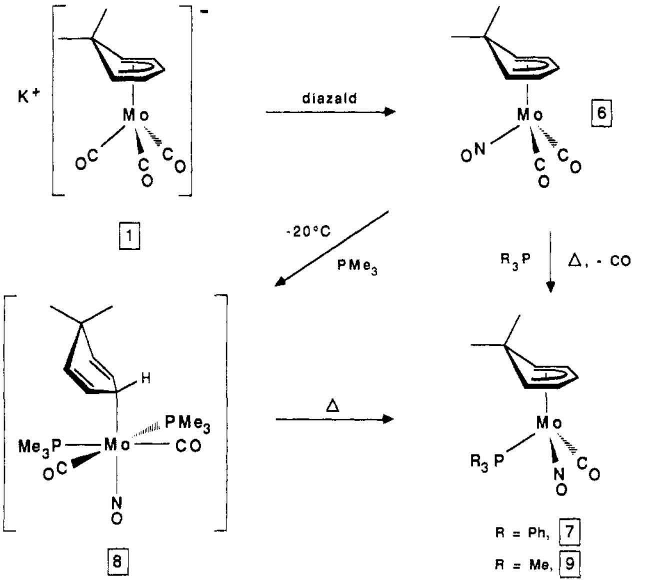
Scheme II



concentrations of (dienyl)$Fe(CO)_2$.

Dimer **4** was only slightly soluble in hexane but dissolved easily in aromatic solvents, where it was indefinitely stable at 25 °C. The intense green color of **4** faded slowly ($\sim$4 h) in THF and rapidly bleached in CH_3CN ($\sim$10 min). The reactivity of $[(dmCh)Mo(CO)_3]_2$ (**4**) is dominated by decarbonylation to form the Mo≡Mo derivative, $[(dmCh)Mo(CO)_2]_2$ (**5**). For example, thermolysis of **4** in hexane for 4 days at 90 °C (or <1 h at 120 °C) produced brick-red **5** quantitatively by ^1H NMR. Heating **4** in the presence of H_2 (0.5 atm), PPh_3, or even CH_3I at 90 °C for extended periods caused only the formation of **5**, while PMe_3 slowly reacted at 25 °C to give a yellow mixture of unidentified products. The decarbonylation was reversible, for solutions of triply bonded **5** slowly ($\sim$1 h) reverted to singly bonded **4** upon exposure to CO (1 atm). A slurry of $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (**1**) and $(dmCh)Mo(CO)_3I$ (**2**) in C_6D_6 (25 °C, 1 day) also resulted in **5** (75% by ^1H NMR) via a pathway that was not investigated.

Triply bonded $[(dmCh)Mo(CO)_2]_2$ (**5**) was remarkably stable, withstanding extensive thermolysis at 135 °C for >2 weeks and the array of reagents described above. Since the metal–metal bond order of 3 was assigned in reference to $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$,[24] **5** was expected to display substantial reactivity. Tolane and 2-butyne failed to react with **5** upon extended heating (120 °C, 2 days), while such reagents are known to readily bridge the Mo≡Mo bond of $[CpMo(CO)_2]_2$.[25] The IR spectrum of **5** manifested two absorptions ($\nu(CO)$ = 1945, 1886 cm^{-1} in C_6H_{12}) at energies lower than those for **4**, yet still within the range of terminal CO stretches. Interestingly, these values are *higher* (by an average of 40 cm^{-1}) than for the comparable Cp, Cp*, and indenyl (η^5-C_9H_7) complexes.[14,15,24] The inert character of **5** and the possible absence of a bridging CO were puzzling. To elucidate the possible structural basis for these results, **5** was characterized via an X-ray crystallographic study (vide infra).

Through the use of the standard, mild nitrosylating agent Diazald (*N*-nitroso-*N*-methyl-*p*-toluenesulfonamide),[26] it was possible to prepare mononuclear derivatives of **1** bearing a terminal NO ligand (Scheme II). Treatment of **1** with Diazald in diethyl ether at 0 °C gave an orange solution, from which red-orange crystals of $(dmCh)Mo(CO)_2(NO)$ (**6**, 46%) were obtained after hexane extraction and sublimation. Nitrosyl **6** was soluble in hydrocarbons, stable to air for short periods, and thermally stable in benzene at elevated temperatures (>5 h, 93 °C), but degraded upon prolonged exposure ($\sim$14 days) to room fluorescent light. Examination of the IR spectrum showed two carbonyl bands (2017, 1957 cm^{-1}) and a stretching vibration in the region expected for a linear, terminal bound nitrosyl group (1678 cm^{-1}).

Further derivatization of **6** was possible through phosphine substitution of a carbonyl. Reflux of a toluene solution containing **6** and equimolar PPh_3 for 16 h afforded, upon cooling, analytically pure red crystals of $(dmCh)Mo(CO)(NO)(PPh_3)$ (**7**, 30%). The IR revealed the expected shift of absorbances to lower energy upon replacement of CO by PPh_3 and the ^1H NMR showed five inequivalent ring-bound protons, indicative of a chiral metal center. It is clear that the disparity in chemical shifts between formerly mirror-related protons (i.e., in **6**) was large. In **7**, the chemical shift difference (*D*) between H_c and $H_{c'}$ (Table II), assigned according to the upfield position and typically large ^3J (8 Hz) of each resonance, was 2.16 ppm. A large *D* reflects the sensitivity of a ligand to factors that foster chemical-shift anisotropy. A detailed study by Coville et al.[27] of chiral $(\eta^5$-$Cp')Fe(CO)(PR_3)I$ (Cp′ = methylcyclopentadienyl) complexes indicated that comparable *D* values were less than 1.8 ppm for all phosphines studied. Given prior work establishing the greater covalent bonding of dmCh relative to Cp and the larger size of the former dienyl, it is not unreasonable to expect substantial chemical shift differences.

Exposure of **6** to 1.0 PMe_3 at 25 °C for 3 h produced $(dmCh)Mo(CO)(NO)(PMe_3)$ (**9**) as a red-orange, slightly impure oil upon evaporation of hexane solvent (>95%, ^1H NMR). Thermolysis of **9** (90 °C, 24 h) with an additional 10 equiv of PMe_3 incurred no further substitution, providing evidence for a particularly stable η^5-dmCh configuration. This derivative proved difficult to purify and crystallize; hence characterization rested on spectroscopic data. NMR spectra consisted of a five-resonance pattern for the dmCh ligand (^1H) and a single ^{31}P resonance at δ −0.48 (CD_2Cl_2). The IR spectrum showed stretching vibrations (1933 (CO), 1625 (NO) cm^{-1}) not significantly perturbed from **7**, analogous to Cp congeners in which the $\Delta\nu$ upon changing from PPh_3 to PMe_3 averages only 5 cm^{-1} (Table I).[16,17] Both **7** and **9** are extremely light- (Hg vapor lamp, 25 °C, 1 day) and temperature-stable (133 °C, 1 day) in C_6D_6 solution.

