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Stereoselective Synthesis of *cis* and *trans* Isomers of $[\{Mo(CO)_3Cl\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2\}]$

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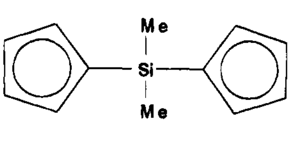
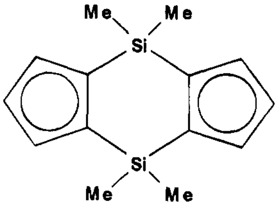
Reaction of $(1,3,5\text{-}C_6H_3Me_3)Mo(CO)_3$ (**1**) and $(C_5H_4(SiMe_2))_2$ in THF (THF = tetrahydrofuran) at room temperature gives the bimetallic complex *cis*-$[\{Mo(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2\}]$ (*cis*-**3**), where the two molybdenum atoms are situated in *cis* positions with respect to the $[\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2]^{2-}$ ligand. In contrast, reaction of **1** with the potassium salt of the $[(C_5H_3(SiMe_2))_2]^{2-}$ anion gives the bimetallic complex *trans*-$K_2[\{Mo(CO)_3\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2\}]$ (*trans*-**2**), where the two molybdenum atoms are situated in *trans* positions with respect to the $[\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2]^{2-}$ ligand. *trans*-**2** can be transformed into *trans*-$[\{Mo(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2\}]$ (*trans*-**3**) by reaction with acetic acid. The hydride complexes *cis*-**3** and *trans*-**3** react with CCl_4 to give *cis*- and *trans*-$[\{Mo(CO)_3Cl\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3(SiMe_2))_2\}]$ (**4**), respectively. The solid-state structures of *cis*-**4** and *trans*-**4** have been determined by single-crystal X-ray analysis. *cis*-**4** crystallizes in the orthorombic space group *Pnma* with Z = 2 in an unit cell of dimensions $a = 11.435(3)$ Å, $b = 18.881(3)$ Å, and $c = 23.535(4)$ Å. *trans*-**4** crystallizes in the monoclinic space group *C*2/*c* with $Z = 4$ in an unit cell of dimensions $a = 17.168(5)$ Å, $b = 10.195(1)$ Å, $c = 16.329(4)$ Å, and $\beta = 119.37(1)°$. The structures have 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 2348 observed reflections to $R = 0.075$ and $R_w = 0.11$, for *cis*-**4**, and on the basis of 2597 observed reflections to $R = 0.033$ and $R_w = 0.057$, for *trans*-**4**.

Introduction

Recently, we have reported the synthesis of dinuclear titanium, zirconium, and molybdenum complexes bridged by a $(C_5H_4)_2SiMe_2$ ligand (**A**),[1−3] which is characterized by its flexibility in relation to the stereochemical disposition of the two metal centers. In contrast, the rigid stereochemistry is well-defined in the doubly bridged cyclopentadienyl ligand **B**, where the two metal centers can be coordinated *cis* or *trans* with respect to the ligand plane. Some homodimetallic complexes have been obtained as *cis* isomers, others as *trans* isomers, and others as *cis* and *trans* mixtures.[4−7] In this article we present results that show the stereoselective synthesis of some molybdenum derivatives.



A



B

Results and Discussion

The mesitylene ligand of $[(1,3,5\text{-}C_6H_3Me_3)Mo(CO)_3]$ (**1**)[8] is easily substituted by the cyclopentadienyl group by reaction with $(C_5H_4(SiMe_2))_2$, 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 *cis*-**3**, as the only isomer observable by ^1H NMR (Scheme 1), where the two metal fragments are *cis* with respect to the ligand plane.

In contrast, the mesitylene complex **1** reacts with the potassium salt of the $[(C_5H_3(SiMe_2))_2]^{2-}$ anion to give *trans*-**2** as the only isomer observable by ^1H NMR. *trans*-**2** can be selectively transformed into the hydride

