Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compound	$(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$	$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$	$(\eta^5\text{-}C_5Me_5)_2Hf(CO)_2$
mol wt	374.4	417.7	505.0
space group	$P2_12_12_1$	$Fmm2$	$Fmm2$
cell constant, a, Å	8.517 (3)	15.137 (4)	15.135 (4)
b, Å	10.774 (4)	16.860 (4)	16.807 (4)
c, Å	22.195 (6)	8.280 (3)	8.268 (3)
cell vol, Å^3	2036.7	2113.1	2103.2
molecules/unit cell	4	4	4
ρ(calcd), g cm^{-3}	1.22	1.31	1.59
μ(calcd), cm^{-1}	4.49	5.23	52.23
radiation	Mo Kα	Mo Kα	Mo Kα
max crystal dimensions, mm	0.75 × 0.40 × 1.50	0.10 × 0.10 × 1.80	0.10 × 0.20 × 1.50
scan width	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$	$0.80 + 0.20 \tan\theta$
standard reflections	400 008	400 060	400 060
decay of standards	±2%	±2%	±2%
reflections measured	2176	548	546
2θ range	50°	50°	50°
obsd reflections	1366	507	544
no. of parameters varied	226	64	64
GOF	1.15	1.09	1.31
R	0.040	0.030	0.032
R_w	0.045	0.034	0.037

and **6**, respectively. In particular, it is noteworthy that the carbonyl stretching frequencies for both the A_1 and B_1 modes of **1**, **2**, and **3** are shifted to ca. 29-41-cm^{-1} lower energy relative to corresponding values for **4**, **5**, and **6**. These shifts are approximately those predicted[28] for the introduction of 10 methyl substituents onto the cyclopentadienyl rings of **4**-**6**, and can be attributed to enhanced π backbonding to the CO ligands as a result of increased electron density on the metal atom caused by the methyl groups. Analogous trends in the case of titanium complexes **1** and **4** have also been observed by Brintzinger and co-workers.[1]

Attempts to promote substitution of the carbonyl ligands in **1**-**3** by phosphines and phosphites under both thermal and photochemical conditions have thus far proved to be largely unsuccessful, in contrast to the cyclopentadienyl analogues **4**-**6**.[16] The results are consistent with enhanced thermal and photochemical stabilities of the permethylated complexes **1**-**3** relative to their cyclopentadienyl counterparts.[29] Further studies concerning the reactivities of **1**-**3** are in progress.

The crystal data for all three compounds and a summary of the refinement parameters are presented in Table II. In each case the hydrogen atoms were included, and all nonhydrogen atoms were refined with anisotropic temperature factors. For the hafnium structure the intensities were corrected for absorption effects.[30]

The molecular structures and atom-numbering schemes for the three compounds are shown in Figure 1. For titanium the molecule contains no crystallographically imposed symmetry, whereas the zirconium and hafnium molecules are isostructural and each metal atom resides on the intersection of two mirror planes. The average Ti-C(π) bond length, 2.384 (12) Å, is larger than the 2.35 (1) Å found in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$[15] despite the fact that the pentamethylcyclopentadienyl ligand is more electron rich. The lengthening is doubtless due to nonbonded methyl-methyl repulsion. This is also evidenced by the fact that the methyl carbon atoms reside 0.2 Å out of the plane of the ring atoms. The average Ti-C(σ) bond distance, 2.01 (1) Å, is shorter than the 2.03 (1) Å value found in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$,[15] as might be expected from the longer ring approach with $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$.

The three unique Zr-C(π) lengths average 2.498 (9) Å compared to 2.48 (1) Å in $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$.[31] However, the Zr-C($\sigma$) bond is much shorter in the title compound: 2.145 (9) Å vs. 2.187 (4) Å in the $\eta^5\text{-}C_5H_5$ complex. Following this trend the Hf-C(σ) distance, 2.14 (2) Å, is marginally shorter than the 2.16(2) Å found in $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$.

Acknowledgment. We are grateful to the National Science Foundation for support of this research program.

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[28] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287-297.

[29] For example, when **3** was photolyzed in C_6D_6 solution for 55 h, starting material was still observed to be present. In contrast, **6** when photolyzed under analogous conditions is completely consumed in 3-4 h.[16]

[30] The method of data collection and computer library have been described previously: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc. Dalton Trans.* **1979**, 46-53.