Close inspection of the reaction between **6** and PMe_3 by ^1H NMR (−20 °C, CD_2Cl_2) revealed the presence of an intermediate, tentatively assigned as $(\eta^1$-$dmCh)Mo(CO)_2(NO)(PMe_3)_2$ (**8**), along the pathway to **9**. If $\sim$1.0 equiv of PMe_3 was used, only $\sim$0.5 equiv of **8** was detected, whereas excess phosphine (i.e., 2.0, 4.0 or $\sim$10 equiv) led to its complete formation, implicating the incorporation of two phosphines. Two inequivalent methyl groups differing by only 0.005 ppm (δ 0.985, 0.990) were observed for **8**. Normally, the methyl shifts are quite dissimilar for an η^5-dmCh, but $(dmCh)_2$ (3-(4,4-dimethyl-2,5-cyclohexadien-1-yl)-6,6-dimethyl-1,4-cyclohexadiene)[9] manifests only a single methyl resonance. The two equivalent PMe_3

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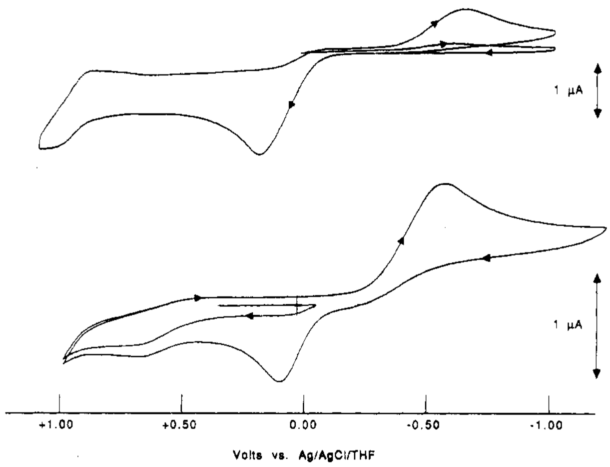

Figure 1. (A) Cyclic voltammogram for oxidation of $[(dmCh)Mo(CO)_3]^-$ (1) beginning with a cathodic scan (scan rate = 200 mV/s). (B) Cyclic voltammogram for reduction of $[(dmCh)Mo(CO)_3]_2$ (4) beginning with an anodic scan (scan rate = 200 mV/s).

groups exhibited an $AX_9A'X'_9$ pattern[28] at δ 1.51 ($|J_{PH} + J_{PH'}|$ = 6.9 Hz) and a singlet at δ −24.4 in the ^{31}P NMR. In comparison, the PMe_3 ligands in *fac*-$(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$[29] display a similar motif ($|J_{PH} + J_{PH'}|$ = 7.7 Hz). Although characteristic of chemically equivalent phosphines, this pattern can be observed for both *cis*- and *trans*-phosphine geometries.

Resonances distinct from other dmCh-containing complexes appeared clustered in the vinylic region. A doublet of doublets at δ 4.63 (J = 9.7, 0.7 Hz) was assigned to $H_{c,c'}$, in contrast to typical positions for an η^5-dmCh (δ 2.2–3.5, Table II). An overlapping set of resonances at δ 5.68, best described as a doublet of doublets superimposed on a complex multiplet, was tentatively assigned to $H_{b,b'}$ (J = 9.7, 4.5 Hz) and H_c (m). Upon warming, **8** reverted to (dmCh)Mo(CO)(NO)(PMe_3) (**9**), concomitant with the loss of CO and PMe_3. The NMR data, while informative, fall short of establishing the exact coordination geometry of **8**, since various structures, including some that contain η^3-dmCh and bent NO ligands, conform to the spectra. However, comparisons with structurally and spectrally characterized Cp analogues (e.g., *fac*-$(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$,[29] $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)(PMe_3)_2$,[30] and *fac*-$(\eta^1\text{-}C_5H_5)M(CO)_2(NO)(PMe_3)_2$ (M = Mo, W))[17] lend credence to a structure containing *cis*-PMe_3 groups, a *trans*-dmCh,NO arrangement, and a linear nitrosyl (Scheme II).

Electrochemistry of $(dmCh)Mo(CO)_3^-$ (1), $[(dmCh)Mo(CO)_3]_2$ (4), and $[(dmCh)Mo(CO)_2]_2$ (5). Since oxidation of $[K(diglyme)_n][(dmCh)Mo(CO)_3]$ (**1**) resulted in the formation of $[(dmCh)Mo(CO)_3]_2$ (**4**), an electrochemical study was initiated to examine their interrelationship. Dissolution of **4** in acetonitrile or CH_2Cl_2 resulted in apparent decomposition; thus THF was employed as the solvent, with 0.2 M $^nBu_4NBF_4$ as supporting electrolyte. Cyclic voltammetry (CV) of anion **1** (Figure 1A), beginning with an initial scan in the cathodic direction (200 mV s^{-1}), revealed no peaks to −1.0 V. The return scan exhibited an electrochemically irreversible oxidation wave at E_a +0.14 V (vs Ag/AgCl/THF) that was devoid of a coupled reduction peak. Upon generation of a second scan, a reduction peak at E_c = −0.63 V was observed without a coupled oxidation wave. Successive scans showed no further changes, establishing the steady-state CV shown. Independent CV scans confirmed the absence of extraneous peaks beyond the potential limits shown (~1.5 to −1.5 V). The complementary CV of the dimer **4** was essentially identical with that of **1**, once a steady state had been established (B). Initial oxidation of **4** showed no peaks to +1.0 V (vs Ag/AgCl/THF), while an irreversible reduction appeared at E_c = −0.60 V. Completion of the scan displayed only the accompanying irreversible oxidation E_a = +0.11 V.

Overall, the cyclic voltammetry closely resembles that of $[CpMo(CO)_3]_2$ and $CpMo(CO)_3^-$, examined recently by Kadish and co-workers,[31] in firmly implicating the intermediacy of the monomer radical, $(dmCh)Mo(CO)_3^{\bullet}$.[32] Two plausible mechanisms involve the reactions indicated in eq 2–6. The cathodic wave corresponds to the 1e$^-$ reduction of $[(dmCh)Mo(CO)_3]_2$ (**4**), generating the dimer radical anion, $[(dmCh)Mo(CO)_3]_2^{\bullet-}$ (**4$^-$**, eq 2). The subsequent dissociation of **4$^-$** to $(dmCh)Mo(CO)_3^-$ (**1**) and $(dmCh)Mo(CO)_3^{\bullet}$ is expected to occur rapidly (k_{diss}, eq 3), followed be either of two events: direct reduction of transient $(dmCh)Mo(CO)_3^{\bullet}$ to **1** (eq 4) or dimerization of the radical monomer to regenerate **4** (k_{dim}, eq 5). Both processes can account for the net 2e$^-$ transfer involved in converting **4** to 2 equiv of **1**. At the potentials required to reduce **4**, electrochemical reduction of $(dmCh)Mo(CO)_3^{\bullet}$ would be favorable. Alternatively, dimerization of the transient radical is expected to be exceedingly fast (e.g., for $CpMo(CO)_3^{\bullet}$, $k_{dim} = 3.1 \times 10^9$ M^{-1} s^{-1}),[33] leading to regeneration of **4** and its ensuing reduction, despite the low concentrations of $(dmCh)Mo(CO)_3^{\bullet}$. Either mechanism is preferable to a second electron transfer to **4$^-$** followed by dissociation to 2 equiv of **1**, since the former step would undoubtedly require greater potential. In total, eq 2–4 represent the common $EC_{diss}E$ pathway, and eq 2, 3, and 5 comprise the related $EC_{diss}C_{dim}$ process.[34] The anodic

$$\underset{\mathbf{4}}{[(dmCh)Mo(CO)_3]_2} + e^- \xrightarrow{E_c} \underset{\mathbf{4^-}}{[(dmCh)Mo(CO)_3]_2^{\bullet-}} \quad (2)$$

$$\underset{\mathbf{4^-}}{[(dmCh)Mo(CO)_3]_2^{\bullet-}} \xrightarrow{k_{diss}} \underset{\mathbf{1}}{(dmCh)Mo(CO)_3^-} + (dmCh)Mo(CO)_3^{\bullet} \quad (3)$$

$$(dmCh)Mo(CO)_3^{\bullet} + e^- \xrightarrow{E_c} \underset{\mathbf{1}}{(dmCh)Mo(CO)_3^-} \quad (4)$$

$$(dmCh)Mo(CO)_3^{\bullet} \xrightarrow{k_{dim}} \underset{\mathbf{4}}{{}^1\!/\!_2[(dmCh)Mo(CO)_3]_2} \quad (5)$$

$$\underset{\mathbf{1}}{(dmCh)Mo(CO)_3^-} \xrightarrow{E_a} (dmCh)Mo(CO)_3^{\bullet} \quad (6)$$

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electrochemistry is less ambiguous; oxidation of **1** produces $(\mathrm{dmCh})\mathrm{Mo(CO)_3}^{\bullet}$ (eq 6), whose dimerization occurs swiftly (eq 5).