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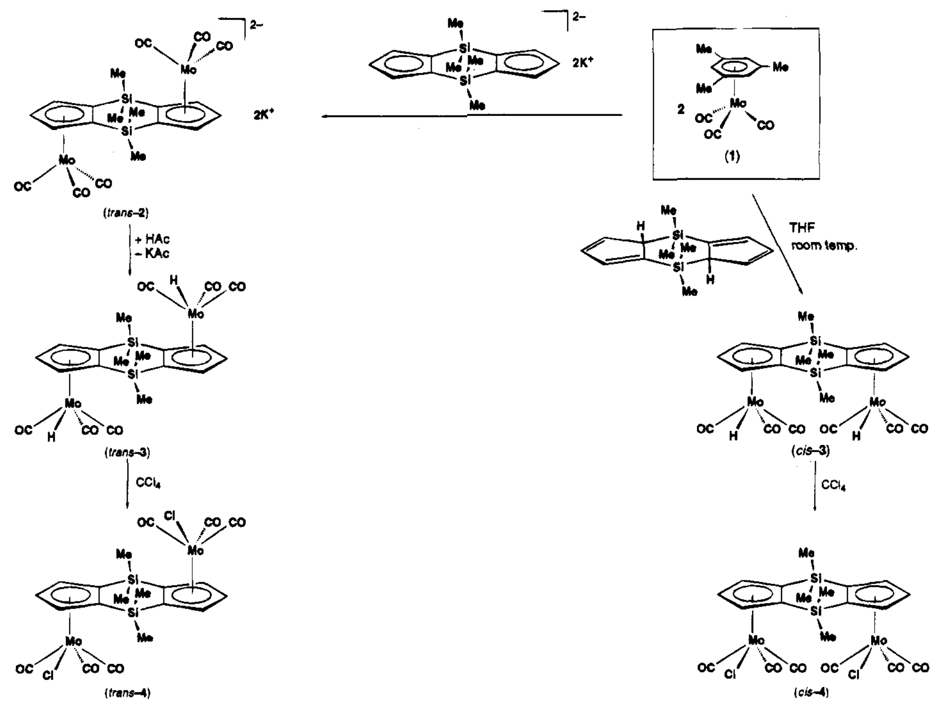
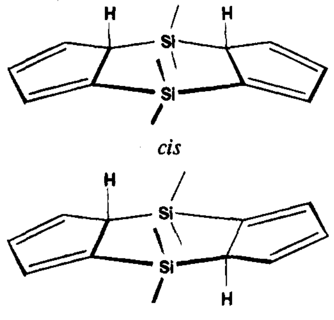
Scheme 1



trans-**3** by reaction with excess acetic acid. Metathetical replacement of hydride by chloride takes place easily when *cis*-**3** or *trans*-**3** is stirred in CCl_4, leading to *cis*-**4** or *trans*-**4**, respectively. The crystal structures of these two isomers have been determined by X-ray diffraction analysis (see below).

Spectroscopic data for all complexes are given in the Experimental Section. The ν(CO) frequencies are in the range 2050−1929 cm^{-1} for neutral complexes **3** and **4** and 1895−1748 cm^{-1} for the anionic complex *trans*-**2**, as expected for terminal carbonyls. The ^1H NMR spectra of *cis*-**3** and *trans*-**3** show high-field hydride singlets at −4.94 and −5.61 ppm, respectively. The cyclopentadienyl ring protons appear in all the complexes, as a triplet due to the proton γ to the $SiMe_2$ bridges and a doublet due to the protons β to the $SiMe_2$ bridges, in the range 4.7−6.6 ppm. The *cis* and *trans* isomers can be easily distinguished by the ^1H and ^{13}C NMR methyl signals of the $SiMe_2$ bridges, because the *cis* isomers show two pairs of equivalent methyl groups while the *trans* isomers show four equivalent methyl groups.[5]

The stereoselective formation of *cis* or *trans* molybdenum complexes reported here depends on the synthetic route employed. It has been reported[4] that the X-ray crystal structure of the lithium salt [$Li_2(TMEDA)_2$-$\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] presents a *trans* arrangement as expected from the electrostatic repulsion of the charges, and it has been pointed out that this arrangement could influence the formation of *trans* derivatives after its reaction with suitable transition-metal compounds. Therefore, we can argue that the same electrostatic interaction induces the formation of *trans*-**2** when the potassium salt of the dianion is used as the starting reagent. It has also been reported[4] that the solutions of the dimethylsilyl-bridged dicyclopentadiene $(C_5H_4(SiMe_2))_2$ ligand show a fluxional behavior caused by 1,2-metallotropic rearrangements which leads to an equilibrium between the *cis* and *trans* isomers in the molar ratio 1/2.4 at 27 °C in C_6D_6:



Therefore, the stereoselective formation of *cis*-**3**, when a solution containing a mixture of both *cis* and *trans* isomers of the ligand is used, only can be explained if the reaction is kinetically controlled, as the *trans* isomer would probably be thermodynamically preferred from steric considerations.

No interconversion has been observed by ^1H NMR between *cis* and *trans* isomers, even when benzene-d_6 solutions of the hydrides *cis*-**3** and *trans*-**3** are warmed to 80 °C for several days (decomposition occurs at higher temperatures). This indicates that there is not a kinetically accessible pathway for the interconversion between both isomers, making it difficult to determine their relative thermodynamical stability. It has been pointed out[5] that the coordination of large metal−ligand fragments such as $(C_5Me_5)M$ seems to favor a *trans* arrangement for steric reasons. However, steric factors do not seem to be important in the stereochemistry of our complexes, as indicated by the crystal structures of *cis*-**4** and *trans*-**4** (see below) where intermolecular distances between metals are even shorter than the intramolecular ones.

