Synthesis of Bimetallic Complexes of Molybdenum Containing Bis(η^5-cyclopentadienyl)dimethylsilane or Bis(η^5-tetramethylcyclopentadienyl)dimethylsilane Bridges. Crystal Structure of $[\{Mo(CO)_3Cl\}_2\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2]$

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Received June 2, 1993[⊗]

Reaction of (arene)$Mo(CO)_3$ (arene = xylene, mesitylene) and $(C_5R_4H)_2SiMe_2$ in THF (THF = tetrahydrofuran) at room temperature gives the bimetallic complexes $[(Mo(CO)_3H)_2(\mu\text{-}(\eta^5\text{-}C_5R_4)_2SiMe_2)]$ (R = H (**2**), Me (**2***)). From **2** or **2***, other dimetallic complexes of molybdenum are obtained in high yields. Reaction of **2** with aqueous H_2O_2 leads to the dimeric carbonyl $[(Mo(CO)_3)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$(*Mo–Mo*) (**3**). Complex **2** reacts with NaH to give the anion $[(Mo(CO)_3)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]^{2-}$ isolated as its sodium (**4**) or tetrabutylammonium (**5**) salt. Reaction of **4** with *p*-$CH_3C_6H_4SO_2N(NO)CH_3$ (Diazald) leads to the nitrosyl derivative $[(Mo(CO)_2(NO))_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$ (**6**), whose oxidation with PCl_5, Br_2, or I_2 gives the halo complexes $[(MoX_2(NO))_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$ (X = Cl (**7**), Br (**8**), I (**9**)), respectively. Complexes **2** and **2*** are easily transformed into the halides $[(Mo(CO)_3Cl)_2(\mu\text{-}(\eta^5\text{-}C_5R_4)_2SiMe_2)]$ (R = H (**10**), Me (**10***)) when dissolved in CCl_4 and can be also oxidized by PCl_5 to the tetrahalides $[(MoCl_4)_2(\mu\text{-}(\eta^5\text{-}C_5R_4)_2SiMe_2)]$ (R = H (**11**), Me (**11***)). The variable-temperature ^1H NMR spectra of complexes **7**–**9** in solution support an 18e structure with two bridging and two terminal halides with fast interchange at room temperature (^1H NMR scale) between *cis* and *trans* isomers through a 16e intermediate. The solid-state structure of **10** has been determined by a single-crystal X-ray analysis. It crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in an unit cell of dimensions $a = 7.934(3)$ Å, $b = 12.305(3)$ Å, $c = 13.166(3)$ Å, $\alpha = 112.32(1)°$, $\beta = 105.48(1)°$, and $\gamma = 90.34(1)°$. The structure has been solved from diffractometer data by a combination of heavy atom, direct methods, and Fourier synthesis and refined by full-matrix least squares on the basis of the 4493 observed reflections to $R = 0.037$ and $R_w = 0.055$. The coordination around the molybdenum atoms is "four-legged piano stool", all the angles and distances having the usual values for this type of structure. The molybdenum atoms are *exo* with respect to the Cp–Si–Cp system, allowing the metals to be situated at a very long distance, 6.491 Å.

Introduction

Increasing attention has been paid to dinuclear metal complexes, due to the significant repercussion that the cooperative effect of both metal centers can have on their reactivity and catalytic applications. Bridged-cyclopentadienyl ligands such as $(C_5H_4)_2SiMe_2$[1] have been recently used as anchoring ligands for bringing two reactive metal centers in close proximity. We have reported the use of this ligand to isolate mononuclear metallocene-type[2] and dinuclear monocyclopentadienyl-[3] and metallocene-type[4] group 4 metal complexes. The synthesis of the molybdenum complexes **3**, **4**, and **10** (Scheme I) and their tungsten analogues has been previously reported,[5–7] but the reactivity of these complexes has been scarcely studied and mostly limited to carbonyl chemistry.[8–10] Moreover, methods used for the synthesis of **3** and **10** involve partial thermal or hydrolytic breaking of the $SiMe_2$ bridge or lead to a mixture that requires further separations leading to lower yields. In this paper we report new methods for preparing complexes **3**, **4**, and **10** in high yields and the synthesis and chemical behavior of new complexes which were characterized by IR and NMR spectroscopy. We report also some preliminary results obtained with the permethylated ligand $(C_5Me_4)_2SiMe_2$ and the X-ray molecular structure of **10**.

Results and Discussion

Preparative Methods. The arene ligand of complexes $[(arene)Mo(CO)_3]$ (arene = 1,3,5-$C_6H_3Me_3$ (**1a**), 1,4-$C_6H_4Me_2$ (**1b**))[11] is easily substituted by the cyclopentadienyl group by reaction with $(C_5H_5)_2SiMe_2$, in THF. The reaction takes place with activation of one C–H bond from each ring and simultaneous transfer of one hydride to each metal center, giving **2** (Scheme I). The reaction is complete in 5 h for **1a** but is instantaneous for **1b**, although the enhanced stability makes **1a** a more convenient starting complex to prepare **2**. The red oil obtained when the

