Four-legged piano stool molybdenum(II) compounds without carbonyl ligands. 2. Reactions of (.eta.5-C5R5)MoCl(PMe3)3 (R = H, Me) with neutral donors

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activation chemistry of the late transition metals. Compounds such as $Cp^*M(PMe_3)(H)(R)$ (M = Rh, Ir; R = alkyl) are thermodynamically less stable than the corresponding phenyl–hydrido derivatives, and their thermal treatment in C_6D_6 proceeds to the formation of the more stable $Cp^*M(PMe_3)(D)(C_6D_5)$ product.[30] In our case, the methyl derivatives **5** and **5*** can be isolated (although they thermally decompose at mild temperatures) and the corresponding phenyl derivative (for the Cp system) cannot. This does not necessarily mean that the order of thermodynamic stability of phenyl vs methyl derivatives is reversed for the molybdenum system (M–Ph bonds are stronger than M-R(sp^3) bonds also for early transition metals, for instance for scandium[31]). A possible rationalization for the observed reactivity is that the cyclometalated forms (**6** and **7***) are thermodynamically more stable than the corresponding non-cyclometalated forms (**5**, **5***, or the corresponding phenyl derivatives), and although the phenyl derivatives probably are *thermodynamically more stable* than those containing the methyl group, they are also (in analogy to the Rh and Ir chemistry mentioned above)[30] *kinetically more labile*.

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Supplementary Material Available: A figure showing observed and simulated second-order $^{31}P\{^1H\}$-NMR spectra for compound **5** (Figure 1S) and tables of complete bond distances and angles, anisotropic thermal parameters, and positional parameters of hydrogen atoms for compound $[1]^+PF_6^-$ (5 pages); a table of observed and calculated structure factors for compound $[1]^+PF_6^-$ (5 pages). Ordering information is given on any current masthead page.

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Four-Legged Piano Stool Molybdenum(II) Compounds without Carbonyl Ligands. 2. Reactions of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H, Me) with Neutral Donors

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Substitution of a PMe_3 ligand of compound $CpMoCl(PMe_3)_3$ (**1**) with L affords $CpMoCl(PMe_3)_2L$ molecules (L = N_2 (**2**), C_2H_4 (**3**)). No analogous products are obtained with propene or butene. Neither does $Cp^*MoCl(PMe_3)_3$ (**1***) react in an analogous fashion with ethylene. NMR investigations show that the dinitrogen complex has a trans configuration of the monodentate ligands in the four-legged piano stool geometry, whereas the ethylene complex is present in solution as a mixture of cis and trans isomers, the cis isomer being the prevalent one (10:1 in benzene-d_6; 33:1 in acetone-d_6). The olefin ligand in the cis isomer does not freely rotate around the Mo–C_2H_4 bond on the NMR time scale, and its conformation has been established by a combination of selective decoupling, NOE, and ^1H–^{13}C COSY-NMR experiments. Interaction of **1** with butadiene affords $CpMoCl(PMe_3)(\eta^4\text{-}C_4H_6)$ (**4**), which can also be obtained directly from $CpMoCl_2$, butadiene, PMe_3, and Na/Hg. No analogous reactions occur with 2,3-dimethylbutadiene or cycloheptatriene. The corresponding Cp* compound, **4***, has been obtained by reduction of $Cp^*MoCl_4(PMe_3)$ with Na/Hg in the presence of butadiene. Compound **1** interacts with diphenylacetylene to afford the salt $[CpMo(PMe_3)_2(PhCCPh)]^+Cl^-$ (**5**). Compound **3** reacts with $LiEt_3BH$ or EtMgBr to afford $CpMoH(C_2H_4)(PMe_3)_2$ (**6**), which is fluxional at room temperature and decoalesces into a 47:53 mixture of cis and trans isomers at low temperature. Compound **6** was also obtained from **1** and EtMgBr. Interaction of **6** with PMe_3 results in C_2H_4 substitution rather than insertion into the Mo–H bond. Alkylation of **3** with MeLi generates $CpMo(CH_3)(C_2H_4)(PMe_3)_2$ (**7**), which is stable at $T \leq 60$ °C and is present exclusively as the cis isomer. Warming transforms the latter compound into $CpMo(\eta^2\text{-}CH_2PMe_2)(C_2H_4)(PMe_3)$ (**8**) with elimination of methane.

Introduction

In the preceding paper[1] we have reported the preparation of $YMoCl(PMe_3)_3$ (Y = Cp (**1**), Cp* (**1***)), a few substitution reactions of the chloro ligand with hydrido, alkyl, and allyl reagents, and the electrochemical and chemical oxidation of **1** to the 17-electron $[CpMoCl(PMe_3)_3]^+$ ion, including the X-ray structure of its PF_6^- salt. In this paper we report the preparation, characterization, and reactivity of derivatives of compounds **1** and **1*** where one or more PMe_3 ligands have been replaced by other neutral donors.

Experimental Section

All operations were conducted under an atmosphere of argon unless otherwise stated. Solvents were dried by conventional methods and distilled under dinitrogen, followed by thorough degassing and saturation with argon prior to use. Instruments used were as follows: NMR, Bruker AF200 and WP200 for routine ^1H, ^{13}C, ^{31}P, and variable-temperature analyses, Bruker AM400 for NOE studies, and Bruker AMX500 for the ^1H–^{13}C COSY investigation; EPR, Bruker ER200; MS, VG 7070E. For the

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Table I. NMR Spectroscopic Data (δ) for All New Compounds