Crystal Structures of *cis*-4 and *trans*-4. The molecular structures of *cis*-**4** and *trans*-**4** based on the X-ray structural analysis are shown in Figures 1 and

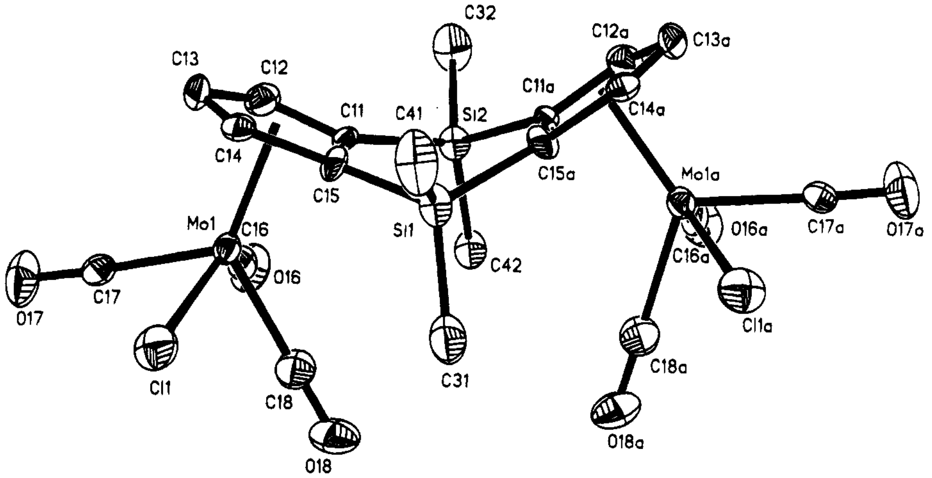


Figure 1. Perspective view of the molecular structure of *cis*-**4** (molecule A) with the atom-numbering scheme.

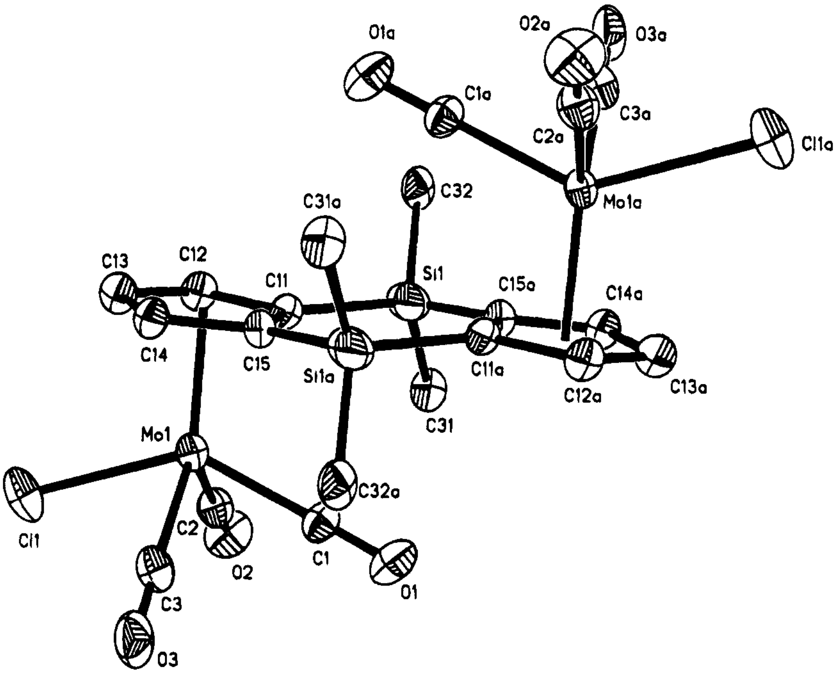


Figure 2. Perspective view of the molecular structure of *trans*-**4** with the atom-numbering scheme.

2, respectively, along with the numbering scheme employed. Atomic parameters for the non-hydrogen atoms are listed in Table 1 and important bond distances and bond angles in Table 2. The crystals of *cis*-**4** were of medium quality (see Experimental Section).

In the asymmetric unit of the unit cell of *cis*-**4** there exist two independent half-molecules that build up the complete molecules through a symmetry plane which contains the silicon atoms and the methyl groups bonded to them (Figure 3). Molecule A is defined as containing Mo(1), Si(1), and Si(2); molecule B contains Mo(2), Si(3), and Si(4). Both molecules A and B are *cis* species in the sense that the two metal atoms are located in the same face of the $(C_5H_3(SiMe_2))_2$ ligand which is bent along the silicon atom line, locating the metals in *exo* positions with respect to the dihedral angle defined by the cyclopentadienyl rings. This bending, reflected by the angles shown at the top of Figure 3, lengthens the intramolecular Mo—Mo distances. From a simple geometric valuation, the calculated Mo—Mo distance would be 5.0 Å for a planar system, while the values found are 6.542(1) Å in *cis*-**4** (A) and 6.72(1) Å in *cis*-**4**(B). It is interesting to note that some intermolecular Mo—Mo distances are shorter than the intramolecular distances, with 6.30(1) Å as the minimum value. We could compare these distances with the Mo—Mo distance of 6.491 Å found[3] in $[\{Mo(CO)_3Cl\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$. These data show that the $(C_5H_3(SiMe_2))_2$ group is actually flexible. In addition to the interaction between the coordination spheres of the metal atoms, the crystal packing or other effects can easily modify the bending of this system.

