Cyclopentadienylmolybdenum(II) and -(III) Complexes Containing Diene and Allyl Ligands. 2. Comparative Reactivity of the Isomeric Complexes CpMo(η-C_3H_5)(η-C_4H_6) with Either *supine* or *prone* Allyl and Either *s-cis* (*Supine*) or *s-trans* Butadiene Ligands toward Protons

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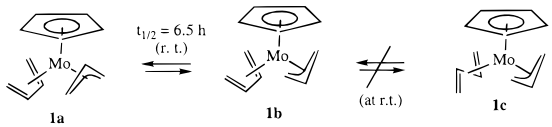
Abstract: The electron-rich isomeric complexes CpMo(η^3-C_3H_5)(η^4-C_4H_6) (**1a**, *prone*-C_3H_5; *supine*-C_4H_6; **1b**, *supine*-C_3H_5; *supine*-C_4H_6; **1c**, *supine*-C_3H_5; *s-trans*-C_4H_6) do not react with neutral ligands under mild conditions. They are, however, easily protonated by a variety of different acids. Protonation of **1a** and **1b** involves attack at the terminal position of the allyl ligand and elimination of propene. Protonations with acetic acid show rates in the order **1a** > **1b** and afford the same product, CpMo(O_2CCH_3)(η^4-C_4H_6), **2**, which can be oxidized to the 17-electron cation [**2**]$^+$. HBF_4 protonation of **1a** in the absence of trapping donor molecules affords [CpMo(η^4-*supine*-C_4H_6)(μ-F_2BF_2)]$_n$, **3**. The latter readily reacts with donor molecules to afford [CpMo(η^4-*supine*-C_4H_6)L_2][BF_4] products (L = MeCN, **4**; Bu^{t}NC, **5**; or L_2 = 1,3-butadiene, **6**), which are also directly and selectively obtained by protonation of **1a** in the presence of the appropriate ligand. Compound **6** has a (*supine*-C_4H_6)(*s-trans*-C_4H_6) configuration and converts into compound **4** when dissolved in MeCN. Protonation of **1c** is much slower relative to the isomers **1a** and **1b**. The observed products depend on the nature of the solvent. Protonation by HBF_4·Et_2O in MeCN affords unstable [CpMo(*supine*-η-C_3H_5)(*syn*-CH_3-*prone*-η-C_3H_4)($NCCH_3$)][BF_4] (**7**), which rapidly exchanges the MeCN ligand. Decomposition of the latter involves a regioselective reductive coupling of the two allyl ligands to generate 3-methyl-1,5-hexadiene quantitatively. In C_6D_6, the HBF_4 protonation of **1c** produces small amounts of propene and a violet precipitate which gives a mixture of **4** and **7** upon treatment in MeCN. In the presence of 1,3-butadiene, protonation of **1c** in THF followed by extraction into acetone affords a mixture of **6** and [CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)(Me_2-CO)][BF_4] (**8**). Compound **8** converts into [CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)(L)][BF_4] (L = MeCN, **9**; PMe_3, **10**) when treated with the appropriate L. Protonation of **1c** in MeCN in the presence of butadiene affords **7** which slowly decomposes, under these conditions, to a mixture of **4** and [CpMo(η^4-*s-trans*-C_4H_6)($MeCN)_2$]$^+$, **11**. The collective results for the protonation of **1c** indicate that the proton attacks the *s-trans* diene ligand in MeCN. The preferred position of attack in nonpolar solvents, on the other hand, is the allyl. The difference of electronic distribution for isomers **1a**−**c** has been investigated by DFT methods. The calculations indicate that the allyl ligand is a stronger donor in the *supine* configuration, while the diene ligand is both a weaker donor and a weaker acceptor when it is coordinated in the *s-trans* mode.

Introduction

Transition metal complexes containing allyl and butadiene ligands have attracted extensive attention due to the fact that they play important roles in catalytic process and in organic syntheses.[2−5] In a previous contribution,[6] we have reported the synthesis and characterization of the title compound in three different isomeric forms (see Scheme 1) and defined the relative thermodynamic stability of the isomers and the barriers to their interconversion through equilibrium and kinetic studies. In short, isomers **1a** and **1c** are the most stable ones and have the same relative free energy (1:1 ratio). On the other hand, the free energy of **1b** is 2.3 kcal/mol higher, being found in equilibrium with **1a** in a ratio of 2:98 at room temperature. The minor isomer has been selectively synthesized by reduction of

Scheme 1



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[**1b**]$^+$. The equilibration of **1a** and **1b** is relatively accessible ($\Delta G^{\ddagger} = 23.6$ kcal/mol), while equilibration with **1c** has a barrier of >30 kcal/mol. Thus, the interconversion between isomers **1a**/**b** and **1c** is essentially frozen at room temperature. The three isomers show different potentials for the electrochemically reversible oxidation processes to the corresponding Mo(III) cations, suggesting that the relative configuration of the ligands regulates the metal electron density in an important way.

Most of the previously reported examples of allyl- and diene-containing molecules are either stable in a single isomeric form, the other form being observed under kinetically controlled conditions, or are observed in two rapidly interconverting forms.[7−14] There are compounds that have been isolated in more than one isomeric form and whose interconversion is slow or frozen under ambient conditions, but their comparative reactivity has not been studied in detail.[13,15−17] Furthermore, no previous example appears to be available where slow isomerization occurs for both the allyl and the diene ligand *in the same molecule*. Therefore, compound **1** is an excellent system to probe the reactivity of both the allyl and the diene ligand as a function of coordination mode. We have in fact observed that the position and rate of proton attack depend on the relative orientation of both allyl and diene ligands, leading to quite different and occasionally complex products. The results of these investigations are reported in the present contribution.

Experimental Section

General Procedures. All reactions were conducted by standard Schlenk-line techniques under a dinitrogen atmosphere. Solvents were dried by conventional methods (THF and Et_2O on Na/benzophenone, toluene and heptane on Na, CH_2Cl_2, on P_4O_{10}) and distilled directly from the drying agent under dinitrogen. All routine NMR experiments were carried out on a Bruker AM400 or WF 200 spectrometers, while 2D-NMR were obtained from a Bruker AMX500 spectrometer. The ^{1}H and ^{13}C NMR data for all new compounds are given in Table 1. EPR spectra were recorded on a Bruker ER200 spectrometer and IR spectra on a Perkin-Elmer FTIR 1600 spectrophotometer. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software; the electrochemical cell was a locally modified Schlenk tube with a Pt counterelectrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with a Ag/AgCl reference electrode and a Pt working electrode. The supporting electrolyte used was 0.1 M $NBu^n_4PF_6$. All potentials are reported vs the Cp_2Fe/Cp_2Fe^+ couple which was introduced into the cell at the end of each measurement. Elemental analyses were performed by Atlantic Microlab, Inc. or the analytical service at the LSEO, Dijon. Compounds CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (**1a**), [CpMo(*supine*-η-C_3H_5)(*supine*-η-C_4H_6)][PF_6] ([**1b**]$^+PF_6^-$), and CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (**1c**) were prepared according to the literature.[6]

Reations of CpMo(η-C_3H_5)(η-C_4H_6) with Nucleophiles. At room temperature, no change in the NMR spectroscopic properties was observed over several days upon mixing compounds CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (**1a**) or CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (**1c**) and excess *tert*-butyl isocyanide (in benzene), methyl lithium (in THF), allylmagnesium bromide (in THF), trimethyl phosphine (in benzene), or carbon monoxide (in benzene).

Reation of CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (1a) with CH_3COOH. Preparation of CpMo(η-CH_3CO_2)(η-C_4H_6) (2). Compound **1a** (300 mg, 1.17 mmol) was dissolved in 20 mL of heptane. To the resulting solution was added 220 μL of acetic acid (3.88 mmol) with a microsyringe at room temperature. The color changed from red-yellow to green upon stirring for 3.5 h. All solvent was removed by evaporation under reduced pressure, and the residue was recrystallized from heptane (5 mL) to yield green crystalline **2** (182 mg, 85% yield). Anal. Calcd for $C_{11}H_{14}MoO_2$: C, 48.18; H, 5.11. Found: C, 48.36; H, 5.15. IR (THF, cm^{-1}): 1529 (m) and 1461 (s). Cyclic voltammogram (versus Fc^+/Fc): irreversible oxidation at $E_{1/2} = -0.45$ V (in CH_2Cl_2) and -0.48 V (in THF).

Oxidation of CpMo(η^2-O_2CCH_3)(η-C_4H_6) (2) by $FcPF_6$, Followed by *in situ* Reduction with Cp_2Co. Compound **2** (4 mg, 0.015 mmol) was dissolved in 0.5 mL of acetone-d_6 and transferred into an NMR tube in which a capillary was placed. The setup was devised to allow the measurements of EPR with the solution inside the capillary and of NMR with the solution inside the NMR tube. The ^{1}H NMR spectrum showed only the presence of compound **2**, while no EPR signal was detected. $FcPF_6$ (5 mg, 0.015 mmol) was added to the NMR tube, causing a color change from green to yellow-brown. The EPR spectrum showed a pentet at $g = 1.996$ ($a_{4H} = 9$ G) with molybdenum satellites ($a_{Mo} = 37$ G), assigned to [**2**]$^+$, while no prominent proton NMR signals were found except for those due to the solvent. At this point, Cp_2Co (10 mg, 0.053 mmol, excess) was added to the solution; the color turned to red-brown. The ^{1}H NMR spectrum showed the regeneration of compound **2**, while no EPR active species was found. The intensity of the NMR signals of compound **2** (relative to the reference solvent signal) became smaller compared to that of the initial spectrum.

Stability of [CpMo(η^2-O_2CCH_3)(η-C_4H_6)][PF_6] ([2][PF_6]) in Acetone. CpMo(η^2-O_2CCH_3)(η-C_4H_6) (2) (2.0 mg, 7.3 μmol) and $FcPF_6$ (2.5 mg, 1 equiv) were placed in EPR tube. Two hundred microliters of acetone was subsequently added, and EPR spectra were recorded periodically. The intensity of [**2**]$^+$ halved in 5.5 h, while the signal became broad.