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[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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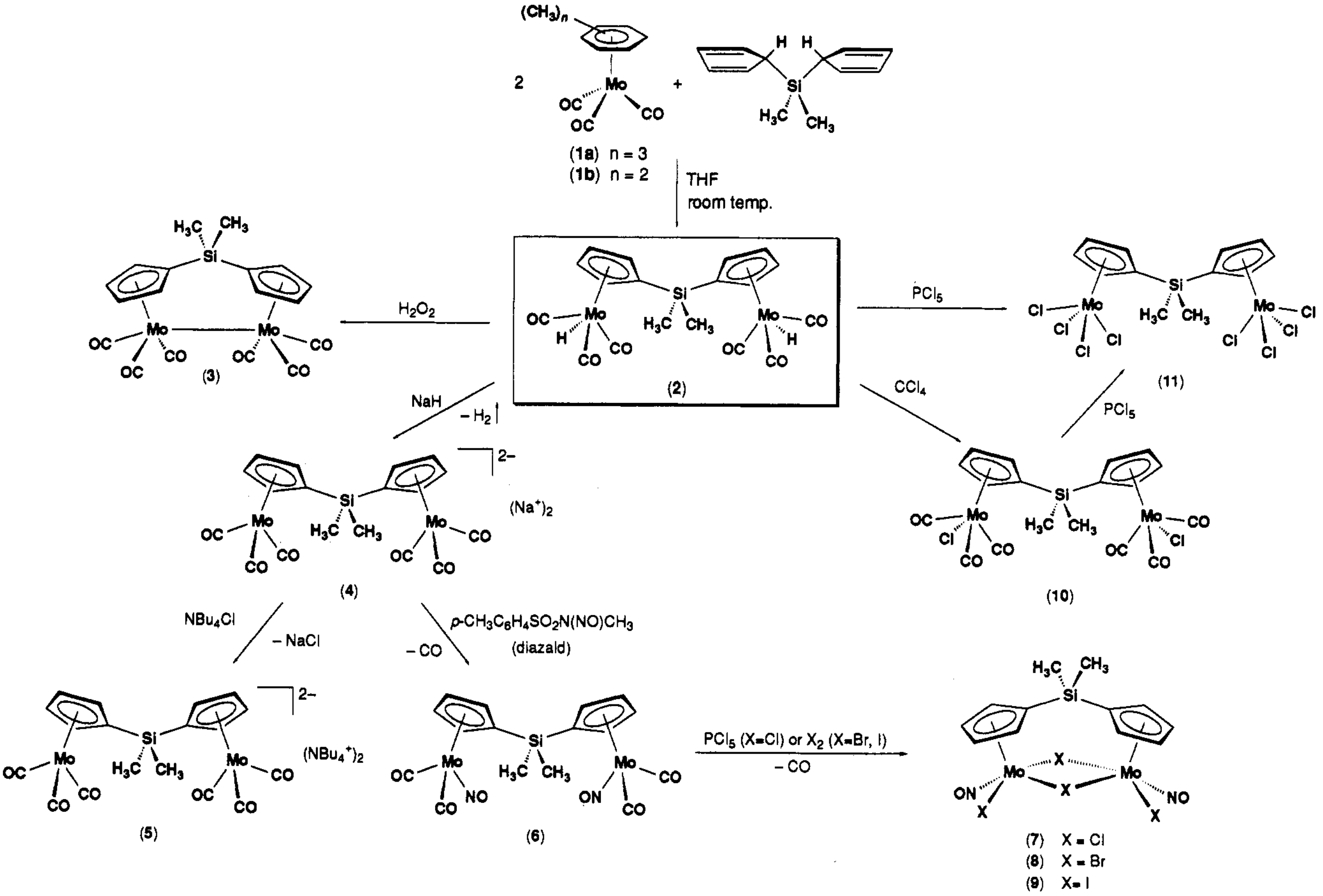
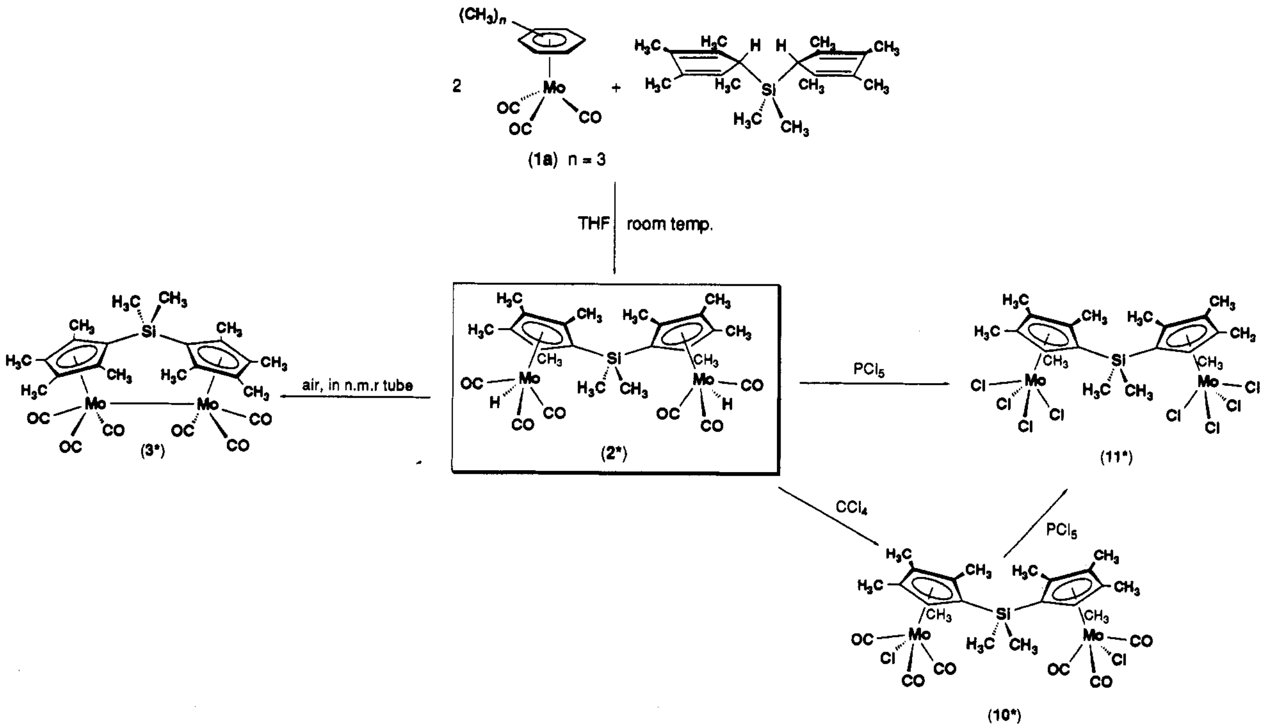
Scheme I



Scheme II



reaction mixture is evaporated to dryness contains pure hydride **2** (^{1}H NMR evidence), which can be crystallized as a white solid only in small yield by washing with cold hexane. The previously reported[7] reaction with $Mo(CO)_3(EtCN)_3$ leads only to $[(C_5H_5)_2Mo(CO)_3]_2$. The same method can be used to prepare **2*** (Scheme II) by starting from the permethylated dimethylsilyl compound. Complexes **2** and **2*** are difficult to isolate as solids and decompose quickly in air and oil after several hours at room temperature. However, the reaction mixtures of **1** and $(C_5H_5)_2SiMe_2$ or $(C_5Me_4H)_2SiMe_2$ are appropriate to prepare other derivatives *in situ*.