[31] Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812-3817.

Transformation of Coordinatively Unsaturated η^1-Vinylmolybdenum Complexes into Three-Electron η^2-Bonded Cyclic Alkylidene Species

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In an elegant series of investigations Bercaw and co-workers were led to postulate[1] a facile rearrangement of coordinatively unsaturated zirconium η^1-acyl complexes into three-electron η^2-bonded zirconium oxycarbene species, which were unstable and underwent further reactions. A driving force for this interesting rearrangement was considered to be the stability of the zirconium-oxygen bond. Recently a similar "switch" in bonding mode has been reported[2] with acylbis(pentamethylcyclopentadienyl)-thorium complexes. In this paper we report that coordinatively unsaturated vinylmolybdenum complexes can undergo a related transformation into stable three-electron η^2-bonded cyclic alkylidene complexes.

Reaction (-78 °C) of a purple tetrahydrofuran solution of bis(trimethyl phosphite)diphenylacetylene(η^5-cyclopentadienyl)-molybdenum tetrafluoroborate[3] with 1 molar equiv of potassium selectride [KBH(*sec*-Bu)$_3$] led to a rapid reaction and the formation of the green crystalline (from tetrahydrofuran at -30 °C) complex **1** [^{1}H NMR (CD_2Cl_2) τ 2.4-3.4 (m, 10 H, Ph), 4.76 (s, 5 H, C_5H_5), 6.17 (dd, 1 H, MoC*H*Ph, $^3J_{\text{trans-PH}} = 13$ Hz, $^3J_{\text{cis-PH}} = 6$ Hz), 6.66 (d, 9 H, PO*Me*, $^3J_{PH} = 11.5$ Hz), 6.76 (d, 9 H, PO*Me*, $^3J_{PH} = 11.5$ Hz); ^{31}P (CD_2Cl_2, ^{1}H decoupled) AB system δ_A 164.7, δ_B 158.1 $J_{PP} = 155$ Hz; ^{13}C (CD_2Cl_2, ^{1}H decoupled) δ 255.5 (d, alkylidene carbon, $^2J_{PC} = 40$ Hz), 157.1, 143.9, 130.9, 128.2, 126.8, 126.3, 121.1 (Ph), 91.4 (C_5H_5), 51.9, 51.7, 51.4, 51.1, 26.8 (d, MoCHPh, $^2J_{PC} = 30$ Hz)]. Elemental analysis and mass

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[1] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121-127.

[2] Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112-7114.

[3] Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365-2371.

0002-7863/81/1503-1267$01.25/0

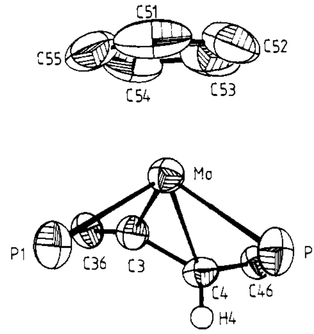


Figure 1. View of complex **1** with substituents omitted for clarity.