compd	solvent	^{1}H	^{31}P{^{1}H}	^{13}C or ^{13}C{^{1}H}
2	C_6D_6	4.46 (d, 5 H, J_{PH} = 1 Hz, Cp), 1.28 (vt,[a] 18 H, J_{PH} = 6.5 Hz, PMe_3)	21.3 (s)	
3c[b]	C_6D_6	4.36 (dd, 5 H, J_{PH} = 4 Hz, J_{PH} = 1 Hz, Cp), 2.34 (m, 1 H, H_a), 2.13 (m, 1 H, H_b), 2.02 (m, 1 H, H_c), 1.63 (m, 1 H, H_d), 1.26 (d, 9 H, J_{PH} = 7.5 Hz, cis-PMe_3), 0.60 (d, 9 H, J_{PH} = 7 Hz, trans-PMe_3)	22.1 (d, J_{PP} = 36 Hz, P_{cis}), 2.4 (d, J_{PP} = 36 Hz, P_{trans})	87.7 (s, Cp), 50.3 (t, J_{PC} = 8 Hz, $CH_{a,b}$), 32.4 (s, $CH_{c,d}$), 19.6 (d, J_{PC} = 23 Hz, PMe_3), 18.4 (d, J_{PC} = 23 Hz, PMe_3)
3t[c]	C_6D_6	4.08 (t, 5 H, J_{PH} = 2.5 Hz, Cp), 0.96 (vt,[a] 18 H, J_{PH} = 7.5 Hz, PMe_3)	9.6 (s)	86.1 (s, Cp)
4[d]	C_6D_6	5.82 (m, 1 H, H_a), 5.29 (m, 1 H, H_b), 4.38 (d, 5 H, J_{PH} = 1 Hz, Cp), 2.92 (d, 1 H, J = 7 Hz, H_c), 1.34 (m, 1 H, H_d), 1.00 (m, 1 H, H_e), 0.85 (d, 9 H, J_{PH} = 8 Hz, PMe_3), 0.13 (m, 1 H, H_f)	10.3 (s)	115.6 (s, CH_a or CH_b), 104.6 (s, CH_b or CH_a), 89.4 (s, Cp), 48.9 (s, $CH_{d,e}$ or $CH_{c,f}$), 39.6 (s, $CH_{c,f}$ or $CH_{d,e}$), 15.6 (d, J_{PC} = 26 Hz, PMe_3)
4*	C_6D_6	6.00 (quint, 1 H, J = 8 Hz, H_a), 5.25 (quart, 1 H, J = 7 Hz, H_b), 2.55 (d, 1 H, J = 7.5 Hz, H_c), 1.45 (s, 15 H, Cp*), 1.06 (d, 1 H, J = 7 Hz, H_d), 0.86 (d, 9 H, J_{PH} = 7.5 Hz, PMe_3), 0.06 (d, 1 H, J = 8.5 Hz, H_e), −0.30 (dd, 1 H, J_1 = 3 Hz, J_2 = 8 Hz, H_f)	4.9 (s)	112.5 (d, J_{HC} = 169 Hz, CH_a or CH_b), 108.8 (d, J_{HC} = 165 Hz, CH_b or CH_a), 97.7 (s, $C_5(CH_3)_5$), 57.8 (t, J_{HC} = 154 Hz, $CH_{d,e}$ or $CH_{c,f}$), 46.8 (t, J_{HC} = 152 Hz, $CH_{c,f}$ or $CH_{d,e}$), 15.0 (dd, J_{PC} = 24 Hz, J_{HC} = 133 Hz, PMe_3), 11.2 (q, J_{HC} = 126 Hz, $C_5(CH_3)_5$)
5	$CDCl_3$	7.4–7.1 (m, 10 H, 2 Ph), 5.60 (t, 5 H, J_{PH} = 1 Hz, 2 PMe_3), 1.56 (vt,[a] 18 H, J_{PH} = 8.5 Hz, 2 PMe_3)	12.8 (s)	221.1 (d, J_{PC} = 12 Hz, $C{\equiv}C$), 128.7 (s, Ph), 127.9 (s, Ph), 126.5 (s, Ph), 93.6 (s, Cp), 23.1 (br, PMe_3)
6	C_6D_6 (20 °C)	4.42 (s, 5 H, Cp), 1.27 (td, 4 H, J_{PH} = 7 Hz, J_{HH} = 3 Hz, C_2H_4), 1.09 (vt,[a] 18 H, J_{PH} = 3.5 Hz, 2 PMe_3), −6.45 (t of quint, 1 H, J_{PH} = 62 Hz, J_{HH} = 3 Hz, Mo–*H*)	22.7 (s)	84.2 (s, Cp), 25.1 (vt,[a] J_{PC} = 11 Hz, 2 PMe_3), 22.2 (t, J_{PC} = 6 Hz, C_2H_4)
	$C_6D_5CD_3$[e] (−93 °C)	4.50 (br s, Cp, **6t**), 4.23 (br s, Cp, **6c**), 2.22 (br, C_2H_4), 1.51 (br, C_2H_4), 1.22 (br s, 2 PMe_3, **6t**), 0.86 (br, C_2H_4), 0.63 (br s, PMe_3, **6c**), 0.39 (br s, PMe_3, **6c**), −6.28 (br t, J_{PH} = 73 Hz, Mo–*H*, **6t**), −7.30 (br d, J_{PH} = 48 Hz, Mo–*H*, **6c**)	28.2 (s, 2 PMe_3, **6t**), 18.3 (d, J_{PP} = 33 Hz, PMe_3, **6c**), 7.1 (d, J_{PP} = 33 Hz, PMe_3, **6c**)	
7	$C_6D_5CD_3$	3.92 (dd, 5 H, J_{PH} = 3.5 Hz, J_{PH} = 1 Hz, Cp), 1.73 (m, 1 H, C_2H_4), 1.40 (m, 1 H, C_2H_4), 1.08 (d, 9 H, J_{PH} = 6.5 Hz, PMe_3), 0.84 (m, 1 H, C_2H_4), 0.70 (d, 9 H, J_{PH} = 6 Hz, PMe_3), 0.60 (m, 1 H, C_2H_4), −1.00 (d, 3 H, J_{PH} = 10.5 Hz, CH_3)	12.3 (d, J_{PP} = 27 Hz, PMe_3), 8.9 (d, J_{PP} = 27 Hz, PMe_3)	83.4 (d, 5 C, J_{HC} = 176 Hz, Cp), 43.6 (tt, J_{PC} = 4 Hz, J_{HC} = 153 Hz, C_2H_4), 31.8 (t, J_{HC} = 151 Hz, C_2H_4), 20.2 (quart of d, J_{PC} = 10 Hz,[f] PMe_3), 18.0 (quart of d, J_{PC} = 10 Hz, J_{HC} = 128 Hz, PMe_3), 6.7 (quart of t, J_{PC} = 9 Hz, J_{HC} = 124 Hz, CH_3)
8	$C_6D_5CD_3$	4.20 (dd, 5 H, J_{PH} = 2 Hz, J_{PH} = 0.2 Hz, Cp), 1.40 (m, 2 H, C_2H_4), 1.22 (d, 3 H, J_{PH} = 7 Hz, PMe), 1.06 (d, 3 H, J_{PH} = 9 Hz, PMe), 0.93 (d, 9 H, J_{PH} = 7 Hz, PMe_3), 0.80 (m, 2 H, C_2H_4), −0.55 (dt, 1 H, J_{HH} = 7.4 Hz, J_{PH} = 2.4 Hz, CH), −2.01 (d, 1 H, J_{HH} = 7.4 Hz, CH)	23.7 (d, J_{PP} = 49 Hz, PMe_3), −36.7 (d, J_{PP} = 49 Hz, PMe_2)	

[a] Intermediate pattern between doublet and virtual triplet. Coupling constant is given on the basis of the two outer peaks. [b] Assignments (see I) and ethylene orientation are based on NOE, ^{1}H{^{31}P, selected ^{1}H}, and ^{1}H–^{13}C COSY-NMR experiments (see text). [c] Other peaks were too weak or masked by the stronger peaks of the cis isomer **3c**. Equilibrium **3c**:**3t** ratio (from integration of ^{1}H Cp and ^{31}P{^{1}H} resonances): 10:1 (C_6D_6); 12:1 ($C_6D_5CD_3$); 33:1 (CD_3COCD_3). [d] Assignments (see II) and butadiene orientation are based on NOE and ^{1}H{^{31}P, selective ^{1}H}-NMR experiments (see text). [e] Other proton peaks were masked by the stronger PMe_3 absorptions. Equilibrium **6c**:**6t** ratio (from integration of ^{1}H hydride and ^{31}P{^{1}H} resonances) is 47:53. [f] J_{HC} not evident in the ^{13}C-NMR spectrum due to overlap with the strong solvent resonance and low signal-to-noise ratio. J_{PC} obtained from the ^{13}C{^{1}H}-NMR spectrum.

electron impact mass spectra, the samples were introduced into the spectrometer with a desorption chemical ionization probe. For the fast atom bombardment mass spectra, a xenon ion source was used.

Elemental analyses were by Galbraith Laboratories, Knoxville, TN. Compounds $CpMoCl(PMe_3)_3$,[1] $Cp^*MoCl(PMe_3)_3$,[1] Cp^*MoCl_4,[2] and $CpMoCl_2(PMe_3)_2$[3] were prepared as described in the literature. $LiEt_3BH$ (1.0 M in THF), LiMe (1.4 M in Et_2O), and EtMgBr (3.0 M in Et_2O) were purchased from Aldrich and were used as received. All the NMR spectra of the new compounds are reported in Table I.