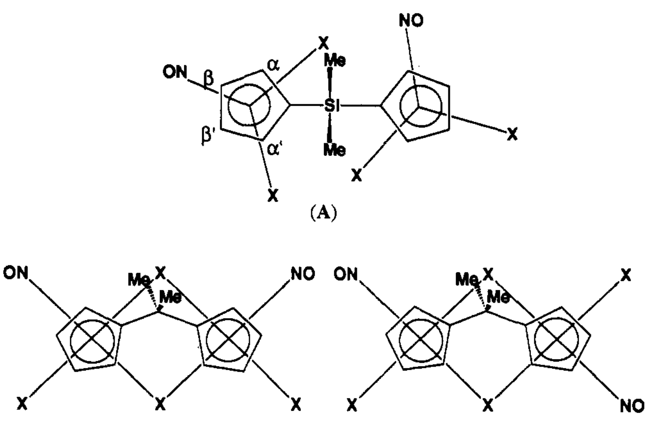
The best method to prepare **3** in high yield is the reaction of the hydride **2** with aqueous hydrogen peroxide in THF, which leads to pure **3**. When **2** is heated, a *ca.* 1:1 mixture of **3** and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ is obtained. Complex **3*** could not be obtained from **2*** by reaction with O_2 or H_2O_2 or by heating. However, a pure sample of **3*** (^{1}H NMR evidence) is obtained when the tube containing **2*** in $CDCl_3$ is exposed several hours to the air.

Addition of NaH to **2** in THF produces **4** as an air-sensitive but nonpyrophoric yellow solid with the evolution of H_2, whereas the previously reported method[6] gives **4** as a pyrophoric solid. Complex **4** crystallizes with a molecule of diethyl ether according to the analytical and ^{1}H NMR evidence. Replacement of sodium with tetrabutylammonium ion by reaction with $(n\text{-Bu})_4NCl$ gives the more stable complex **5**, facilitating its complete characterization.

Complex **6** can be prepared by using the same method reported[12-15] for $CpMo(CO)_2NO$ (Cp = C_5H_5, C_5Me_5, etc.). As for the related cyclopentadienyl derivatives,[13,15,16] **6** is oxidized by halogens or PCl_5, losing CO to give the diamagnetic complexes **7**–**9**, showing that the $SiMe_2$ bridge resists the halogenation. Metathetical replacement of hydride by chloride takes place easily when **2** is stirred in CCl_4, leading to the diamagnetic complex **10**. Total decarbonylation of **2** is produced by oxidation with the stoichiometric amount of PCl_5 to give the paramagnetic (μ_{eff} = 2.16 μ_B at room temperature) molybdenum(V) complex **11**, which is better obtained as a highly pure compound by oxidation of **10** with PCl_5. Complexes **10*** and **11*** were prepared similarly. As for C_5H_5 and C_5Me_5, the substitution of $(C_5H_4)_2SiMe_2$ by $(C_5Me_4)_2SiMe_2$ enhances the solubility of these complexes.

Structural Study. Spectroscopic data for all complexes are given in the Experimental Section. The ν(NO) frequencies for **6**–**9** are in the range 1669–1701 cm^{-1}, as expected for linear nitrosyls.[17-19] The ν(CO) frequencies are in the range 1743–2049 cm^{-1}, as expected for terminal carbonyls. The ^{1}H NMR spectra of **2** and **2*** show high-field hydride singlets at −5.63 and −5.39 ppm, respectively. The ^{1}H NMR spectra for all the complexes show one singlet between 0.76 and −0.02 ppm, due to the methyl protons of the silyl group. The ^{1}H NMR spectrum of **3** that shows four broad signals in the range 4.2–5.2 ppm has been analyzed in ref 7. The cyclopentadienyl ring protons appear in all the complexes, except **3**, as two groups of three resonances (the AA′ and BB′ parts of a AA′BB′ spin system) in the range 4.2–7.2 ppm, whereas two singlets in the range 1.5–2.1 ppm are observed for permethylated rings. The simulation of the second-order spectra[20] for the complexes with a AA′BB′ spin system shows that the chemical shifts of the AA′ and BB′ parts match approximately the position of the central resonance of each group of three resonances.

Chart I



(A)

(*cis*-**B**) (*trans*-**B**)

The ^{1}H and $^{13}C\{^1H\}$ NMR data show that the four α- and the four β-carbons (see Chart I) and their substituents are chemically equivalent at room temperature in all the complexes except **3**. This chemical equivalence implies the existence of two planes of symmetry (planes Me–Si–Me and cp–Si–cp; cp = centroid of the cyclopentadienyl ring) in the structure of a rigid molecule or in the average structure of a fluxional molecule. Complexes **7**–**9** show a dynamic ^{1}H NMR behavior. In CD_2Cl_2, at low temperatures, a main species is observed whose cyclopentadienyl protons appear as four groups of resonances of an ABCD spin system. Other minor resonances are observed at low temperature, but only for the iodide complex **9** can these be unequivocally assigned to a minor species which has all eight ring protons nonequivalent (the ratio between the minor and the main species is 0.4:1). All the resonances coalesce at high temperatures in two groups of resonances of an AA′BB′ spin system. The free energies ($\Delta G_c^{\ddagger}$) calculated at the coalescence temperatures for the transformation of the ABCD into the AA′BB′ spin system are 51.4 kJ mol^{-1} for **7**, 52.1 kJ mol^{-1} for **8**, and 57.9 kJ mol^{-1} for **9**.