Irreversible electrochemical events are implicated in the mechanisms addressed (i.e., $E_iC_iE_i$, $E_iC_iC_i$) due to the rapid chemical reactions that succeed e^- transfer. Since $\mathbf{4}^-$ was deemed likely to possess a significant lifetime, the scan rate (ν) was increased to 500 V s^{-1} in an attempt to observe reversibility in the cathodic wave. No corresponding oxidation was noted, placing an approximate lower limit on k_{diss} (ca. > 10^3 s^{-1}).[35] A value of 1.06×10^3 s^{-1} has been measured for the dissociation of $[\mathrm{CpFe(CO)_2}]_2^-$. Davies et al. determined this value by means of the derivative CV technique,[36] but the use of this method in the $\mathbf{4}/\mathbf{4}^-$ system requires electrochemical reversibility at high CV scan rates, which has not been achieved. In principle, for an $E_iC_iE_i$ or related process and suitable value of k_{diss}, the technique of potential step chronoamperometry[34,37] can determine the time regime in which the C_i step occurs, providing rate information about the dissociation. This technique is equally suitable when applied to an irreversible or reversible electron-transfer step and thus is more reliable than CV. Using a platinum bead working electrode, the chronoamperometric method was applied to the cathodic wave ($\mathbf{4} \rightarrow \mathbf{4}^-$). Unfortunately, rapid coating of the electrode surface proved troublesome, and the experiment merely suggested that the cleavage of $\mathbf{4}^-$ occurred at a rate too great to measure. The related scission of a fulvalene-bridged hexacarbonyldimolybdenum radical anion has been studied by Bard et al.,[38] and rapid-scan CV placed a lower limit on the process as $k_{\mathrm{diss}} > 600$ s^{-1}.

Further comparisons of the electrochemistry with corresponding data pertaining to Cp analogues reveal some differences.[31] Oxidation of $[\mathrm{CpMo(CO)_3}]_2$ occurs at $E_p \sim +1.0$ V (vs Ag/AgCl in THF), providing an unstable monocation that cleaves into $\mathrm{CpMo(CO)_3}^{\bullet}$ and $\mathrm{CpMo(CO)_3}^+$. The latter is persistent on the CV time scale (~4 s, using a 200 mV s^{-1} scan rate), as shown by its subsequent reduction at −0.47 V. In contrast, only a small, irreversible wave that could correspond to oxidation of **4** was noticed in CV scans taken to the periphery of the anodic solvent breakdown potential, at which point rapid decolorization of the intense green solution was seen. Comparisons can be drawn between redox potentials for $[\mathrm{CpMo(CO)_3}]_2$ ($\mathrm{Mp_2}$) and **4**. The reduction of $\mathrm{Mp_2}$ occurs at −1.15 V in contrast to −0.60 V for **4**, each vs Ag/AgCl in THF. Vahrenkamp and co-worker have established a linear correlation of the electrochemical reduction potential of group 6 dimers with the energies of their $\sigma \rightarrow \sigma^*$ transitions; the higher the transition energy, the more cathodic the potential.[39] The data for **4** fall close to the line established for those homo- and heterobimetallic dimers. Similarly, the oxidation of Mp^- (−0.12 V) occurs at potentials more cathodic than that of **1** (+0.14 V).[31] Although the electrochemical irreversibility of all four cited peaks precludes any true thermodynamic assessment, the data are consistent with the contention that dmCh is more covalent and thus "softer" than Cp.[40] Dimer **4** is more prone to reduction and **1** less prone to oxidation than the Mp analogues, because electron delocalization is aided by the presence of the dmCh ring. In comparison, Cp* (η^5-$\mathrm{C_5Me_5}$) is substantially better at donating electron density to the Mo center, and hence $[\mathrm{Cp^*Mo(CO)_3}]_2$ is more difficult to reduce and $\mathrm{Cp^*Mo(CO)_3}^-$ easier to oxidize than the Cp compounds.[41]

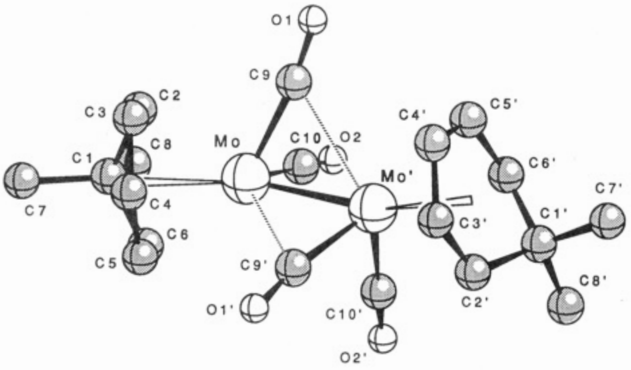

Figure 2. Molecular structure of $[(\mathrm{dmCh})\mathrm{Mo(CO)_2}]_2$ (**5**).

Calculations by Hoffmann et al. on $[\mathrm{CpMo(CO)_2}]_2$ suggest that the HOMO is metal–metal π-bonding in character, whereas the LUMO is Mo$\equiv$Mo π^*, yet virtually nonbonding.[42] Assuming electrochemical potentials can be correlated with HOMO and LUMO energies, a view advanced by Bursten[43] and supported by Bard,[38] the cyclic voltammetry of $[(\mathrm{dmCh})\mathrm{Mo(CO)_2}]_2$ (**5**) provided some important information about its Mo$\equiv$Mo bond. The CV of **5** displayed a reversible reduction at $E^\circ_{1/2} = -1.10$ V (vs Ag/AgCl in THF, $\Delta E_p = 240$ mV at $\nu = 200$ mV s^{-1}; cf. $\Delta E_p(\mathrm{Cp_2Fe/Cp_2Fe^+}) = 220$ mV) yet no oxidation peak appeared when electrolysis was carried to the anodic solvent breakdown (>+1.50 V). Since $[(\mathrm{dmCh})\mathrm{Mo(CO)_2}]_2^{\bullet -}$ ($\mathbf{5}^-$) is stable on the CV time scale, the reversible reduction is indicative of weakly antibonding or nonbonding Mo$\equiv$Mo π^*-orbitals in **5**, assuming these constitute the LUMO. If this orbital possesses substantial dmCh character, as expected, delocalization of the added electron will limit the effect reduction has on the metal–metal bond order. The ability of dmCh to accept electron density also adds stability to the Mo$\equiv$Mo bonding framework, and hence the absence of an observable oxidation for **5** may be attributed to the more covalent nature of dmCh. Oddly, a recent, brief report[44] of the redox behavior attributed to $[\mathrm{CpMo(CO)_2}]_2$ asserted that its cyclic voltammogram is virtually identical with its singly bonded kin ($[\mathrm{CpMo(CO)_3}]_2$),[41] with minor variations of peak potentials. Analogous cathodic and anodic ECE processes occur, complete with scission of anion $[\mathrm{CpMo(CO)_2}]_2^-$, oxidative cleavage, etc.

