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Reactions of the Doubly Bridged Bis(cyclopentadienyl) Dinuclear Molybdenum Complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ with a Carboxylate-Substituted Allene

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Reaction of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) with equivalent molar amount of allene $H_2C{=}C{=}CHCO_2Me$ in refluxing toluene gave four products: complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}HC{\equiv}CCH_2CO_2Me)]$ (**3**) (10 %) with a crosswise substituted alkyne bridge, $\eta^2\text{-}\eta^2\text{-}HC{\equiv}CCH_2CO_2Me$ derived from a 1,3-hydrogen shift of $H_2C{=}C{=}CHCO_2Me$, complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_2(O)_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(CO_2Me)CHCH_2\}]$ (**6**) (16 %) with a bridging $\eta^1,\eta^3\text{-}C(CO_2Me)CHCH_2$ allylic group, and allene C–C coupled complexes $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^3\text{-}\eta^3\text{-}\{MeO_2CCH(CH_2)C\}(CHCHCHCO_2Me)\}]$ (**4**) (7 %) and $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^3\text{-}\eta^3\text{-}\{MeO_2CCH(CH_2)C\}_2\}]$ (**5**) (13 %), in which the two allene molecules were coupled in head-to-center and center-to-center coupling modes, respectively. When **1** was treated with an excess amount of $H_2C{=}C{=}CHCO_2Me$, only C–C coupled products **4** (10 %) and **5** (22 %) were obtained. In comparison, reaction of the singly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2$ (**2**) with $H_2C{=}C{=}CHCO_2Me$ only gave the $\eta^2\text{-}\eta^2$ coordinated complex $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}H_2CCCHCO_2Me)]$ (**7**) (21 %). These results marked the different reactivities of doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex **1** and the corresponding singly bridged analogue **2**. The formation of these complexes was discussed and the molecular structures of **3**–**7** were determined by X-ray diffraction.

Introduction

Transition-metal-catalyzed reactions of allenes have received great interest in recent years.[1,2] The chemistry of complexes containing allene or its dimer as a ligand have been intimately involved with the development of organometallic chemistry, for they represent one of the most important fundamental steps in catalytic reactions of allenes[3] or basal models for species involved in oligomerization and polymerization of hydrocarbons at metal centers.[4]

Allenes have been reported to bridge a pair of metal atoms in six different ways (Figure 1). There are three $\mu\text{-}\eta^2\text{-}\eta^2$ forms, two with M–M bonds, including C_2 symmetric form **A**[5] and C_{2v} symmetric form **B**,[6] and form **C** without a M–M bond.[7] There are also two $\mu\text{-}\eta^1\text{-}\eta^3$ forms with or without a M–M bond (form **D**[8] and **E**[6a,6c,8c,8g,9]), which have C_s symmetry. There are at least two examples of $\mu\text{-}\eta^1\text{-}\eta^1$ form **F**,[8d,8f] which also has C_s symmetry.

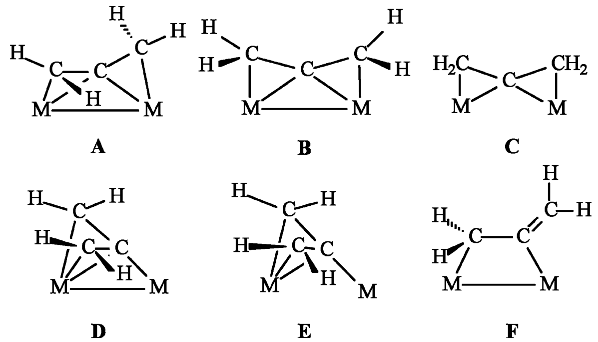

Figure 1. Forms of allene bridging two metals.

Three coupling modes of the dimeric allenes bridging two or more metals were reported (Figure 2). The first is a center-to-center coupling mode, including the $\mu\text{-}\eta^3\text{-}\eta^3$ diallyl with or without a M–M bond (form **G**[8e,10] and **H**[5g,11]) and the $\mu\text{-}\eta^1\text{-}\eta^1$ form **I**,[12] which was found to support a nonbonded diruthenium system. The second is a head-to-head coupling mode with a $\mu\text{-}\eta^2\text{-}\eta^2$ form **J**.[12] The third is a head-to-center coupling mode, which includes the $\mu\text{-}\eta^1\text{-}\eta^3$ form **K**[5g] and the $\mu\text{-}\eta^1\text{-}\eta^2\text{-}\eta^3$ form **L** that partakes in a trimetal system.[13]

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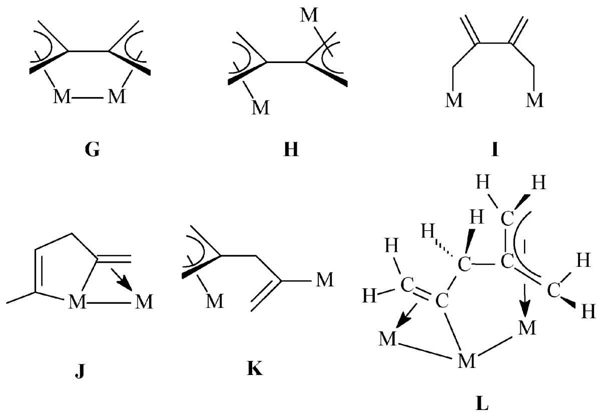


Figure 2. Forms of dimeric allenes bridging two or more metals.

Substituted bridging allenes generally assume one of these basic forms,[14] although distortion will be introduced by the effects of the substituting group. However, two new forms emerged when substituted allenes were involved (Figure 3). Reaction of 1,1-difluoroallene with $Mn_2(CO)_{10}$ yielded a complex with head-to-head coupling mode in μ-η^1-η^1 form **M**.[14j] A new μ-η^1-η^3 form **N**, which is derived from allene, appeared in the complex $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)NiMo(CO)_2[\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(Me)C(Me)CH_2]$[14h,15] with the head carbon atom σ bonded to the metal atom.

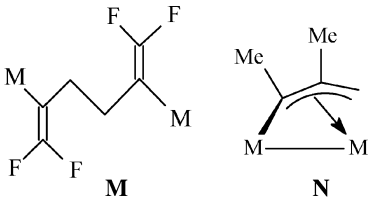
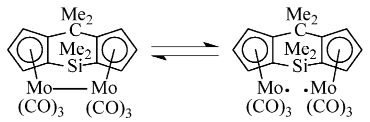


Figure 3. Two new forms of substituted allenes bridging two metals.

Bridged bis(cyclopentadienyl) dinuclear metal complexes in which two reactive metal centers are held in close proximity could potentially exhibit cooperative electronic and steric effects that would be useful in catalysis.[16] In comparison with singly bridged bis(cyclopentadienyl) metal complexes, doubly bridged bis(cyclopentadienyl) ligands are more rigid, and they lock the two metals on either the same or opposite faces of the ligand. They also maintain the two metal centers in close proximity even after metal–metal bond cleavage, which could result in unique structures, reactivities, and catalytic properties.[17] Recently, we reported the reaction of a certain type of doubly bridged bis(cyclopentadiene) with metal carbonyls.[18] A series of dinuclear metal complexes with unusually long M–M bond lengths were obtained. In particular, the Me_2C and Me_2Si doubly bridged bis(cyclopentadienyl) dinuclear molybdenum carbonyl complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) [Mo–Mo = 3.4328(12) Å] exhibited a distinct EPR signal (g = 2.160) in its microcrystalline state (Scheme 1).[18a]



Scheme 1.