Reaction of CpMo(*supine*-η-C_3H_5)(*supine*-η-C_4H_6) (1b) with CH_3COOH. Compound **1b** was prepared *in situ* in a 5 mm NMR tube from 16.0 mg of compound [**1b**]$^+PF_6^-$ (40 μmol) and 7.5 mg of cobaltocene (1 equiv) in 0.5 mL of C_6D_6. The rapid reduction of [**1b**]$^+$ to **1b** by Cp_2Co has been described previously.[6] The mixture was vigorously shaken for 5 min, followed by centrifugation and filtration into a new NMR tube. Then 2 μL of acetic acid (33 μmol) was added to the filtrate. ^{1}H NMR integration against the acetic acid resonances showed only 17 μmol of **1b** in the reaction solution. The conversion of compound **1b** to compound **2** was monitored by ^{1}H NMR, yielding a half-life $t_{1/2} = 26$ min. Under similar conditions, the reaction of isomer **1a** (4.4 mg, 17 μmol) with 2 equiv of acetic acid gave a $t_{1/2}$ of 10 min.

Reaction of CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (1c) with CH_3COOH. (i) To a solution of **1c** (8 mg, 31 μmol) in 0.5 mL or C_6D_6 was added 1.8 μL of acetic acid (1 equiv). No significant change was observed by ^{1}H NMR for 28 h. **(ii)** Five milligrams of **1c** (20 μmol) was dissolved in 0.5 mL of C_6D_6, and 100 μL of acetic acid (50 equiv) was added. No reaction was detected by ^{1}H NMR in 10 min. Prolonged standing for 24 h only resulted in decomposition, giving both propene and 3-methyl-1,5-hexadiene in a 2.5:1 ratio.

Reaction of CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (1a) with HBF_4 in benzene. Preparation of [CpMo(η^4-C_4H_6)(μ-F_2BF_2)]$_n$ (3). To a benzene solution of compound **1a** (50 mg, 0.195 mmol in 0.5 mL) was added 34 μL of HBF_4·Et_2O (85%, 0.195 mmol), yielding a pale yellow solid. The mixture was centrifuged and the supernatant was filtered off. The pale yellow crystalline solid was dried under vacuum

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for 0.5 h. IR (Nujol, cm^{-1}): 1097 (m), 1055 (m), and 1012 (m). Further characterization of this species was hampered by its insolubility in either benzene or chloroform and its extreme sensitivity toward air and reactivity toward donor solvents.

When the same experiment was carried out in C_6D_6, the formation of propene was observed by ^{1}H NMR: δ 5.70 (m, 1H, vinyl), 4.95 (m, 2H, vinyl), 1.54 (dt, $J_d = 7$ Hz, $J_t = 1.6$ Hz).

Reaction of CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (1a) with HBF_4 in Acetonitrile. Preparation of [CpMo(CH_3CN)$_2$(*supine*-η-C_4H_6)]BF_4 (4). One hundred milligrams of compound **1a** (0.391 mmol) was dissolved in 5 mL of MeCN, and 70 μL of HBF_4·Et_2O (85%, 1 equiv) was added by syringe. A red-violet solution formed accompanying gas evolution. After stirring for 0.5 h the solvent was completely removed under reduced pressure. The residue was recrystallized from CH_3CN/THF, giving brick-red crystalline **4** (141 mg, 93%). Anal. Calcd for $C_{13}H_{17}BF_4MoN_2$: C, 40.66; H, 4.46. Found: C, 40.02; H, 4.63. Compound **4** has also been obtained in 73% yield by dissolving compound **3** in acetonitrile.

Reaction of CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (1a) with HBF_4 in the presence of Bu^{t}NC. Preparation of [CpMo(CNBu^t)$_2$(C_4H_6)]BF_4 (5). Compound **1a** (57 mg, 0.19 mmol) was dissolved in 0.5 mL of C_6H_6. To the resulting solution was added by syringe, in the order, CNBu^t (150 mL, 1.33 mmol) and HBF_4·Et_2O (39 mL, 85%, 0.19 mmol). A maroon oily precipitate formed accompanying gas evolution. The light red supernatant was filtered off, and the oily solid was washed with 2 × 1 mL of heptane. The oily material was dried under vacuum for 2 h (yield 85 mg, 82%). Anal. Calcd for $C_{19}H_{29}BF_4MoN_2$: C, 48.74; H, 6.24. Found: C, 49.01; H, 6.80. The same product could also be obtained by the reaction of compound **3** with *tert*-butyl isocyanide.

Reaction of CpMo(*prone*-η-C_3H_5)(*supine*-η-C_4H_6) (1a) with HBF_4 in the presence of Butadiene. Preparation of [CpMo(*supine*-η-C_4H_6)(*s-trans*-η-C_4H_6)][BF_4] (6). Compound **1a** (0.900 g, 3.52 mmol) was dissolved in 20 mL of THF. To the resulting solution was added butadiene by condensation of the gaseous reagent until the volume had increased by ca. 10 mL. After cooling to −78 °C, HBF_4·Et_2O (0.61 mL, 85%, 3.52 mmol) was added, causing the precipitation of a yellow solid. The mixture was stirred for 0.5 h at −78 °C and then for another 0.5 h at room temperature. The colorless supernatant was decanted off, and the yellow solid was washed with 2 × 20 mL of THF. The yellow solid was dried under vacuum for 4 h (yield 1.240 g, 94%). Anal. Calcd for $C_{13}H_{17}BF_4Mo$·$0.25C_4H_8O$: C, 44.96; H, 5.12. Found: C, 44.59; H, 5.40. The presence of THF was confirmed by ^{1}H NMR spectroscopy. This product can also be synthesized in a low yield (36%) by addition of butadiene to compound **3**.

Reaction of CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (1c) with HBF_4·Et_2O in acetonitrile. Formation and Stability of [CpMo(η-C_3H_5)(syn-η-$C_3H_4CH_3$)($NCCD_3$)][BF_4] (7). Dissolution of compound **1c** (7.5 mg, 29 μmol) in CD_3CN (0.5 mL), followed by the addition of 5 μL of HBF_4·Et_2O (85%, 29 μmol), generated a yellow-brown solution. The resulting solution was investigated by ^{1}H NMR, indicating the formation of compound **7** (80% on the basis of integration against the solvent standard) (see Table 1 and Discussion for the resonance assignment) and an unidentified species (20%), as well as free propene (20%). The resonances of **7** gradually decreased, while those of 3-methyl-1,5-hexadiene (δ (ppm), 5.77 (m, 2H), ca 4.96 (m, 4H), 2.20 (m, 1H), 2.10 (m, 2H), 0.97 (d, 3H)) appeared within 30 min. After standing at room temperature overnight, complex **7** completely decomposed to quantitatively yield 3-methyl-1,5-hexadiene and other uncharacterized metal-containing species. The ^{1}H NMR signal of the acetonitrile ligand was detected when regular acetonitrile was used for the reaction, followed by removal of the solvent under reduced pressure and dissolution of the residue in CD_3CN. Following the rapid recording of the latter ^{1}H NMR spectrum, the signal due to the CH_3CN ligand disappeared within 30 min.

Reaction of CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (1c) with HBF_4·Et_2O in Benzene. Compound **1c** (7.5 mg, 29 μmol) was dissolved in C_6D_6 (0.5 mL) in a 5 mm NMR tube, followed by the addition of 5 μL of HBF_4·Et_2O (85%, 29 μmol). A violet precipitate immediately formed. The ^{1}H NMR spectrum showed the formation of propene (ca. 20% on the basis of integration against the solvent standard). After transfer into a Schlenk tube via cannula, the liquid was filtered off, and the solid was dried under vacuum for 10 min. The solid was dissolved in 0.5 mL of CD_3CN, and the resulting solution was tranferred back into an NMR tube. A ^{1}H NMR spectrum showed the formation of three complexes in ca. 1:1:1 ratio: complexes **4** and **7** and an unidentified species with the Cp resonance at δ 5.22.

Reaction of CpMo(*supine*-η-C_3H_5)(*s-trans*-η-C_4H_6) (1c) with HBF_4·Et_2O in the Presence of Excess Butadiene. (i) In THF. Compound **1c** (340 mg, 1.33 mmol) was dissolved in 5 mL of THF. Ca. 5 mL (liquid volume) of butadiene was condensed into the mixture at −196 °C. HBF_4·Et_2O (227 μL, 85 %, 1.31 mmol) was then added by microsyringe, yielding a violet-brown precipitate. After the supernatant was decanted off, the solid was washed with 5 mL of THF and dried under vacuum for 0.5 h. The violet-brown solid was not soluble in chloroform. When the violet-brown solid (5 mg) was treated with acetone-d_6 (0.5 mL), a mixture of **6** and [CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)(Me_2CO)][BF_4] (**8**) (ca. 1:1 ratio) was detected by ^{1}H NMR. Compound **8** slowly decomposes in acetone. Attempts to separate these two products by selective crystallization failed. The product was also soluble in acetonitrile, and subsequent ^{1}H NMR inspection in CD_3CN showed the formation of **4** and [CpMo(η-allyl-CH_2CH_2-η-allyl)($NCCH_3$)][BF_4] (**9**) (ca. 1:1 ratio), in addition to free butadiene. Attempts to separate the two products by selective crystallization failed. To the CD_3CN solution containing complexes **4** and **9** was added 1 μL of PMe_3 (10 μmol). After 24 h, the proton NMR showed that compound **8** has been converted to a new species, [CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)(PMe_3)][BF_4] (**10**), while complex **4** remained unchanged.

(ii) In C_6D_6. Fifteen milligrams of **1c** (58 μmol) was dissolved in a mixture of C_6D_6 and butadiene (0.5 mL/0.5 mL), to which 10 μL of HBF_4·Et_2O (85%, 58 μmol) was syringed, causing the formation of a violet precipitate and a colorless supernatant. Propene in the supernatant was detected by ^{1}H NMR. After removal of all solvents, the solid was dried under vaccum for 10 min, and then 0.5 mL of CD_3CN was added. A ^{1}H NMR spectrum showed the formation of compounds **4** and **9** (ca. 1:1 ratio), accompanied by an unidentified species. No 3-methyl-1,5-hexadiene could be detected.