The *trans*-**4** molecule consists of halves related by a symmetry center located at the center of the $(C_5H_3(SiMe_2))_2$ system. This system is only slightly folded compared with the situation described above for *cis*-**4**. The central ring formed by C(11)—C(15)—Si(1)—C(11a)—C(15a)—Si(1a) is planar and makes an angle of 7.8° with the plane defined by each cyclopentadienyl ring (Figure 3). The silicon atoms and the methyl groups define a plane which divides the molecule into two equivalent parts. O(1) is located practically in this plane and is equidistant from two methyl groups with distances of 2.68 and 2.78 Å to one hydrogen of each

Table 1. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of *cis*-4 and *trans*-4

atom	x	y	z	B^a (Å^2)
cis-4				
Mo(1)	1.0021(1)	0.07676(5)	0.12089(4)	2.68(2)
Mo(2)	1.4927(1)	0.42961(5)	−0.13130(4)	2.59(2)
Cl(1)	0.8185(4)	0.0402(2)	0.0711(2)	4.85(9)
Cl(2)	1.6433(4)	0.4785(2)	−0.1981(2)	5.5(1)
Si(1)	0.9390(5)	0.250	0.0411(2)	3.2(1)
Si(2)	1.1630(5)	0.250	0.1517(2)	2.8(1)
Si(3)	1.5532(5)	0.250	−0.2075(2)	3.2(1)
Si(4)	1.3904(5)	0.250	−0.0791(2)	2.8(1)
C(16)	1.069(1)	0.0674(7)	0.1986(6)	4.0(3)
O(16)	1.111(1)	0.0621(5)	0.2430(4)	5.5(3)
C(17)	1.003(1)	−0.0273(7)	0.1321(5)	3.2(3)
O(17)	1.006(1)	−0.0882(5)	0.1365(5)	6.5(3)
C(18)	0.877(1)	0.1173(8)	0.1722(6)	4.4(3)
O(18)	0.8058(9)	0.1411(6)	0.2001(5)	6.2(3)
C(26)	1.446(2)	0.4344(8)	−0.0498(6)	5.0(4)
O(26)	1.416(1)	0.4366(6)	−0.0032(4)	5.9(3)
C(27)	1.479(1)	0.5340(7)	−0.1224(5)	3.2(3)
O(27)	1.464(1)	0.5948(5)	−0.1181(5)	6.2(3)
C(28)	1.645(1)	0.4053(8)	−0.0919(7)	4.3(3)
O(28)	1.729(1)	0.3935(7)	−0.0700(5)	7.4(3)
C(11)	1.126(1)	0.1726(6)	0.1041(5)	2.3(2)
C(12)	1.189(1)	0.1093(7)	0.0971(6)	3.5(3)
C(13)	1.147(1)	0.0716(6)	0.0503(6)	3.7(3)
C(14)	1.058(1)	0.1103(7)	0.0271(5)	2.7(3)
C(15)	1.035(1)	0.1730(6)	0.0605(5)	2.7(3)
C(21)	1.458(1)	0.3262(6)	−0.1821(5)	2.5(2)
C(22)	1.414(1)	0.3836(7)	−0.2167(5)	3.9(3)
C(23)	1.324(1)	0.4187(6)	−0.1873(6)	3.9(3)
C(24)	1.305(1)	0.3835(7)	−0.1344(5)	3.3(3)
C(25)	1.389(1)	0.3239(6)	−0.1308(5)	2.4(2)
C(31)	0.801(2)	0.250	0.079(1)	5.7(6)
C(41)	0.903(2)	0.250	−0.0366(9)	5.4(6)
C(32)	1.327(2)	0.250	0.162(1)	5.2(6)
C(42)	1.080(2)	0.250	0.2209(8)	3.8(5)
C(33)	1.568(3)	0.250	−0.2869(8)	7.1(7)
C(43)	1.702(2)	0.250	−0.177(1)	6.2(7)
C(34)	1.255(3)	0.250	−0.037(1)	7.1(7)
C(44)	1.517(2)	0.250	−0.0312(9)	5.2(6)
trans-4				
Mo(1)	0.11912(1)	0.23954(2)	0.57705(2)	2.802(6)
Cl(1)	0.18771(5)	0.02206(8)	0.57827(7)	5.15(2)
Si(1)	0.10014(4)	0.59176(7)	0.50929(4)	2.64(1)
O(1)	0.1153(1)	0.4323(3)	0.7237(1)	5.23(6)
O(2)	0.3243(2)	0.3001(3)	0.7081(2)	5.58(7)
O(3)	0.0532(2)	0.0637(3)	0.6899(2)	5.63(6)
C(1)	0.1170(2)	0.3635(3)	0.6712(2)	3.66(6)
C(2)	0.2507(2)	0.2765(3)	0.6620(2)	3.89(7)
C(3)	0.0783(2)	0.1265(3)	0.6496(2)	3.95(7)
C(11)	0.0689(1)	0.4153(3)	0.4763(2)	2.67(5)
C(12)	0.1115(2)	0.3291(3)	0.4410(2)	3.18(5)
C(13)	0.0626(2)	0.2118(3)	0.4119(2)	3.66(6)
C(14)	−0.0098(2)	0.2196(3)	0.4304(2)	3.10(6)
C(15)	−0.0089(1)	0.3449(3)	0.4689(2)	2.57(5)
C(31)	0.2109(2)	0.6161(3)	0.6165(2)	4.40(7)
C(32)	0.1074(2)	0.6766(3)	0.4128(2)	4.06(6)