Partial Conversion of $CpMoCl(PMe_3)_3$ (1) to $CpMoCl(PMe_3)_2(N_2)$ (2). A 210-mg sample of compound 1 (0.496 mmol) was dissolved in *n*-heptane (30 mL) and heated to 50–60 °C while the solution was purged with dinitrogen. Additional *n*-heptane was added as the solvent evaporated. Small amounts of an insoluble yellow-brown precipitate formed. After 3.5 h the soild was removed by filtration, the solution was evaporated to dryness, and the residue was investigated by NMR spectroscopy in C_6D_6. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra indicated a 1:1 mixture of **1** and **2**.

Preparation of $CpMoCl(PMe_3)_2(C_2H_4)$ (3). (a) From Compound 1. Compound 1 (100 mg, 0.24 mmol) was dissolved in *n*-heptane (10 mL). The solution was warmed to 50 °C, and ethene was passed rapidly through the solution. After 1 h the solution was orange-brown and a red microcrystalline precipitate had formed. The precipitate was filtered off and dried to give 64 mg of **3**. Cooling the filtrate to −20 °C overnight gave a further crop of 5 mg. Total yield: 78%. The spectroscopic properties of this material are identical to those of the analyzed sample, obtained as described below.

(b) From a Mixture of Compounds 1 and 2. Compound **1** (320 mg, 0.75 mmol) was partially converted to compound **2** as described above. The resulting *n*-heptane solution was warmed to 60 °C in a water bath, and ethene was bubbled through it for 1.5 h. Similar workup as described above for the synthesis of **3** from pure **1** gave 0.25 g (86% yield) of compound **3**. Anal. Calcd

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for $C_{13}H_{27}ClMoP_2$: C, 41.4; H, 7.2. Found: C, 41.2; H, 7.2.

Reaction of Compound 1 with Propene. Compound 1 (320 mg, 0.75 mmol) was dissolved in 40 mL of toluene and heated to 90 °C. Propene was bubbled through the stirred solution for ca. 1.5 h, during which time the color of the solution changed from purple to red-brown. After filtration, the solution was concentrated to ca. 4 mL and treated with *n*-heptane (15 mL), followed by cooling to −20 °C. The red-brown crystals that formed (78 mg) were shown to be of compound $CpMoCl_2(PMe_3)_2$ by comparison of their NMR and EPR spectroscopic properties with those reported in the literature.[4] NMR analysis of the mother liquor (evaporation of an aliquot to dryness, followed by redissolution in C_6D_6) did not show resonances attributable to an olefin complex analogous to compound **3**.

Reaction between Compound 3 and PMe_3 in a 1:1 Ratio. A solution of compound **3** (37 mg, 9.8×10^{-2} mmol) in ca. 1 mL of C_6D_6 was transferred in an NMR tube. To this was added 10 μL of PMe_3 (0.1 mmol) via a microsyringe, and the tube was flame sealed under vacuum at the liquid-nitrogen temperature. After thawing, the tube was immersed in a warm oil bath (T = 65 °C) and its contents periodically monitored by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy. The growth of the characteristic peaks of compound **1** was observed over a period of ca. 24 h until a ratio of **1**/**3** of 10:90 was reached. The characteristic resonances of free PMe_3 remained the prominent features in the NMR spectra. Further monitoring (3 days at the same temperature) did not show a significant variation of the spectra.

Preparation of $CpMoCl(\eta^4\text{-}C_4H_6)(PMe_3)$ (4). (a) From Compound 1 and C_4H_6. A crystalline sample of compound **1**, obtained as described previously[1] from $CpMoCl_2$ (641 mg, 2.76 mmol), PMe_3 (860 μL, 8.6 mmol), and Na/Hg (63 mg, 2.74 mmol, 0.5% w/w) in 20 mL of THF, was dissolved in *n*-heptane (50 mL). The resulting solution was warmed in a water bath to 65 °C, and butadiene was bubbled through for 5 min. The color of the solution changed from dark purple to a lighter purple while minor amounts of a tan precipitate formed. Upon cooling to room temperature, the purple product crystallized out. Purification from the tan byproduct was accomplished by dissolution in toluene, followed by filtration and recrystallization by diffusion of *n*-heptane. Yield: 187 mg (20.7% based on $CpMoCl_2$). The NMR spectroscopic properties of this material are identical with those of the product obtained by the procedure described below.

(b) From $CpMoCl_2(PMe_3)_2$, Na/Hg, and C_4H_6. PMe_3 (0.45 mL, 4.3 mmol) was added to a slurry of $CpMoCl_2$ (0.50 g, 2.2 mmol) in THF (20 mL). After the formation of $CpMoCl_2(PMe_3)_2$ was complete (ca. 1 h), the solution was transferred via cannula onto sodium amalgam (50 mg, 2.15 mmol, 0.5% wt). The solution was heated to 60 °C and stirred, and C_4H_6 was passed through the solution for 1 h. Additional THF was added as the solvent evaporated. The initially red-brown solution changed color to orange-red. After evaporation to dryness, the residue was extracted with toluene (2 × 10 mL). The solution was filtered, concentrated to 2–3 mL, and layered with *n*-heptane (10 mL). Dark purple crystals of compound **4** slowly deposited. They were filtered off, washed with *n*-heptane, and dried under vacuum. Yield: 80 mg (11%). MS (FAB, glycerol): envelope corresponding to M^+, % intensity of highest peak (m/e 328) = 37.2. The mother solution gave more crystalline material upon cooling to 0 °C. By NMR inspection, this material consisted of a 9:1 mixture of compounds **1** and **4**. After removal of the second crop, NMR inspection of the mother solution revealed the presence of compound **1**, $CpMoH(PMe_3)_3$, and other unidentified paramagnetic materials as suggested by broad peaks at ca. δ −1, −3.5, and −9.

A similar experiment with 2,3-dimethylbutadiene or cycloheptatriene or cycloheptatriene gave no η^4-product. Only **1** was isolated in low yields (30–40%).

Preparation of $Cp^*MoCl(\eta^4\text{-}C_4H_6)(PMe_3)$ (4*). Cp^*MoCl_4 (1.258 g, 3.37 mmol) was slurried with 50 mL of THF and cooled to −78 °C. Excess C_4H_6 was condensed in the Schlenk tube (ca. 10 min), followed by the addition of PMe_3 (0.33 mL, 3.3 mmol). The solution turned dark orange-brown. The mixture was then treated with Na/Hg (0.5%, 235 mg, 10.2 mmol) and stirred while being warmed to room temperature. Over a period of a few hours, the color changed to purple-brown, then dark green, and finally blue-green. The solution was decanted off the precipitate of Hg and NaCl and was evaporated to dryness. The residue was extracted with pentane (50 mL), and the resulting solution was filtered and concentrated to ca. 20 mL. Cooling to −78 °C afforded gray-blue crystals of compound **4***, which were separated by decanting off the mother liquor, washed with cold pentane, and dried under vacuum. Yield: 725 mg, 54%. MS (FAB, glycerol): envelope corresponding to M^+, % intensity of highest peak (m/e 398) = 55.3. Envelopes corresponding to $(M - Cl)^+$, $(M - C_4H_6)^+$, and $(M - PMe_3)^+$ were also clearly identified. Solutions of **4*** in pentane or benzene are green-blue but turn brown slowly over 1–2 days with no apparent change in the ^1H- or ^{31}P-NMR spectra.

Reaction of 1 with PhCCPh. Formation of $[CpMo(PMe_3)_2(PhCCPh)]^+Cl^-$ (5). $CpMoCl(PMe_3)_3$ (100 mg, 0.24 mmol) and PhCCPh (50 mg, 0.29 mmol) were stirred in 1:1 toluene/*n*-heptane (10 mL) for 16 h. A green microcrystalline precipitate deposited. Cooling to −20 °C gave more green microcrystals. The product was filtered off, washed with toluene, and dried in vacuo. Yield: 41 mg, 33%. Characterization of the compound is based on comparison of the NMR spectroscopic properties with those of similar compounds (see Results).