Two different structures can be envisaged for complexes **7**–**9**. Structure A (Chart I) involving two 16e molybdenum centers, as found[21] for $[(C_5Me_5)W(NO)I_2]$ in the solid state, does not agree with the activation barriers found, because the equivalence between α- and β-substituents could be achieved by simple rotation about the cp–Si and cp–Mo axes. In fact, the coalescence has not been observed in CD_2Cl_2 in the range of +25 to −70 °C for **10**, for which the equivalence is expected to be achieved by this type of process. The dynamic ^{1}H NMR behavior observed is better explained by the structural arrangement B (*cis* and *trans*) that has two halide bridges and two 18e molybdenum centers, as found[15] for $[(C_5Me_5)Mo(NO)Br_2]_2$ in the solid. In this structural arrangement, the halide bridges determine the Mo···Mo distance (4.168 Å in $[(C_5Me_5)Mo(NO)Br_2]_2$) and probably force the $SiMe_2$ bridge to be seated unsymmetrically over the $Mo(\mu\text{-}X)_2Mo$ moiety (see Crystal Structure discussion and Table III). The static structure *trans*-**B** would show eight nonequivalent ring protons, as observed at low temperature for the minor species, whereas the static structure *cis*-**B** would have only four nonequivalent protons as observed at low temperature for the main species. The transformation at room temperature of the four and eight groups of resonances of each isomer into

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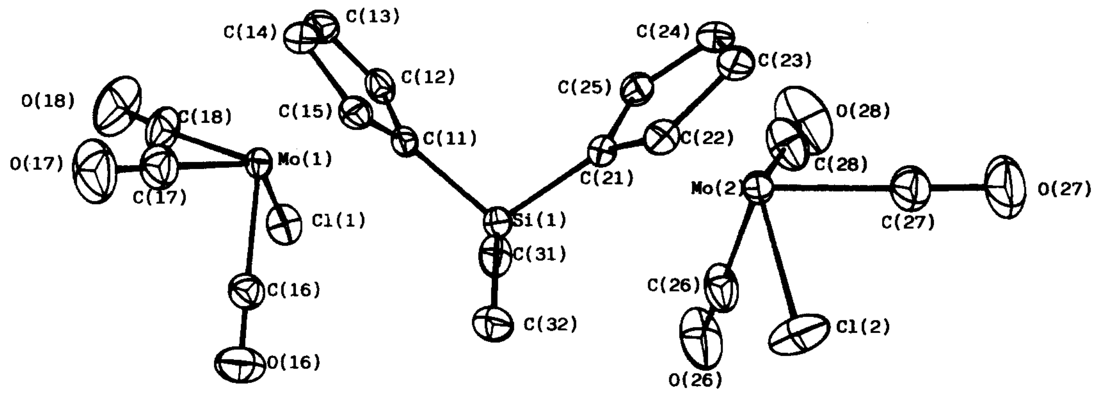
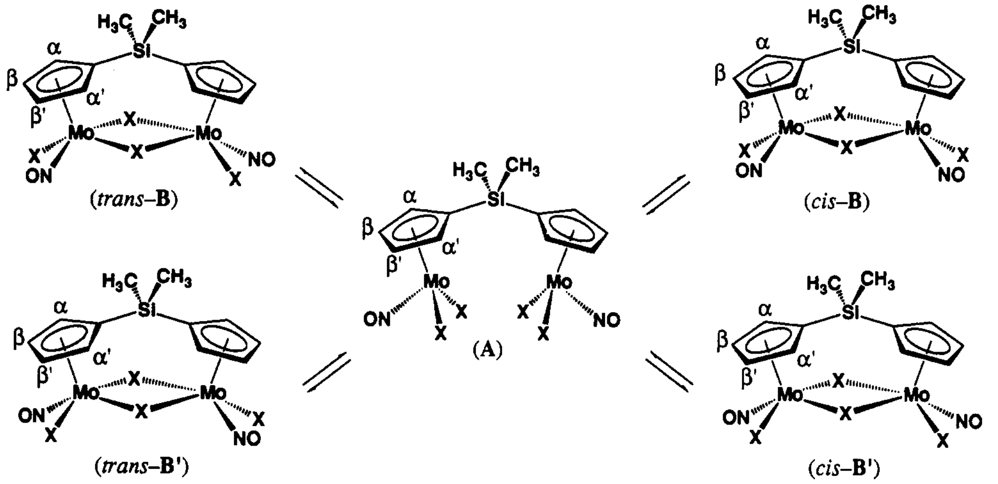


Figure 1. Perspective view of the molecular structure of $[(Mo(CO)_3Cl)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$(**10**) with the atom-numbering scheme.

Scheme III



a single AA′BB′ spin system could be explained by the rapid interchange of the nitrosyl and terminal halide positions through a 16e intermediate (Scheme III). This process would make equivalent the α- and β-protons of the main *cis* isomer through the *cis*-**B** ⇌ *cis*-**B**′ conversion, the α- and β-protons of the minor *trans* isomer through the *trans*-**B** ⇌ *trans*-**B**′ conversion, and the α- and β-protons of both isomers through the *trans*-**B** ⇌ *cis*-**B** conversion.

Crystal Structure of 10. The molecular structure of **10** based on the X-ray structural analysis is shown in Figure 1 with the numbering scheme employed. Atomic parameters for the non-hydrogen atoms are listed in Table I and important bond distances and bond angles in Table II. The molecular structure consists of a dinuclear system with the two Mo atoms bridged only by the $(C_5H_4)_2SiMe_2$ ligand. Each Mo atom has a "four-legged piano stool" coordination, where the legs are three CO groups and a chlorine atom. If the centroid of each Cp ring is taken as a coordination site, the angles around Mo between this point and the legs range from 109 to 128° and between consecutive legs range from 76.0 to 78.7°. These figures are usual for this type of structure. The CO ligand has a linear arrangement with angles Mo–C–O from 173.8 to 178.7°. Distances Mo–C and C–O are normal for terminal CO groups.

The most interesting feature of this structure is the position of both Mo atoms *exo* with respect to the Cp–Si–Cp system. This arrangement allows the metals to be situated at a very long distance, 6.491 Å. The positions of the two molybdenum atoms are not completely symmetrical with respect to the $(C_5H_4)_2SiMe_2$ ligand, because Mo(1) is in the plane defined by Si(1), C(21), and C(11) but Mo(2) is situated at −0.299 Å with respect to them. The chlorine atoms are in *trans* positions with respect to this plane or the Mo–Mo line. On the other hand, both Mo atoms have the same distance (3.74 Å) to the plane C(31), Si(1), C(32).