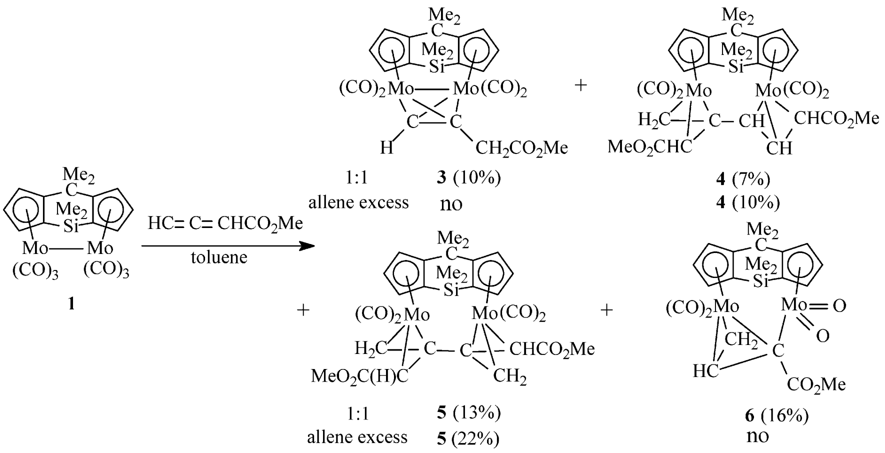
The thermal or photolytic reactions of various allenes with $[CpMo(CO)_3]_2$ only afforded simple allene adducts, in which the allene molecule bridged the Mo–Mo bond in a μ-η^2-η^2 form.[5a,5b,5j,14a,14d,19] Kreiter and coworkers reported the photolysis of $FvMo_2(CO)_6$ (Fv = fulvalene, μ-η^5-η^5-$C_{10}H_8$) with $H_2C{=}C{=}CH_2$,[19] in which the allene acted as η^2-C_3H_4, μ-η^1-η^3-C_3H_4, μ-η^2-η^2-C_3H_4 ligands, or μ-η^1-η^2-η^3-C_6H_8 ligands of its dimer. To further understand the effect of the Me_2C and Me_2Si doubly bridged bis(cyclopentadienyl) ligand on the reactivity of the Mo–Mo bond, in this paper the reaction of **1** with a carboxylate-substituted allene $H_2C{=}C{=}CHCO_2Me$ was studied and a variety of complexes in four different coordination forms were obtained. The reaction of $H_2C{=}C{=}CHCO_2Me$ with the singly bridged analogue $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2$ (**2**) was also examined for comparison.

Results and Discussion

Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with $H_2C{=}C{=}CHCO_2Me$

Reaction of **1** with an equivalent molar amount of $H_2C{=}C{=}CHCO_2Me$ in refluxing toluene produced four products: $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}HC{\equiv}CCH_2CO_2Me)]$ (**3**) (10%), $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^3\text{-}\eta^3\text{-}\{MeO_2CCH(CH_2)C\}(CHCHCHCO_2Me)\}]$ (**4**) (7%), $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4\{\mu\text{-}\eta^3\text{-}\eta^3\text{-}\{MeO_2CCH(CH_2)C\}_2\}]$ (**5**) (13%), and $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_2(O)_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(CO_2Me)CHCH_2\}]$ (**6**) (16%) (Scheme 2). When **1** was treated with a large excess of $H_2C{=}C{=}CHCO_2Me$ (**1**/allene, 1:10), only allene C–C coupled products **4** and **5** were obtained in 10 and 22% yields, respectively. The products were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy; elemental analysis; and single-crystal X-ray diffraction analysis.

Complex **3** has a crosswise substituted alkyne bridge η^2-η^2-$HC{\equiv}CCH_2CO_2Me$ (Figure 4), which is derived evidently from the allene $H_2C{=}C{=}CHCO_2Me$ after a 1,3-hydrogen shift. This type of allene rearrangement in reactions with transition metals has not yet been reported. The dimensions of the Mo_2C_2 core is similar to that in the $Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR)$ analogue.[20] The bridging alkyne is tipped over to the CMe_2 bridge side of the doubly bridged ligand and the MeO_2CCH_2 group points away from the doubly bridged ligand (Figure 4, right). It is interesting that complex **3** has no symmetry in the solid state, but its ^1H NMR spectrum only exhibits three resonances for the Cp protons, which is suggestive of C_s symmetry. This can be attributed to the equilibrium of the free rotation around



Scheme 2.

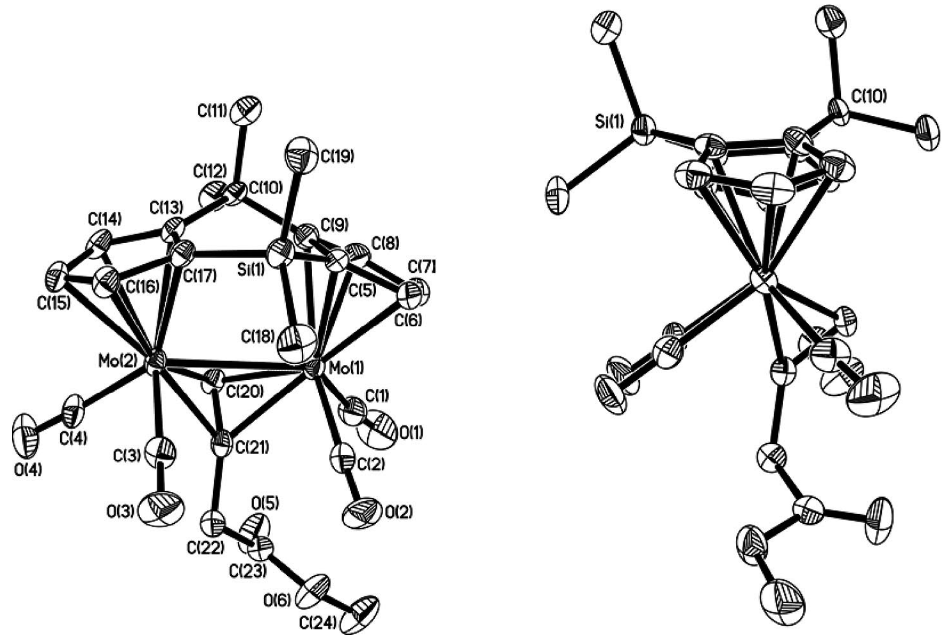


Figure 4. ORTEP diagram of complex **3**. Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity; (left) view perpendicular to the Mo–Mo bond; (right) view down the Mo–Mo axis. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 2.9511(8), Mo(1)–C(20) 2.160(5), Mo(1)–C(21) 2.198(5), Mo(2)–C(20) 2.163(5), Mo(2)–C(21) 2.201(5), C(20)–C(21) 1.362(7), Mo(1)–Cp(centroid) 2.012, Mo(2)–Cp(centroid) 2.012; Mo(1)–C(20)–Mo(2) 86.11(18), Mo(1)–C(21)–Mo(2) 84.27(18), Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 0.5, Cp–Cp fold angle 137.3.

the C–C bond of the CH_2–CO_2Me group in solution. The ^1H and ^{13}C NMR spectroscopic characterization of the $HC{\equiv}CCH_2CO_2Me$ bridge is similar to that found in complex $Cp'_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}HC{\equiv}CCH_2OMe)$ ($Cp' = C_5H_4Me$).[14c] The IR spectrum of **3** shows four strong terminal carbonyl absorptions at 1980~1876 cm^{-1}, which is in the range typical for the carbonyl absorption bands in the analogues $Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR)$,[20] and an absorption at 1736 cm^{-1} assigned to the C=O stretching frequency of the carboxylate group.