Molecular Structure of $[(\mathrm{dmCh})\mathrm{Mo(CO)_2}]_2$ (5). Examination of the IR and electrochemical data pertaining to $[(\mathrm{dmCh})\mathrm{Mo(CO)_2}]_2$ (**5**) suggested that its structure was significantly different than the Cp[24] and related derivatives.[15,45] Slow evaporation (25 °C, 4 days) of a hexane solution of **5** provided red needles suitable for X-ray analysis. The structure was solved routinely via the heavy-atom method, and standard refinement in space group $P\bar{1}$ resulted in an R of 0.049 ($R_w = 0.036$, GOF = 1.163). Figure 2 illustrates the molecular geometry of **5**,

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[35] Estimated from $\nu/\Delta E_p$, where ΔE_p is the peak-to-peak separation found for $\mathrm{Fc/Fc^+}$ couple in the system at hand.

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for [(dmCh)Mo(CO)$_2$]$_2$ (5)[a]

Distances

Mo–Mo′	2.508 (1)	C1–C8	1.540 (11)
Mo–C4	2.316 (7)	C4–C5	1.432 (8)
Mo′–C2′	2.419 (8)	C1′–C6′	1.493 (9)
Mo′–C5′	2.320 (7)	C2′–C3′	1.374 (9)
Mo–C10	1.997 (7)	C5′–C6′	1.406 (10)
O1–C9	1.143 (7)	Mo···C9′	2.573 (9)
O2′–C10′	1.105 (9)	Mo′···C10	3.112 (10)
C1–C7	1.533 (11)	Mo–C3	2.325 (7)
C3–C4	1.421 (9)	Mo–C6	2.414 (7)
C1′–C2′	1.520 (10)	Mo′–C4′	2.281 (7)
C1′–C8′	1.530 (8)	Mo–C9	1.962 (6)
C4′–C5′	1.420 (12)	Mo′–C10′	2.008 (7)
R′–Mo′	1.935 (1)	O1′–C9′	1.156 (9)
Mo···C10′	3.056 (10)	C1–C6	1.517 (9)
Mo–C2	2.396 (7)	C2–C3	1.371 (9)
Mo–C5	2.313 (7)	C5–C6	1.379 (10)
Mo′–C3′	2.321 (8)	C1′–C7′	1.539 (13)
Mo′–C6′	2.434 (8)	C3′–C4′	1.380 (11)
Mo′–C9′	1.950 (7)	R–Mo	1.927 (1)
O2–C10	1.122 (10)	Mo′···C9	2.640 (9)
C1–C2	1.543 (8)		

Angles

Mo′–Mo–R	160.1 (2)	Mo–Mo′–C10	39.8 (3)
C9–Mo–C10	87.4 (3)	C2–C1–C7	111.1 (5)
Mo–Mo′–R′	162.1 (2)	C6–C1–C8	112.4 (5)
C9′–Mo′–C10′	87.7 (3)	C2–C3–C4	119.8 (5)
Mo–C9–O1	170.4 (6)	C1–C6–C5	119.2 (5)
Mo′–C10′–O2′	178.2 (9)	C2′–C1′–C8′	111.5 (6)
Mo′–C9′–Mo	65.7 (3)	C7′–C1′–C8′	108.1 (7)
Mo′–Mo–C9′	45.1 (3)	C3′–C4′–C5′	119.0 (6)
C2–C1–C6	101.7 (5)	C10–Mo–R	109.3 (3)
C6–C1–C7	111.4 (6)	C10–Mo–Mo′	86.6 (3)
C1–C2–C3	118.5 (5)	C10′–Mo′–R′	110.3 (3)
C4–C5–C6	119.7 (5)	C10′–Mo′–Mo	84.4 (3)
C2′–C1′–C7′	110.9 (6)	Mo′–C9′–O1′	169.3 (6)
C6′–C1′–C8′	111.8 (6)	Mo–C10–Mo′	53.6 (3)
C2′–C3′–C4′	120.2 (7)	Mo–Mo′–C9	44.7 (3)
C1′–C6′–C5′	117.8 (6)	Mo′–Mo–C10′	40.8 (3)
C9–Mo–R	120.3 (3)	C2–C1–C8	111.4 (6)
C9–Mo–Mo′	71.2 (2)	C7–C1–C8	108.7 (6)
C9′–Mo′–R′	119.9 (3)	C3–C4–C5	117.5 (6)
C9′–Mo′–Mo	69.2 (2)	C2′–C1′–C6′	103.7 (6)
Mo–C10–O2	178.9 (7)	C6′–C1′–C7′	110.8 (6)
Mo–C9–Mo′	64.1 (3)	C1′–C2′–C3′	118.3 (6)
Mo′–C10′–Mo	54.8 (3)	C4′–C5′–C6′	119.0 (6)

[a] An estimated standard deviation of the least significant figure for each distance (in Å) is given in parentheses. R and R′ are centroids of the dmCh rings, defined as the centers of triangles C2–C4–C6 and C2′–C4′–C6′, respectively.

and Table III lists pertinent interatomic distances and angles. Although both halves of the triply bonded complex are crystallographically distinct, the molecule possesses virtual C_2 symmetry, containing a pseudo-2-fold axis that bisects the C10–Mo–Mo′–C10′ dihedral angle and passes through the center of the 2.508 (1) Å Mo$\equiv$Mo bond. Each metal center assumes a distorted three-legged piano-stool geometry comprised of the triple bond and a linear semibridging CO[46] (C9–O1, C9′–O1′) that is 87.6 (2)° (av) from a terminal CO (C10–O2, C10′–O2′). The C9–Mo–Mo′ angle of 71.2 (2)° ($\angle$(C9′–Mo′–Mo) = 69.2 (2)°) is clearly different from the corresponding angle of the terminal CO ($\angle$(C10–Mo–Mo′) = 86.6 (3)°, $\angle$(C10′–Mo′–Mo) = 84.4 (3)°), revealing the semibridging nature of C9–O1 (C9′–O1′).

Planes consisting of the methyls and adjoining carbons of each dmCh "envelop flap" (C7–C1–C8, C7′–C1′–C8′) are aligned with the terminal carbonyls (C10–O2, C10′–O2′) of the respective molybdenums (Mo, Mo′). The C4 and C4′ positions of the dmCh rings are thus anti to the terminal carbonyls, whereas C6 and C6′ are essentially anti to the semibridging CO ligands (C9–O1, C9′–O1′). As previously observed in (dmCh)$_2$TiCO,[9] the C3, C4, and C5 (C3′, C4′, C5′) positions of the dmCh ring are approximately equidistant from the molybdenums (2.313 (16) Å (av)) yet are about 0.1 Å closer than the remaining bound carbons, C2 and C6 (C2′, C6′; 2.416 (16) Å (av)).[47] Despite this slight cant, the bound carbons of each dmCh ligand (C2–C6, C2′–C6′) are basically planar ($\sum\sigma^2$ = 0.001 Å). In viewing the bonding of the dmCh unit, the resemblance to the indenyl ligands in [(indenyl)Mo(CO)$_2$]$_2$ became apparent.[15] In the latter the Mo–"allyl" distances (2.339 (8) Å (av)) are 0.06 Å shorter than those attributed to the carbons shared by both the Cp and benzene rings (2.399 (4) Å (av)).