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

group. Probably this interaction forces a small angular displacement of the Cp ring with respect to the planarity. This situation is similar to that described for *trans*-[$Li_2(TMEDA)_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$], where the angle between the planes is 7.1°,[4] while *trans*-[$(TiCl_3)_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] is completely planar.[7] The small or no folding in the *trans* complexes is in contrast with the important folding found in the metallocene-type species *trans*-[$\{Cr(C_5H_5)\}_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] and *trans*-[$\{Fe(C_5Me_5)\}_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] complexes (folding angles between the Cp rings 45.7 and 44°, respectively).[5,6] The intramolecular Mo—Mo distance in *trans*-4 is 6.416 Å, and also some intermolecular Mo—Mo distances are shorter than the intramolecular distance, with 6.068 Å as a minimum value.

Each Mo atom in *cis*-4 (A,B) and *trans*-4 has a "four-legged piano-stool" coordination. 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 111.1 to 130.1° for *cis*-4 and from 110.6 to 126.7° for *trans*-4. The angles between contiguous legs range from 76 to 80° for *cis*-4 and from 76.5(1) to 78.3(1)° for *trans*-4. These figures are typical for this type of structure. The CO ligands have a linear arrangement, with Mo—C—O angles from 178 to 179.5°. Mo—C and C—O distances are normal for terminal CO groups. The Mo—C(ring) distances range from 2.30(1) to 2.38(1) Å in *cis*-4(A), from 2.32(1) to 2.36(1) Å in *cis*-4(B), and from 2.295(2) to 2.393(3) Å in *trans*-4.

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 cannulas through Subaseals. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium benzophenone ketyl; hexane from sodium; CCl_4 over $CaCl_2$. 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 ^1H 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 $SiMe_4$, and coupling constants are in Hz. C, H, and N analyses were performed with a Perkin-Elmer 240-B instrument. Mass spectra were recorded with a Hewlett-Packard 5988A spectrometer.

Syntheses. The compounds (1,3,5-$C_6H_3Me_3$)$Mo(CO)_3$ (**1**) and $(C_5H_4(SiMe_2))_2$ were prepared according to reported methods.[4,8]

Preparation of *cis*-[$\{Mo(CO)_3H\}_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] (*cis*-3). $(C_5H_4(SiMe_2))_2$ (0.30 g, 1.22 mmol) and **1** (0.73 g, 2.45 mmol) are dissolved in THF (50 mL). The solution is stirred until the ν(CO) absorptions of **1** at 1959 and 1874 cm^{-1} disappear (*ca.* 4 h). Then, the solvent is evaporated to dryness and the residue extracted with hexane (50 mL). The solvent is partially evaporated (*ca.* 25 mL) and the solution cooled to −40 °C overnight to give *cis*-**3** as a white or pale yellow solid, both with the same analytical composition (0.66 g, 90%, mp 126−127 °C). Anal. Calcd for $C_{20}H_{20}O_6Si_2Mo_2$: C, 39.7; H, 3.3. Found: C, 39.5; H, 3.5. MS: *m/e* 580 (M^+ − CO). IR (THF): ν(CO) 2020 s, 1929 vs. ^1H NMR (C_6D_6): δ 5.02 (t, 1 H, C_5H_3, ^3J(HH) = 2), 4.78 (d, 2 H, C_5H_3), 0.46 (s, 3 H, SiMe_2), −0.02 (s, 3 H, SiMe_2), −4.94 (s, 1 H, Mo−*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 227.0 (s, *C*O), 104.0 (s, C_5H_3 α to the $SiMe_2$ bridges), 98.1 (s, C_5H_3 γ to the $SiMe_2$ bridges), 96.6 (s, C_5H_3 β to the $SiMe_2$ bridges), 3.7 (s, SiMe_2), 3.0 (s, SiMe_2).

Preparation of *cis*-[$\{Mo(CO)_3Cl\}_2\{\mu$-η^5:η^5-$(C_5H_3(SiMe_2))_2\}$] (*cis*-4). A solution of *cis*-**3** is prepared by reaction of **1** (1.56 g, 5.2 mmol) and $(C_5H_4(SiMe_2))_2$ (0.63 mL, 2.6 mmol) in THF (50 mL) as described previously. The solution is evaporated to dryness, and the yellow oil is dissolved in CCl_4 (*ca.* 50 mL). An orange precipitate appears (5 min). The stirring is continued overnight. Then, the orange solid (1.58 g, 90% , dec pt 175 °C) is filtered and dried *in vacuo*. Anal. Calcd for $C_{20}H_{18}O_6Si_2Cl_2Mo_2$: C, 35.65; H, 2.7. Found: C, 35.9; H, 2.6 IR (THF): ν(CO) 2050 s, 1966 vs. ^1H NMR (acetone-