Complexes **4** and **5** are isomers. It is difficult to assign their structures from their ^1H NMR spectra. So, their molecular structures were determined by single-crystal X-ray diffraction analysis (Figures 5 and 6). The most interesting structural features of **4** and **5** are the bridging $\mu\text{-}\eta^3\text{-}\eta^3$-biallyl ligands. In complex **4**, two allene units are coupled in a head-to-center mode, which is associated with a 1,2-hydrogen shift [from C(25) to C(26)]. The head-to-center coupling mode once appeared in the $\mu\text{-}\eta^1\text{-}\eta^3$ form **K** (Figure 2, M = Mn)[5g] and the trimetal system with a $\mu\text{-}\eta^1\text{-}\eta^2\text{-}\eta^3$ form **L** (Figure 2, M = Os).[13] In the latter case, two allene molecules were coupled through simple C–C bond formation without any hydrogen shift. So, complex **4** represents a new form of the head-to-center coupling mode of two allene molecules: the $\mu\text{-}\eta^3\text{-}\eta^3$ biallyl form **O**, which bridges two metal atoms without a M–M bond (Figure 7). In **4**, the

Mo···Mo distance of 4.663 Å is much longer than that in **1** [3.4328(12) Å] and the sum of the covalent radius of two molybdenum atoms (3.24 Å),[21] which indicates the absence of a Mo–Mo bond. The allene dimer acts as a six-electron donor, which also demands cleavage of the Mo–Mo bond. In **4**, the M–C_{allyl} distances are in the order of Mo–C_H av. 2.39 Å > Mo–C_E av. 2.32 Å > Mo–C_C av. 2.28 Å (Table 1). It is reasonable that the Mo–C_C bonds are the shortest, but the Mo–C_E distances are 0.06~0.08 Å shorter than the Mo–C_H distances. This is probably due to the fact that the Mo–C_E bonds are close to a σ bond (η^1), whereas the C_C–C_H bonds are more likely π bonded (η^2) to the Mo atom. The longer bond length of C_E–C_H (av. 1.44 Å) than that of C_C–C_H (av. 1.40 Å) further supports this theory. All of the allylic C–C bond lengths approach typical C(sp^2)–C(sp^2) single-bond lengths (1.46 Å),[22] whereas the coupling C(21)–C(25) bond length [1.484(4) Å] is longer than that. The $(Me_2C)(Me_2Si)(\eta^5\text{-}C_5H_3)_2$ ligand is almost in a flat conformation. The remarkable variety in the dihedral angle between the two Cp rings, which ranges from 149.3° in **1** to 173.7° in **4**, also results from cleavage of the Mo–Mo bond by insertion of an allene dimer. The two allyl units of the dimeric ligand are not parallel to each other, as indicated by a dihedral angle of 51.2°.

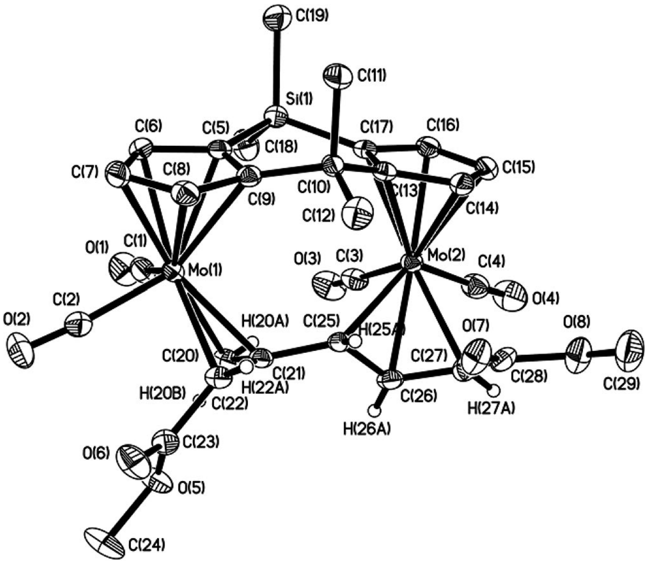


Figure 5. ORTEP diagram of complex **4**. Thermal ellipsoids are shown at the 30% level; all hydrogen atoms except that of the η^3-allyl moiety are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 4.663, Mo(1)–Cp(centroid) 2.043, Mo(2)–Cp(centroid) 2.011; C(20)–C(21)–C(22) 118.5(3), C(25)–C(26)–C(27) 119.9(3), Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 2.1, Cp–Cp 173.7. For the Mo–C_{allyl} and C_{allyl}–C_{allyl} bond lengths, see Table 1.

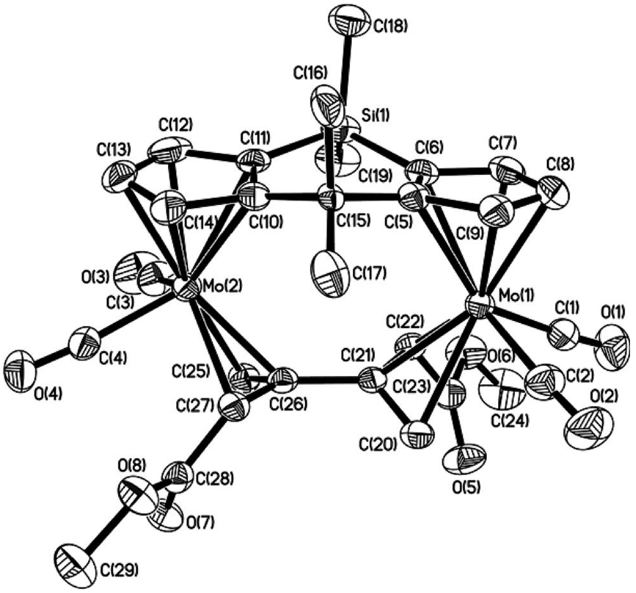


Figure 6. ORTEP diagram of complex **5**. Thermal ellipsoids are shown at the 30% level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 4.911, Mo(1)–Cp(centroid) 2.025, Mo(2)–Cp(centroid) 2.022; C(20)–C(21)–C(22) 116.9(5), C(25)–C(26)–C(27) 115.5(5), Mo(1)–C(21)–C(26)–Mo(2) 26.3(10), Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 6.8, Cp–Cp 172.5. For the Mo–C_{allyl} and C_{allyl}–C_{allyl} bond lengths, see Table 1.

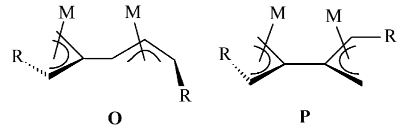


Figure 7. Two new forms of substituted allenes bridging two metals.

Complex **4** is stable in the solid state, but somewhat sensitive to air in solution. In the ^{1}H NMR spectrum of **4**, the cyclopentadienyl hydrogen atoms occur as six sets of well-resolved multiplets; in addition, there are six resonances for the allylic protons at δ = 5.0–2.8 ppm, which suggest the asymmetry of the structure and are consistent with its solid-state molecule. Its ^{1}H NMR spectrum also shows the existence of another minor isomer (see Experimental Section

Table 1. Selected bond lengths [Å] in complexes **4** and **5**.