The asymmetry of the carbonyls in 5 can be rationalized by using arguments based on the trans influence of segments of the dmCh ligand. The C4 and C4′ positions are more strongly bound to Mo and Mo′, and thus the carbonyls opposite these sites (C10–O2, C10′–O2′) are terminal. In contrast, C9–O1 and C9′–O1′ are effectively trans to the more weakly bound C6 and C6′ carbons of dmCh and experience greater σ-bonding and π-backbonding, leading to the linear semibridging mode[46] of ligation. In addition, the steric influence of the dimethyl group on each dmCh may play a role. Note that the more sterically demanding terminal CO ligands are situated beneath the "open" C2··C6 and C2′··C6′ ends (2.372 (2) Å (av)) of the dmCh groups while the semibridging CO's are naturally displaced away from the dienyl.

The best planes of each dmCh ring are not parallel with respect to each other but deviate inward at C4 and C4′, forming a dihedral angle of 25.3°. In contrast, [CpMo(CO)$_2$]$_2$ contains rigorously parallel Cp ligands, and the vector between the centroids of both Cp ligands is collinear with the intermetallic axis (i.e., Cp–Mo–Mo angle = 180°).[24] Defining the centroids R and R′ as the geometric means of C2-C4-C6 and C2′-C4′-C6′, the analogous R–Mo–Mo′ and R′–Mo′–Mo angles are 160.1 (2)° and 162.1 (2)°, respectively. Interestingly, the rings in 5 are not syn-eclipsed (χ = 0°) but closer to the gauche-eclipsed (χ = 60°) ideal, with the actual χ = 68.9 (5)°.

The relatively long 2.508 (1) Å Mo$\equiv$Mo bond distance is a feature that depends critically on bridging character of the carbonyls. Bond distances of comparable (dienyl)(CO)$_2$Mo$\equiv$Mo(CO)$_2$(dienyl) complexes span a somewhat abbreviated range, but the Mo$\equiv$Mo unit of 5 is clearly the longest: 2.448 (1) Å,[24] dienyl = Cp (ν(CO) = 1889, 1859 cm^{-1});[14,24] 2.488 (1) Å,[45] Cp* (1874, 1846 cm^{-1});[14] 2.500 (1) Å,[15] indenyl (1893, 1858 cm^{-1}).[15] Note that in each case, the CO stretching frequencies are appreciably lower than those of 5 (ν(CO) = 1945, 1886 cm^{-1}, Table I). The structural details parallel the IR results. With use of Curtis' criteria ($\alpha = (d_2 - d_1)/d_1$; d_2, d_1 are M–C and M′–C distances where $\alpha > 0$; an α of 0 indicates a symmetrical bridge)[24] for judging the semibridging nature of the carbonyl ligands, the following order exists, based on average α values of all carbonyls present: Cp ($\alpha \sim 0.20$)[24] < Cp* ($\alpha \sim 0.07, 0.35$)[45] < indenyl ($\alpha \sim 0.28, 0.41$)[15] < dmCh ($\alpha \sim 0.35, 0.54$). In [(dmCh)Mo(CO)$_2$]$_2$ (5), both C10–O2 and C10′–O2′ are clearly terminal ($\angle$(Mo–C10–O2) = 178.9 (7)°, α = 0.56; ($\angle$(Mo′–C10′–O2′) = 178.2 (9)°, α = 0.52), while C9–O1 and C9′–O1′ are slightly semibridging ($\angle$(Mo–C9–O1) = 170.4 (6)°, α = 0.35; $\angle$(Mo′–C9′–O1′) = 169.3 (6)°, α = 0.35), with d_2(Mo′–C9) = 2.572 (5) Å and d_2(Mo–C9′)

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= 2.640 (6) Å compared to d_1(Mo–C9) = 1.962 (6) Å and d_1(Mo–C9′) = 1.950 (7) Å. The close resemblance of [(indenyl)Mo(CO)$_2$]$_2$ and **5** may be partly a consequence of the similar bonding geometries of the ligands, as previously addressed.

The data persuasively show that the greater the semibridging character of the carbonyl ligands, the shorter the Mo$\equiv$Mo bond, although the magnitude of the change is relatively minor. Presumably, this correlation is due to the geometric constraints imposed by the linear semibridging mode of CO binding. Note that Mo–C9 and Mo′–C9′ distances (1.956 (9) Å (av)) are slightly shorter than their terminal counterparts, Mo–C10 and Mo′–C10′ (2.003 (8) Å (av)). The ability of bridging groups to constrain or dictate the degree and distance of metal–metal interactions has been the subject of numerous discussions.[48] Surprisingly, the tris(pyrazolyl)borate complex [TpMo(CO)$_2$]$_2$ (Tp = HB(C$_3$N$_2$H$_3$)$_3$, ν(CO) = 1970, 1905, 1856, 1842 cm^{-1})[49] most closely resembles **5**, including an analogous pseudo C_2 axis that bisects the Mo$\equiv$Mo bond. The Mo$\equiv$Mo bond length is 2.507 (1) Å, and each Mo contains one semibridging (α = 0.27, $\angle$(MoCO) = 171°) and one terminal (α = 0.41, 175°) CO.

Curtis observed that the Mo$\equiv$Mo bond lengths correlate inversely with the cone angle of the dienyl or Tp ligand; extrapolating to this case, dmCh should approach 180°, a value that is not borne out by models or structural studies. Nonetheless, dmCh is a large ligand that can exert a great deal of steric influence, although perhaps not quite as encumbering as Cp*. Interestingly, the Mo–C(carbonyl) bond lengths in [CpMo(CO)$_2$]$_2$ are 2.13 (4) and 2.56 (5) Å, while [(dmCh)Mo(CO)$_2$]$_2$ (**5**) contains significantly shorter Mo–CO distances (2.003 (8), 1.956 (9) Å) but a slightly longer semibridging distance, 2.61 (5) Å. It would seem that steric influences on the Mo–carbonyl distances are at best minimal.

The question remains as to why the ligation by dmCh renders the CO ligands less able to bridge, leading to a longer Mo$\equiv$Mo bond. The dimethylcyclohexadienyl ligand is considered to be stronger field than Cp[9] and can act as a significant π-acceptor, akin to pentadienyl units. Recall that Hoffmann showed that the linear semibridging CO ligands result from acceptance of electron density from the dimolybdenum fragment.[50] When dmCh is present, it is not necessary to delocalize excess electron density into just the carbonyls, as is the case in [CpMo(CO)$_2$]$_2$. The dmCh competes effectively with the CO ligands for electron density, thereby lessening the back-donation into the carbonyls. Since electron density is being disseminated into the peripheral π-hydrocarbons, the Mo$\equiv$Mo bond is weaker and longer than in the Cp case.