Preparation of $CpMoH(C_2H_4)(PMe_3)_2$ (6). (a) From Compound 3 and $LiEt_3BH$. A 102-mg sample of compound **3** (0.27 mmol) was treated with $LiEt_3BH$ (0.27 mL, 1 M in THF, 0.27 mmol) in 10 mL of toluene while the mixture was purged with C_2H_4. After 1 h of stirring at room temperature, the mixture was evaporated to dryness, the residue was extracted with pentane (15 mL), and the resulting solution was filtered from the pale red residue, which was shown by NMR spectroscopy to contain some unreacted **3**, and evaporated to dryness to leave a yellow solid. Yield: 63 mg, 68%. NMR properties of this material are identical to those of the same compound obtained by the procedure described below, on which mass spectral data were obtained to further support its formulation as **6**.

If the above procedure is carried out without C_2H_4 purging, a complex mixture of hydride products results, including $CpMoH(PMe_3)_3$ and $CpMoH_3(PMe_3)_2$, as indicated by NMR spectroscopy.

(b) From Compound 3 and EtMgBr. Compound **3** (70 mg, 0.18 mmol) was dissolved in THF and treated with EtMgBr (185 μL, 1 M in Et_2O, 0.185 mmol) at 20 °C with stirring. In less than 1 min the color changed from red to yellow. After evaporation to dryness, the residue was extracted with pentane (2 × 10 mL), and the resulting solution filtered and evaporated to dryness, to leave an oily material which turned into a solid upon prolonged standing under dynamic vacuum. Yield: 49 mg, 90%. The reaction is shown to be quantitative in solution by ^1H-NMR monitoring in THF-d_8. MS (FAB, glycerol): envelope corresponding to $(M - H)^+$, % intensity of highest peak (m/e 343) = 2.9.

(c) From Compound 1 and EtMgBr. Compound **1** (30 mg, 0.07 mmol) was dissolved in 3 mL of pentane, cooled to 0 °C, and treated with EtMgBr (1 M in Et_2O) dropwise until the solution is yellow. After further stirring at 0 °C for 20 min, the solution was filtered and evaporated to dryness. NMR inspection of the residue in C_6D_6 shows that this consists of a mixture of $CpMoH(PMe_3)_3$ and compound **6** in a 1:2 approximate ratio.

When an identical experiment was repeated, but the yellow solution was allowed to stir for 2 h before being evaporated to dryness, the $CpMoH(PMe_3)_3$/**6** ratio was found to be ca. 2:1.

Preparation of $CpMo(CH_3)(C_2H_4)(PMe_3)_2$ (7). Compound **3** (15 mg, 0.04 mmol) was treated with MeLi (30 μL, 1.4 M in Et_2O, 0.04 mmol), in Et_2O (5 mL) at room temperature. An immediate color change from red to yellow was observed. After evaporation to dryness, the residue was extracted with pentane (10 mL) and the resulting solution was filtered and evaporated to dryness to leave the product as a yellow microcrystalline solid. Yield: 12 mg, 85%. An NMR investigation showed that the compound is contaminated by a small amount of compound **6** (<5%). MS (EI, 70 eV): envelope corresponding to $(M - 3H)^+$, % intensity of highest peak (m/e 355) = 11.7%; an additional envelope (highest peak at m/e 341, 4.6%) may correspond to further loss of CH_4 or to the loss of 3 H from the product of thermal decomposition of **7**, i.e. compound **8** (vide infra).

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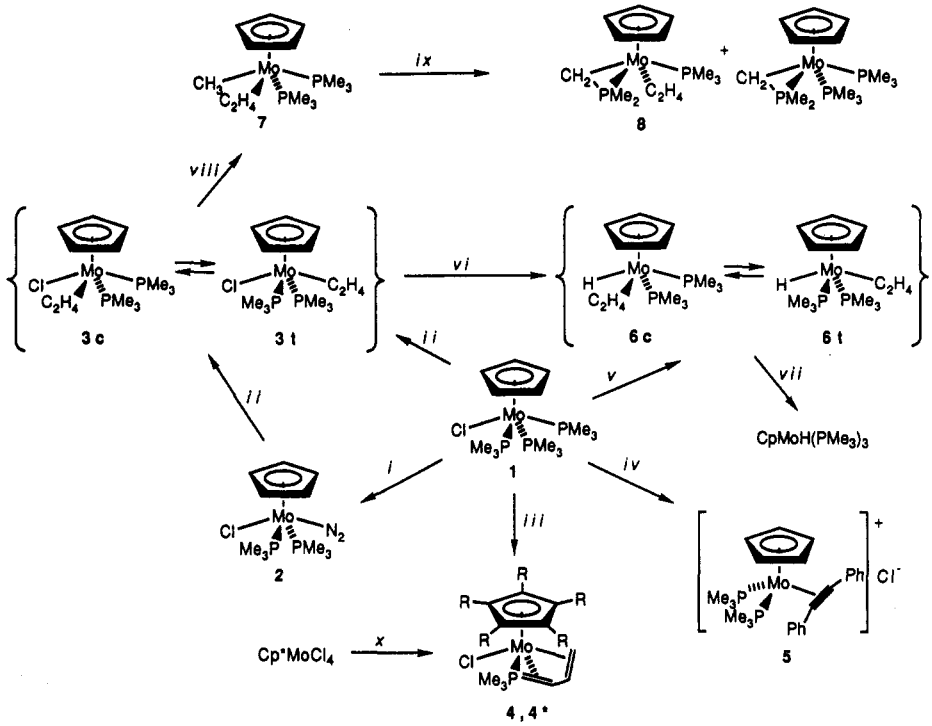
Scheme I[a]



[a] Unstarred numbers refer to R = H; starred numbers refer to R = Me. Key: (i) N_2 purge, heptane, ≥50 °C; (ii) C_2H_4 purge, heptane, ≥50 °C; (iii) C_4H_6 purge, heptane, 65 °C; (iv) PhCCPh, toluene/heptane, rt; (v) EtMgBr, pentane, 0 °C; (vi) $LiEt_3BH$, toluene, C_2H_4, rt or EtMgBr, THF, rt; (vii) PMe_3, rt; (viii) MeLi, Et_2O, rt; (ix) toluene, 120 °C, 2 h; (x) PMe_3, C_4H_6, Na/Hg, THF, rt.

Thermolysis of Compound 7. A sample (ca. 5 mg) of compound 7 was heated in toluene-d_8 in a sealed NMR tube. Heating to 60 °C overnight did not result in any observable change in the NMR spectroscopic properties of the solution. Further heating for 2 h at ca. 120 °C resulted in conversion to a 3:2 mixture of $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)(C_2H_4)$ (8) and $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$,[1] as the only organometallic species observable by NMR methods. The formation of methane (and the absence of CH_3D) is suggested by the growth of a singlet at δ 0.17 in the ^{1}H-NMR spectrum. An insoluble brown solid also formed during the thermolysis.

Results

The reactions described in this paper are summarized in Scheme I.

Substitution of a PMe_3 ligand with dinitrogen in compound 1 proceeds sluggishly. The reaction was carried out under a continuous N_2 purge through the heptane solution, which was kept at ca. 60 °C in order to remove the volatile PMe_3 that was formed. We could not obtain a sample of compound 2 that was not contaminated by unreacted 1. Under the same experimental conditions, 1* did not generate any of the previously reported[5,6] dinitrogen complex $Cp^*MoCl(PMe_3)_2(N_2)$ (2*). An attempt to generate 2 by direct reduction of $CpMoCl_2(PMe_3)_2$ under dinitrogen also failed to produce 2. Rather, compound 1 was obtained from this reaction in modest yields as the only isolable material.