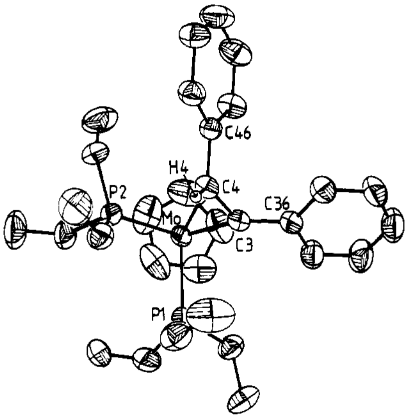


Figure 2. Molecular structure of **1**. Pertinent molecular parameters include Mo–P(1) = 2.340 (1), Mo–P(2) = 2.326 (1), Mo–C(3) = 1.950 (3), Mo–C(4) = 2.300 (3), Mo–C(51) = 2.347 (4), Mo–C (52) = 2.386 (4), Mo–C(53) = 2.376 (3), Mo–C(54) = 2.345 (4), Mo–C(55) = 2.338 (4), C(4)–C(3) = 1.434 (4), C(4)–H(4) = 0.854 (24), C(4)–C(46) = 1.482 (4), C(3)–C(36) = 1.457 (4) Å; P(1)–Mo–P(2) = 91.4 (0.1), P(1)–Mo–C(3) = 87.2 (0.1), P(1)–Mo–C(4) = 99.5 (0.1), P(2)–Mo–C(3) = 109.6 (0.1), P(2)–Mo–C(4) = 73.1 (0.1), C(3)–Mo–C(4) = 38.3(0.1), Mo–C(3)–C(4) = 84.1 (0.2), Mo–C(3)–C(36) = 144.1 (0.2), C(4)–C(3)–C(36) = 129.8 (0.3), Mo–C(4)–C(3) = 57.5 (0.1), Mo–C(4)–H(4) = 113.9 (1.9), Mo–C(4)–C(46) = 123.8 (0.2), C(3)–C(4)–H(4) = 120.3 (1.7), C(3)–C(4)–C(46) = 122.5 (0.2), H(4)–C(4)–C(46) = 110.0 (1.9)°.

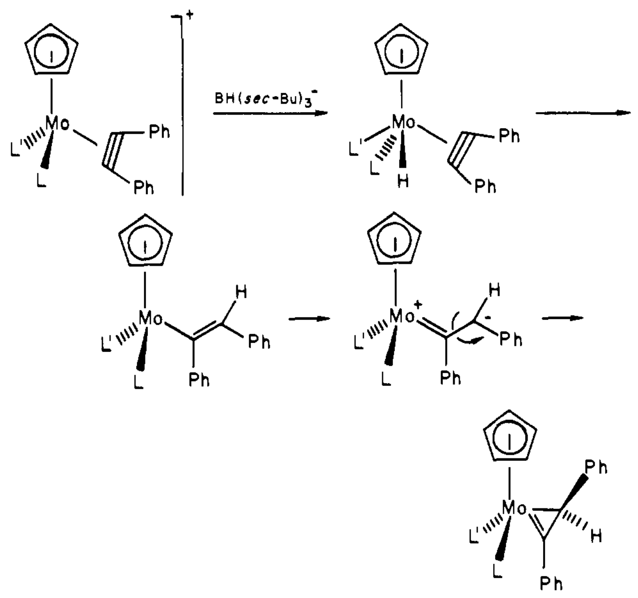
spectroscopy showed that **1** had the molecular formula [Mo(CHPhCPh)[P(OMe)$_3$]$_2$(η^5-C_5H_5)]. In order to confirm the indications from the NMR spectra that **1** was an alkylidene complex, a single-crystal X-ray diffraction study was undertaken.

Crystal data for (1): $C_{25}H_{34}O_6P_2Mo$, M = 588.1, monoclinic, space group $P2_1/c$, a = 12.258 (3), b = 13.123 (2), c = 17.000 (4) Å; β = 103.26°; U = 2 661 (1) Å^3; Z = 4; $F(000)$ = 1216 electrons, μ(Mo K$\bar{\alpha}$) = 6.3 cm^{-1}.

Of a total of 4213 independent reflection intensities measured (Syntex R3m diffractometer, Mo Kα radiation, $\bar{\lambda}$ = 0.710 69 Å) to $2\theta_{max}$ = 55°, 3966 [$I > 2.0\sigma(I)$] were used to solve (Patterson and difference Fourier techniques) and refine[4] (full matrix blocks, blocked cascade method) the structure to R = 0.028 and R_w = 0.029.

The two views of the molecule illustrated in Figures 1 and 2 show that **1** is an alkylidene complex containing the unusual three-electron η^2-bonded system Mo═CPhCHPh where the molybdenum is in a distorted square-pyramidal environment with angles P(1)–Mo–P(2) = 91.4 (1) and C(4)–Mo–C(3) = 38.3(1)°. The molybdenum is not bonded symmetrically to all five carbon atoms of the cyclopentadienyl ligand as indicated by a Mo–C range of 2.338 (4)–2.386 (4) Å. Comparison of the Mo–C(3) bond length of 1.950 (3) Å with that calculated from the covalent radii (Mo–C = 2.07 Å) for a single molybdenum carbon bond indicates substantial double character consistent with its formulation as an alkylidene system, whereas the rather long single bond Mo–C(4) at 2.300 (3) Å shows the presence of strain in the three-membered ring. The ^{13}C chemical shift of C(4) is in the region normally associated with saturated carbon, whereas C(3) is typical of an alkylidene carbon. This difference is also reflected by the overall geometry of the CPhCHPh fragment as illustrated by the parameters listed in Figure 1, the asymmetry being reflected in the relative magnitude of the distances Mo–P(2) = 2.326(1) and Mo–P(1) = 2.340 (1) Å.