The M(1)–cp(1)–Si–cp(2) and M(2)–cp(2)–Si–cp(1) dihedral angles θ_1 and θ_2 (Table III; cp is the centroid of the cyclopentadienyl ring) can rationalize the arrangement of the metal centers in the structures of bimetallic $(C_5H_5)_2$-$SiMe_2$-bridged complexes. Table III shows the results of a simple model calculation of the variation of the Mo···Mo distance with changes in θ of the same absolute value and equal sign (*transoid* arrangement) or opposite sign (*cisoid* arrangement). In complex **10**, where metal–metal bond and ligand bridges (other than the $(C_5H_5)_2SiMe_2$ bridge) are absent, the values of the θ angles are close to 180° (178.3 and 169.3°); i.e., the two metal centers are situated almost at the maximum distance. However, the potential curve for the variation of dihedral angles is expected to be rather shallow; therefore, the angles θ observed in solid **10** will be variable in solution. Note that in the crystal structure of $[((\eta^5\text{-}C_5Me_5)TiCl_2)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$ that has bulky C_5Me_5 ligands bonded to the titanium centers, the θ angles are farther from 180° (166.5 and 125.4)°.[4] A metal–metal bond or ligand bridge requires the two metal centers to be placed close to one another, implicating smaller θ angles. This is shown by the solid-state structure of $[(W(CO)_3)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$(*W–W*), where the two metals are in a *transoid* arrangement,[5] and of $[(TiCl)_2$-

Table I. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of 10

atom	x	y	z	B^a (Å^2)
Mo(1)	0.03121(3)	0.29162(2)	0.71736(2)	2.858(2)
Mo(2)	0.38432(3)	0.19081(2)	1.25419(2)	2.921(5)
Si(1)	0.29383(9)	0.26686(6)	0.99136(6)	2.81(1)
Cl(1)	0.1088(1)	0.50907(7)	0.83542(7)	5.09(2)
Cl(2)	0.6666(1)	0.1236(1)	1.2166(1)	6.39(3)
C(11)	0.0912(3)	0.2298(2)	0.8658(2)	2.77(5)
C(12)	–0.0647(4)	0.2897(3)	0.8695(2)	3.84(6)
C(13)	–0.1984(4)	0.2256(3)	0.7672(3)	5.00(7)
C(14)	–0.1333(4)	0.1293(3)	0.6991(3)	4.58(7)
C(15)	0.0460(4)	0.1291(2)	0.7592(2)	3.29(5)
C(16)	0.2783(4)	0.3200(3)	0.7084(3)	4.01(7)
O(16)	0.4156(3)	0.3289(3)	0.7035(2)	6.30(7)
C(17)	0.0264(5)	0.1875(3)	0.5570(3)	5.06(9)
O(17)	0.0269(5)	0.1271(3)	0.4664(2)	8.4(1)
C(18)	–0.1308(6)	0.3672(3)	0.6188(3)	6.1(1)
O(18)	–0.2315(6)	0.4056(3)	0.5695(3)	10.8(1)
C(21)	0.2331(3)	0.1815(2)	1.0710(2)	2.71(5)
C(22)	0.2704(3)	0.0645(2)	1.0580(2)	2.96(5)
C(23)	0.1864(4)	0.0239(2)	1.1207(2)	3.50(6)
C(24)	0.0930(4)	0.1151(3)	1.1745(2)	3.84(6)
C(25)	0.1207(3)	0.2115(2)	1.1432(2)	3.42(6)
C(26)	0.5373(6)	0.3458(3)	1.3095(3)	5.84(9)
O(26)	0.6209(5)	0.4324(3)	1.3379(3)	9.8(1)
C(27)	0.4750(6)	0.1253(3)	1.3727(3)	5.78(9)
O(27)	0.5234(5)	0.0832(3)	1.4372(3)	10.1(1)
C(28)	0.2958(7)	0.2929(4)	1.3826(3)	6.3(1)
O(28)	0.2424(6)	0.3490(3)	1.4560(3)	10.8(1)
C(31)	0.3287(5)	0.4283(3)	1.0794(3)	4.84(8)
C(32)	0.4896(4)	0.2140(3)	0.9447(3)	4.62(7)

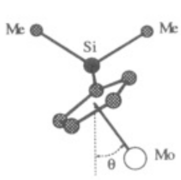
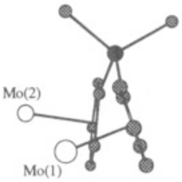
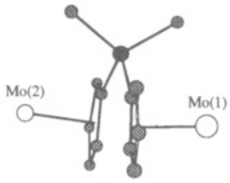
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for 10

	Distances		
Mo(1)–Cl(1)	2.5102(8)	Mo(2)–Cl(2)	2.500(1)
Mo(1)–C(11)	2.338(3)	Mo(2)–C(21)	2.348(2)
Mo(1)–C(12)	2.378(3)	Mo(2)–C(22)	2.365(2)
Mo(1)–C(13)	2.361(4)	Mo(2)–C(23)	2.349(2)
Mo(1)–C(14)	2.296(4)	Mo(2)–C(24)	2.291(3)
Mo(1)–C(15)	2.291(3)	Mo(2)–C(25)	2.288(3)
Mo(1)–C(16)	2.013(3)	Mo(2)–C(26)	2.021(4)
Mo(1)–C(17)	1.963(3)	Mo(2)–C(27)	1.991(4)
Mo(1)–C(18)	2.030(4)	Mo(2)–C(28)	1.990(4)
Mo(1)–cp(1)[a]	1.995	Mo(2)–cp(2)[a]	1.991
Si–C(11)	1.878(2)	Si–C(21)	1.880(3)
Si–C(31)	1.855(3)	Si–C(32)	1.852(3)
C(11)–C(12)	1.447(4)	C(21)–C(22)	1.427(4)
C(11)–C(15)	1.427(3)	C(21)–C(25)	1.423(4)
C(12)–C(13)	1.407(3)	C(22)–C(23)	1.407(5)
C(13)–C(14)	1.389(5)	C(23)–C(24)	1.413(4)
C(14)–C(15)	1.432(4)	C(24)–C(25)	1.429(5)
C(16)–O(16)	1.116(4)	C(26)–O(26)	1.128(5)
C(17)–O(17)	1.142(4)	C(27)–O(27)	1.140(6)
C(18)–O(18)	1.115(6)	C(28)–O(28)	1.142(6)
	Angles		
C(11)–Si–C(21)	102.0(1)	C(31)–Si–C(32)	111.8(2)
Mo(1)–C(16)–O(16)	176.0(3)	Mo(2)–C(26)–O(26)	178.4(3)
Mo(1)–C(17)–O(17)	178.8(4)	Mo(2)–C(27)–O(27)	177.1(3)
Mo(1)–C(18)–O(18)	173.8(5)	Mo(2)–C(28)–O(28)	178.2(4)
cp(1)–Mo(1)–Cl(1)	113.4	cp(2)–Mo(2)–Cl(2)	111.5
cp(1)–Mo(1)–C(16)	127.8	cp(2)–Mo(2)–C(26)	127.7
cp(1)–Mo(1)–C(17)	111.0	cp(2)–Mo(2)–C(27)	126.6
cp(1)–Mo(1)–C(18)	123.7	cp(2)–Mo(2)–C(28)	108.6
C(16)–Mo(1)–Cl(1)	78.3	C(26)–Mo(2)–Cl(2)	77.7
Cl(1)–Mo(1)–C(18)	76.7	Cl(2)–Mo(2)–C(27)	78.2
C(18)–Mo(1)–C(17)	78.0	C(27)–Mo(2)–C(28)	77.6
C(17)–Mo(1)–C(16)	76.0	C(28)–Mo(2)–C(26)	78.7