Compound 2 was identified by its NMR and IR spectroscopic properties in solution. The N–N stretching vibration is found at 1972 cm^{-1} (vs 1949 cm^{-1} in 2*).[6] The ^{1}H-NMR spectrum shows a single resonance for the PMe_3 protons as an intermediate pattern between a doublet and a virtual triplet, which is typical for PMe_3 ligands occupying relative trans positions in four-legged piano stool structures.[1] The trans configuration for compound 2 is also suggested by the single $^{31}P\{^1H\}$ resonance at δ 21.3 (cf. 14.7 for 2*).[6]

Substitution of PMe_3 with an ethylene molecule in compound 1 is more facile than the substitution with N_2 and affords the ethylene complex $CpMoCl(PMe_3)_2(C_2H_4)$ (3) in good yield. This may reflect the higher affinity of the metal for ethylene versus N_2 and/or the fact that compound 3 is only partially soluble in heptane and precipitates as it forms. When compound 3 is interacted with the equimolar amount of PMe_3 in an homogeneous solution and in a sealed tube (so as to avoid loss of volatiles), an equilibrium is reached containing compounds 1 and 3 in an approximate 1:9 ratio.

Compound 3 is present in solution as a mixture of cis and trans isomers (Scheme I), the cis isomer being largely prevalent. The assignment of the cis structure to the major isomer is straightforward because of the predominance of the two doublets in the $^{31}P\{^1H\}$-NMR spectrum due to the two inequivalent phosphorus nuclei, which is paralleled by two prominent doublets in the ^{1}H-NMR spectrum for the phosphorus-coupled PMe_3 proton resonances. The minor isomer shows a single resonance in the ^{31}P-NMR spectrum and a pattern for the corresponding protons (intermediate between a doublet and a virtual triplet) analogous to those of 2 and to the two trans PMe_3 ligands in the precursor 1. Of the two $^{31}P\{^1H\}$-NMR doublets observed for the major isomer, 3c, we assign the downfield shifted one (at δ 22.1) to the phosphorus donor which is located trans with respect to the chloro ligand and the upfield shifted one (at δ 2.5) to the phosphorus donor which is located trans with respect to the C_2H_4 ligand. This is based on the comparison with the $^{31}P\{^1H\}$-NMR spectrum of compound 1, which shows the lower field resonance (triplet, 25.8 δ) for the unique phosphine ligand located trans with respect to the chloride.[1] $^1H\{$selective-$^{31}P\}$-NMR experiments allow the assignment of the PMe_3

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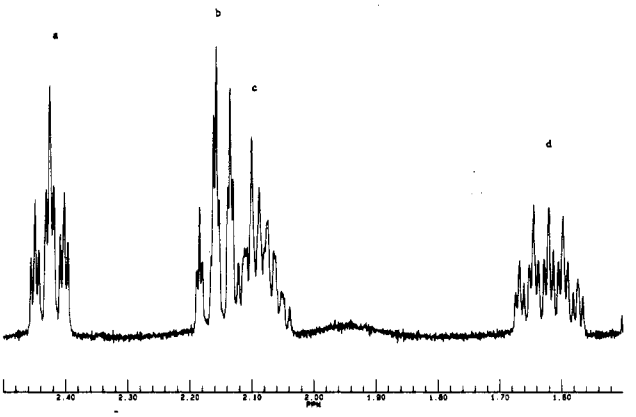
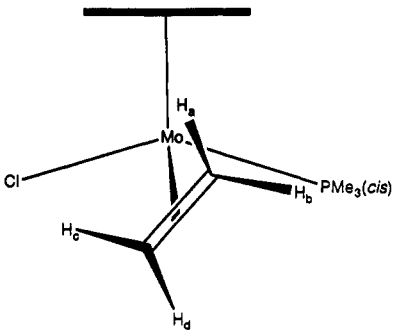


Figure 1. ^{1}H-NMR spectrum of compound **3** at 400 MHz in the ethylene proton resonance region (solvent = C_6D_6).

proton resonances as shown in Table I.

The ethene proton resonances in **3t** were obscured by the resonances of the same protons in the major isomer **3c**. For the ethene ligand in the cis isomer, the inequivalence of the four protons (see Figure 1) is consistent with the ligand being present in an upright conformation, in a parallel one, or at any angle in between. However, the observation of four independent resonances shows that the ethylene ligand is *not* freely rotating, as if that were the case, each pair of trans hydrogens in the ethylene ligand would become equivalent. This was found to be the case for the closely related $[CpMo(Pom\text{-}Pom)(CO)(C_2H_4)]^+$ complex (Pom-Pom = 1,2-bis(dimethoxyphosphino)-ethane).[7a] Since we were not able to grow suitable single crystals for compound **3** for an X-ray analysis, we have obtained more details on the conformation of the ethylene ligand from a combination of selective homo- and heteronuclear decoupling, NOE, and ^{1}H–^{13}C COSY-NMR experiments. Selective saturation of each phosphorus resonance shows that all ethylene protons are coupled to both phosphorus nuclei. For instance, both resonances a and b (Figure 1), which look like triplets of triplets, are reduced to triplets of doublets (small doublet coupling) upon saturation of either phosphorus nucleus. The H–H large couplings are shown to be J_{ac}, J_{ad}, J_{bc}, J_{bd} by triple resonance (broad band ^{31}P, selective ^{1}H decoupling) experiments. H_a is not significantly coupled to H_b, and H_c and H_d are also weakly coupled to each other. This coupling pattern suggests that H_a and H_b are located on the same carbon, and so obviously are H_c and H_d ($J_{trans} > J_{cis} > J_{gem}$). This is confirmed by a ^{1}H–^{13}C COSY-NMR experiment, which shows that H_a and H_b are located on the carbon that resonates at δ 32.4 (singlet) in the ^{13}C NMR spectrum, whereas H_c and H_d are located on the carbon that resonates at δ 50.3 (triplet). The coupling pattern does not allow one to establish whether H_a is located trans to H_c or H_d and, correspondingly, whether H_b is trans to H_d or H_c.

The structure is assigned as shown in I on the basis of the results of ^{1}H-NOE-difference NMR experiments. Saturation of the Cp protons enhances the resonance due to H_a the most, followed by H_b and H_c, whereas H_d is hardly affected at all. This result suggests an intermediate conformation between the upright and horizontal ones and also suggests that H_a is located trans to H_d. Saturation of the PMe_3 proton resonance at δ 0.60 (the one assigned to the cis-PMe_3 ligand; vide supra) enhances the reso-

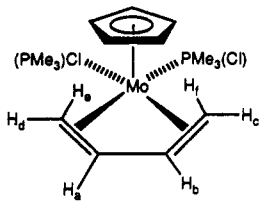


I

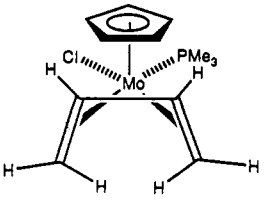
nances due to H_b and H_d but not those of H_a and H_c. It is worth noting that theoretical calculations carried out on *cis*-$[CpMo(PH_3)_2(CO)(C_2H_4)]^+$ predict a lowest energy conformation for the ethylene ligand that is neither upright nor parallel.[7b]

An analogous olefin complex could not be obtained from the reaction of compound **1** and propene, which is somewhat surprising since placing the extra methyl group in the position occupied by H_d in structure I should not be too large a steric perturbation. Analogously, no similar derivative was obtained from **1*** and C_2H_4 (this reaction gave a mixture of paramagnetic, unidentified products).