(iii) In CD_3CN. Formation of Compound [CpMo(CD_3CN)$_2$(*s-trans*-η-C_4H_6)]BF_4 (11). **1c** (7.5 mg, 29 μmol) was placed in an NMR tube in 0.5 mL of CD_3CN. Butadiene (0.5 mL) was subsequently condensed in the tube at low temperature. Further addition of 5 μL of HBF_4·Et_2O (85%, 29 μmol) at room temperature caused a color change from yellow to yellow-brown. The immediate recording of a ^{1}H NMR (<10 min) showed the formation of complexes **7** and propene in a ratio of ca. 3:1 (spectroscopic yield: 60% and 20%, respectively). Small resonances attributable to the decomposition products **4** and **11** (see below) were already observable. After standing overnight, the resonances of complex **7** had been completely replaced by the resonances attributed to compounds [CpMo(CD_3CN)$_2$(*supine*-η-C_4H_6)]BF_4 (**4**) and [CpMo(CD_3CN)$_2$(*s-trans*-η-C_4H_6)]BF_4 (**11**) in an approximate 1:1 ratio, accompanied by minor unidentified species with Cp resonances at δ 5.67 and 5.81. The concomitant release of 3-methyl-1,5-hexadiene was also shown by the ^{1}H NMR spectrum. Complexes **4** and **11** are moderately stable in acetone or acetonitrile. No change of the relative intensity of these species was observed at room temperature over 16 h in either solvent. The resonances for the MeCN ligands in both complexes **4** and **11** were detected by repeating the experiment in CH_3CN.

Molecular Orbital Calculations. The geometries of compounds **1a**−**c** were optimized at the DFT-B3LYP level.[18] The starting geometries of compounds **1a** and **1c** were taken from the X-ray determined structures,[6] while the geometry of **1b** was generated from that of **1a** by a 180° rotation of the allyl ligand around the axis that joins the Mo atom and the center of gravity of the allyl ligand. The calculations were run using GAUSSIAN 94[19] on the SGI Power Challenge at the Université de Bourgogne. The LanL2DZ basis set used includes both Dunning and Hay's D95 sets for H and C[20] and the relativistic Electron Core Potential (ECP) sets of Hay and Wadt for the Mo atom.[21−23] Electrons outside the core were all those of H and

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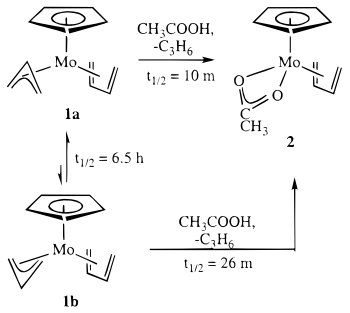
Scheme 2



C atoms and the 4*s*, 4*p*, 4*d*, and 5s electrons for Mo. Single point calculations were also carried out at the LanL2DZ-optimized geometries, after extending the basis set as follows: the *s*, inner *p*, and *d* functions on the Mo atom of the LanL2DZ set was decontracted, thus yielding a valence ⟨5*s* 4*p* 3*d*⟩ set, and one *d* function (exponent 1.2) was added to the basis for C.

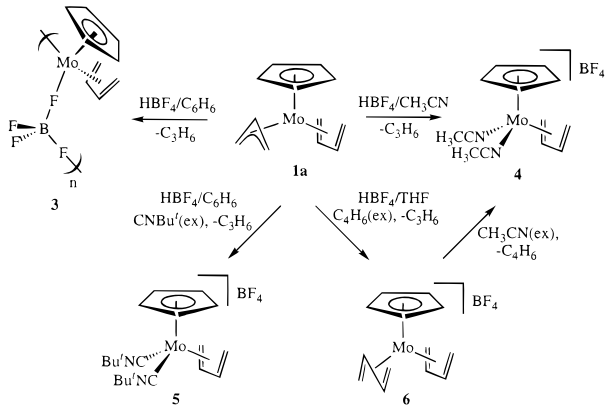
Results

Protonation of Isomers 1a and 1b. The protonation reaction of **1a** and **1b** has been investigated with a variety of proton sources and under different conditions. In all cases, attack at the allyl ligand with subsequent elimination of propene (confirmed by ^{1}H NMR) occurs. When acetic acid is used, the allyl ligand is replaced by the acetate group to afford compound CpMo(η-O_2CCH_3)(*supine*-η-C_4H_6), **2** (see Scheme 2). A comparison of the measured half lives of reaction indicates that the *prone* allyl ligand in **1a** is protonated faster than the *supine* allyl ligand in **1b**. On the other hand, comparison with the previously measured[6] half-life of the **1b**/**1a** isomerization suggests that the protonation of **1b** occurs directly and not via isomerization to **1a**. Under the assumption of a rate-determining protonation of the allyl ligand, the data suggest that the allyl terminal carbon atoms carry a higher negative charge in **1a** relative to **1b**.

The bidentate binding mode of the acetato ligand is indicated by the IR bands at 1529 and 1461 cm^{-1}. The *supine* conformation of the butadiene ligand is indicated by the downfield shifted central protons of the butadiene ligand. For the alternative *prone* butadiene configuration, the central protons would be shifted upfield due to the shielding of the cyclopentadiene ring current, as it is found for *supine* and *prone* allyl ligands. Furthermore, the indiscernible geminal coupling constant (<1 Hz) also suggests the *supine* conformation. This criterion has also been used to determine the conformation of allyl complexes.[7]

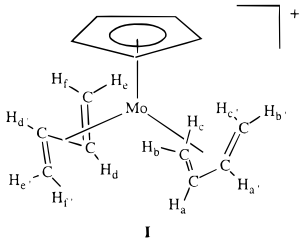
When the benzene solution of **1a** is treated with HBF_4·OEt_2, a brown powder of [CpMo(η^4-C_4H_6)(μ-F_2BF_2)]$_n$ (**3**) immediately precipitates out of solution (Scheme 3). This product is extremely sensitive, immediately turning black upon exposure to air. It is insoluble in hydrocarbons (including chlorinated ones) and reactive toward donor solvents. Its characterization rests only on IR analysis and the results of further derivatization

Scheme 3



reactions (*vide infra*). The assignment of a bidentate bridging coordination mode for the tetrafluoroborato ligand is supported by the IR data, in comparison with the IR bands reported for complexes [Cu(bpy)$_2$F$_2$BF$_2$][BF$_4$] and SnMe$_3$F$_2$BF$_2$.[24,25] Compound **3** is reactive toward nucleophiles, such as acetonitrile and *tert*-butyl isocyanide as well as butadiene. These ligands displace the coordinated BF_4 ligand from **3** to yield the adducts [CpMo(η^4-C_4H_6)L_2]$^+$. The same complexes can best be obtained directly by HBF_4 protonation of **1a** in the presence of an excess of the desired ligand, see Scheme 3.

The spectroscopic properties of complexes **4** and **5** are straightforward. As is the case for compound **2**, the *supine* conformation of the diene ligand in **4** and **5** is indicated by both proton chemical shifts and the small value of the geminal coupling in the ^{1}H NMR (see Table 1). Compound **6**, on the other hand, shows a more complex NMR pattern because of the low symmetry, the larger number of inequivalent protons, and the complex coupling pattern. The complete assignment reported in Table 1 (see drawing **I** for the proton nomenclature) was assisted by homonuclear decoupling experiments and a 2-D ^{1}H−^{13}C correlation spectrum. From the NMR analysis, we can also conclude that compound **6** is obtained in a single isomeric form. Compound **6** is not stable in acetone at room temperature, decomposing to uncharacterized products. Dissolution in acetonitrile, on the other hand, affords the acetonitrile complex **4a** quantitatively with loss of the *trans*-butadiene ligand (Scheme 3).



Protonation of Isomer 1c in the Absence of Butadiene. The reaction of isomer **1c** with 1 equiv of acetic acid is very slow in comparison with the corresponding protonations of **1a** and **1b** shown above. No reaction is detected by ^{1}H NMR for 28 h. With a large excess of acetic acid and prolonged standing, on the other hand, only decomposition takes place. Among the decomposition products, 3-methyl-1,5-hexadiene and propene in a 1:2.5 ratio were identified by ^{1}H NMR. The reaction of

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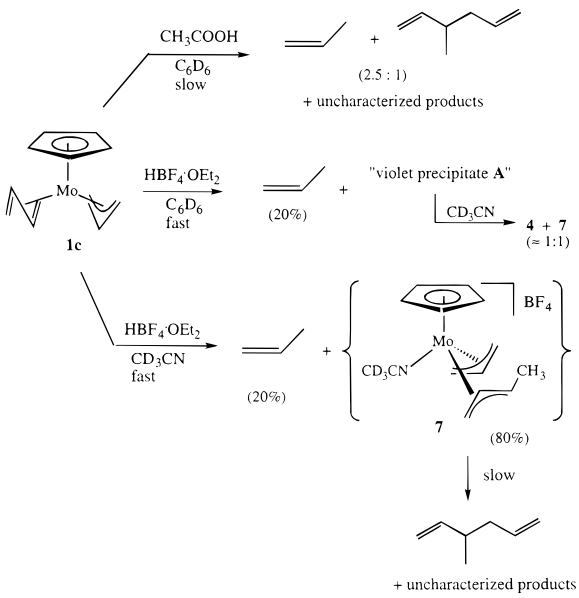
Scheme 4

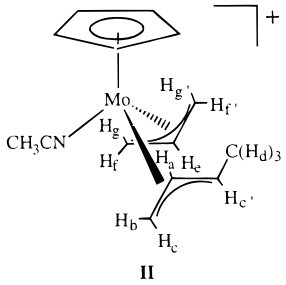


1c with $HBF_4.OEt_2$ in C_6D_6, on the other hand, immediately yields a violet precipitate (**A**). Propene (20% yield) is the only organic product detected by NMR in the supernatant. After dissolution of **A** in CD_3CN, a 1:1 mixture of compounds **4** and an unstable intermediate, [CpMo(η-C_3H_5)(*syn*-η-$C_3H_4CH_3$)-($NCCH_3$)][BF_4] (**7**), is obtained (see Scheme 4). Thus, the violet precipitate **A** is presumably constituted by a 1:1 mixture of [CpMo(η^4-C_4H_6)(μ-F_2BF_2)]$_n$, **3** (resulting from allyl attack, propene elimination, and diene isomerization), and CpMo(η^3-C_3H_5)(η^3-*syn*-C_3H_4-1-CH_3)(FBF_3) (resulting from the *apparent* butadiene attack) or related agostic complexes (see Discussion). Note that a diene isomerization *must* have taken place before the addition of CD_3CN to **A**, because a hypothetical [CpMo-(η^4-*s-trans*-C_4H_6)(η^2-F_2BF_2)]$_n$ compound would lead to a [CpMo-(η^4-*s-trans*-C_4H_6)(CD_3CN)$_2$]$^+$ product which is not observed among the reaction products. Such a compound indeed exists and does not isomerize to **4** (*vide infra*).