Scheme I



1, L = L = P(OMe)$_3$
2, L = CO; L' = PMe$_2$Ph

It is interesting that the reaction leading to **1** is regioselective, forming only the isomer with the phenyl group on the saturated carbon C(4) pointing toward the cyclopentadienyl ligand; examination of the NMR spectrum of the reaction mixture showed the presence of only one isomer.

A similar reaction between potassium selectride and the unsymmetrical cation [Mo(CO)(PMe$_2$Ph)(PhC$_2$Ph)(η^5-C_5H_5)]BF$_4$[5] afforded the less stable though still isolable green crystalline complex **2** [^{1}H NMR (CD_2Cl_2) τ 2.6–3.4 (m, 15 H, Ph), 4.59 (s, 5 H, C_5H_5), 6.32 (d, 1 H, MoC*HPh*, $^2J_{PH}$ = 3 Hz), 8.47 (d, 6 H, P*Me*, $^2J_{PH}$ = 8 Hz)]. If it is assumed that $^2J_{trans\text{-}PH} > {}^2J_{cis\text{-}PH}$, then the presence of a ^{31}P–^1H coupling of 3 Hz on the MoC*HPh* proton suggests that the dimethylphenylphosphine ligand is trans to the alkylidene carbon present in **2**.

We have previously[6] shown that reaction of NaBH$_4$ or potassium selectride with [Mo[P(OMe)$_3$]$_2$(t-BuC$_2$H)(η^5-C_5H_5)]BF$_4$ in the presence of trimethyl phosphite affords the stable σ-vinyl complex [Mo(*trans*-CH═CH-*t*-Bu)[P(OMe)$_3$]$_3$(η^5-C_5H_5)], the corresponding reaction with NaBD$_4$ giving MoCH═CD-*t*-Bu. In view of this we suggest that in the formation of **1** an initially formed molybdenum hydride undergoes an "insertion" reaction to give a coordinatively *unsaturated* σ-vinyl species (Scheme I). While in the case of the reaction with the 3,3-dimethylbut-1-yne containing cation an additional molecule of trimethyl phosphite was available to occupy the coordination site created by the "insertion" of the acetylene into a Mo–H bond, this pathway to a stable species was not available with the diphenylacetylene system. We suggest that the σ-vinyl group Mo(*cis*-CPh═CHPh) accommodates itself to this situation by back-bonding with the molybdenum, thus allowing rotation about the carbon–carbon bond of the vinyl group and achieving the conformation required to allow

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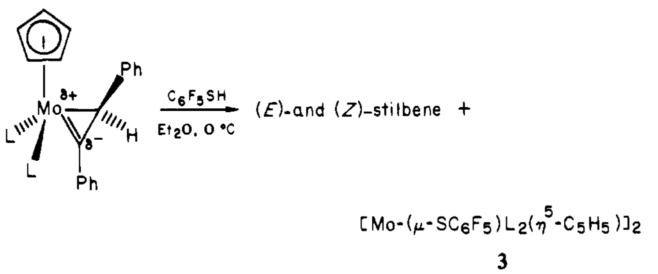
(4) Sheldrick, G. M. SHELXTL structure analysis system, Göttingen, Federal Republic of Germany, 1980.

(5) Prepared by reaction (CH_2Cl_2, room temperature) of the cation[3] [Mo(CO)(PhC$_2$Ph)$_2$(η^5-C_5H_5)]BF$_4$ with dimethylphenylphosphine: Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Muir, Lj. M.; Muir, K. W. *J. Chem. Soc., Dalton Trans.*, in press.

(6) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795–5796.

Scheme II



$L = P(OMe)_3$

collapse to the 18-electron cyclic alkylidene three-electron η^2-bonding mode.