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-4 and *trans*-4

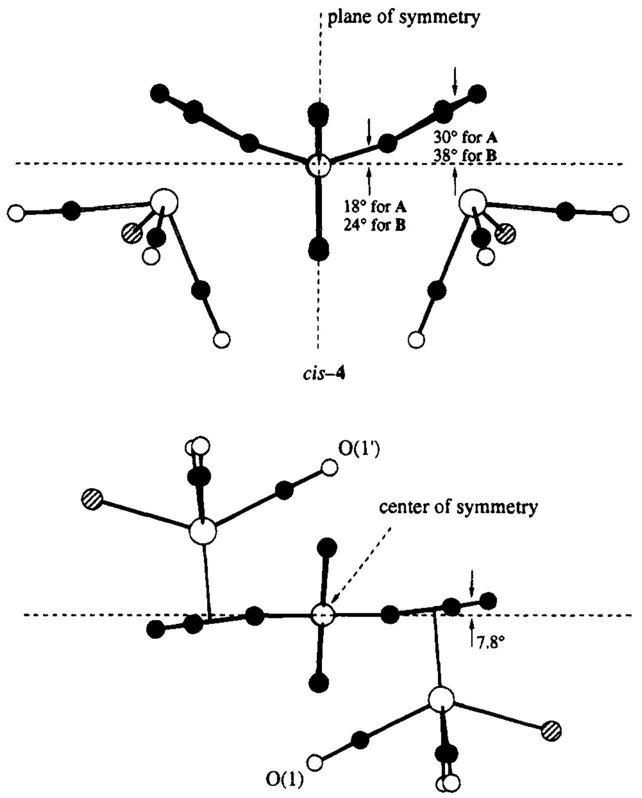
cis-4					
molecule A		molecule B		*trans*-4	
		Distances			
Mo(1)—Cl(1)	2.502(4)	Mo(2)—Cl(2)	2.508(4)	Mo(1)—Cl(1)	2.5060(9)
Mo(1)—C(11)	2.33(1)	Mo(2)—C(21)	2.32(1)	Mo(1)—C(11)	2.295(2)
Mo(1)—C(12)	2.30(1)	Mo(2)—C(22)	2.37(1)	Mo(1)—C(12)	2.345(3)
Mo(1)—C(13)	2.35(1)	Mo(2)—C(23)	2.35(1)	Mo(1)—C(13)	2.393(3)
Mo(1)—C(14)	2.39(1)	Mo(2)—C(24)	2.32(1)	Mo(1)—C(14)	2.340(2)
Mo(1)—C(15)	2.34(1)	Mo(2)—C(25)	2.32(1)	Mo(1)—C(15)	2.301(2)
Mo(1)—C(16)	1.99(1)	Mo(2)—C(26)	1.99(1)	Mo(1)—C(1)	2.005(3)
Mo(1)—C(17)	1.98(1)	Mo(2)—C(27)	1.99(1)	Mo(1)—C(2)	2.023(3)
Mo(1)—C(18)	2.02(1)	Mo(2)—C(28)	2.02(1)	Mo(1)—C(3)	2.009(4)
Mo(1)—cp(1)[a]	2.002	Mo(2)—cp(2)[a]	1.99	Mo(1)—cp(1)[a]	1.994
Si(1)—C(15)	1.88(1)	Si(3)—C(21)	1.90(1)	Si(1)—C(11)	1.879(3)
Si(2)—C(11)	1.89(1)	Si(4)—C(28)	1.85(1)		
Si(1)—C(31)	1.81(3)	Si(3)—C(33)	1.88(2)	Si(1)—C(31)	1.865(2)
Si(1)—C(41)	1.87(2)	Si(3)—C(43)	1.85(2)	Si(1)—C(32)	1.854(4)
Si(2)—C(32)	1.89(2)	Si(4)—C(34)	1.84(3)		
Si(2)—C(42)	1.89(2)	Si(4)—C(44)	1.84(3)		
C(11)—C(12)	1.41(2)	C(21)—C(22)	1.44(2)	C(11)—C(12)	1.433(4)
C(11)—C(15)	1.46(2)	C(21)—C(25)	1.44(2)	C(11)—C(15)	1.467(4)
C(12)—C(13)	1.40(2)	C(22)—C(23)	1.41(2)	C(12)—C(13)	1.403(4)
C(13)—C(14)	1.36(2)	C(23)—C(24)	1.43(2)	C(13)—C(14)	1.417(5)
C(14)—C(15)	1.45(2)	C(24)—C(25)	1.49(2)	C(14)—C(15)	1.421(4)
C(16)—O(16)	1.15(2)	C(26)—O(26)	1.15(2)	C(1)—O(1)	1.119(4)
C(17)—O(17)	1.16(2)	C(27)—O(27)	1.16(2)	C(2)—O(2)	1.135(4)
C(18)—O(18)	1.14(2)	C(28)—O(28)	1.11(2)	C(3)—O(3)	1.143(5)
		Angles			
Mo(1)—C(16)—O(16)	178(1)	Mo(2)—C(26)—O(26)	178(2)	Mo(1)—C(1)—O(1)	179.5(3)
Mo(1)—C(17)—O(17)	177(1)	Mo(2)—C(27)—O(27)	177(1)	Mo(1)—C(2)—O(2)	178.1(3)
Mo(1)—C(18)—O(18)	178(1)	Mo(2)—C(28)—O(28)	178(1)	Mo(1)—C(3)—O(3)	178.4(3)
cp(1)—Mo(1)—Cl(1)	111.1	cp(2)—Mo(2)—Cl(2)	112.5	cp(1)—Mo(1)—Cl(1)	110.6
cp(1)—Mo(1)—C(16)	111.5	cp(2)—Mo(2)—C(26)	107.1	cp(1)—Mo(1)—C(1)	112.0
cp(1)—Mo(1)—C(17)	123.1	cp(2)—Mo(2)—C(27)	125.8	cp(1)—Mo(1)—C(2)	125.9
cp(1)—Mo(1)—C(18)	129.1	cp(2)—Mo(2)—C(28)	130.1	cp(1)—Mo(1)—C(3)	126.7
Cl(1)—Mo(1)—C(17)	78.1(4)	Cl(2)—Mo(2)—C(27)	75.9(4)	Cl(1)—Mo(1)—C(2)	78.3(1)
Cl(1)—Mo(1)—C(18)	77.0(4)	Cl(2)—Mo(2)—C(28)	77.3(4)	Cl(1)—Mo(1)—C(3)	77.7(1)
C(16)—Mo(1)—C(17)	77.7(5)	C(26)—Mo(2)—C(27)	80.4(6)	C(1)—Mo(1)—C(2)	77.9(1)
C(16)—Mo(1)—C(18)	75.9(6)	C(26)—Mo(2)—C(28)	78.3(7)	C(1)—Mo(1)—C(3)	76.5(1)