The butadiene complex **4** was obtained from either compound **1** and butadiene or by direct reduction of $CpMoCl_2(PMe_3)_2$ with Na/Hg in the presence of butadiene. The analogous Cp* complex, **4***, forms by direct reduction of Cp^*MoCl_4 with 3 equiv of Na/Hg in the presence of butadiene and PMe_3. Both compounds **4** and **4*** show six independent resonances for the butadiene ligand. In analogy with the allyl complexes $YMo(\eta^3\text{-}C_3H_5)(PMe_3)_2$ (Y = Cp, Cp*) reported in the previous paper,[1] two configurations (supine, II, and prone, III) are



II



III

possible for the butadiene in these complexes, and the NMR spectroscopic properties are consistent with either a single isomer in solution or with a mixture of isomers in rapid equilibrium with each other. Since the pattern of the butadiene proton resonances is similar for compounds **4** and **4***, and since the ^{1}H-NMR spectrum of **4*** does not change upon cooling to 193 K, we suspect that a single isomer is present at all temperatures.

The assignment of the structure as the supine isomer (II) is based on investigations similar to those presented for the assignment of structure I to complex **3** (see above), which have been carried out on the Cp complex, **4**. The general pattern of the ^{1}H-NMR spectrum of **4*** is similar to that of **4**, and it is therefore likely that the two complexes have a similar structure. Comparison with other literature butadiene complexes allows the assignment of the most downfield shifted butadiene resonances (at δ 5.82, H_a, and 5.29, H_b, for **4**) to the inner protons. The other observed butadiene resonances, at δ 2.92 (H_c), 1.34 (H_d), 1.00 (H_e), and 0.13 (H_f) are assigned to the outer protons. Triple resonance (broad band phosphorus and selective proton decoupling) experiments show the following as large (≥3 Hz) couplings: J_{ab}, J_{ad}, J_{ae}, J_{bc}, and J_{bf}. All the other couplings are small or undetectable. This places the H_d

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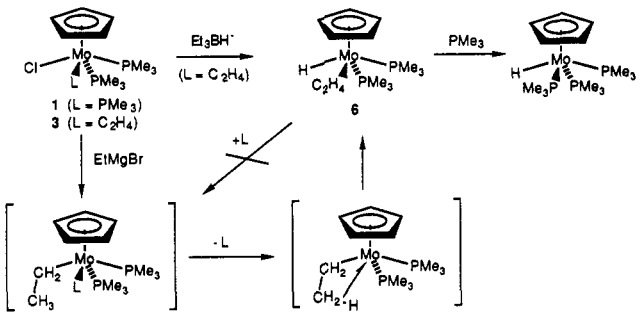
and H_e protons on the terminal carbon which is adjacent to $C(H_a)$ and the H_c and H_f protons on the terminal carbon which is adjacent to $C(H_b)$. As for the case of complex **3c**, the J_{HH} pattern does not allow a clear assignment of the stereochemistry at the two terminal carbon atoms (i.e., whether H_d or H_e is trans to H_a and whether H_c or H_f is trans to H_b). A ^{1}H-NOE-difference NMR experiment, which was carried out with saturation of the Cp proton resonance, shows the stronger enhancement for resonances H_e and H_f, an intermediate enhancement for resonances H_c and H_d, and a negligible effect on resonances H_a and H_b. This suggests that the butadiene ligand adopts the supine geometry and that protons H_e and H_f are closest to the Cp ring, thus presumably trans with respect to the corresponding inner protons H_a and H_b, as shown in II. The relative location of the Cl and PMe_3 ligands with respect to the two C–C double bonds remains uncertain. Saturation of the ^{31}P-NMR resonance of the PMe_3 ligand shows that the strongest P–H couplings are experienced by H_a, H_d, and H_f, whereas P–H coupling is weak or not observed for H_b, H_c, and H_e. No discernible P–C coupling was observed for any of the butadiene C atoms in the $^{13}C\{^1H\}$-NMR spectrum.

Similar butadiene complexes have been reported in the literature. $[CpMo(CO)_2(diene)]^+$ cations (diene = butadiene and homologues) and fluxional at room temperature, and two mechanisms for signal averaging (a more facile rotational motion of the diene ligand and a less facile "flip" through an intermediate metallacyclopentene structure) have been identified.[8] $CpW(CH_3)(CO)(diene)$ complexes are likewise fluxional at room temperature, and the supine/prone equilibrium ratio, which is close to 1:1 for the butadiene complex, was found to increase with the steric encumbering of the diene moiety.[9] On the other hand, the $[CpMo(dppe)(\eta^4\text{-}C_4H_6)]^+$ ion shows the two isomers in a 1:1 ratio "frozen" at room temperature.[10] The solid-state structure of $Cp^*Mo(CH_3)(CO)(\eta^4\text{-}C_4H_6)$ shows a supine conformation of the butadiene ligand,[11] as do the structures of $(\eta^5\text{-}C_9H_7)MoBr(PMe_3)(\eta^4\text{-}CH_2{=}C{=}C(Me)\text{-}C(Me){=}CHMe)$,[12] $[CpMo(dppe)(\eta^4\text{-}C_6H_8)]^+$,[13a] and $CpMoI[P(OMe)_3](\eta^4\text{-}CH_2{=}CH{-}CH{=}CH{-}CH_2Bu^t)$.[13b]

Treatment of compound 1 with diphenylacetylene results in the formation of the ionic compound $[CpMo(PhCCPh)(PMe_3)_2]Cl$ (**5**). The bonding mode of the acetylene ligand as a 4-electron donor is clearly indicated by the low-field ^{13}C-NMR resonance for the sp-hybridized carbon at δ 221.1. The similar complexes $[CpMoL_2(MeCCMe)]^+$ (L = PMe_2Ph; L_2 = $Ph_2PCH{=}CHPPh_2$) have the same resonance at δ 216 and 229, respectively.[14] This parameter is highly diagnostic for the bonding mode of alkynes, since complexes where an 18-electron count is achieved with only 2 electrons being provided by the alkyne ligand are characterized by sp-^{13}C resonances at much higher fields, for instance δ 112.8 for $Pt(MeCCMe)(PPh_3)_2$[15] and δ 44 for $[CpFe(CO)_2(MeCCMe)]^+$.[16]

Scheme II



The hydride–ethylene complex $CpMoH(C_2H_4)(PMe_3)_2$ (**6**) has been obtained in three different ways: (i) replacement of a chloride in compound **3** with a hydride ligand (provided by $LiEt_3BH$); (ii) reaction of compound **3** with EtMgBr; (iii) reaction of compound **1** with EtMgBr. Method i gives the best results under a C_2H_4 purge; when the reaction is conducted under argon, a complex mixture of hydride products, including $CpMoH(PMe_3)_3$ and $CpMoH_3(PMe_3)_2$, is obtained. This might seem to suggest that the reaction(s) leading to the formation of the by-products is (are) initiated by dissociation of the C_2H_4 ligand. It is interesting to observe that the excess C_2H_4 does not induce formation of an ethyl group by insertion of the ethylene ligand into the Mo–H bond (see Scheme II) as found, for instance, for the reaction of (triphos)-$RhCl(C_2H_4)$ with $LiEt_3BH$.[17] In fact, quite the opposite takes place, since an attempt to obtain the ethyl complex $CpMo(Et)(PMe_3)_2(C_2H_4)$ by reaction of **3** with EtMgBr resulted in clean conversion to compound **6** (method ii). Method iii is, in our opinion, the most interesting one of the three. The interaction between **1** and EtMgBr did not give the expected $CpMo(Et)(PMe_3)_3$ but rather a mixture of **6** and $CpMoH(PMe_3)_3$. Soon after the addition of the Grignard reagent, compound **6** is the prevalent hydride product, but subsequently the ratio of the two hydride products changes in favor of $CpMoH(PMe_3)_3$. This is consistent with the mechanism shown in Scheme II, which involves formation of **6** as the kinetic product through β-H elimination from the ethyl ligand following dissociation of a PMe_3 ligand.