An important question remaining is the polarity of the molybdenum carbon double bond present in these molecules. The complex **1** in diethyl ether reacted instantaneously at 0 °C with the weak acid C_6F_5SH to give a mixture of *cis*- and *trans*-stilbene and the dinuclear complex **3**[7] (Scheme II). This shows that the alkylidene carbon carries a partial negative charge as found by Schrock and his co-workers[8] for a number of tantalumalkylidene complexes.

Transition-metal-vinyl complexes have been implicated in a number of organometallic reactions, and the establishment of a pathway from coordinatively *unsaturated* σ-vinyl complexes to an unusual[9] strained cyclic alkylidene complex has a number of important implications.

Acknowledgment. We thank the S.R.C. for support.

Supplementary Material Available: Atomic positional and thermal parameters for complex **1** (6 pages). Ordering information is given on any current masthead page.

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[7] Satisfactory elemental analyses and IR and NMR spectra have been observed for this complex.

[8] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

[9] Recently (Davidson, J. L.; Shiratian, M.; Muir, Lj. M.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30–32) it has been reported that $[\overline{WC(O)C}(CF_3){=}\overline{C}(CF_3)SMe(CO)_2(\eta^5\text{-}C_5H_5)]$ rearranges to $[\overline{W}C(CF_3){=}C(CF_3)\overline{C}(O)SMe(CO)_2(\eta^5\text{-}C_5H_5)]$ via a species $[\overline{WC(CF_3)C}(CF_3).C(O)SMe(CO)_2(\eta^5\text{-}C_5H_5)]$, which is structurally related to complexes **1** and **2**. However, these molecules carry strongly electron-withdrawing groups, and the rearrangement has been interpreted in terms of a 1,3 shift of a mercapto group. A more relevant comparison can be drawn with the interconversion of the η^1-ketenyl complex $[W[C(CO)R](CO)(PMe_3)_2(\eta^5\text{-}C_5H_5)]$, formed from reaction of the carbyne $[W{\equiv}CR(CO)_2(\eta^5\text{-}C_5H_5)]$ with PMe_3, into a η^2-ketenyl system $[W\{O{\cdots}C{\cdots}C{\cdots}R\}(CO)(PMe_3)(\eta^5\text{-}C_5H_5)]$ (Vedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376–3389). It could be argued that, whereas Kreissl's complex is a metalacyclopropenone, the complexes **1** and **2** are metallacyclopropenes.

Linking of Four Acetylene Molecules at a Dimolybdenum Center and the Protonation of the Resulting Metallacyclononatetraene To Form a Cation Containing a Bridging MoHC System

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The reaction of acetylenes with transition-metal complexes has commanded the attention of organometallic chemists for a number of years. One of the principal reasons for this continued interest in the remarkable observation by Reppe and his co-workers that certain nickel complexes catalyze the conversion of acetylene into cyclooctatetraene.[1] Recently,[2,3] there have been indications that this catalytic reaction might require two adjacent metal centers. While exploring the chemistry of the cationic complex bis(but-2-yne)carbonyl(η^5-cyclopentadienyl)molybdenum tetrafluoroborate,[4,5] we have observed an unusual cyclotetramerization reaction of coordinated but-2-yne.

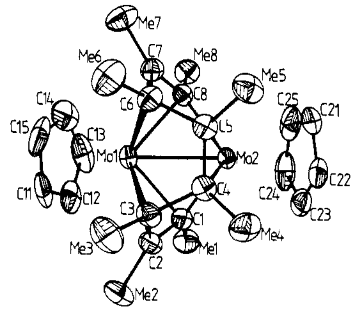

Figure 1. Drawing[19] of **2** showing 50% probabiity ellipsoids; all methyl and cyclopentadienyl hydrogens are omitted for clarity. Only the major (77.3%) orientation of the disordered cyclopentadienyl ring attached to Mo(1) is shown. Bond lengths: Mo(1)–C(1) = 2.237 (2), Mo(1)–C(2) = 2.346 (3), Mo(1)–C(3) = 2.313 (3), Mo(2)–C(4) = 2.234 (3), Mo(2)–C(5) = 2.231 (2), Mo(1)–C(6) = 2.317 (2), Mo(1)–C(7) = 2.348 (2), Mo(1)–C(8) = 2.234 (2), C(1)–C(2) = 1.412 (4), C(2)–C(3) = 1.427 (3), C(3)–C(4) = 1.507 (3), C(4)–C(5) = 1.439 (3), C(5)–C(6) = 1.509 (3), C(6)–C(7) = 1.434 (4), C(7)–C(8) = 1.412 (4) Å.