[a] cp(1) is the centroid of C(11)–C(15); cp(2) is the centroid of C(21)–C(25).

Table III. Mo···Mo Distance vs the Mo(1)–cp(1)–Si–cp(2) and the Mo(2)–cp(2)–Si–cp(1) Dihedral Angles θ_1 and θ_2[a]

	Mo···Mo dist (Å)	
$\lvert\theta_1\rvert = \lvert\theta_2\rvert$[b] (deg)	*cisoid* arrangement	*transoid* arrangement
		
0	2.86	
45	3.52	4.47
90	5.11	6.45
135	6.71	7.25
180	7.37	

[a] An idealized geometry is proposed with cp–Si–cp = 109.5°, Si–cp–Mo = 90°, Mo–cp = 1.95 Å, and cp–Si = 3.13 Å; cp is the centroid of the cyclopentadienyl ring. [b] Only the cases in which angles θ_1 and θ_2 have the same absolute value and signs are equal (*transoid* arrangement) or opposite (*cisoid* arrangement) are analyzed.

$(\mu\text{-O})(\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2)]_2(\mu\text{-O})_2$, where the planar Ti_4O_4 core forces a *cisoid* arrangement with similar θ angles for both metals.[3] The Mo(μ-X)$_2$Mo core in complexes **7–9** would also impose a *cisoid* arrangement with similar θ angles for both metals. This structure is in agreement with their NMR data (see above). When the M···M distance cannot be adjusted by modification of the θ angles, this can be achieved by deformation of the C(ring)–Si–C(ring)′ and cp–C(ring)–Si angles, as in $[\text{Yb}_2(\mu\text{-Br})_2(\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2)_2]$, where the second $(\text{C}_5\text{H}_4)_2\text{SiMe}_2$ bridge imposes θ angles of *ca.* 0°.[22]

Experimental Section

Reagents and General Techniques. All reactions were carried out in dried Schlenk tubes under argon or nitrogen, and the manipulations were carried out using syringes or cannulae through Subaseals. Solvents were dried and distilled under nitrogen: dietyl ether and tetrahydrofuran from sodium benzophenone ketyl; toluene, pentane, and hexane from sodium; CH_2Cl_2 over P_4O_{10}. Unless otherwise stated, reagents were obtained from commercial sources and used as received. IR spectra were recorded in Nujol mulls for solids or in CaF_2 cells for solutions, over the range 4000-200 cm^{-1} on a Perkin-Elmer 583 spectrophotometer. IR data are given in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded at 299.95 and 75.43 MHz, respectively, on a Varian Unity 300 spectrometer; chemical shifts, in ppm, are positive downfield relative to external SiMe_4. C, H, and N analyses were performed with a Perkin-Elmer 240-B instrument. Mass spectra were recorded in a Hewlett-Packard 5988A spectrometer.

Syntheses. The compounds (arene)MO(CO)$_3$ (arene = 1,3,5-$\text{C}_6\text{H}_3\text{Me}_3$ (**1a**), $\text{C}_6\text{H}_4\text{Me}_2$ (**1b**)), $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$, and $(\text{C}_5\text{Me}_4\text{H})_2\text{SiMe}_2$ were prepared according to reported methods.[11,23,24]

Preparation of $[(\text{Mo(CO)}_3\text{H})_2(\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2)]$ (2). Bis(cyclopentadienyl)dimethylsilane (0.32 mL, 1.7 mmol) is added at room temperature to a solution of **1a** (1.00 g, 3.33 mmol) in THF (30 mL). The yellow solution stirred over 5 h turns pale orange, or red if traces of oxygen are present (if **1b** is used instead of **1a**, the reaction is instantaneous). The solvent is evaporated to dryness, and the resulting orange oil is characterized by IR and ^{1}H NMR as **2**. Complex **2** can be isolated in small amounts as a white solid (20–30 mg, 2–3%) by crystallization of the oil with some drops of cold hexane. However, this solid turns to an oil again after several hours at room temperature and its chemical behavior is the same as that observed by using the crude oil.

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Anal. Calcd for $C_{18}H_{16}O_6SiMo_2$: C, 39.4; H, 2.9. Found: C, 37.8; H, 3.0. IR (THF): ν(CO) 2020 s, 1931 vs. ^{1}H NMR (C_6D_6): δ 4.72, 4.68 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.15 (s, 3 H, SiMe_2), −5.63 (s, 1 H, Mo–*H*).