	4				**5**			
Mo–C_H[a]	Mo(1)–C(20)	2.386(3)	Mo(2)–C(25)	2.398(3)	Mo(1)–C(20)	2.381(6)	Mo(2)–C(25)	2.354(6)
Mo–C_C[b]	Mo(1)–C(21)	2.264(3)	Mo(2)–C(26)	2.302(3)	Mo(1)–C(21)	2.292(6)	Mo(2)–C(26)	2.257(5)
Mo–C_E[c]	Mo(1)–C(22)	2.301(3)	Mo(2)–C(27)	2.336(3)	Mo(1)–C(22)	2.276(6)	Mo(2)–C(27)	2.295(5)
C_H–C_C	C(20)–C(21)	1.404(5)	C(25)–C(26)	1.396(4)	C(20)–C(21)	1.396(8)	C(25)–C(26)	1.420(8)
C_E–C_C	C(21)–C(22)	1.446(4)	C(26)–C(27)	1.422(5)	C(21)–C(22)	1.444(8)	C(26)–C(27)	1.432(8)
C_P–C_P[d]	C(21)–C(25)	1.484(4)			C(21)–C(26)	1.520(8)		

[a] C_H represents the H-substituted carbon atom of the allyl. [b] C_C represents the center carbon atom of the allyl. [c] C_E represents the CO_2Me-substituted carbon atom of the allyl. [d] C_p represents the coupling carbon of the allyl.

for details, and this will be discussed together with complex **6** below). The obvious diversity of the resonances of the four CH carbon atoms in the biallyl ligand is in accordance with the head-to-center coupling mode of the two allene molecules. The IR spectrum of **4** displays three strong terminal carbonyl bands and one absorption due to the C=O stretching frequency of the carboxylate group.

In complex **5**, the two allene molecules are coupled in a center-to-center mode. It (form **P**, Figure 7) resembles form **H** very much, except that it has two Mo atoms located on the same side of the biallyl ligand, as a result of the locking effect of the doubly bridge ligand. The Mo···Mo distance of 4.911 Å is even longer than that of **4**, presumably due to the center-to-center coupling mode in **5** with the unexpected long coupling C(21)–C(26) bond length of 1.520(8) Å. The two allyl planes are twisted by 42.4° around the C(21)–C(26) bond. Two molybdenum atoms and C(21), and C(26) are almost coplanar, and none of them deviate by more than 0.0648 Å from the mean plane. The Cp–Cp fold angle (172.5 vs. 173.7°) decreased slightly, whereas its torsion angle Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) (6.8 vs. 2.1°) increased in comparison with those of **4**.

The spectroscopic data of **5** is consistent with its structure. Four strong resonances at 1976~1878 cm^{-1} due to terminal carbonyl absorptions and an absorption at 1699 cm^{-1} attributed to the C=O stretching frequency of the carboxylate group are observed in its IR spectrum, which are very similar to those of complex **4**. The ^1H NMR spectrum of **5** comprises five sets of resonances for the allene protons with a ratio of 1:1:2:1:1, two resonances for the CO_2Me groups, and six sets of well-resolved multiplets for the Cp protons, all of which indicates the absence of symmetry in the complex. The asymmetry of the structure is also recognized by its ^{13}C NMR spectrum, in which resonances due to the CH_2 (δ = 65.4 and 35.5 ppm) and CH (δ = 60.3 and 38.1 ppm) carbon atoms of the allyl group are separated distinctly. The resonance of the coupling carbon atom is in the range typical for complexes containing the similar biallyl ligand, such as $Fe_2(CO)_6(\mu\text{-}\eta^3\text{-}\eta^3\text{-}CH_3SCHCCH_2)_2$,[14g] whereas the low-field resonance of the CH_2 carbon atom and the high-field resonance of the CH carbon atom are not consistent with other complexes.[10a,14g]

Compound **6** is the one remaining compound obtained from the reaction of **1** with an equivalent molar amount of $H_2C=C=CHCO_2Me$. There are two crystallographically independent molecules in the unit cell of **6**. Figure 8 shows one of the molecules. It contains a bridging $\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(CO_2Me)CHCH_2$ allylic group in form **N**. The other example of form **N** is the $(\eta^5\text{-}Cp)(\eta^5\text{-}C_5H_4Me)NiMo(CO)_2[\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(Me)C(Me)CH_2]$ complex, which was obtained from $(\eta^5\text{-}Cp)(\eta^5\text{-}C_5H_4Me)NiMo(CO)_2[\mu\text{-}\eta^1\text{-}\eta^3\text{-}C(CMe_2)\text{-}(CH_2)]$ after a 1,4-hydrogen shift that occurred on the surface of the silica (Scheme 3).[14h,15] The $\mu\text{-}\eta^1\text{-}\eta^3$-allylic ligand here was obtained by an easy 1,2-hydrogen shift on the allene. The allene ligand is η^3 or π bonded to Mo(1) and η^1 or σ bonded to Mo(2) with the CH_2CO_2Me-substituted C(20) atom. It should be noted that Mo(2) is oxidized. The Mo(1)–C(allyl) bonds in **6** are significantly different from each other and range from 2.174(5) to 2.347(5) Å. These values are unexceptional, as wide variations in the Mo–C bond lengths have been observed in other allyl complexes.[23] The Mo···Mo distance of 3.955 Å indicates the absence of a Mo–Mo bond. The dihedral angle (154.2°) between the two Cp rings is larger than that of **1** (149.3°), but much smaller than those of **4** and **5** (173.7 and 172.5°). The twist of the bridging ligand is evident, as reflected by the large torsion angle Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) (23.1°).

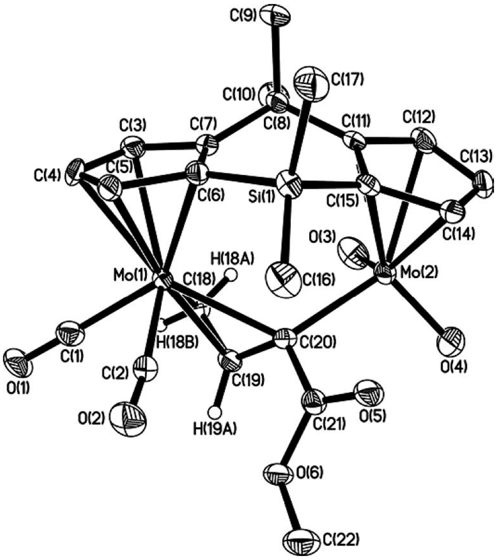
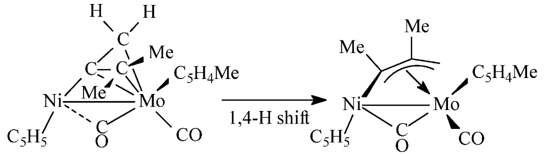


Figure 8. ORTEP diagram of complex **6**. Thermal ellipsoids are shown at the 30% level; all hydrogen atoms except that of η^3-allyl are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 3.955, Mo(1)–C(18) 2.332(5), Mo(1)–C(19) 2.269(5), Mo(1)–C(20) 2.347(5), Mo(2)–C(20) 2.174(5), Mo(2)–O(3) 1.711(5), Mo(2)–O(4) 1.698(4), C(18)–C(19) 1.391(8), C(19)–C(20) 1.451(8), Mo(1)–Cp(centroid) 2.018, Mo(2)–Cp(centroid) 2.143, Mo(2)–C(20)–Mo(1) 122.0(2), C(18)–Mo(1)–C(20) 64.00(17), Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 23.1, Cp–Cp 154.2.

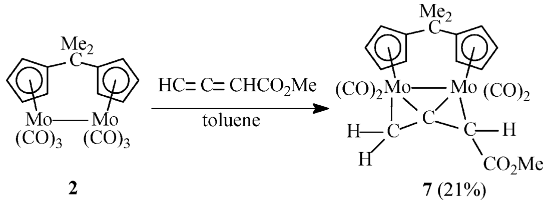


Scheme 3.