When **1c** is protonated with HBF_4·OEt_2 directly in acetonitrile, the instantaneous formation of **7** occurs in 80% spectroscopic yield, and no complex **4** is observed. The reaction is accompanied by the formation of propene and an uncharacterized Mo-containing species (Cp resonance at δ 5.67) in ca. 20% spectroscopic yield. Thus, the nature of the solvent has an effect on the ratio between the two reaction pathways. Compound **7** subsequently evolves to selectively produce 3-methyl-1,5-hexadiene and uncharacterized Mo-containing products. The allyl coupling process is apparently 100% regioselective, as no trace of the other possible product, namely 1,5-heptadiene, could be observed spectroscopically.

The complexity of the ^{1}H NMR spectrum of **7** required the use of homonuclear decoupling experiments for a complete assignment (see Table 1 and drawing **II** for the proton nomenclature). The coupling constants of the allyl protons fall into the expected ranges. No precise stereochemical knowledge is implied in drawing **II**, other than the *syn*-position of the allyl methyl group, which is indicated by the large *trans* coupling constant of $J_{HaHc'}$ (12.5 Hz). The conformation adopted by the two allyl ligands cannot be determined with certainty, and the compound is too unstable for isolation and structural studies either in the solid state or in solution. Fluxional rearrangements may also occur (see also compounds **8**−**10** below).

Protonation of Isomer 1c in the Presence of Butadiene. When the protonation of **1c** by HBF_4·OEt_2 is carried out in THF



in the presence of 1,3-butadiene as trapping agent, a mixture of compound **6** and a new compound, [CpMo(η^3-C_3H_4-CH_2-CH_2-η^3-C_3H_4){O=C(CD_3)$_2$}][BF_4], **8**, are observed in a 1:1 ratio by ^{1}H NMR upon investigating an aliquot of the solution in acetone-d_6 (see Scheme 5). An attempt to detect the acetone ligand in **8** was not successful. Dissolution of the reaction residue in regular acetone, followed by removal of the solvent and NMR analysis in $CDCl_3$ yielded no proton signal for compound **8**, presumably because of a solvent-induced radical decomposition. The formation of compound **8** involves coupling of two *s-trans* butadiene ligands. A similar process has been previously described for the reaction of butadiene with $Ni(COD)_2$,[26] $[Cp_2V]^-$,[27] $CpCr(\eta^3$-$C_3H_5)_2$,[28] and $Cp^*Cr(\eta^3$-$C_3H_5)_2$.[29]

When the same experiment is carried out in C_6D_6, an insoluble violet precipitate (**B**) is generated, and the evolution of propene in ca. 50% spectrocopic yield is observed by ^{1}H NMR. No 3-methyl-1,5-hexadiene, nor any other organic product, is observed during this process. Dissolution of **B** in CD_3CN affords a mixture of compounds **4** and [CpMo(η^3-C_3H_4-CH_2-CH_2-η^3-C_3H_4)(MeCN)][BF_4], **9**, in an approximate 1:1 ratio, plus free butadiene, see Scheme 5. The violet precipitate **B** presumably contains a 1:1 mixture of compounds **6** and a precursor to **8** such as CpMo(η^3-C_3H_4-CH_2CH_2-η^3-C_3H_4)(FBF_3) and is therefore different than the violet precipitate **A**. The conversion of **6** to **4** with release of butadiene is established, see Scheme 3. The second component of **B** cannot be CpMo(η^3-C_3H_5)(η^3-*syn*-C_3H_4-1-CH_3)(FBF_3) (i.e., identical to the proposed component of **A** that derives from the proton attack on the diene ligand), because the formation of **9** from such a compound would also require the formation of 3-methyl-1,5-hexadiene (not verified experimentally) and the presence of free butadiene, whereas the process takes place from dried **B** after complete removal of excess butadiene. When the solid mixture of **6** and **8** obtained in acetone-d_6 is treated with acetonitrile, compounds **4** and **9** are formed again in a 1:1 ratio, accompanied by loss of butadiene, as shown by ^{1}H NMR.

Finally, when the HBF_4 protonation of **1c** in the presence of butadiene is carried out directly in CD_3CN, the immediate formation of propene and compound **7** (20% and 60% spectroscopic yields, respectively) is observed by ^{1}H NMR (Scheme 5). Subsequently, the slow formation of 3-methyl-1,5-hexadiene (*cf.* Scheme 4) is accompanied by the formation of an isomeric mixture of [CpMo($NCCD_3$)$_2$(*supine*-η-C_4H_6)][BF_4] (**4**) and [CpMo($NCCD_3$)$_2$(*s-trans*-η-C_4H_6)][BF_4] (**11**) in an 1:1 ratio. In addition to a Cp signal at 6.12 ppm, complex **11** shows six proton signals, three of them overlapping in the 4.1−3.8 ppm range, as shown by ^{1}H{selective-^{1}H} NMR experiments (see

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Scheme 5

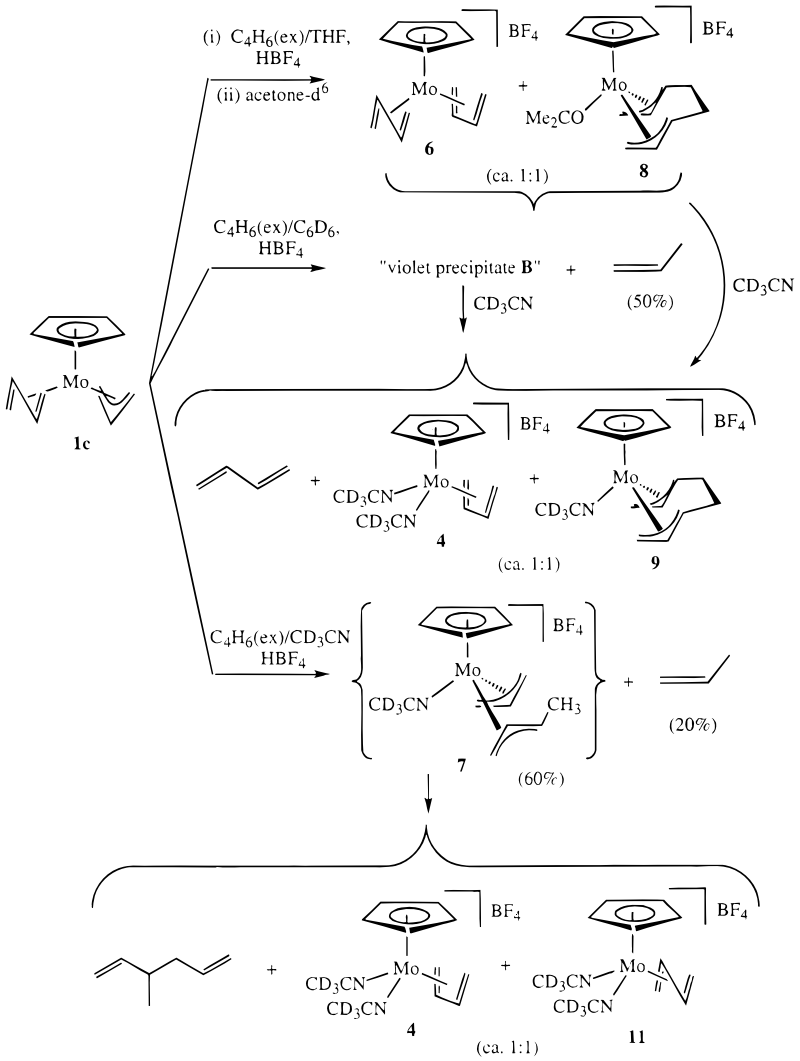
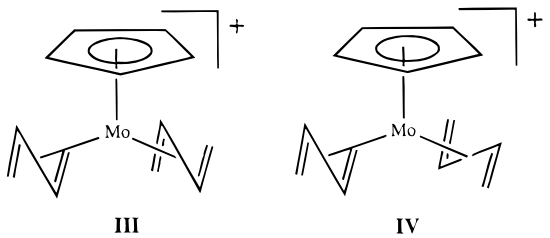


Table 1, the proton and carbon nomenclature is the same as for the *s-trans* butadiene ligand in compound **6**, see **I**). Furthermore, the ^{13}C NMR resonances for the butadiene carbon atoms in complex **11** compare well with those assigned to the same atoms in complex **6**. When the protonation is carried out in regular MeCN, followed by NMR analysis in acetone-d_6, two distinct resonances attributable to the MeCN ligands in **11** are observed by both ^{1}H and ^{13}C NMR, in agreement with the lack of symmetry imposed by the *s-trans* butadiene ligand. Attempts to separate compounds **4** and **11** have been fruitless. Upon prolonged standing at room temperature, the relative ratio of **4** and **11** does not significantly change. Analogously, no formation of **11** occurs upon prolonged standing of pure **4** (obtained as shown in Scheme 3) at room temperature. This demonstrates that the isomerization of the butadiene ligand in compounds **4** and **11** is a difficult process (the same is found for compounds **1a** and **1c**,[6] see Introduction).

It was initially difficult to assign the spectrum of **8** to a bis-allyl complex of Mo(IV) as opposed to a hypothetical $[CpMo(\eta^4\text{-}s\text{-}trans\text{-}C_4H_6)_2]^+$ complex of Mo(II), which would be formed by coordination of two 1,3-butadiene ligands in the *s-trans* configuration. This complex could exist in two possible conformations (**III** with mirror symmetry and **IV** with local C_2 symmetry for the $Mo(C_4H_6)_2$ moiety), both of which would lead to the observation of six proton resonances for the two diene ligands. Indeed, only six proton resonances are observed for the organic moiety in compounds **8**, and the presumed fast exchange of the coordinated acetone did not allow its direct observation in the NMR spetrum. Compound **9** also shows only six resonances for the organic ligand system, but the acetonitrile ligand exchanges relatively slowly ($t_{1/2}$ ca. 1/2 h) and its direct observation in the NMR spectrum became possible. Finally, addition of PMe_3 results in the formation of the ligand substitution product, $[CpMo(\eta\text{-}C_3H_4\text{-}CH_2CH_2\text{-}\eta\text{-}C_3H_4)(PMe_3)][BF_4]$ (**10**) (Scheme 6), which has the PMe_3 ligand firmly coordinated to the metal center and shows a greater number of resonances (see Table 1). Structures **III** and **IV** are electronically saturated, thus they are not expected to allow coordination of an additional ligand.