Preparation of [(Mo(CO)$_3$)$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)](*Mo–Mo*) (3). A solution of complex **2** is prepared by reacting **1a** (1.00 g, 3.33 mmol) and $(C_5H_5)_2SiMe_2$ (0.32 mL, 1.7 mmol) in THF (30 mL) as described previously. Then, a 35% solution of H_2O_2 (0.16 mL, 1.7 mmol) is added. The pale yellow solution immediately turns dark red. After 1 h of stirring, anhydrous Na_2SO_4 is added, the mixture is stirred over 1 h, and the solution is filtered and evaporated to dryness *in vacuo*. The oil obtained is crystallized as a red solid with hexane and dried *in vacuo* (0.68 g, 75%). Anal. Calcd for $C_{18}H_{14}O_6SiMo_2$: C, 39.6; H, 2.6. Found: C, 39.2; H, 2.8. IR and ^{1}H NMR data are in agreement with those previously reported.[7]

Preparation of Na$_2$[(Mo(CO)$_3$)$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (4). A solution of **2** is prepared by reacting **1a** (1.00 g, 3.33 mmol) and $(C_5H_5)_2SiMe_2$ (0.32 mL, 1.7 mmol) in THF (30 mL) as described previously. The solution is added dropwise at −78 °C to a suspension of NaH (0.10 g, 4.2 mmol) in THF (25 mL). Evolution of gas (H_2) is observed while the solution turns yellow, and after 1 h, the solution is filtered and evaporated *in vacuo* to dryness. A yellow oil is then obtained, from which complex **4** (1.03 g, 93%) can be crystallized as a diethyl ether solvate (**4**·OEt$_2$) by washing several times with cold diethyl ether. Anal. Calcd for $C_{22}H_{24}O_7Na_2SiMo_2$: C, 39.65; H, 3.6. Found: C, 39.5; H, 4.1. IR and ^{1}H NMR data are in agreement with those previously reported.[6]

Preparation of (Bu$_4$N)$_2$[(Mo(CO)$_3$)$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (5). Solid (Bu$_4$N)Cl (0.92 g, 3.3 mmol) is added to a solution of **4**·OEt$_2$ (1.10 g, 1.65 mmol) in THF (40 mL). The mixture is stirred over 48 h. The NaCl precipitated is filtered through Celite, and the solution is evaporated *in vacuo* to dryness. Complex **5** (0.80 g, 47%) is crystallized as a yellow solid by addition of diethyl ether. Anal. Calcd for $C_{54}H_{86}N_2O_6SiMo_2$: C, 58.2; H, 8.4; N, 2.7. Found: C, 58.5; H, 9.2; N, 2.6. IR (CH_2Cl_2): ν(CO) 1891 s, 1774 vs, br. ^{1}H NMR (CD_2Cl_2): δ 5.20, 5.15 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.34 (s, 3 H, SiMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 236.4 (s, *C*O), 95.2 (s, C_5H_4), 94.2 (s, C_5H_4), 88.4 (s, C_5H_4), 1.1 (s, SiMe_2).

Preparation of [(Mo(CO)$_2$(NO))$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (6). A solution of *p*-$CH_3C_6H_4SO_2N(NO)CH_3$ (Diazald; 1.43 g, 6.67 mmol) in THF (60 mL) is added dropwise (15–30 min) to a solution of **4**·OEt$_2$ (2.22 g, 3.33 mmol) in THF (40 mL). The yellow solution turns progressively orange, while evolution of CO is observed and a white precipitate is formed. The stirring is continued overnight. The solution is filtered and evaporated *in vacuo* to dryness, the residue extracted with diethyl ether (3 × 20 mL), this solution evaporated *in vacuo* to dryness, and the residue extracted with 20-mL fractions of hexane until colorless. The solution is evaporated to *ca.* 5 mL and stored at −40 °C overnight. Complex **6** is obtained as an orange microcrystalline solid (1.10 g, 60%). Anal. Calcd for $C_{16}H_{14}N_2O_6SiMo_2$: C, 34.9; H, 2.6; N, 5.1. Found: C, 35.4; H, 2.6; N, 4.8. IR (THF): ν(CO) 2017 s, 1944 vs; ν(NO) 1669 s. ^{1}H NMR (C_6D_6): δ 5.02, 4.79 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.14 (s 3 H, SiMe_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 227.3 (s, CO), 101.2 (s, C_5H_4), 100.3 (s, C_5H_4), 95.7 (s, C_5H_4), −0.8 (s, SiMe_2).

Preparation of [(MoCl$_2$(NO))$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (7). At 0 °C, a solution of **6** (0.20 g, 0.36 mmol) in diethyl ether (20 mL) is added dropwise to a suspension of PCl_5 (0.15 g, 0.73 mmol). Evolution of a gas is observed while the solution turns green and an orange solid precipitates. The mixture is stirred over 2 h. Then, the solution is filtered and the orange solid (0.15 g, 72%) is washed with diethyl ether (2 × 20 mL) and dried *in vacuo*. Anal. Calcd for $C_{12}H_{14}N_2O_2SiCl_4Mo_2$: C, 24.85; H, 2.4; N, 4.8. Found: C, 24.6; H, 2.6; N, 4.7. IR (CH_2Cl_2): ν(NO) 1701 s. ^{1}H NMR (acetone-d_6): δ 6.50, 6.27 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.69 (s, 3 H, SiMe_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 131.1 (s, C_5H_4), 126.0 (s, C_5H_4), 106.5 (s, C_5H_4), −2.6 (s, SiMe_2).

Table IV. Crystallographic Data for 10

formula	$C_{18}H_{14}Cl_2Mo_2O_6Si$
cryst habit	prismatic
color	orange
symmetry	triclinic, $P\bar{1}$
unit cell determn	least-squares fit from 25 rflns
unit cell dimens	
a, b, c, Å	7.934(3), 12.305(3), 13.166(3)
α, β, γ, deg	112.32(1), 105.48(1), 90.34(1)
packing	
V, Å^3	11.37
D_{calcd}, g cm^{-3}	1.80
M_r	617.18
F(000)	604
μ, cm^{-1}	13.90
technique	four-circle diffractometer; bisecting geometry, graphite-oriented monochromator; Mo Kα $\omega/2\theta$ scans; θ_{max} = 27°
no. of rflns	
measd	5433
indep	4950
obsd	4493; $I \geq 3\sigma(I)$
range of *hkl*	*h*, 0 to 10; *k*, −15 to +15; *l*, −16 to +16
std rflns	2 rflns every 120 min; no variation
R	0.037
R_w	0.055
goodness of fit indicator	2.278
largest param shift/error	0.01
max peak in final diff map, e Å^{-3}	1.4 (near Mo)
min peak in final diff map, e Å^{-3}	0.87

Preparation of [(MoBr$_2$(NO))$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (8). A solution of Br_2 (0.06 mL, 1.1 mmol) in CH_2Cl_2 (20 mL) is added dropwise to a solution of **6** (0.30 g, 0.545 mmol) in CH_2Cl_2 (20 mL) at −78 °C. Evolution of gas is observed while the solution darkens. When the addition of Br_2 is finished, the solution is stirred for 1 h. Then, toluene (40 mL) is added and the orange precipitate (0.35 g, 85%) filtered, washed with toluene, and dried *in vacuo*. Anal. Calcd for $C_{12}H_{14}N_2O_2SiBr_4Mo_2$: C, 19.0; H, 1.9; N, 3.7. Found: C, 19.3; H, 2.0; N, 3.5. IR (THF): ν(NO) 1681 s. ^{1}H NMR (THF-d_8): δ 6.49, 6.45 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.64 (s, 3 H, SiMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 118.5 (br, C_5H_4), 111.6 (br, C_5H_4), 109.2 (br, C_5H_4), −2.1 (s, SiMe_2).