Conclusions

An investigation into the ancillary character of the 6,6-dimethylcyclohexadienyl ligand (dmCh) has been undertaken via the preparation of (dmCh)MoL$_n$ species. Given the ability of dmCh to stabilize Ti(II) and V(II),[9] it is somewhat surprising to note that the chemistry delineated closely parallels that of cyclopentadienyl in this system. However, subtle variations in spectral, structural, and electrochemical behavior support the contention that dmCh can accept and donate electron density to a substantially greater extent than Cp. Arguments assessing the electrochemical and structural evidence have been previously addressed, while the data in Table I provide an opportunity to scrutinize the effect of dmCh (vs Cp) on CO stretching frequencies. For species possessing several electron-withdrawing carbonyls, such as [Mp′]$^-$, Mp′I, [Mp′]$_2$Hg, and Mp′$_2$ (Mp′ = (dienyl)Mo(CO)$_3$), dmCh donates more electron density to each metal center than Cp, and hence the ν(CO) bands of **1**–**4** are slightly lower in energy than their counterparts. In contrast, when fewer carbonyls are present, as in (dienyl)Mo(CO)(NO)PR$_3$, or when the metal center is more electron rich due to multiple metal–metal bonding, as in [(dienyl)Mo(CO)$_2$]$_2$, the dmCh ligand can accept a greater amount of electron density than Cp, and hence the carbonyl stretches for these complexes (**5**, **7**, and **9**) are higher in energy. The contention that dmCh is a "softer" ligand[40] is borne out by these observations, which show how the ligand can compensate for variations in electron density at the Mo center by behaving in an electronically amphoteric fashion. Although the properties of the dmCh ligand are not as dramatically manifested by this molybdenum system relative to previously prepared (dmCh)$_2$M complexes, the data consistently portray the dienyl as a strong-field, yet ancillary ligand.

Experimental Section

General Considerations. All manipulations were performed using either glovebox or high-vacuum line techniques. Ethereal and hydrocarbon solvents were distilled from purple benzophenone ketyl and vacuum transferred from same prior to use. CH$_2$Cl$_2$ was similarly dried over P$_2$O$_5$. Benzene-d_6, toluene-d_8, CD$_2$Cl$_2$, and THF-d_8 were dried over activated 4-Å molecular sieves, vacuum transferred, and stored over N$_2$. Mo(CO)$_6$ was purchased from Climax, Diazald (*N*-nitroso-*p*-toluenesulfonamide) from Aldrich, and HgI$_2$ from Mallinckrodt; each was used without further purification. [Cp$_2$Fe]PF$_6$,[51] (diglyme)Mo(CO)$_3$,[11] and (dmCh)K[9] were prepared by using published procedures.

NMR spectra were recorded on Varian XL-200 and XL-400 instruments and referenced to TMS (^{1}H, ^{13}C{^{1}H}, δ 0.0) or external P(OMe)$_3$ (^{31}P{^{1}H}, δ 140.4). Monitoring of reactions by NMR was carried out using sealed tubes as in procedures 8 and 9. Infrared spectra were obtained on a Mattson FT-IR spectrometer interfaced to a AT&T PC7300 computer. Elemental analyses were conducted by Analytische Laboratorien, Elbach, West Germany.

Procedures. 1. [(dmCh)Mo(CO)$_3$]K(diglyme)$_n$ (1). To a mixture of (diglyme)Mo(CO)$_3$ (1.080 g, 3.44 mmol) and K(dmCh) (0.503 g, 3.44 mmol) at –78 °C was added 40 mL of THF. The resulting slurry was stirred 4 h, allowed to warm to 25 °C, and stirred an additional 2 h. The resulting brown solution was filtered and reduced to 5 mL, and 15 mL of hexane added. Rapid stirring of the resulting two phases effected the dispersal of a tan solid. Filtration and washing with Et$_2$O provided 1.247 g (85%) of **1** (n = 0.74 by ^{1}H NMR). Anal. Calcd for C$_{15.44}$H$_{21.36}$O$_{5.22}$KMo: C, 43.58; H, 5.06. Found: C, 43.27; H, 4.90.

2. (dmCh)Mo(CO)$_3$I (2). Method a. To a slurry of **1** (536 mg, 1.26 mmol) in 10 mL of THF at –78 °C was added a solution of I$_2$ (0.0504 M; 1.26 mmol, 25 mL THF). The reaction mixture was stirred 2 h, warmed to 25 °C, and stirred an additional hour. The THF was removed, 35 mL of hexane was added, and the solution filtered to give a dark red–brown filtrate. Crystallization from hexane gave 52 mg (10%) of red–orange **2**. **Method b.** To a solution of [(dmCh)Mo(CO)$_3$]$_2$Hg (**3**, 876 mg, 1.13 mmol) in CH$_2$Cl$_2$ at 0 °C was added a solution of I$_2$ (0.12 M, CH$_2$Cl$_2$; 2.4 mmol, 20 mL) over 1 min. The mixture was stirred 1 h, warmed to 25 °C, and stirred an additional 12 h. The CH$_2$Cl$_2$ was removed, 20 mL of hexane added, and the solution filtered. Crystallization from hexane provided 152 mg (65%) of **2**: ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 29.19, 39.05 (Me), 36.43 (CMe$_2$) 83.96 (C$_{c,c'}$), 90.73 (C$_a$), 100.48

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($C_{b,b'}$), 215.83 (CO). Anal. Calcd for $C_{11}H_{11}O_3MoI$: C, 31.91; H, 2.68. Found: C, 31.82; H, 2.79.

3. [(dmCh)Mo(CO)$_3$]$_2$Hg (3). To a mixture of 1 (1.19 g, 2.79 mmol) and HgI_2 (634 mg, 1.39 mmol) at −78 °C was added 35 mL of THF. After 5 min, the solution was warmed to 0 °C and stirred an additional 3 h. Removal of THF, addition of 10 mL of benzene, filtration, and addition of 20 mL of hexane provided yellow 3 (832 mg, 77%) as a light- and temperature-sensitive powder.

4. [(dmCh)Mo(CO)$_3$]$_2$ (4). To a solution of 1 (974 mg, 2.29 mmol) in 25 mL of THF at −78 °C was added [Cp_2Fe]PF_6 (741 mg, 2.24 mmol) from a solid addition funnel. The resulting deep green slurry was rapidly stirred, warmed to 0 °C over 30 min, and allowed to warm to 25 °C. After THF was removed and 30 mL of benzene added, the solution was filtered, and the volatiles were pumped off to yield orange–brown and purple crystals. Ferrocene (363 mg, 87%) was removed via sublimation, and the residue crystallized from toluene/pentane to yield 375 mg (57%) of purple 4. When dissolved or pulverized, 4 appears dark green. Similar results may be obtained by using [Cp_2Fe]BPh_4 as the oxidant; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 29.26, 34.36 (Me), 73.19 ($C_{c,c'}$), 99.17 ($C_{b,b'}$), 98.88 (C_a), 223.65 (CO), *C*Me$_2$ unobserved. Anal. Calcd for $C_{22}H_{22}O_6Mo_2$: C, 46.01; H, 3.86. Found: C, 46.10; H, 3.97.

5. [(dmCh)Mo(CO)$_2$]$_2$ (5). A sample of 4 (365 mg, 0.64 mmol) was transferred to a 200-mL glass bomb reactor fitted with a needle valve adapter, and 25 mL of hexane was added. The solution was degassed and immersed in a 90 °C bath for 4 days. The solution was then periodically degassed while hot (~6 times) and further degassed upon cooling, resulting in a red solution. Filtration and crystallization at −78 °C afforded 265 mg (80%) of brick-red 5: $^{13}C\{^1H\}$ NMR (C_6D_6) δ 29.76, 34.91 (Me), 67.82 ($C_{c,c'}$), 93.28 (C_a), 104.12 ($C_{b,b'}$), 235.0 (CO), *C*Me$_2$ unobserved. Anal. Calcd for $C_{20}H_{22}O_4Mo_2$: C, 46.35; H, 4.28. Found: C, 46.23; H, 4.42.