Like compound **3**, compound **6** is also present as a mixture of cis (**6c**) and trans (**6t**) isomers in solution. However, for compound **6** the isomerization reaction is faster and only average NMR spectroscopic properties are observed at room temperature. Signals attributable to the two individual isomers (approximate 1:1 ratio) are observed at −93 °C by ^{1}H- and $^{31}P\{^1H\}$-NMR (see Table I). In particular, the hydride resonance, which is observed at room temperature as a triplet of quintets due to equivalent coupling to the two phosphorus nuclei and to the four ethylene protons, decoalesces to a broad triplet (**6t**) and a broad doublet (**6c**) at low temperature.

The interaction between **3** and MeLi gives the isolable methyl–ethylene complex, $CpMo(CH_3)(PMe_3)_2(C_2H_4)$ (**7**). This exists in solution exclusively in the cis geometry. The resonance patterns in the ^{1}H-, ^{31}P-, and ^{13}C-NMR spectra indicate that the structure is similar to that of compound **3c**. In particular, the four distinct resonances for the ethylene protons indicate frozen rotation around the $Mo\text{–}C_2H_4$ axis, and the J_{PC} pattern for the ^{13}C resonances of the ethylene carbon atoms (triplet signal for the

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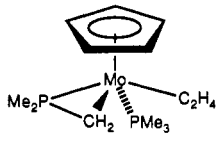
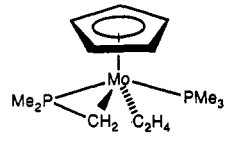
downfield carbon; no observed PC coupling for the upfield shifted carbon) are similar for compounds **3c** and **7**. The four ethylene proton resonances are, on the average, upfield shifted with respect to those found for compound **3**. This effect may be attributed to the higher donor power of CH_3 with respect to Cl, which results in a shielding effect on the ethylene protons through the more electron-rich nature of the metal. The pattern of the four resonances is also slightly different: whereas for compound **3** $\delta_a \gg \delta_b > \delta_c \gg \delta_d$, for compound **7** we have $\delta_a > \delta_b \gg \delta_c > \delta_d$. This might indicate a different orientational preference for the C_2H_4 ligand in the two compounds.

Compound **7** is not a catalyst for ethylene polymerization at room temperature. No significant amounts of polyethylene were formed upon stirring a solution of compound **7** at room temperature under ethylene at atmospheric pressure for 16 h. Compound **7** is thermally more stable than its analogue $CpMo(CH_3)(PMe_3)_3$ described in the previous paper.[1] While the latter decomposes at ≥20 °C to afford the product of phosphine metalation, $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$, compound **7** is stable at 60 °C. However, it decomposes in refluxing toluene in analogy to the tris-PMe_3 derivative to give $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)(C_2H_4)$ (**8**) and $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ in an approximate 3:2 ratio with elimination of methane. The mechanism of formation of compound **8** from **7** is probably identical to the formation of $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ from $CpMo(CH_3)(PMe_3)_3$, as discussed in the previous paper.[1] Dissociation of a phosphine ligand from compound **7** would be followed by oxidative addition of a C–H bond of the remaining PMe_3 ligand; then reductive elimination of CH_4 occurs, and finally the PMe_3 ligand that had dissociated recoordinates to generate the product. Which PMe_3 ligand is the one that initially dissociates (the one trans to the methyl group or the one trans to the ethylene ligand) cannot be established on the basis of our observations. The formation of compound $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ from **7** probably follows the formation of **8** and is probably due to the occurrence of secondary decomposition pathways which release free PMe_3 in solution and generate uncharacterized insoluble materials.

The intimate geometry of compound **8**, i.e. whether the CH_2 group is located cis or trans relative to the C_2H_4 ligand (see IV and V), remains undefined. The NMR properties



IV



V

of the analogous compound $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ are consistent with fluxional behavior involving rotation or rocking of the $\eta^2\text{-}CH_2PMe_2$ moiety between the two limiting orientations, which makes the two pairs of diastereotopic Me groups and CH_2 protons look equivalent.[1] In the case of compound **8**, a similar fluxional process would not alter the symmetry of the molecule; thus the observation of inequivalent Me groups and CH_2 protons for the $\eta^2\text{-}CH_2PMe_2$ moiety is consistent with either a single isomer or with a rapidly scrambling mixture. On the basis of a comparison with compound **7**, where C_2H_4 is selectively located cis with respect to the hydrocarbyl ligand, we would like to suggest that structure IV may be thermodynamically preferred for compound **8**. Consistent with this conclusion is also the observation of the Cp proton resonance as a doublet of doublets with a large (2 Hz) and a small (0.2 Hz) coupling. Because of the "angular trans influence",[18] the Cp–Mo–P angle is expected to be significantly larger for the metalated phosphine than for the PMe_3 ligand in structure IV. If the structure were as in V, the two P donors would be located at a similar Cp–Mo–P angle and the two couplings to the Cp protons would also be expected to be similar. In other similar compounds, significant coupling for the Cp protons has been observed only to phosphorus donors that are located trans relative to π neutral or donor ligands.[1,19]

Discussion

This paper reports a number of four-legged piano stool Mo(II) complexes formally obtained from compounds **1** and **1*** by replacing PMe_3 ligands with other neutral ligands. Contrary to what was found in the exchange studies of the chloride ligand, where similar reactivity was observed for the Cp and Cp* systems,[1] we find that the replacement of PMe_3 proceeds more readily in the Cp complexes. This could be due to either (or both) a thermodynamic factor associated with the higher steric bulk of the Cp* system or a kinetic factor. The steric factor proves important even within the Cp system, since the facile formation of the ethylene complex, $CpMoCl(PMe_3)_2(C_2H_4)$, is not paralleled by the formation of the analogous complex of propene. However, there is evidence to suggest that complex **1*** may also be kinetically more inert than complex **1**. In fact, replacement of PMe_3 with N_2 should certainly relieve steric hindrance in the molecule, and the synthetic method utilized (continuous N_2 purge with removal of PMe_3 at a temperature higher than its boiling point) should circumvent the possible thermodynamic preference for the PMe_3 ligand due to electronic factors. Nevertheless, although compound **1** reacts (although sluggishly) with N_2 to afford complex **2**, no reaction between **1*** and N_2 takes place under the same conditions. The hypothetical substitution product, $Cp^*MoCl(N_2)(PMe_3)_2$, is a stable compound and has been obtained by an alternative route.[5,6] The replacement of PMe_3 by C_2H_4 may occur for **1***, but the ultimate products are paramagnetic and were not characterized.

Within the series having the formula $CpMoXL(PMe_3)_2$ (X = Cl, H, Me; L = N_2, C_2H_4), the difference in stereochemistry deserves some consideration. Compound **2** (X = Cl, L = N_2) has a trans geometry, compound **6** (X = H, L = C_2H_4) is a 53:47 mixture of trans and cis isomers, compound **3** (X = Cl, L = C_2H_4) is also a mixture of isomers, but with the cis one strongly prevailing, and finally compound **7** is present exclusively as the cis isomer. That in the case of compounds **2** and **7** we are observing nonequilibrium situations does not seem likely, on the basis of the following consideration. In the case of compound **6**, the fast equilibration can be attributed to the small size of the hydride ligand, but in the case of compound **3** both the X and the L ligand are at least as bulky as for compounds **2** and **7**, and nevertheless by running multiple experiments, we always observe the same ratio of isomers, which is solvent dependent (10:1 in C_6D_6, 12:1 in $C_6D_5CD_3$, and 33:1 in CD_3COCD_3), indicating fast equilibration.