Preparation of [(MoI$_2$(NO))$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (9). This complex is obtained by the same procedure described for **8** by starting from I_2 (0.14 g, 0.55 mmol) and **6** (0.15 g, 0.27 mmol) as a red solid (0.18 g, 70%). Anal. Calcd for $C_{12}H_{14}N_2O_2SiMo_2I_4$: C, 15.2; H, 1.5; N, 3.0. Found: C, 14.9; H, 1.6; N, 2.9. IR (THF): ν(NO) 1678 s. ^{1}H NMR (acetone-d_6): δ 7.24, 5.95 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.72 (s, 3 H, SiMe_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 121.1 (br, C_5H_4), 109.5 (br, C_5H_4), 102.1 (br, C_5H_4), −2.9 (s, SiMe_2).

Preparation of [(Mo(CO)$_3$Cl)$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (10). A solution of **2** is prepared by reaction of **1a** (2.00 g, 6.66 mmol) and $(C_5H_5)_2SiMe_2$ (0.64 mL, 3.33 mmol) in THF (30 mL) as described previously. The solution is evaporated to dryness, and the orange oil is dissolved in CCl_4. An orange solid precipitates from the solution. The stirring is continued for 1 h. Then, the orange solid (1.60 g, 78%) is filtered and dried *in vacuo*. Anal. Calcd for $C_{18}H_{14}O_6SiCl_2Mo_2$: C, 35.0; H, 2.3. IR and ^{1}H NMR data are in agreement with those previously reported.[7]

Preparation of [(MoCl$_4$)$_2$(μ-(η^5-C_5H_4)$_2$SiMe$_2$)] (11). A solution of **2** is prepared by reaction of **1a** (1.00 g, 3.33 mmol) and $(C_5H_5)_2SiMe_2$ (0.32 mL, 1.66 mmol) in THF (30 mL) as described previously. The solvent is eliminated *in vacuo* and toluene (30 mL) added. The solution is mixed with a suspension of PCl_5 (1.55 g, 7.46 mmol) in toluene (30 mL). A purple solid precipitates immediately, while evolution of gas is observed. The mixture is stirred for 3 days at 60 °C and the purple solid separated by filtration, washed with toluene, and dried *in vacuo* (0.76 g, 69%).

Highly pure **11** can also be prepared in toluene from **10**, by a similar method (96% yield). Anal. Calcd for $C_{12}H_{14}SiCl_8Mo_2$: C, 21.8; H, 2.1. Found: C, 21.3; H, 2.2.

Preparation of the Permethylated Complexes 2*, 10*, and 11*. These complexes are obtained by the same procedures described for **2**, **10** and **11**, respectively, from **1a** (1.00 g, 3.33 mmol) and $(C_5Me_4H)_2SiMe_2$ (0.50 g, 1.66 mmol).

Data for 2*: complex **2*** is used without previous isolation (see Discussion). IR (THF): ν(CO) 2009 s, 1923 vs. ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 6 H, $C_5\mathit{Me}_4$), 1.98 (s, 6 H, $C_5\mathit{Me}_4$), 0.76 (s, 3 H, $Si\mathit{Me}_2$) −5.39(s, 1 H, Mo–*H*).

Data for 10*: orange solid; yield 70%. Anal. Calcd for $C_{26}H_{30}O_6SiCl_2Mo_2$: C, 42.8; H, 4.1. Found: C, 42.6; H, 4.0, IR (THF): ν(CO) 2041 s, 1959 vs. ^{1}H NMR (C_6D_6): δ 1.40 (s, 6 H, $C_5\mathit{Me}_4$), 1.54 (s, 6 H, $C_5\mathit{Me}_4$), 0.55 (s, 3 H, $Si\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 244.5 (s, *C*O), 225.2 (s, *C*O), 118.4 (s, C_5Me_4), 112.0 (s, C_5Me_4), 95.4 (s, C_5Me_4), 14.2 (s, $C_5\mathit{Me}_4$), 10.7 (s, $C_5\mathit{Me}_4$), 4.0 (s, $Si\mathit{Me}_2$).

Data for 11*: Purple solid; yield 66%. Anal. Calcd for $C_{20}H_{30}SiCl_8Mo_2$: C, 31.0; H, 3.9. Found: C, 30.8; H, 4.3.

Data for 3* (see Discussion). IR (THF): ν(CO) 2039 s, 1978 vs, 1960 vs. ^{1}H NMR (C_6D_6): δ 2.00 (s, 6 H, $C_5\mathit{Me}_4$), 1.85 (s, 6 H, $C_5\mathit{Me}_4$), 0.67 (s, 3 H, $Si\mathit{Me}_2$).

Crystal Structure of $[(Mo(CO)_3Cl)_2(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)]$ (10). A suitably sized orange crystal of **10** was obtained by crystallization from CH_2Cl_2/hexane. The crystal was mounted in a Enraf-Nonius CAD-4 automatic four-circle diffractometer. Crystallographic and experimental details are summarized in Table IV. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by a combination of heavy atoms, direct methods, and Fourier synthesis. The structure was refined on F by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found in the Fourier difference map and refined for one cycle isotropically. Final $R = 0.037$ and $R_W = 0.055$ values with $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma(F_o)^2]^2$ were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref 25. Calculations were performed with the SDP Enraf-Nonius package,[26] MULTAN,[27] and DIRDIF[28] on a Microvax II computer.

Acknowledgment. We gratefully acknowledge financial support from the Comisión Asesora de Investigación Científica y Técnica (ref. PB89/0208).

Supplementary Material Available: For **10**, tables of positional parameters for hydrogen atoms and thermal parameters (2 pages). Ordering information is given on any current masthead page.

OM930368N

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