III **IV**

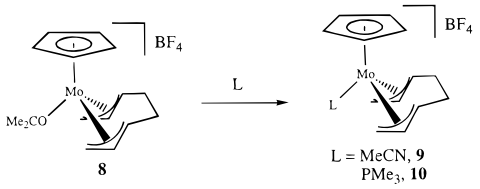
Additional NMR evidence in favor of the formulation given for compounds **8**−**10** is the typical sp^3 J_{CH} constant (129 Hz) for C_{ig} in the ^{13}C NMR (refer to drawing **V**). This would not be consistent with a bis(butadiene) formulation. Furthermore, while the proton signals of H_d, H_e, and H_f exhibit typical chemical shift and coupling patterns pertinent to a π-coordinated

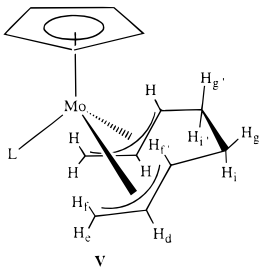
Table 1. ^{1}H-NMR Data for Compounds

compd	^{1}H-NMR (δ)	^{13}C-NMR (δ)
CpMo(η-CH_3CO_2)(*supine*-η-C_4H_6) (**2**)[a]	6.98 (2H_a, m), 4.52 (5H, Cp, s), 2.73 (2H_b, d, $^3J_{HH_a}$ = 13 Hz), 1.40 (3H, CH_3CO_2, s), 0.15 (2H_c, d, $^3J_{HH_a}$ = 14.5 Hz)	
[CpMo($NCCH_3$)$_2$(*supine*-η-C_4H_6)][BF_4] (**4**)[b]	6.23 (2H_a, m), 4.97 (5H, Cp, s), 2.42 (2H_b, d, $^3J_{HH_a}$ = 7 Hz), 2.29 ($NCCH_3$, 6H, s), 0.84 (2H_c, d, $^3J_{HH_a}$ = 6.5 Hz)	
[CpMo(CNBu^t)$_2$(*supine*-η-C_4H_6)][BF_4] (**5**)[b]	5.48 (2H_a, m), 5.07 (5H, Cp, s), 2.26 (2H_b, d, $^3J_{HH_a}$ = 7 Hz), 1.00 (2H_c, d, $^3J_{HH_a}$ = 7.5 Hz), 1.38 (18H, CNBu^t, s)	161.8 (2C, CNBu^t), 101.7 (2C_a, dm, ^1J = 169 Hz), 87.8 (5H, Cp, dm, ^1J = 181 Hz), 58.9 (2C, $CNC(CH_3)_3$, m), 44.3 (2C_{bc}, tm, ^1J = 160 Hz), 30.2 (6C, $CNC(CH_3)_3$, qm, ^1J = 129 Hz)
[CpMo(*supine*-η-C_4H_6)(*s-trans*-η-C_4H_6)][BF_4] (**6**)[c]	5.85 (5H, Cp, s); 5.70 (1H_a, dddd, $^3J_{HH_b}$ = 7 Hz, $^3J_{HH_c}$ = 9.5 Hz, $^3J_{HH_{a'}}$ = 6 Hz, $^4J_{HH_{c'}}$ = 2.5 Hz), 5.16 (1$H_{a'}$, dddd, $^3J_{HH_{b'}}$ = 8 Hz, $^3J_{HH_{c'}}$ = 11 Hz, $^3J_{HH_a}$ = 6 Hz, $^4J_{HHc}$ = 3 Hz), 4.51 (1H_d, ddd, $^3J_{HH_e}$ = 7 Hz, $^3J_{HH_f}$ = 15 Hz, $^3J_{HH_{d'}}$ = 10 Hz), 3.95 (1H_f, d, $^3J_{HH_d}$ = 15 Hz), 3.87 (1H_e, d, $^3J_{HH_d}$ = 7 Hz), 3.64 (1$H_{d'}$, ddd, $^3J_{HH_d}$ = 10 Hz, $^3J_{HH_{f'}}$ = 13 Hz, $^3J_{HH_{e'}}$ = 8 Hz), 3.18 (1H_b and 1$H_{b'}$, m), 2.91 (1$H_{f'}$, dd, $^3J_{HH_{d'}}$ = 13 Hz, $^2J_{HH_{e'}}$ = 3 Hz), 2.62 (1$H_{e'}$, dd, $^3J_{HH_{d'}}$ = 8 Hz, $^2J_{HH_{f'}}$ = 3 Hz), 2.07 (1H_c, overlap with the solvent peak), 1.99 (1$H_{c'}$, ddd, $^3J_{HH_{a'}}$ = 11 Hz, $^2J_{HH_{b'}}$ = 2 Hz, $^4J_{HH_a}$ = 2.5 Hz)	118.8 (1$C_{a'}$), 107.2 (1C_a), 104.7 (1C_d), 95.8 (5C, Cp), 79.6 (1$C_{d'}$), 77.8 (1C_{ef}), 48.9 (1$C_{b'c'}$), 48.1 (1C_{bc}), 45.6 (1$C_{e'f'}$)
[CpMo(*supine*-η-C_3H_5)(*syn*-CH_3-*prone*-η-C_3H_4)($NCCH_3$)][BF_4] (**7**)[d]	5.26 (5H, s, Cp), 4.83 (1H_a, ddd, $^3J_{HH_b}$ = 8 Hz, $^3J_{HH_c}$ = 11.5 Hz, $^3J_{HH_{c'}}$ = 12.5 Hz), 4.76 (1H_e, dddd, $^3J_{HH_f}$ = 6.6 Hz, $^3J_{HH_{f'}}$ = 7 Hz, $^3J_{HH_g}$ = 10 Hz, $^3J_{HH_{g'}}$ = 10 Hz), 4.14 (1$H_{c'}$, dq, $^3J_{HH_a}$ = 12.5 Hz, $^3J_{HH_d}$ = 6.5 Hz), 3.23 (1H_f, dd, $^3J_{HH_e}$ = 6.5 Hz, $^3J_{HH_{f'}}$ = 3 Hz), 2.93 (1H_g, d, $^3J_{HH_e}$ = 10 Hz), 2.69 (1$H_{f'}$, dd, $^3J_{HH_e}$ = 7 Hz, $^3J_{HH_f}$ = 3 Hz), 2.24 (3H, b, CH_3CN), 2.04 (1H_b, dd, $^3J_{HH_a}$ = 8 Hz, $^3J_{HH_c}$ = 3.5 Hz), 1.95 (3H_d, d, $^3J_{HH_e}$ = 6.5 Hz) 0.93 (1$H_{g'}$, d, $^3J_{HH_e}$ = 10 Hz), 0.38 (1H_c, dd, $^3J_{HH_a}$ = 11.5 Hz, $^3J_{HH_b}$ = 3.5 Hz)	
[CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)-(Me_2CO)][BF_4] (**8**)[c]	5.85 (5H, Cp, s), 4.70 (2H_d, ddt, $^3J_{HH_e}$ = 6.5 Hz, $^3J_{HH_f}$ = 10 Hz, $^3J_{HH_{f'}}$ = 11 Hz), 4.41 (2$H_{f'}$, ddm, $^3J_{HH_d}$ = 11 Hz, $^3J_{HH_i}$ = 4 Hz, complicated coupling-pattern with H_g), 3.46 (2H_f, d, $^3J_{HH_d}$ = 10 Hz), 2.85 (2H_i, m), 2.43 (2H_g, m), 1.88 (2H_e, d, $^3J_{HH_d}$ = 6.5 Hz)	
[CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)-($NCCH_3$)][BF_4] (**9**)[d]	5.54 (5H, Cp, s), 4.24 (2H_d, ddt, $^3J_{HH_e}$ = 6.5 Hz, $^3J_{HH_f}$ = 10 Hz, $^3J_{HH_{f'}}$ = 11 Hz), 4.11 (2$H_{f'}$, ddm, $^3J_{HH_d}$ = 11 Hz, $^3J_{HH_i}$ = 4 Hz, complicated coupling-pattern with H_g), 2.79 (2H_f, d, $^3J_{HH_d}$ = 10 Hz), 2.63 (2H_i, m), 2.42 (2H_g, m), 2.33 (2H_e, d, $^3J_{HH_d}$ = 6.5 Hz), 2.16 (3H, b, CH_3CN)	97.7 (5C, Cp, dm, $^1J_{CH}$ = 180 Hz), 92.8 (2C_d, dm, $^1J_{CH}$ = 159 Hz), 83.4 (2$C_{f'}$, d, $^1J_{CH}$ = 169 Hz), 63.5 (2C_{ef}, t, $^1J_{CH}$ = 163 Hz), 36.7 (2C_{gi}, t, $^1J_{CH}$ = 129 Hz)
[CpMo(η-C_3H_4-CH_2CH_2-η-C_3H_4)-(PMe_3)][BF_4] (**10**)[d]	5.42 (5H, Cp, s), 4.13 (1H_d and 1$H_{d'}$, ddd, $^3J_{H_dH_e}$ = $^3J_{H_{d'}H_{e'}}$ = 6 Hz, $^3J_{H_dH_h}$ = $^3J_{H_{d'}H_{h'}}$ = 10 Hz, $^3J_{H_dH_f}$ = $^3J_{H_{d'}H_{f'}}$ = 10 Hz), 3.94 (1H_h and 1$H_{h'}$, dm, $^3J_{H_hH_d}$ = $^3J_{H_{h'}H_{d'}}$ = 10 Hz), 2.50 (1H_g and 1$H_{g'}$ and 1H_i and 1$H_{i'}$, m), 2.11 (1H_f, d, $^3J_{HH_d}$ = 10 Hz), 2.09 (1$H_{f'}$, d, $^3J_{HH_{d'}}$ = 10 Hz), 1.88 (1H_e, d, $^3J_{HH_d}$ = 6 Hz), 1.82 (1$H_{e'}$, d, $^3J_{HH_{d'}}$ = 6 Hz), 1.46 (9H, $P(CH_3)_3$, $^2J_{HP}$ = 9 Hz)	96.8 (5C, Cp, dm, $^1J_{CH}$ = 178 Hz), 86.7 and 86.6 (1C_d and 1$C_{d'}$; 1C_h and 1$C_{h'}$, $^1J_{CH}$ = 170 Hz), 49.4 and 49.2 (1C_{ef} and 1$C_{e'f'}$, $^1J_{CH}$ = 167 Hz), 35.5 (1C_{gi} and 1$C_{g'i'}$, $^1J_{CH}$ = 128 Hz), 17.2 (3C, PMe_3, dq, $^1J_{CP}$ = 32 Hz, $^1J_{CH}$ = 129 Hz) [Note: ^{31}P{^{1}H} NMR signal is at 18.5 ppm]
[CpMo($NCCH_3$)$_2$(*s-trans*-η-C_4H_6)]-[BF_4] (**11**)[c]	6.12 (5H, Cp, s), 4.67 (1H_d, ddd, $^3J_{HH_{d'}}$ = $^3J_{HH_e}$ = 9 Hz, $^3J_{HH_f}$ = 13 Hz), 4.35 (1$H_{f'}$, d, $^3J_{HH_{d'}}$ = 20 Hz), 4.1−3.8 (1H_e, 1$H_{d'}$, and 1$H_{e'}$), 3.71 (1H_f, $^3J_{HH_d}$ = 13 Hz), 2.62 (3H, s, CH_3CN), 2.51 (3H, s, CH_3CN)	101.4 (5H, Cp), 99.4 (1C_d), 87.2 (1$C_{d'}$), 78.4 (1C_{ef}), 42.7 (1$C_{e'f'}$), 4.39 (1C, $\underline{C}H_3CN$), 4.25 (1C, $\underline{C}H_3CN$)