Three resonances for the allylic protons and five resonances for the Cp protons are exhibited in the ^1H NMR spectrum of **6**. In the ^{13}C NMR spectrum, the resonances of the tertiary and quaternary carbon atoms of the allyl ligand are greatly shifted to lower field in comparison with those of **5**. The spectrum also shows that another minor isomer exists for **6** (see Experimental Section for details). Because of the difference of the two bridging atoms, the exchange of the CMe_2 and $SiMe_2$ groups of the doubly bridged ligands is assumed to be the cause for the two isomers. The two isomers could not be separated by column chromatograph, or by recrystallization. Such a phenomenon was also observed in complex **4**. The IR spectrum of **6** (as a mixture of two isomers) contains four strong absorptions at 1970~1888 cm^{-1} for the terminal carbonyl groups and an absorption at 1663 cm^{-1} for the carboxylate group. The absorptions at 926 and 889 cm^{-1} are attributed to the *ν*(Mo=O) frequency.[24]

Reaction of $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2$ (2) with $H_2C{=}C{=}CHCO_2Me$

The reaction of **2** with $H_2C{=}C{=}CHCO_2Me$ was carried out for comparison. Only the $(Me_2C)[(\eta^5\text{-}C_5H_4)_2Mo_2(CO)_4\text{-}(\mu\text{-}\eta^2\text{-}\eta^2\text{-}H_2CCCHCO_2Me)]$ (**7**) product was obtained in 21% yield (Scheme 4). This is consistent with the result of the reaction of $Cp_2Mo_2(CO)_4$ with allene.[5a,5b,5j,14a,14d] Complex **7** consists of a $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_2]_2$ unit bridged by $\eta^2\text{-}\eta^2\text{-}H_2CCCHCO_2Me$ (Figure 9). As expected, the C_3 unit is nonlinear with a C–C–C bond angle of 139.3(3)°. The Mo–Mo bond length of 3.0791(5) Å is much shorter than that of $[Cp_2Mo_2(CO)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}H_2CCCH_2)]$ [3.117(1) Å][5a,5b] and $[Cp_2Mo_2(CO)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}H_2CCCF_2)]$ [3.162(1) Å].[14a] The CO_2Me substitution results in an unsymmetrical situation of the Mo–C distances to the allene ligand: the Mo(2)–C(7) [2.341(3) Å] distance is much longer than that of Mo(1)–C(5) [2.316(3) Å]. The spectroscopic data is consistent with its solid-state molecule. Eight resonances for the Cp protons are observed in the ^1H NMR spectrum, which is indicative of the asymmetry of the molecule and attributed to the locking effect of the bridge. In addition, four strong carbonyl and one carboxylate absorptions are shown in the IR spectrum.



Scheme 4.

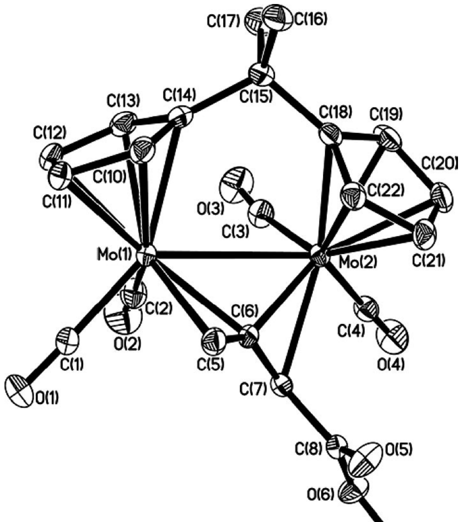
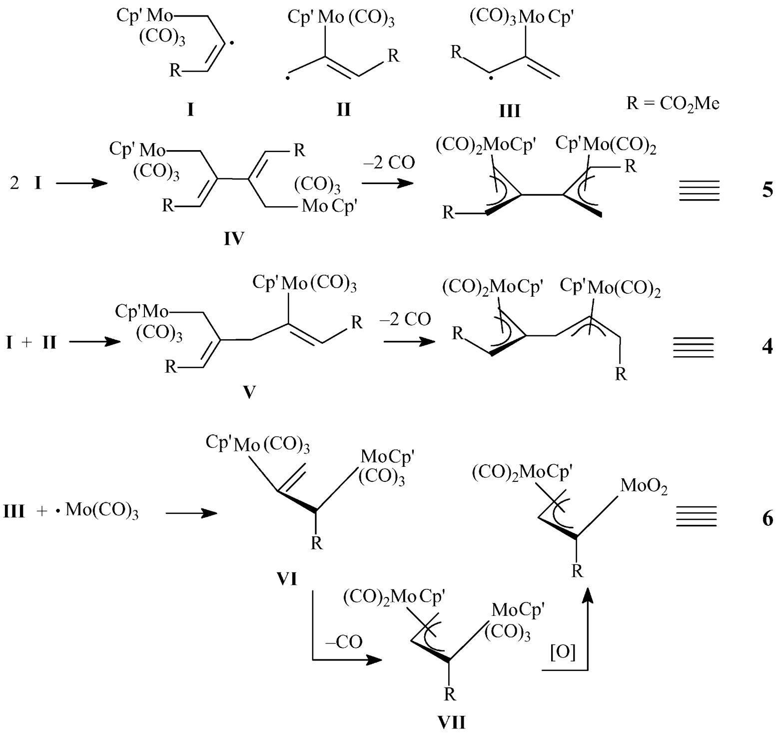


Figure 9. ORTEP diagram of complex **7**. Thermal ellipsoids are shown at the 30% level; all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–Mo(2) 3.0791(5), Mo(1)–C(5) 2.316(3), Mo(1)–C(6) 2.204(3), Mo(2)–C(6) 2.097(3), Mo(2)–C(7) 2.341(3), C(5)–C(6) 1.397(4), C(6)–C(7) 1.408(4), C(5)–C(6)–C(7) 139.3(3), Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 33.0, Cp–Cp 124.5.

Proposed Mechanism

Kreiter and coworkers[5g] proposed that $Mn_2(CO)_{10}$ could react with allene ($H_2C{=}C{=}CH_2$) under irradiation in two different ways. One way is the initial photoactivation, which involves homolytic metal–metal bond fission of $Mn_2(CO)_{10}$ to generate two $Mn(CO)_5$ radicals. The metal radical could then attack allene to produce a carbon radical, which can then couple with each other to form $Mn_2(CO)_8[\mu\text{-}\eta^3\text{-}\eta^3\text{-}(H_2CCCH_2)_2]$ and $Mn_2(CO)_9[\mu\text{-}\eta^1\text{-}\eta^3\text{-}\{C(=CH_2)(CH_2)\}(H_2CCCH_2)]$ in center-to-center and head-to-center coupling modes, respectively. The other way is loss of a CO ligand from $Mn_2(CO)_{10}$ to give $Mn_2(CO)_9$, which can further react with allene to produce $Mn_2(CO)_8\text{-}[\mu\text{-}\eta^2\text{-}\eta^2\text{-}(H_2CCCH_2)]$. As mentioned above, because of the rigidity of the doubly bridged bis(cyclopentadienyl) ligand, complex **1** contains an unusually long Mo–Mo bond, which even exists partially as Mo radicals in the crystal state.[18a] So, the radical pathway might account for the formation of complexes **4**–**6**. The proposed mechanism is outlined in Scheme 5. Three kind of radicals (**I**, **II**, and **III**) might exist when the $Cp'Mo(CO)_3$ (Cp′ represents a Cp ligand of the doubly bridged ligand) radical is treated with $H_2C{=}C{=}CHCO_2Me$ if the doubly bridged ligand is not concerned. Complex **5** can then be formed via intermediate **IV** with the coupling of **I**. Apparently, coupling of **I** and **II** with each other results in the formation of **4**. Among the three radicals, radical **III** is the most stable, but no product derived from the coupling of radical **III** with **I** or **II** was isolated. The steric effect of the R group might be responsible for this fact. Radical **III** can react with the $Cp'Mo(CO)_3$ radical to afford complex **6** via intermediates **VI** and **VII** after oxidation. No $Cp'Mo(CO)_3$ radical exists freely when an excess amount of the allene is used, so the formation of complex **6** is suppressed in the reaction of **1** with excess allene.