Cis–trans isomerism in four-legged piano stool structures has been observed in a great many instances, and discussions of the factors which influence the cis/trans ratio have been presented. There is, however, lack of a complete understanding of these factors.[19b] Steric interactions have

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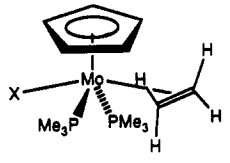
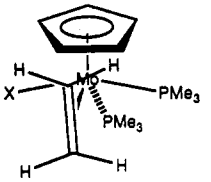
(19) (a) Poli, R.; Krueger, S. T.; Abugideiri, F.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1991**, *10*, 3041. (b) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

been advocated as very important in the determination of the cis/trans ratio of four-legged piano stool isomers. Comparison of compounds **3**, **6**, and **7** (same set of L ligands) shows that the cis/trans ratio depends on the nature of the X group in a manner that correlates better with the steric bulk of X than with its electronic properties. In fact, the hydride and the methyl systems, which are electronically more similar to each other than to the chloride system, represent the extremes of the scale of cis/trans ratios. It is important to consider the preferred orientation of the ethylene ligand in both cis and trans structures. In our recent analysis of the molecular distortions in four-legged piano stool structures,[18] we have described what we have termed "angular trans influence", which results from the observation that π-acidic ligands (such as CO or phosphines) display a higher (ring)–M–L angle (θ angle) when they are located trans relative to another π-acidic ligand (typically 120–130° vs 115–120° when trans relative to π-neutral ligands and 110–115° for the π-neutral ligands themselves).[18] Ethylene is a typical π-acid; thus, it is expected to follow the above trends of θ angles. When ethylene is located trans to a poor π-acid or to a π-neutral ligand as in the *trans*-$CpMoX(C_2H_4)(PMe_3)_2$ compounds (low θ angle), the best π-back-bonding is accomplished upon interaction with the d_{xy} orbital, which is the SHOMO, resulting in a predicted parallel geometry (as in VI). On



VI



VII

the other hand, when the ethylene is located trans to a stronger π-acid as in *cis*-$CpMoX(C_2H_4)(PMe_3)_2$ (high θ angle),[20] the best π-back-bonding is accomplished upon interaction with the d_{z^2} orbital, which is the HOMO. Thus, an upright geometry is predicted (as in VII). Unfortunately, no structure of a *trans*-[(ring)$ML_2L'(C_2H_4)$] molecule [L = π-acidic ligand, L' = π-neutral or π-donor ligand) has been determined to the best of our knowledge. $CpWH(CO)_2$(olefin) complexes have a trans geometry,[21,22] but no studies aimed at elucidating the orientation of the olefin ligand (i.e. perpendicular or parallel) have been carried out. On the other hand, one structure for a *cis*-[(ring)$ML_2L'(C_2H_4)$] complex has been reported, i.e. $[CpMo(Pom\text{-}Pom)(CO)(C_2H_4)]^+$,[7a] which shows an upright ethylene configuration, as expected on the basis of the rationale given above. It is clear that structure VI is sterically less favored than structure VII. Thus, the bulkier the X ligands, the greater the proportion of cis isomer.

The steric argument might also explain the difference between complexes **2** (all trans) and **3** (mainly cis): in compound **2** the two bulkiest ligands (the two PMe_3 ligands) are farthest away from each other, and the L ligand sitting in between them (N_2) is quite small. For compound **3** a parallel C_2H_4 ligand would occupy more room so that the preferred structure is the one that places the two PMe_3 ligands cis relative to each other, as discussed above.

For the cis structures of compounds $CpMoX(PMe_3)_2(C_2H_4)$ (X = H, slightly disfavored; Cl, major; CH_3, only observed isomer), structure VII would be predicted. However, at least for compound **3**, the observed geometry deviates somewhat from the ideal upright conformation (see I). It is possible that this distortion is caused by the different steric requirements of the Cl and PMe_3 ligand. It is also possible, however, that the different nature of these ligands sufficiently perturbs the metal orbitals so that the best Mo–C_2H_4 back-bonding is achieved when the ethylene is in a slightly diagonal geometry. A diagonal geometry has been calculated for the model compound *cis*-$[CpMo(PH_3)_2(CO)(C_2H_4)]^+$.[7b] It is clear from the NMR experiments that the ethylene ligand in compound **3** has hindered rotation around the metal–ligand axis. For the analogous compounds $[CpMo(L\text{-}L)(CO)(C_2H_4)]^+$ (L-L = dppe, Pom-Pom), on the other hand, rotation about this axis is fast on the NMR time scale.[7a] The reason for this difference is probably related to a stronger Mo–C_2H_4 π-interaction in compound **3**, since in the cationic complexes the ethylene ligand competes for π-electron density with stronger π-acids and, in addition, the metal is more electron poor because of the positive charge and the presence of poorer σ-donors.

Another interesting observation is the resistance of the ethylene–hydride complex **6** to undergo insertion to produce an ethyl derivative. This contrasts with the very similar reaction between $CpMoH(CO)_2(C_2H_4)$ and PPh_3, which proceeds to the ethyl derivative, $CpMo(Et)(CO)_2(PPh_3)$.[21] On the other hand, the ruthenium system $Cp^*RuH(PMe_3)_2$ has been prepared from $Cp^*RuCl(PMe_3)_2$ and RMgCl (R = *i*-Pr, *t*-Bu), thus behaving similarly to our Mo(II) system (see Scheme II). In that case, the intermediacy of a hydride–olefin complex was not observed.[23] Another similar system is the arene complex $[(\eta^6\text{-}C_6H_6)Mo(dmpe)H(C_2H_4)]^+$, which behaves in an even more complex manner: interaction with PMe_3 gives the product of insertion, followed by ethyl migration onto the arene ring, $[(\eta^6\text{-}C_6H_5Et)Mo(dmpe)H(PMe_3)]^+$.[24] NMR analysis of $[(\eta^6\text{-}C_6H_6)Mo(dmpe)H(C_2H_4)]^+$ showed that the complex has a cis geometry and that the hydride ligand scrambles at room temperature with the olefin protons.[24] In the case of compound **6**, the complex is fluxional at room temperature due to the cis/trans isomerization, but the H/C_2H_4 scrambling is frozen on the NMR time scale, because the hydride resonance, although averaged because of the pseudoequivalence of the two phosphine ligands, is decoalesced from the ethylene proton resonances. This shows that, in compound **6**, migration of the hydride onto the ethylene ligand is not only thermodynamically less favored but also kinetically less accessible.

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Registry No. **1**, 138784-79-9; **2**, 138784-80-2; **3c**, 138784-81-3; **3t**, 138874-93-8; **4**, 138784-82-4; **4***, 138784-87-9; **5**, 138784-83-5; **6c**, 138784-84-6; **6t**, 138874-94-9; **7**, 138784-85-7; **8**, 138784-86-8; $CpMoCl_2$, 80042-47-3; $CpMoCl_2(PMe_3)_2$, 123934-31-6; Cp^*MoCl_4, 96055-87-7; propene, 115-07-1; butene, 25167-67-3; 2,3-dimethylbutadiene, 513-81-5; cycloheptatriene, 544-25-2.

(20) The role of trialkylphosphines as π-acids has long been criticized. Recent structural studies show that the M–PR_3 π-interaction, although probably not of primary importance in a thermodynamic sense, is sufficient to induce significant structural distortions; see refs 18 and 19a and also: (a) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206. (b) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653.

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