[a] C_6D_6. [b] $CDCl_3$. [c] Acetone-d_6. [d] Acetonitrile-d_3.

Scheme 6



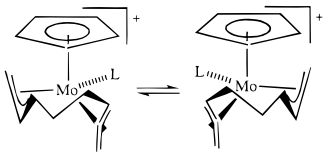


V

vinyl group, the coupling patterns of $H_{f'}$, H_g, and H_i are more complicated. For instance, while both H_e and H_f are only coupled to H_d and not to each other, affording clean doublets, protons H_i and H_g show complex coupling patterns. This is, of course, consistent with our proposed formulation, since H_i and H_g will also couple with their symmetry-equivalent $H_{i'}$ and $H_{g'}$.

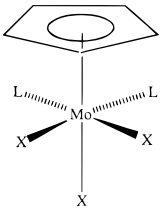
As mentioned above, the PMe_3 derivative **10** shows more resonances than compounds **8** and **9**. In particular, the doublets assigned to the allyl terminal protons H_e and H_f in compounds **8** and **9** are split into two equal doublets in compound **10**. A way to rationalize this behavior is to assume a low symmetry structure, which would be common to all derivatives, but which is only frozen for the PMe_3 adduct. On the other hand, the two ends of the bis(allyl) ligand could readily equalize for the acetone and MeCN adducts. This equalization probably occurs intramolecularly, in which case the slower fluxional process for **10** would be in agreement with the greater bulk of the PMe_3 ligand. The alternative possibility of assistance by ligand dissociation is ruled out by the demonstrated slow (ca. 1/2 h)

Scheme 7



MeCN exchange for compound **9**. The activation barrier for this scrambling process must be quite different for the three compounds, because no coalescence of pseudoequivalent resonances for **10** is observed upon warming to 100 °C, while no decoalescence of the resonances of **8** and **9** is observed upon cooling to −90 °C.

Given the established pseudo-octahedral geometry for 18-electron half-sandwich derivatives of Mo(IV) (see **VI**),[30−34] it is tempting to speculate that the equalization involves a process such as that depicted in Scheme 7. The ground state geometry would involve occupation of two *pseudo*equatorial positions by one allyl moiety and one *pseudo*equatorial and one *pseudo*axial position by the other. The interconversion between the two limiting geometries would involve only minimal rearrangements. There is indeed a structurally characterized complex, CpMo(CO)Br_2(η^3-C_3H_4-2-Me), having a structure of type **VI** with pseudoequatorial Br and CO ligands, whereas the allyl ligand formally occupies one pseudoequatorial and the pseudoaxial positions.[35] It is also interesting to observe that the related W complexes (η^5-C_5H_4R)W(η^3-C_3H_5)$_2$(η^1-C_3H_5) (R = H, Me)[36] show distinct resonances for all protons at low temperature and scrambling of the two η^3-allyl ligands at room temperature. This fluxional process does not involve the η^1-allyl ligand.[36] This behavior is consistent with a fluxional mechanism analogous to that proposed for **8**−**10** in Scheme 7. In spite of several attempts, we have not been able to find a convenient method to separate compounds **8**−**10** from compound **6** or its derivative **4**.



VI

Redox Behavior of CpMo(η-CH_3CO_2)(*supine*-η-C_4H_6) (2). Cyclic voltammetric studies on complex **2** reveal a quasi-reversible oxidation wave at −0.45 V in CH_2Cl_2 (−0.48 V in THF) versus Fc^+/Fc. Chemical oxidation with ferrocenium hexafluorophosphate gives the 17-electron species [CpMo(η-CH_3CO_2)(*supine*-η-C_4H_6)]$^+$, [**2**]$^+$, see Scheme 8. Compound [**2**]$^+$ exhibits a pentet EPR signal (g = 2.003) due to the coupling of the unpaired electron with the butadiene terminal hydrogen nuclei (a_H = 9 G), in addition to the expected molybdenum satellites (a_{Mo} = 36 G), see Figure 1. Following the complete

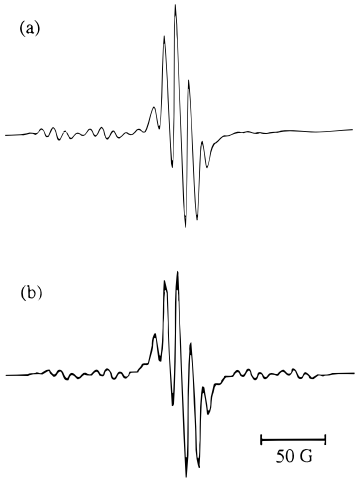
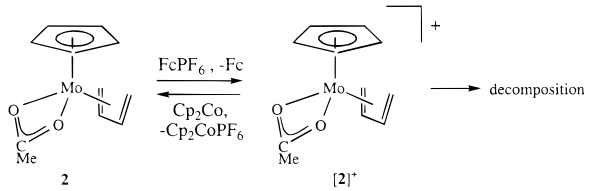


Figure 1. Experimental (a) and simulated (b) spectrum for complex [**2**]$^+$. Solvent = acetone.

Scheme 8



in situ oxidation, immediate reduction by cobaltocene regenerates complex **2** at a lower concentration relative to the starting solution. This indicates that partial decomposition of the cationic complex [**2**]$^+$ has occurred, which is confirmed by a stability test of [**2**]$^+$ in acetone.

Discussion

Reactivity toward Nucleophiles. The title compound, in either isomeric form, does not readily exchange the butadiene ligand with other donors. The compound is electronically saturated and electron-rich in all geometries, as shown by the facile oxidation to the corresponding 17-electron cationic Mo(III) complex (half-wave potentials are −0.46, −0.81, and −0.34 V for **1a**−**c**, respectively).[6] Therefore, a ligand substitution reaction is not likely to occur associatively. Our previously reported study[6] shows that the diene isomerization, which involves partial dissociation of the diene via a 16-electron intermediate, is essentially inaccessible at room temperature, while a half-life of ca. 50 min is estimated at 100 °C. The diene substitution is likely to occur via the same initial intermediate, and accordingly it does not take place at room temperature.

Relative Electrophilic Reactivity and Position of Attack. Contrary to the lack of reactivity toward nucleophiles at room temperature, facile electrophilic attack of compound **1** by Brønsted acids occurs. Protonation studies with the weak acid CH_3COOH establishes a relative rate in the order **1a** > **1b** ≫ **1c**. The marked difference in electrophilic reactivity of isomers **1a** and **1c** allows us to rationalize their initially fortuitous[6] separation by chromatography on silica gel: while isomer **1a** is trapped on the very first layer of the silica gel column, isomer **1c** migrates though the adsorbant and is recovered unchanged at the end of the column. It is therefore clear that the acidity of the surface silanol groups is sufficient to protonate the allyl ligand in **1a**, probably generating a silica-grafted [CpMo(η^4-diene)]$^+$ moiety after propene elimination, but not to rapidly protonate the allyl or diene ligands in **1c**.

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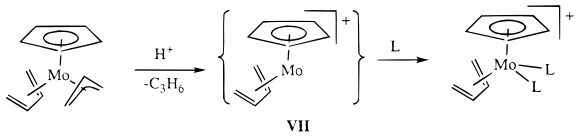
(36) Azevedo, M. C.; Brock, T. H.; Jolly, P. W.; Rufinska, A.; Schroth, G. *Polyhedron* **1991**, *10*, 459−462.

Scheme 9

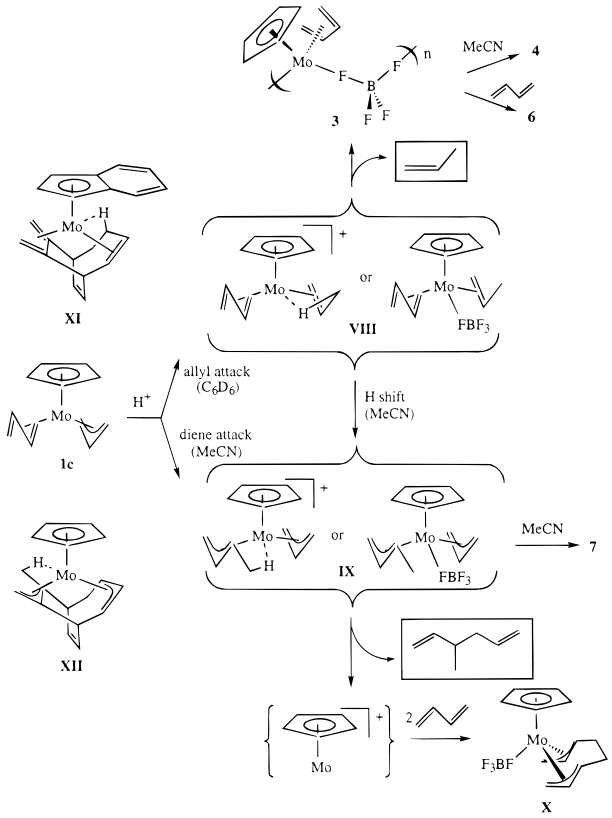


The fate of the protonated material depends on the configuration of the butadiene ligand in an interesting way. For the isomers containing *s-cis* butadiene (**1a** and **1b**), the reaction selectively yields products of propene elimination, evidently resulting from proton attack at a terminal allyl position. In a homogeneous solution, the 14-electron intermediate **VII** (see Scheme 9), formally generated by protonation and propene elimination from isomers **1a** or **1b**, is stabilized by weakly coordinating counterions or solvent molecules (i.e., compound **3**). These intermediates are subsequently trapped by coordinating ligands to afford the observed products **4**−**6**. The coordination of the diene ligand in these products remains *s-cis*. Rather curiously, the second diene ligand in compound **6** selectively adopts the *s-trans* configuration. This behavior is in sharp contrast with what has been previously observed for the isoelectronic neutral niobium complex $CpNb(\eta^4\text{-}C_4H_6)_2$,[37] which is obtained as a mixture of *s-cis*(*supine*)-*s-trans* and *s-cis*(*supine*)-*s-cis*(*prone*) isomers. Furthermore, analogous Nb complexes with bulkier diene and/or cyclopentadienyl ligands only afford the bis-*s-cis* isomer.[37] The selective formation of **4** (and no trace of **11**) when **6** is dissolved in MeCN shows that the *s-trans* butadiene ligand is more labile than the *s-cis*.