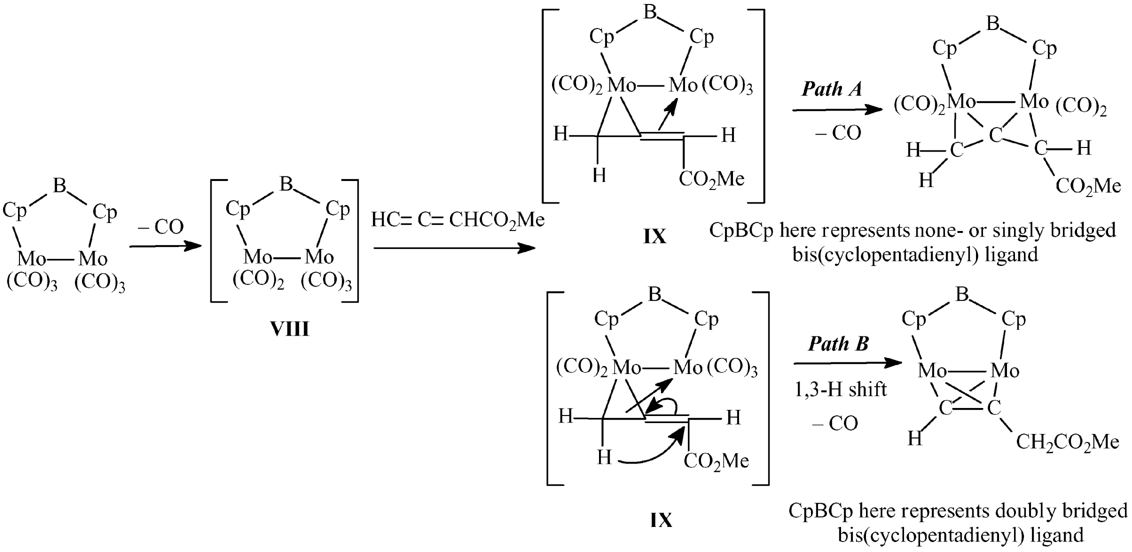
As regards the formation of complexes **3** and **7**, the CO-loss pathway is preferred (Scheme 6). After decarbonylation, resulting intermediate **VIII** reacts with $H_2C{=}C{=}CHCO_2Me$ to give intermediate **IX**, which can then go through two different paths depending on the type of cyclopentadienyl ligand. When the cyclopentadienyl ligand (CpBCp) has no bridge or a single bridge, the reaction follows *Path A* to afford the μ-η^2-η^2-allene product. If the ligand (CpBCp) is doubly bridged, it adopts *Path B* to give the μ-η^2-η^2-alkyne product through 1,3-H shift. In μ-η^2-η^2-



Scheme 5.

allene product **7**, the twist of the two Cp rings around the Mo–Mo axis is evident [Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) torsion angle 33.0°]. The singly bridged cyclopentadienyl ligand can supply such a large torsion to accommodate the allene in an approximate criss-cross arrangement with the Mo–Mo bond, but the rigidity of the doubly bridged bis(cyclopentadienyl) ligand restricts the twist of the two Cp rings to meet the $\mu\text{-}\eta^2\text{-}\eta^2$-allene arrangement. This viewpoint is also supported by the demands of the short Mo–Mo bond length of the $\mu\text{-}\eta^2\text{-}\eta^2$-allene complex [for example in complex **7**, Mo–Mo 3.0791(5) Å], whereas Mo–Mo bond complex **1** can hardly reach such an arrangement owing to the rigidity of the doubly bridged bis(cyclopentadienyl) ligand.[18] So, treatment of **1** with $H_2C{=}C{=}CHCO_2Me$ affords the $\mu\text{-}\eta^2\text{-}\eta^2$-alkyne product instead of the $\mu\text{-}\eta^2\text{-}\eta^2$-allene product.

When the reaction of **1** is performed with a large excess of allene, the radical pathway is favored instead of the CO-loss pathway, as they generate the more active intermediate radicals (**I** and **II**) and the equilibrium cited in Scheme 1 goes towards the radicals on the right-hand side. Thus, complex **3** is not formed in the reaction of **1** with an excess



Scheme 6.

amount of allene, whereas in the reaction of **2** with allene, only the CO-loss pathway occurs, and it is less sensitive to the concentration of the allene.

Conclusions

Reaction of the singly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2$ (**2**) with $H_2C{=}C{=}CHCO_2Me$ only gave the η^2-η^2 coordinated complex **7**, but the reaction of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) with allene $H_2C{=}C{=}CHCO_2Me$ gave four unexpected products. The rigidity of the doubly bridged bis(cyclopentadienyl) ligand plays an essential role in the reaction. Alkyne isomerization from allene was observed in complex **3**. The C–C coupling of two allene molecules in center-to-head and center-to-center coupling modes was found in complexes **4** and **5**. The reactions may undergo two different pathways: the radical pathway and the CO-loss pathway. The results indicated the different reactivity of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex **1** from those of the corresponding singly bridged and nonbridged analogues. This will help us to further study its potential application in synthesis and catalysis.

Experimental Section

General Procedures: Schlenk and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under an atmosphere of argon prior to use. ^1H NMR spectra were recorded with a Bruker AV300 instrument. $^{13}C\{^1H\}$ NMR experiments were carried out with a Varian Mercury VX300 instrument at 75.5 MHz. The spectra of complexes **4**–**6** were assigned with the aid of $^1H,^{13}C$ correlation through gHSQC experiments. The $^{13}C\{^1H\}$ NMR of complex **7** was not obtained because of its low solubility. IR spectra were recorded as KBr disks with a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$[18a] (**1**) and $(Me_2C)[(\eta^5\text{-}C_5H_4)Mo(CO)_3]_2$[25] (**2**) were prepared by literature methods. $H_2C{=}C{=}CHCO_2Me$ was provided by Professor Shengming Ma (Shanghai Institute of Organic Chemistry).

Reaction of 1 with an Equivalent Molar Amount of $H_2C{=}C{=}CHCO_2Me$: A solution of **1** (117 mg, 0.20 mmol) and $H_2C{=}C{=}CHCO_2Me$ (20 mg, 0.20 mmol) in toluene (30 mL) was heated at reflux for 10 h. The color of the solution changed from deep-green to brown. After the solvent was removed in vacuo, the residue was chromatographed on an alumina column (petroleum ether/CH_2Cl_2) to give three bands. The first band (yellow-green) gave unreacted **1** (9 mg, 8%). The second band (green) afforded **3** (12 mg, 10%) as green crystals. The third band (yellow) afforded **4** (9 mg, 7%) as orange crystals as a mixture of two isomers in a 3:1 ratio. The fourth band (orange) (eluted by acetone/CH_2Cl_2) gave **5** (17 mg, 13%) as orange crystals. The fifth band (purple) (eluted by acetone) afforded **6** (18 mg, 16%) as purple crystals as a mixture of two isomers in a 1:1 ratio.