In refluxing acetonitrile the complex $[Mo(CO)(MeC_2Me)_2(\eta^5\text{-}C_5H_5)]BF_4$ loses one molecule of carbon monoxide to form $[Mo(NCMe)(MeC_2Me)_2(\eta^5\text{-}C_5H_5)]BF_4$ (**1**).[6,7] Electrochemical observations[8] showed that this cation readily and irreversibly accepted *one* electron. In seeking to find suitable chemical reagents capable of providing one electron, the reaction of **1** with sodium dicarbonylcyclopentadienyliron in tetrahydrofuran at room temperature was examined. A rapid reaction occurred affording $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ together with a purple crystalline dimolybdenum complex **2**. [^{1}H NMR (C_6D_6) τ 4.91 (s, 5 H, C_5H_5), 6.20 (s, 5 H, C_5H_5), 7.60 (s, 6 H, Me), 7.75 (s, 6 H, Me), 8.00 (s, 6 H, Me), 9.01 (s, 6 H, Me); ^{13}C (C_6D_6, ^{1}H decoupled) δ 174.3, 119.6, 97.4 (C_5H_5), 91.3 (C_5H_5), 71.0, 69.0, 33.0 (Me), 25.2 (Me), 22.0 (Me), 18.4 (Me)]. Elemental analyses and mass spectroscopy indicated that **2** had the molecular formula $[Mo_2(MeC_2Me)_4(\eta^5\text{-}C_5H_5)_2]$ in agreement with the NMR data. In order to define the structure a single-crystal X-ray diffraction study was undertaken.

Crystal Data for 2. $C_{26}H_{34}Mo_2$, $M = 537.9$, triclinic, space group $P\bar{1}$, $a = 8.449$ (1), $b = 10.114$ (2), $c = 14.872$ (3) Å; $\alpha = 86.66$ (2), $\beta = 80.88$ (1), $\gamma = 63.78$ (1)°; $U = 1125.6$ (4) Å^3; $Z = 2$; $D_c = 1.587$ g cm^{-3}; $F(000) = 2548$; μ(Mo Kα) = 11.0 cm^{-1}. Current $R = 0.0201$ ($R = 0.0199$)[9] for 4635 absorption-corrected, observed [$I > 3\sigma(I)$] intensities (Syntex P2$_1$ diffractometer) with $3° < 2\theta < 60°$ and weight $w = 1/\sigma^2(F_o)$. As shown in Figure 1, the molecule contains an octamethyl-substituted molybdenacyclononatetraene bonded to a second molybdenum atom. The C_8 chain begins and ends with σ bonds to Mo(2); atoms C(1),

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[1] Reppe, W; Schlichting, O; Klager, K; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1–92.

[2] Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677–690.

[3] Knox, S. A. R; Stansfield, R. F. D; Stone, F. G. A; Winter, M. J; Woodward P. *J. Chem. Soc., Chem. Commun.* **1978**, 221–223.

[4] Bottrill, M; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365–2371.

[5] Bottrill, M; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795–5796.

[6] Allen, S. R; Baker, P. K; Barnes, S. G; Green, M; Trollope, L; Muir, Lj. M; Muir, K. W. *J. Chem. Soc., Dalton Trans.*, in press.

[7] The formation of the corresponding hexafluorophosphate salt was described (Watson, P. L; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698–2703) during the preparation of this manuscript.

[8] Allen, S. R; Green, M; Norman, N. C., unpublished observations.

[9] The X-ray structures of **2** and **3** were solved by conventional heavy-atom Patterson and difference Fourier techniques and the nonhydrogen framework readily established for both. All hydrogen atoms in **2** except those on the disordered cyclopentadienyl group attached to Mo(1) were located and subsequently constrained to idealized geometries with C–H = 0.96 Å. In **3** all methyl and cyclopentadienyl hydrogens were likewise located and refined.