The mixture of products obtained by protonation of **1c** in C_6D_6 (Scheme 4) could *in principle* be interpreted as deriving from competive protonations of the allyl and the diene terminal positions, both of which are precedented in the literature. Proton attack at the terminal allyl carbon atom has been previously observed for $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ by HBF_4 to afford a stable and reactive η^2-propene complex, $CpMo(CO)_2(\eta^2\text{-}CH_2{=}CHCH_3)\text{-}FBF_3$.[38] Incidentally, a comparison of that result with our finding of the immediate propene elimination from protonated **1a** or **1c** shows that the replacement of two CO ligands by a butadiene ligand labilizes the Mo−propene bond. Attack at the terminal diene carbon has previously been reported for complexes $CpMo(NO)(\eta^4\text{-}s\text{-}trans\text{-diene})$,[39] which are isoelectronic with compound **1**, to yield $CpMo(NO)(\eta^3\text{-allyl})X$ products. To the best of our knowledge, the protonation of the corresponding isomeric $CpMo(NO)(\eta^4\text{-}s\text{-}cis\text{-diene})$ complexes has not been studied.

For the protonation of **1c**, allyl attack would yield a diene-propene Mo(II) intermediate **VIII** followed by propene elimination to afford **3**, whereas butadiene attack would yield a bis-allyl Mo(IV) intermediate **IX** (see Scheme 10). In the absence of butadiene, compound **3** is stable and remains as a component of precipitate **A**, whereas in the presence of butadiene it transforms to **6** (a proposed component of precipitate **B**). Compound **IX**, in turn, would remain unchanged in precipitate **A** or proceed to compound **X** (a proposed component of precipitate **B**) in the presence of butadiene. Both intermediates **VIII** and **IX** could be stabilized in C_6D_6 by the counterion or by agostic interactions, as indicated by the reported X-ray structures of the related compounds **XI** and **XII**.[12] An important

Scheme 10



difference between the protonation of **1c** and that of the precursors to **XI** and **XII** concerns the configuration of the diene ligand: *trans* for the former, *cis* for the latter. A closer analysis of the results for the protonation of **1c** in C_6D_6 in the presence of butadiene, however, shows that a competitive attack is not occurring in this solvent. In particular, the formation of **X** from the diene attack pathway *must imply formation of 3-methyl-1,5-hexadiene* (see Scheme 10), whereas this allyl−allyl coupling product is not formed, *neither during the formation of the violet precipitate **B** nor after dissolution of the latter in CD_3CN.*

A way to reconcile these contrasting results is to assume a *reversible* hydrogen shift between the butadiene-propene and the bis-allyl intermediates, **VIII** and **IX**. A reversible hydrogen shift has already been demonstrated by Michael Green for a related system derived from the protonation of a CpMo(II)-bound macrocyclic ligand that contains both an allyl and a diene function: the diene-alkene Mo(II) form (i.e., **XI**) was found to be preferred in the solid state, while the bis-allyl Mo(IV) form was preferred in solution.[12] It is important to emphasize that, because of this equilibrium process, it is impossible to establish whether the solvent also determines the initial site of attack, or whether this only influences the relative free energy of the two possible products.[12] Adapting the Green scheme to the protonation of **1c**, protonation in the nonpolar C_6D_6 medium would take place at the allyl position to afford **VIII**, whereas protonation in MeCN could occur directly at the diene ligand to afford **IX**, or the latter could form by H-shift from **VIII** after an initial allyl attack. Thus, the violet precipitate **A** is better interpreted as a mixture of **3** (since the formation of propene is already observed *during* the formation of **A**) and **VIII**, both deriving from protonation of the allyl ligand. Upon dissolution in MeCN, the former would evolve to compound **4**, whereas the latter would evolve to **IX** by hydrogen shift and then to **7**

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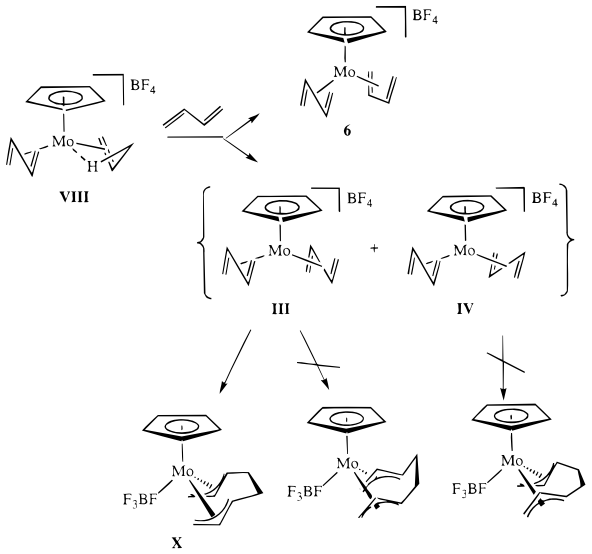
Scheme 11



(see Scheme 10). The diene protonation product, however, is obtained selectively when the process is carried out in MeCN.

The results obtained in the presence of butadiene can now be easily rationalized. The reaction of **1c** with HBF_4 in MeCN leads to **7** as it did in the absence of the diene because the protonation occurs directly at the diene ligand. In a nonpolar solvent, on the other hand, only protonation at the allyl terminal carbon would occur to afford **VIII**, but this could further evolve leading directly to the exchange of propene with butadiene. The coordination mode of the latter would then regulate the subsequent transformations to all observed products. If the butadiene ligand coordinates in the *s-cis* mode, compound **6** is obtained directly. This product could also result from the coordination of a *s-trans* butadiene after isomerization of **VIII** to **3** (*vide infra*). If, on the other hand, butadiene coordinates in the *s-trans* mode to **VIII** *before* this can isomerize to **3**, a hypothetical bis(*s-trans*-diene) complex (**III** or **IV**) would be obtained (see Scheme 11). Such a complex could be unstable, evolving directly to the C−C coupled bis-allyl Mo(IV) complex **X**, *without formation of 3-methyl-1,5-hexadiene*.

It is to be remarked that a diene isomerization from *s-trans* to *s-cis* occurs upon transforming **VIII** to **3**. This is because trapping of this product with MeCN affords only **4** and none of its isomeric complex **11**. All the literature precedents seem to show that isomerization of a coordinated diene ligand is faster for electron poorer complexes: the rate qualitatively decreases in the order $[CpMo(diene)(CO)_2]^+$ > CpMo(NO)(diene) > CpMo(allyl)(diene) > $CpNb(diene)_2$.[6,37,40,41] It appears counterintuitive that a ligand dissociation might occur faster on an electronically poorer or less saturated complex, but we have also previously proven that the diene isomerization process occurs more easily in a 17-electron Mo(III) complex (via a 15-electron intermediate) than in the corresponding 18-electron Mo(II) complex.[6] We have rationalized this behavior by assuming a more important weakening of the metal-ene π back-bonding component relative to the strengthening of the σ bonding component for electron-poorer systems.[6] Thus, it seems reasonable that the diene in complex **3** might rapidly isomerize. The diene ligand, however, does not appear to isomerize *before* the transformation of **VIII** to **3**. Although a subsequent H shift to give an *anti*-allyl isomer of **IX** would be unconsequential on the regio- and stereochemistry of the allyl−allyl coupling, trapping of precipitate **A** by MeCN shows the formation of a single isomer of **7**, with a *syn*-methylallyl ligand.

The spectroscopic properties of the products of ligand addition to **X** (i.e., **8**−**10**) are in best accord with a *syn-supine-syn-supine* configuration for the bis-allyl ligand, although a fluxional process is probably taking place (see Results, Scheme 7). Thus, C−C coupling probably occurs at the terminal butadiene carbons located farther from the Cp ring in intermediate **III**. C−C coupling for an intermediate such as **IV** would lead to an unobserved asymmetric *syn-prone-syn-supine* configuration. It cannot be excluded, however, that the *syn-prone-syn-supine* and *syn-prone-syn-prone* coupling products form but then rapidly isomerize to the more stable *syn-supine-syn-supine* isomer **X**. It is also to be pointed out that a hydrogen shift such as that proposed in Scheme 10 does not occur for the first intermediate resulting from the protonation of **1a**, because no stable Mo(IV) bis-allyl complex of formula $[CpMo(\eta^3\text{-}C_3H_5)(\eta^3\text{-}anti\text{-}C_3H_4\text{-}1\text{-}CH_3)(MeCN)]^+$, nor any 3-methyl-1,5-hexadiene or 1,5-heptadiene is generated during the reaction of **1a** in MeCN.

A final remark concerns the formation of a mixture of the isomeric complexes **4** and **11** upon decomposition of **7** in the presence of butadiene. This is consistent with the idea that, following reductive coupling and elimination of 3-methyl-1,5-hexadiene from **7**, the open coordination sites can be blocked by coordination of butadiene either in the *s-cis* or *s-trans* configuration. After coordination of MeCN has taken place, the isomerization of **11** to **4** does not occur at observable rates (see Results, Scheme 5). Neither does isomerization of **4** to **11** occur when the former is selectively obtained from **3** or **6** in MeCN. Again, this observation indicates that the component of **A** leading to **4** already has a *s-cis* butadiene ligand.