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

Table 3. Crystallographic Data for *cis*-4 and *trans*-4

	cis-4	*trans*-4
formula	$C_{20}H_{18}O_6Si_2Cl_2Mo_2$	$C_{20}H_{18}O_6Si_2Cl_2Mo_2$
cryst habit	prismatic	prismatic
color	orange	orange
symmetry	orthorhombic, *Pnma*	monoclinic, *C2/c*
unit cell determn	least-squares fit from 25 rflns	least-squares fit from 25 rflns
unit cell dimens		
a, Å	11.435(3)	17.168(5)
b, Å	18.881(3)	10.195(1)
c, Å	23.535(4)	16.329(4)
β, deg		119.37(1)
packing: V, Å^3; Z	5082(3); 8	2490(1); 4
D_{calcd}, g cm^{-3}	1.76	1.795
M_r	673.32	673.32
$F(000)$	2656	1328
μ, cm^{-1}	13.0	13.27
technique	four-circle diffractometer; bisecting geometry, graphite-oriented monochromator; Mo Kα; $\omega/2\theta$ scans; $\theta_{max} = 27°$	
no. of rflns		
measd	5608	5923
indep-obsd	2348 ($I \geq 3\sigma(I)$)	2500 ($I \geq 2\sigma(I)$)
range of *hkl*	h, 0−13; k, 0−22; l, 0−28	h, −21 to +21; k, 0−13; l, 0−20
std rflns	2 rflns every 120 min; no variation	
R	0.075	0.033
R_w	0.11	0.057
goodness-of-fit indicator	2.27	2.342
largest param shift/error	0.09	0.05
max peak in final diff map, e Å^{-3}	1.5 (near Mo)	0.523
min peak in final diff map, e Å^{-3}	2.1	0.272

d_6): δ 6.54 (t, 1 H, C_5H_3, ^3J(HH) = 3), 5.92 (d, 2 H, C_5H_3), 0.71 (s, 3 H, SiMe_2), 0.52 (s, 3 H, SiMe_2). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 244.1 (s, *CO trans* to Cl), 225.2 (s, *CO cis* to Cl), 111.4 (s, C_5H_3 β to the SiMe$_2$ bridges), 106.6 (s, C_5H_3 α to the SiMe$_2$ bridges), 99.9 (s, C_5H_3 γ to the SiMe$_2$ bridges), 4.0 (s, SiMe_2), 0.2 (s, SiMe_2).



cis–4

trans–4

Figure 3. (Top) Drawing of *cis*-**4** showing the plane of symmetry that relates one half-molecule with the other. The angles between a plane perpendicular to the plane of symmetry and the planes defined by Si(1)–C(11)–C(15)–Si(2) and by the cyclopentadienyl ring are shown. (Bottom) Drawing of *trans*-**4** showing the center of symmetry that relates one half-molecule with the other. The angle between the Si(1)–C(11)–C(15)–Si(1a)–C(11a)–C(15a) ring plane and the cyclopentadienyl ring plane is shown.