Complex 3: M.p. 191 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.42 (m, 2 H, Cp-H), 5.31 (m, 2 H, Cp-H), 5.11 (m, 2 H, Cp-H), 4.12 (s, 2 H, CH_2), 3.97 (br. s, 1 H, C≡CH), 3.65 (s, 3 H, CO_2CH_3), 1.60 (s, 3 H, CMe), 1.19 (s, 3 H, CMe), 0.59 (s, 3 H, SiMe), 0.30 (s, 3 H, SiMe) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 232.0, 226.1 (CO), 171.9 (C=O), 135.7, 105.8, 96.6, 96.4 (Cp), 88.6 (≡CH), 87.0, 86.9, 83.0, 82.8 (Cp), 51.5 (d, *J* = 7.8 Hz, ≡C), 49.4 (OMe), 41.5 (CH_2), 37.2 (d, *J* = 7.3 Hz, C*Me*$_2$), 35.0 (*C*Me$_2$), 24.0 (d, *J* = 6.0 Hz, C*Me*$_2$), 6.4, 1.1 (Si*Me*$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 1980 (s) (ν_{CO}), 1950 (s) (ν_{CO}), 1904 (s) (ν_{CO}), 1876 (m) (ν_{CO}), 1736 (m) ($\nu_{C=O}$) cm^{-1}. $C_{24}H_{24}Mo_2O_6Si$ (628.42): calcd. C 45.87, H 3.85; found C 45.70, H 3.48.

Complex 4: M.p. 177 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$) major isomer: δ = 6.02 (m, 1 H, Cp-H), 5.80 (m, 1 H, Cp-H), 5.59 (m, 1 H, Cp-H), 5.15 (m, 1 H, Cp-H), 5.00 (d, *J* = 11.0 Hz, 1 H, CH), 4.95 (m, 1 H, Cp-H), 4.79 (m, 1 H, CH), 4.21 (m, 1 H, Cp-H), 4.16 (d, *J* = 2.4 Hz, 1 H, CH_2), 4.04 (d, *J* = 2.4 Hz, 1 H, CH_2), 3.57 (s, 3 H, OCH_3), 3.56 (s, 3 H, OCH_3), 3.38 (d, *J* = 6.45 Hz, 1 H, CH), 2.82 (s, 1 H, CH), 1.42 (s, 3 H, CMe), 1.40 (s, 3 H, CMe), 0.46 (s, 3 H, SiMe), 0.35 (s, 3 H, SiMe) ppm. ^1H NMR (300 MHz, $CDCl_3$) the minor isomer: δ = 5.89 (d, *J* = 11.0 Hz, 1 H, CH), 5.79 (m, 2 H, Cp-H), 5.56 (m, 1 H, Cp-H), 5.39 (m, 1 H, Cp-H), 5.29 (m, 1 H, Cp-H), 4.68 (m, 1 H, CH), 4.37 (br. s, 2 H, CH_2), 4.14 (m, 1 H, Cp-H), 3.58 (s, 3 H, OCH_3), 3.55 (s, 3 H, OCH_3), 3.32 (d, *J* = 6.45 Hz, 1 H, CH), 2.77 (s, 1 H, CH), 1.51 (s, 3 H, CMe), 1.39 (s, 3 H, CMe), 0.75 (s, 3 H, SiMe), 0.29 (s, 3 H, SiMe) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) major isomer: δ = 240.2, 238.6, 236.1, 234.2 (CO), 177.3, 176.5 (C=O), 143.4, 140.4, 107.1, 101.5 (Cp), 96.1 (d, *J* = 7.3 Hz, CH), 96.7 (H_2C*C*CH), 94.0, 91.5, 87.6 (Cp), 87.4 (CH), 87.1, 84.4 (d, *J* = 13.0 Hz) (Cp), 52.6 (d, *J* = 8.5 Hz, CH), 51.2, 50.8 (OMe), 48.0 (CH_2), 42.8 (d, *J* = 6.2 Hz, C*Me*$_2$), 39.6 (d, *J* = 9.5 Hz, CH), 35.5 (*C*Me$_2$), 22.5 (d, *J* = 6.2 Hz, C*Me*$_2$), 3.2, 0.6 (Si*Me*$_2$) ppm. As a result of decomposition, the $^{13}C\{^1H\}$ NMR spectrum of the minor isomer was not clear. IR (KBr) mixture of isomers: $\tilde{\nu}$ = 1969 (s) (ν_{CO}), 1950 (s) (ν_{CO}), 1874 (s) (ν_{CO}), 1697 (m) ($\nu_{C=O}$). $C_{29}H_{30}Mo_2O_8Si$ (726.52): calcd. C 47.94, H 4.16; found C 47.71, H 3.97.

Complex 5: M.p. 182 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88 (m, 1 H, Cp-H), 5.77 (m, 1 H, Cp-H), 5.61 (m, 1 H, Cp-H), 5.41 (m, 1 H, Cp-H), 5.23 (m, 1 H, Cp-H), 5.08 (m, 1 H, Cp-H), 3.95 (s, 1 H, CH_2), 3.93 (d, *J* = 1.75 Hz, 1 H, CH_2), 3.81 (br. s, 2 H, CH), 3.75 (d, *J* = 1.75 Hz, 1 H, CH_2), 3.73 (s, 1 H, CH_2), 3.61 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 1.41 (s, 3 H, CMe), 1.32 (s, 3 H, CMe), 0.57 (s, 3 H, SiMe), 0.28 (s, 3 H, SiMe) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 235.3, 235.0, 233.2, 232.4 (CO), 178.8, 178.0 (C=O), 135.8, 133.5, 103.0, 102.7 (Cp), 96.7 (coupling-C), 92.1 (d, *J* = 14.9 Hz), 90.0, 89.0, 88.8, 86.2, 85.5 (d, *J* = 13.2 Hz) (Cp), 65.4 (CH_2), 60.3 (CH), 50.9, 50.8 (OMe), 42.9 (d, *J* = 7.0 Hz, C*Me*$_2$), 38.1 (CH), 35.5 (CH_2), 35.0 (*C*Me$_2$), 27.1 (d, *J* = 7.4 Hz, C*Me*$_2$), 3.6, –1.1 (Si*Me*$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 1967 (s) (ν_{CO}), 1952 (s) (ν_{CO}), 1896 (s) (ν_{CO}), 1878 (m) (ν_{CO}), 1699 (m) ($\nu_{C=O}$) cm^{-1}. $C_{29}H_{30}Mo_2O_8Si$ (726.52): calcd. C 47.94, H 4.16; found C 47.49, H 4.58.

Complex 6: M.p. 181 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$) isomer 1: δ = 6.50 (m, 2 H, Cp-H), 6.27 (m, 1 H, Cp-H), 5.89 (m, 1 H, Cp-H), 5.80 (m, 1 H, Cp-H), 5.29 (m, 1 H, Cp-H), 4.94 (m, 1 H, CH), 3.66 (s, 3 H, OCH_3), 3.05 (d, *J* = 6.47 Hz, 1 H, CH_2), 2.81 (d, *J* = 10.4 Hz, 1 H, CH_2), 1.62 (s, 3 H, CMe), 1.44 (s, 3 H, CMe), 0.65 (s, 3 H, SiMe), 0.48 (s, 3 H, SiMe) ppm. ^1H NMR (300 MHz, $CDCl_3$) isomer 2: δ = 6.45 (m, 1 H, Cp-H), 6.34 (m, 2 H, Cp-H), 6.11 (m, 1 H, Cp-H), 5.35 (m, 2 H, Cp-H), 5.14 (m, 1 H, CH), 3.60 (s, 3 H, OCH_3), 3.07 (d, *J* = 6.47 Hz, 1 H, CH_2), 2.89 (d, *J* = 10.4 Hz, 1 H, CH_2), 1.82 (s, 3 H, CMe), 1.67 (s, 3 H, CMe), 0.47 (s, 3 H, SiMe), 0.39 (s, 3 H, SiMe) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 238.3, 237.5, 237.0 (CO, mixture), 179.6, 179.1 (C=O,

Table 2. Crystal data and summary of X-ray data collection for **3**–**7**.