In summary, the results obtained do not provide any strong evidence either for or against the direct kinetic proton attack at the butadiene position for complex **1c**. However, they do show that, at least in nonpolar solvents, the thermodynamics favors allyl protonation, while in polar solvents the product of diene protonation becomes predominant.

Electronic Structure of Isomers 1a−c. The results discussed above still leave a number of unanswered questions. (i) Why is complex **6** stable, while the corresponding derivative with two *s-trans* butadiene ligands (**III** or **IV**) is not? (ii) How do the butadiene and allyl coordination modes influence the electronic properties and the relative electrophilic reactivity of the precursor complex **1**? (iii) How does the butadiene coordination mode affect the position of electrophilic attack? To help provide answers to these questions, we have carried out electronic structure calculations on compounds **1a**−**c**. In particular, we were interested in calculating effective charges on the ligand carbon atoms, as protonation reactions are typically charge-controlled. The geometries of **1a** and **1c** are known from X-ray crystallography[6] and that of **1b** can be easily constructed from the other two. However, the location of the hydrogen atoms from X-ray data is inaccurate, and the electronic distribution is quite sensitive to the position of these atoms. Therefore, the geometries of all compounds were fully optimized at the DFT-B3LYP level. This computational method has been proven to provide quite accurate geometries for organometallic complexes.[42,43] Indeed, the optimized positions of the heavy atoms for **1a** are very close to those determined by X-ray

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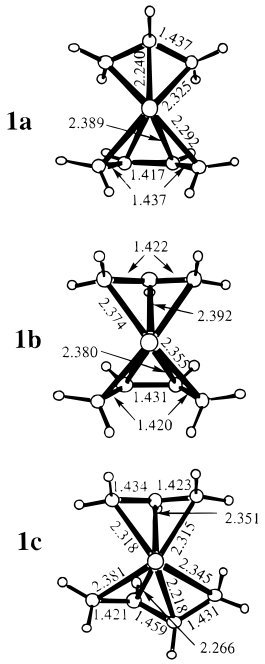

Figure 2. DFT-B3LYP optimized bonding parameters for the Mo(allyl)(butadiene) moieties in compounds **1a**−**c**.

crystallography (see Supplementary Information). The comparison is less significant for **1c**, since the precision of the allyl and diene ligands location in the X-ray structure was affected by disorder.[6] The relevant optimized parameters for the Mo(allyl)(butadiene) moieties are shown in Figure 2.

The effective atomic charges shown in Figure 3 for compounds **1a**−**c** result from a natural population analysis of the B3LYP natural bond orbitals.[44] The two different sets of values refer to calculations with two different basis sets, the values in parentheses referring to the larger one. The more sophisticated calculation shows greater separation of charges (greater positive charge for Mo and greater negative charge for all C atoms), but the overall trends on going from one isomer to another are the same. Several considerations can be made on the basis of these effective charges. (*i*) The position carrying the largest calculated negative charge is the terminal allyl position for all compounds. However, this charge decreases in the order **1a** > **1b** > **1c**. This agrees with the observed relative protonation rates with acetic acid. (*ii*) The relative charges on the Cp carbon atoms indicate that the Mo−Cp interactions are essentially identical in the three compounds. (*iii*) A comparison between **1a** and **1b** shows a greater ionic character for the Mo−allyl interaction in the former compound. This difference is consistent with both the observed faster protonation and the more difficult oxidation[6] for **1a** relative to **1b**. (*iv*) A comparison between charges and bond lengths in the Mo−diene moieties for the three compounds shows important differences. A smaller negative charge on the lateral carbon atoms in the order **1c** < **1b** < **1a** is paralleled by a larger negative charge on the internal diene carbon atoms. This is consistent with a smaller degree of donation from the diene π_2 Huckel orbital to the Mo center and a smaller degree of back-donation from the Mo center to the diene π_3* Huckel orbital in the same order. In simple words, the diene becomes both a weaker donor and a weaker acceptor in going from **1a** to **1b** to **1c**. This trend is fully consistent with the trend of optimized C−C distances in Figure 2. A previous MO study by the Fenske-Hall method on CpMo(NO)(η^4-C_4H_6) isomers, on the other hand, had established that the *cis*-diene is a weaker donor and a stronger acceptor than the *trans*-diene for that system.[41] The results of the calculations for **1c** are consistent with the observed greater lability of the *s-trans* ligand relative to the *s-cis* ligand in compound **6**. Also, the combination of two more weakly bonded *s-trans* butadiene ligands in an intermediate such as **III** or **IV** may be expected to lead to a thermodynamically less stable system, which could gain stability by evolving to the product of C−C coupling according to Scheme 11. The effective metal charge in **1c** is greater than in **1b**, suggesting an overall electron withdrawing effect of the *s-trans* diene relative to the *s-cis*. This charge difference agrees with the greater oxidation potential for **1c** relative to **1b**. (*v*) The asymmetric *s-trans* butadiene has a greater negative charge on the terminal *exo* carbon atom. This suggests that the proton attack should prefer this position over the alternative *endo* position.

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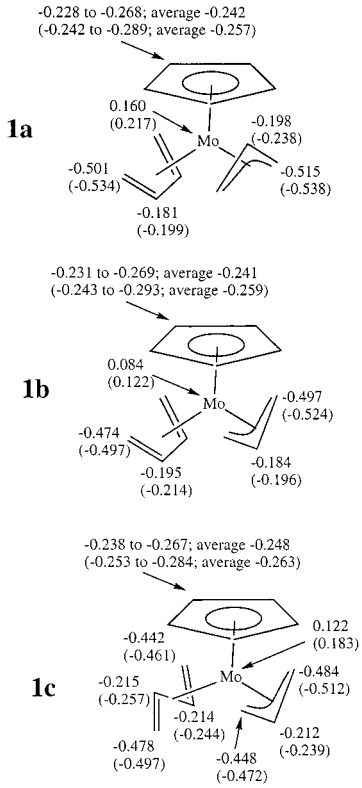


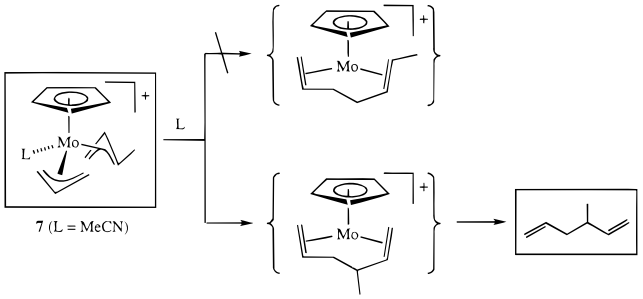
Figure 3. Effective atomic charges for compounds **1a**−**c** from DFT-B3LYP calculations. The values without parentheses refer to the calculation with the LANL2DZ basis set. Values in parentheses refer to the calculation with the extended basis set (see Experimental Section).

Ally−Allyl Coupling. An interesting feature of the protonation reaction of **1c** is the allyl−allyl coupling induced by polar

solvents. Metal-assisted coupling of allyl ligands to afford 1,5-hexadiene products is a widely known reaction.[45−47] The only precedent for this reaction on molybdenum appears to be the interaction of a "violet solution", presumaby containing (η^6-C_6H_6)Mo(η^3-C_3H_5)(μ-Cl)$_2$AlClEt, with propene to ultimately afford a 2,4-hexadiene complex via formation of an intermediate containing coordinated 1,5-hexadiene.[48] The proposed bis(allyl) Mo(IV) intermediate, i.e., [(η^6-C_6H_6)Mo(η^3-C_3H_5)$_2$(C_3H_7)]$^+$, however, was not directly observed. In our case, the bis(allyl) Mo(IV) complex, albeit unstable toward allyl−allyl coupling, can be observed in MeCN. The hexadiene formation involves a formal two-electron reduction of the metal and is therefore facilitated by systems that gain stability upon reduction. For instance, a spontaneous coupling has been reported to occur upon ligand addition to the Cr(III) complex CpCr(η^3-C_3H_5)$_2$,[49] while the corresponding Mo complex does not undergo a similar process,[50] in accord with the expected greater stability of the heavier metal in the higher oxidation state. The oxidation state IV for molybdenum, however is sufficient to induce this coupling process.

A remarkable feature of this allyl−allyl coupling process is its regioselectivity to afford 3-methyl-1,5-hexadiene, no trace of the other expected product (1,5-heptadiene) being observed (see Scheme 12). This regioselectivity is probably due to stereocontrol at the level of intermediate **7**, but this compound is unfortunately too unstable for a structural study. As a final point of interest, we would like to point out the difference of stability between complex **7** and complex **9**. Both complexes are MeCN-stabilized bis-allyl derivatives of CpMo(IV); they differ only in the presence of a backbone linking the two allyl ligands in complex **9**. The presence of this backbone is probably responsible for the increased stability, since it may prevent the two allyl moieties from reaching a suitable configuration for the reductive C−C coupling process. Further studies of this reductive coupling are warranted, since this system is an ideal model for the transition-metal catalyzed butadiene dimerization process.[26]

Scheme 12



Conclusions

It has been established that the relative configuration of allyl and diene ligands in compound **1** induces drastic changes in the reactivity toward protons. While the attack occurs selectively at the allyl terminal position when the diene is coordinated in the *s-cis* mode (compounds **1a** and **1b**), a solvent dependent competition between terminal allyl attack and terminal diene attack is observed when the diene is coordinated in the *s-trans* mode (compound **1c**). The experimental results also suggest a facile solvent-dependent H-shift process between the protonated allyl and diene ligands for the product of protonation of compound **1c**, generalizing a similar observation for the protonation of a system where the coordinated allyl and diene ligands are part of the same macrocycle.[12]

An insight into the electronic differences between the precursor complexes is provided by a DFT analysis. The calculations indicate that the allyl ligand transfers more electron density to the metal center in the *supine* relative to the *prone* conformation, whereas the diene ligand is both a weaker donor and a weaker acceptor, but overall a stronger electron-withdrawing ligand, in the *s-trans* configuration.

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Supporting Information Available: Tables with relevant optimized parameters for compounds **1a**−**c** (4 pages). See any current masthead page for ordering and web access instructions.

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