Preparation of *trans*-K$_2$[{Mo(CO)$_3$}$_2${μ-η^5:η^5-(C$_5$H$_3$(SiMe$_2$))$_2$}] (*trans*-2). A mixture of K$_2$[(C$_5$H$_3$(SiMe$_2$))$_2$] (1.31 g, 4.11 mmol), prepared by reaction of KH and (C$_5$H$_4$(SiMe$_2$))$_2$, and **1** (2.47 g, 8.23 mmol) is stirred for 7 h in THF (50 mL). The mixture is filtered, and the solution is evaporated *in vacuo* to dryness. The pale yellow solid then obtained (2.63 g, 94%) is washed several times with hexane to eliminate mesitylene. Anal. Calcd for C$_{20}$H$_{18}$O$_6$Si$_2$K$_2$Mo$_2$: C, 35.3; H, 2.7. Found: C, 35.3; H, 3.0. IR (THF): ν(CO) 1895 s, 1789 vs, 1748 vs. ^{1}H NMR (acetone-d_6): δ 5.24 (d, 2 H, C$_5$$H_3$, ^3J(HH) = 2), 5.00 (t, 1 H, C$_5$$H_3$), 0.34 (s, 6 H, Si$Me_2$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 236.3 (s, CO), 101.6 (s, C$_5$H$_3$ α to the SiMe$_2$ bridges), 95.3 (s, C$_5$H$_3$ β to the SiMe$_2$ bridges), 94.2 (s, C$_5$H$_3$ γ to the SiMe$_2$ bridges), 6.0 (s, SiMe_2).

Preparation of *trans*-[{Mo(CO)$_3$H}$_2${μ-η^5:η^5-(C$_5$H$_3$(SiMe$_2$))$_2$}] (trans-3). Glacial acetic acid (5 mL, 87 mmol) is added to a solution of *trans*-**2** (0.45 g, 0.66 mmol) in THF (50 mL). The solution is stirred for 15 min and then evaporated to dryness. The residue is extracted with hexane (50 mL) and the solution partially evaporated and cooled at −40 °C to give a white solid that is characterized as *trans*-**3** (0.35 g, 90%, mp 108–109 °C). Anal. Calcd for C$_{20}$H$_{20}$O$_6$Si$_2$Mo$_2$: C, 39.7; H, 3.3. Found: C, 40.0; H, 3.5 MS: *m/e* 608 (M$^+$). IR (THF): ν(CO) 2027 s, 1945 vs. ^{1}H NMR (C$_6$D$_6$): δ 4.9 (m, 3 H, C$_5$$H_3$), 0.23 (s, 6 H, Si$Me_2$), −5.61 (s, 1 H, Mo–$H$). ^{13}C{^{1}H} NMR (C$_6D_6$): δ 227.2 (s, CO), 103.7 (s, C_5H$_3$ α to the SiMe$_2$ bridges), 99.1 (s, C_5H$_3$ β to the SiMe$_2$ bridges), 97.2 (s, C$_5$H$_3$ γ to the SiMe$_2$ bridges), 3.1 (s, SiMe_2).

Preparation of trans-[{Mo(CO)$_3$Cl}$_2${μ-η^5:η^5-(C$_5$H$_3$(SiMe$_2$))$_2$}] (*trans*-4). This complex is obtained as a red-orange solid (0.58 g, 80%, dec pt 138 °C) from *trans*-**3** (0.65 g, 1.09 mmol) by the same procedure described for *cis*-**4**. Anal. Calcd for C$_{20}$H$_{18}$O$_6$Si$_2$Cl$_2$Mo$_2$: C, 35.7; H, 2.7. Found: C, 35.4; H, 2.5. IR (THF): ν(CO) 2049 s, 1972 vs. ^{1}H NMR (CDCl$_3$): δ 6.29 (t, 1 H, C$_5$$H_3$, ^3J(HH) = 3), 5.61 (d, 2 H, C$_5$$H_3$), 0.54 (s, 6 H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 242.5 (s, CO *trans* to Cl), 223.1 (s, CO *cis* to Cl), 108.8 (s, C_5H$_3$ β to the SiMe$_2$ bridges), 103.6 (s, C_5H$_3$ α to the SiMe$_2$ bridges), 102.2 (s, C$_5$H$_3$ γ to the SiMe$_2$ bridges), 1.4 (s, SiMe_2).

Crystal Structures of *cis*-4 and *trans*-4. Suitably sized orange crystals of *trans*-**4** were obtained by crystallization from CH$_2$Cl$_2$/diethyl ether. After several recrystallizations from CH$_2$Cl$_2$/hexane, only poor quality crystals of *cis*-**4** were obtained. The crystals were mounted in sealed tubes under argon in an Enraf-Nonius CAD-4 automatic four-circle diffractometer. Crystallographic and experimental details are summarized in Table 3. 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 structures were solved by a combination of heavy atoms, direct methods, and Fourier synthesis. The structures were refined on F by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included from the geometrical calculations and refined for one cycle isotropically. Final $R = 0.075$ and $R_w = 0.11$ 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 for *cis*-**4** and $R = 0.033$ and $R_w = 0.057$ values for *trans*-**4**. Anomalous dispersion corrections and atomic scattering factors were taken from ref 9. Calculations were performed with the SDP Enraf-Nonius package,[10] MULTAN,[11] and DIRDIF[12] on a Microvax II computer.

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Supplementary Material Available: For *cis*-**4** and *trans*-**4**, tables of positional parameters for hydrogen atoms and thermal parameters (4 pages). Ordering information is given on any current masthead page.

OM940329R

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