	3	**4**·CH_2Cl_2	**5**	**6**	**7**
Empirical formula	$C_{24}H_{24}Mo_2O_6Si$	$C_{30}H_{32}Cl_2MoO_8Si$	$C_{29}H_{30}Mo_2O_8Si$	$C_{22}H_{24}Mo_2O_6Si$	$C_{22}H_{20}Mo_2O_6$
Fw	628.40	811.43	726.50	604.38	572.26
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2(1)$	$P2(1)/n$
a [Å]	10.022(2)	9.8647(15)	36.826(5)	9.6173(12)	14.167(2)
b [Å]	10.377(2)	11.0399(18)	9.6174(13)	16.310(2)	9.4266(14)
c [Å]	12.011(2)	16.568(3)	20.476(3)	14.5586(18)	15.848(2)
α [°]	98.015(3)	73.557(2)	90	90	90
β [°]	102.659(3)	80.401(2)	123.78	93.231(2)	105.825(2)
γ [°]	93.180(3)	70.342(2)	90	90	90
V [Å^3]	1202.0(4)	1624.6(4)	5292(3)	2280.1(5)	2799(5)
Z	2	2	8	4	4
D_{calcd} [g cm^{-3}]	1.736	1.659	1.601	1.761	1.867
μ [mm^{-1}]	1.131	1.021	0.919	1.188	1.269
F(000)	628	816	2928	1208	1136
Crystal size [mm]	0.26 × 0.20 × 0.14	0.32 × 0.28 × 0.16	0.28 × 0.26 × 0.20	0.22 × 0.18 × 0.10	0.24 × 0.22 × 0.16
Max. 2θ [°]	50.02	50.00	52.80	53.74	52.68
No. of reflections collected	6166	8315	16379	13187	10869
No. of independent reflections/R_{int}	4224/0.0285	5680/0.0182	6136/0.0433	5401/0.0259	4124/0.0284
No. of parameters	303	394	367	569	274
GOF on F^2	1.004	1.049	1.107	1.035	1.094
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0370, 0.0803	0.0291, 0.0694	0.0519, 0.1050	0.0338, 0.0739	0.0255, 0.0573
$R1$, $wR2$ (all data)	0.0638, 0.0919	0.0409, 0.0761	0.0900, 0.1192	0.0441, 0.0794	0.0419, 0.0640
Largest peak in final diff map [e Å^{-3}]	0.516	0.734	0.904	0.702	0.518

mixture), 160.4 (HC*C*CO$_2$Me, mixture), 143.4, 135.9, 131.2, 128.8 (Cp, mixture), 114.7 (d, J = 15.2 Hz, Cp, isomer 2), 110.7 (d, J = 17.1 Hz, Cp, isomer 1), 109.8 (Cp, mixture), 109.4 (Cp, isomer 2), 109.2 (Cp, isomer 1), 108.5 (d, J = 17.0 Hz, Cp, isomer 2), 107.0 (d, J = 16.7 Hz, Cp, isomer 1), 100.1 (d, J = 17.1 Hz, CH, isomer 2), 98.9 (d, J = 19.0 Hz, CH, isomer 1), 95.6 (Cp, isomer 1), 95.3 (Cp, mixture), 94.8 (Cp, isomer1), 93.1 (d, J = 10.8 Hz, Cp, isomer 2), 91.0 (d, J = 13.6 Hz, Cp, isomer 1), 90.2 (d, J = 12.4 Hz, Cp, isomer 2), 87.2 (d, J = 12.9 Hz, Cp, isomer 2), 50.9, 50.8 (OMe, mixture), 41.7 (CH$_2$, mixture), 40.3 (d, J = 9.5 Hz, C*Me*$_2$, isomer 1), 36.5, 36.2 (*C*Me$_2$, mixture), 35.8 (d, J = 9.3 Hz, C*Me*$_2$, isomer 2), 25.2 (d, J = 7.8 Hz, C*Me*$_2$, isomer 2), 24.3 (d, J = 9.0 Hz, C*Me*$_2$, isomer 1), 4.5 (Si*Me*$_2$, isomer 2), 1.8 (Si*Me*$_2$, isomer 1), –2.0 (Si*Me*$_2$, isomer 1), –4.4 (Si*Me*$_2$, isomer2) ppm. IR (KBr) mixture of isomers: $\tilde{\nu}$ = 1969 (s) (ν_{CO}), 1956 (s) (ν_{CO}), 1902 (s) (ν_{CO}), 1888 (s) (ν_{CO}), 1663 (m) ($\nu_{C=O}$) cm^{-1}. $C_{22}H_{24}Mo_2O_6Si$ (604.39): calcd. C 43.72, H 4.00; found C 43.75, H 4.16.

Reaction of 1 with an Excess Amount of $H_2C{=}C{=}CHCO_2Me$: A solution of **1** (117 mg, 0.20 mmol) and $H_2C{=}C{=}CHCO_2Me$ (200 mg, 2.0 mmol) in toluene (30 mL) was heated at reflux for 5 h. The color of the solution changed from deep-green to dark-orange. After the solvent was removed in vacuo, the residue was chromatographed on an alumina column (petroleum ether/CH$_2$Cl$_2$) to give a yellow band, which afforded **4** (15 mg, 10%) as orange crystals. The use of acetone/CH$_2$Cl$_2$ as the eluent afforded an orange band, which gave **5** (32 mg, 22%) as orange crystals.

Reaction of 2 with $H_2C{=}C{=}CHCO_2Me$: A solution of **2** (200 mg, 0.37 mmol) and $H_2C{=}C{=}CHCO_2Me$ (400 mg, 4.0 mmol) in toluene (50 mL) was heated at reflux for 12 h. The color of the solution changed from deep-red to black. After the solvent was removed in vacuo, the residue was chromatographed on an alumina column (petroleum ether/CH$_2$Cl$_2$) to give a blue band, which afforded **7** (45 mg, 21%) as green crystals. M.p. 165 °C (dec.). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.53 (m, 1 H, Cp-H), 5.31 (m, 1 H, Cp-H), 5.11 (m, 1 H, Cp-H), 4.98 (m, 1 H, Cp-H), 4.88 (m, 1 H, Cp-H), 4.51 (m, 1 H, Cp-H), 4.42 (m, 1 H, Cp-H), 3.99 (s, 1 H, CH), 3.80 (m, 1 H, Cp-H), 3.70 (br. s, 3 H, OCH$_3$), 3.05 (s, 1 H, CH$_2$), 3.83 (s, 1 H, CH$_2$), 1.57 (s, 3 H, CMe), 1.54 (s, 3 H, CMe) ppm. IR (KBr): 1977 (s) (ν_{CO}), 1940 (s) (ν_{CO}), 1886 (s) (ν_{CO}), 1855 (m) (ν_{CO}), 1686 (m) ($\nu_{C=O}$)cm^{-1}. $C_{22}H_{20}Mo_2O_6$ (572.28): calcd. C 46.17, H 3.52; found C 46.46, H 3.20.

Crystallographic Studies: Single crystals of complexes **3**–**7** suitable for X-ray diffraction were obtained from hexane/CH$_2$Cl$_2$ solutions. Data collection was performed with a Bruker SMART 1000 by using graphite-monochromated Mo-K_α radiation (ω-2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were performed with the SHELXL-97 program system. The molecular structure of **4** contains a CH$_2$Cl$_2$ molecule of solvation. The crystal data and summary of X-ray data collection are presented in Table 2.

CCDC-636563, -636564, -636565, -636566 and -661650 for compounds **3**–**7** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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