6. (dmCh)Mo(CO)$_2$NO (6). To a slurry of 1 (296 mg, 0.695 mmol) in Et_2O at −78 °C was added an ethereal solution of Diazald (0.035 M; 20 mL, 0.70 mmol). The reaction mixture was warmed and allowed to stir at 25 °C for 20 h. Removal of Et_2O followed by hexane extraction and evaporation of solvent left a volatile yellow solid. Sublimation (25 °C, 10^{-4} Torr) yielded 98 mg (49%) of crystalline 6. Anal. Calcd. for $C_{10}H_{11}NO_3Mo$: C, 41.54; H, 3.83. Found: C, 41.57; H, 3.83.

7. (dmCh)Mo(CO)(NO)PPh$_3$ (7). Triphenylphosphine (46 mg, 0.18 mmol) and 6 (51 mg, 0.18 mmol) were dissolved in 10 mL of toluene and heated to reflux for 16 h. Cooling of the solution to 0 °C provided 28 mg (30%) of red, crystalline 7: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 49.4 (s). Anal. Calcd for $C_{27}H_{26}NO_2PMo$: C, 61.96; H, 5.01. Found: C, 61.89; H, 5.15.

8. (η^1-dmCh)Mo(CO)$_2$(NO)(PMe$_3$)$_2$ (8). To an NMR tube fitted with a ground-glass joint attached to a needle valve adapter was added 17 mg (0.058 mmol) of 6 and 0.4 mL of CD_2Cl_2. The tube was evacuated and cooled to 77 K, and PMe_3 (0.12 mmol) was admitted via a gas bulb. Upon slowly warming to −20 °C over 30 min, resonances attributable to 8 were noted by ^1H NMR (CD_2Cl_2, −20 °C): δ 0.985 (s, Me, 3 H), 0.990 (s, Me, 3 H), 1.51 ($AX_9A'X'_9$, PMe_3, 18 H, $|J_{PH} + J_{PH'}|$ = 6.9 Hz), 4.63 (dd, $H_{c,c'}$, 2 H, *J* = 9.7, 0.7 Hz), 5.68 (dd, $H_{b,b'}$, 2 H, *J* = 9.7, 4.5 Hz), 5.68 (m, H_a(tentative)); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ −24.4.

9. (dmCh)Mo(CO)(NO)(PMe$_3$) (9). To an NMR tube fitted with a ground-glass joint attached to a needle valve adapter was added 17 mg (0.058 mmol) of 6 and 0.4 mL of C_6D_6. The tube was evacuated and cooled to 77 K, and PMe_3 (0.058 mmol) was admitted via a gas bulb. After the tube was sealed with a torch and allowed to stand for 1 h at 25 °C, quantitative conversion to orange (dmCh)Mo(CO)(NO)PMe$_3$ (9) was noted. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −0.48 (s).

Electrochemical Studies of 1 and 4. Electrochemical measurements were recorded using a BAC-CV-27 instrument and Soltec 6423S *X–Y* recorder. Reference electrodes consisted of a cracked-bead outer shell containing a silver wire immersed in a saturated solution of $AgCl/Me_4NCl$ in THF. Cyclic voltammograms were recorded in a single-compartment cell, using either a 0.02- or 0.03-in. Pt disk working electrode and a 0.03-in. Pt wire auxiliary electrode.

Starting with either 1 or 4, the [Mo] was ~1 mM in THF with ~0.1 M [^{n}Bu$_4$N]BF_4 as a supporting electrolyte. The working electrode was a 0.3-in. Pt wire, and the reference electrode was either Ag/AgCl or a Ag wire pseudoreference. Calibration: $Cp_2Fe^{+/0}$ is +0.82 V vs Ag/AgCl/THF/25 °C; $Cp_2Fe^{+/0}$ is +0.84 V vs Ag wire/THF/25 °C. The $Cp_2Fe^{+/0}$ couple is defined as 0.31 V vs saturated calomel electrode in nonaqueous solvents at 25 °C.[51]

Table IV. Fractional Coordinates and Thermal Parameters[a] for [(dmCh)Mo(CO)$_2$]$_2$ (5)

atom	*x*	*y*	*z*	*B*(iso), Å^2
Mo	0.71722 (4)	0.18269 (5)	0.79841 (2)	2.37 (1)
Mo′	0.86085 (3)	−0.01873 (5)	0.76300 (3)	2.48 (1)
O1	1.0428 (5)	0.3473 (6)	0.8978 (4)	4.9 (1)
O2	0.7492 (9)	0.3043 (8)	0.5762 (5)	7.1 (2)
O1′	0.6383 (6)	−0.1778 (6)	0.8823 (5)	5.2 (2)
O2′	0.6163 (8)	−0.1175 (9)	0.5416 (5)	7.8 (2)
C1	0.4978 (7)	0.3919 (8)	0.7742 (5)	3.7 (2)
C2	0.6554 (6)	0.4262 (7)	0.8507 (5)	3.3 (2)
C3	0.6846 (7)	0.3437 (8)	0.9405 (5)	3.6 (2)
C4	0.6005 (7)	0.1893 (8)	0.9374 (5)	3.6 (2)
C5	0.4924 (7)	0.1227 (7)	0.8365 (6)	3.7 (2)
C6	0.4660 (6)	0.2131 (8)	0.7500 (5)	3.6 (2)
C7	0.3918 (8)	0.4456 (9)	0.8335 (7)	4.6 (2)
C8	0.4898 (9)	0.4754 (9)	0.6690 (6)	5.1 (2)
C9	0.9268 (7)	0.2742 (7)	0.8604 (5)	3.5 (2)
C10	0.7373 (9)	0.2590 (9)	0.6556 (6)	4.5 (2)
C1′	1.0186 (7)	−0.2222 (8)	0.6567 (5)	3.7 (2)
C2′	0.9331 (7)	−0.2688 (8)	0.7398 (5)	3.9 (2)
C3′	0.9901 (9)	−0.1997 (9)	0.8471 (5)	4.7 (2)
C4′	1.0805 (8)	−0.0512 (11)	0.8701 (6)	5.2 (2)
C5′	1.1109 (7)	0.0297 (8)	0.7813 (7)	4.4 (2)
C6′	1.0513 (8)	−0.0455 (8)	0.6728 (6)	4.2 (2)
C7′	1.1611 (10)	−0.2852 (11)	0.6811 (7)	5.7 (3)
C8′	0.9290 (10)	−0.2874 (10)	0.5386 (6)	5.1 (2)
C9′	0.7159 (7)	−0.1052 (7)	0.8387 (5)	3.4 (2)
C10′	0.7021 (9)	−0.0804 (9)	0.6205 (6)	5.0 (2)

[a] From the anisotropic thermal parameters in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; the *B* (isotropic equivalent) values are derived by $B(\text{iso}) = 4.0[V^2 \det(B_{ij})]^{1/3}$.

Single-Crystal X-ray Diffraction Analysis of [(dmCh)Mo(CO)$_2$]$_2$ (5). A truncated cylinder (0.12 × 0.15 × 0.35 mm) of [(dmCh)Mo(CO)$_2$]$_2$ (5), obtained via hexane evaporation, was sealed in a Lindemann capillary. Preliminary X-ray diffraction photographs displayed triclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer-measured 2θ values at 25 °C, were *a* = 9.654 (1) Å, *b* = 8.658 (1) Å, *c* = 12.608 (2) Å, α = 93.44 (1)°, β = 104.80 (1)°, γ = 100.79 (1)°. The cell volume was 994.88 (22) Å^3, with a calculated density of 1.730 g/cm^3, where *Z* = 2. The space group was determined to be $P\bar{1}$, and the asymmetric unit consisted of $C_{20}H_{22}O_4Mo_2$. All unique diffraction maxima (*h,k,l*) with 2θ ≤ 114° were measured on a four-circle automated diffractometer, with a variable-speed, 1° ω scan (0.1–30°/min) using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at 25 °C. After correction for Lorentz polarization and background effects, 2518 (93.7%) of the unique data (2997) were judged observed ($|F_o| \geq 3\sigma|F_o|$).[52] The structural solution using the heavy-atom method positioned the Mo atoms (two cycles, *R* = 0.25), and non-hydrogen light atoms were revealed by successive Fourier syntheses. Standard block-diagonal least-squares refinements converged to a residual (*R*) of 0.106. Included in this refinement were all non-hydrogen atoms; the H atomic positions were generated from assumed geometries and were not refined. At the end of this isotropic refinement, an empirical absorption correction (after Walker and Stuart)[53] was applied, dropping *R* to 0.069. The minimum, maximum, and average absorption corrections were 0.816, 1.874, and 1.025. A final difference Fourier map revealed no peaks greater than 0.31 e$^-$/Å^3. For 2518 observed reflections, the final residuals were *R* = 0.049 and (R_w) = 0.036, with GOF = 1.163.[54] Fractional coordinates and thermal parameters for 5 are given in Table IV.

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

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Registry No. 1, 125520-06-1; 2, 125520-07-2; 3, 125520-08-3; 4, 125520-09-4; 5, 125520-10-7; 6, 125520-11-8; 7, 125520-12-9; 8, 125520-13-0; 9, 125520-14-1; (diglyme)Mo(CO)$_3$, 18177-90-7; K(dmCh), 82360-21-2; HgI$_2$, 7774-29-0; [Cp$_2$Fe]PF$_6$, 11077-24-0; [Cp$_2$Fe]BPh$_4$, 11057-46-8; ferrocene, 102-54-5; Diazald, 80-11-5.

Supplementary Material Available: Information pertaining to the X-ray structural investigation of [(dmCh)Mo(CO)$_2$]$_2$ (**5**): a summary of crystal data encompassing data collection and solution/refinement and listings of atomic coordinates, hydrogen atom coordinates, isotropic and anisotropic temperature factors, bond lengths, and bond angles (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Reactions of Alkynes with Coordinatively Unsaturated (η^5-C$_5$Me$_5$)Ru Derivatives. X-ray Crystal Structures of (η^5-C$_5$Me$_5$)Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)Ru(η^5-C$_5$Me$_5$) and (η^5-C$_5$Me$_5$)$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC$\equiv$CSiMe$_3$)

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Reaction of acetylene with Cp*Ru(P^{i}Pr$_3$)Cl or [Cp*Ru(μ_3-Cl)]$_4$ (Cp* = η^5-C$_5$Me$_5$) gives good yields of the dinuclear ruthenacyclopentadiene complex Cp*Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**1**). Compound **1** crystallizes in space group $P\bar{1}$, with a = 8.673 (6) Å, b = 9.632 (7) Å, c = 16.17 (1) Å, α = 96.72 (4)°, β = 92.39 (4)°, γ = 95.95 (4)°, V = 1332 (2) Å^3, Z = 2, R_F = 4.42%, and R_{wF} = 6.53%. Alkylation of **1** with MeMgBr affords the dimethyl complex Cp*Me$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**2**). Reaction of [Cp*Ru(μ_3-Cl)]$_4$ with 8 equiv of Me$_3$SiC$\equiv$CH produces the cyclobutadiene complex Cp*Ru[η^4-C$_4$H$_2$(SiMe$_3$)$_2$]Cl (**3**) as the major product (67% yield). A minor product in this reaction, formed in 5% yield, is a ruthenacyclopentadiene complex analogous to **1**, Cp*Cl$_2$Ru[η^2:η^4-μ_2-C$_4$H$_2$(SiMe$_3$)$_2$]RuCp* (**4**). This species was characterized in solution by NMR spectroscopy. If [Cp*Ru(μ_3-Cl)]$_4$ is allowed to react with a limited amount of Me$_3$SiC$\equiv$CH (ca. 1 equiv), a triruthenium cluster containing one alkyne ligand may be isolated in high yield. This compound, Cp*$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC$\equiv$CSiMe$_3$) (**5**), is unstable in solution but was characterized in the solid state by X-ray crystallography. Compound **5** crystallizes in space group $P2_1/n$, with a = 12.568 (6) Å, b = 17.195 (9) Å, c = 18.307 (9) Å, β = 96.46 (3)°, V = 3931 (3) Å^3, Z = 4, R_F = 4.21%, and R_{wF} = 6.74%. Finally, [Cp*Ru(μ_3-Cl)]$_4$ and dimethyl acetylenedicarboxylate (DMAD) react to give a diruthenium complex containing DMAD and C$_6$(CO$_2$Me)$_6$ ligands, Cp*$_2$Ru$_2$Cl$_2$(MeO$_2$CC$\equiv$CCO$_2$Me)[C$_6$(CO$_2$Me)$_6$] (**6**). Possible structures for this species are discussed.

Introduction

It is well established that coordinatively unsaturated transition-metal species have a rich reaction chemistry with alkynes.[1] We have been investigating coordinatively unsaturated Cp*Ru (Cp* = η^5-C$_5$Me$_5$) species, particulary with respect to (1) eliminations in organosilicon ligands[2] and (2) the chemistry of alkoxide derivatives.[3] Convenient starting points for these studies are the 16-electron complexes Cp*Ru(PR$_3$)Cl (R = Cy, ^{i}Pr)[4] and the labile cluster [Cp*Ru(μ_3-Cl)]$_4$,[5] which serve as synthetic equivalents for the 14-electron fragment Cp*RuCl. As part of a survey of the reaction chemistry of these starting materials, we have investigated their reactions with alkynes. As expected, Cp*Ru(P^{i}Pr$_3$)Cl and [Cp*Ru(μ_3-Cl)]$_4$ are quite reactive toward alkynes, and a number of different reaction products can be observed. In this paper we report the synthesis and characterization of dinuclear ruthenacyclopentadiene complexes Cp*X$_2$Ru(η^2:η^4-μ_2-CRCHCRCH)RuCp* (X = Cl, R = H (**1**); X = Me, R = H (**2**); X = Cl, R = SiMe$_3$ (**4**)), a cyclobutadiene complex, Cp*Ru[η^4-C$_4$H$_2$(SiMe$_3$)$_2$]Cl (**3**), a triruthenium cluster with a bridging alkyne, Cp*$_3$Ru$_3$(μ_2-Cl)$_2$(μ_3-Cl)(η^2-μ_2-HC$\equiv$CSiMe$_3$) (**5**), and a dinuclear arene complex, Cp*$_2$Ru$_2$Cl$_2$(MeO$_2$CC$\equiv$CCO$_2$Me)[C$_6$(CO$_2$Me)$_6$] (**6**).

Results

Blue toluene solutions of the coordinatively unsaturated complex Cp*Ru(P^{i}Pr$_3$)Cl[4] rapidly turn red when pressurized with acetylene (15 psi) at room temperature. Workup of the reaction mixture results in isolation of the metallacyclopentadiene complex Cp*Cl$_2$Ru(η^2:η^4-μ_2-C$_4$H$_4$)RuCp* (**1**), which crystallizes from toluene as red prisms. Compound **1** was characterized spectroscopically and by X-ray crystallography (vide infra). The lability of

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