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**FOUR-LEGGED PIANO STOOL MOLYBDENUM(II)
COMPOUNDS WITHOUT CARBONYL LIGANDS—3[†]
CYCLOPENTADIENYL AND INDENYL COMPLEXES
CONTAINING THE TRIDENTATE LIGAND
Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂ (TRIPHOS) VIA REDUCTION
OF MOLYBDENUM(III) PRECURSORS**

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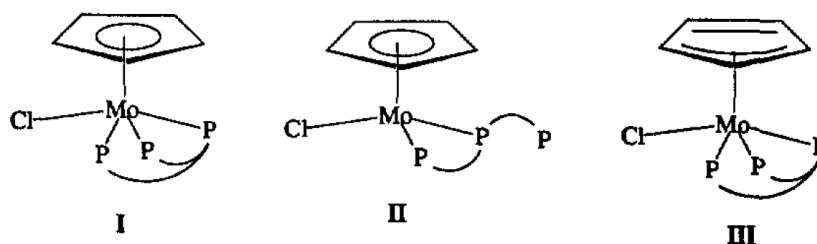
[†] For part 2, see Ref. 1.

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Abstract - The carbonyl-free, half-sandwich molybdenum(II) complexes CpMoCl(triphos) (**1**) and IndMoX(triphos) [X = Cl (**2**); I (**3**); triphos = Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂; Ind: η⁵-C₇H₉ or indenyl] have been synthesized by either reduction of CpMoCl₂ in the presence of triphos or by reduction and transmetallation of MoX₃(triphos) (X = Cl, I) with CpNa or IndNa. The spectroscopic properties indicate a saturated, 18-electron structure in each case. All compounds are susceptible to oxidation in chlorinated hydrocarbons and the oxidation of **1** has been studied in detail both chemically and electrochemically. Compound [I]⁺PF₆⁻ has been obtained by oxidation of **1** with AgPF₆, whereas the corresponding AlCl₄⁻ salt has been prepared in a one-pot reaction from CpMoCl₂, triphos and AlCl₃. The structure of **1** has been confirmed by X-ray crystallography as a four-legged piano stool with an η⁵-cyclopentadienyl ring and a tridentate triphos ligand.

Low oxidation state transition metals are usually compatible with strong π-acidic ligands such as CO, the latter being able to relieve the metal from the excess electron density via the π back-bonding mechanism. Application of the general principle of electroneutrality² leads to the expectation that low-valent complexes will easily dissociate ligands and therefore display enhanced reactivity when they are completely surrounded by strongly donor and weakly π-acceptor ligands. For instance, the complexes Mo(PMe₃)₆,³ W(PMe₃)₆,⁴ and Os(PMe₃)₅,⁵ isoelectronic with the respective zero-valent binary carbonyls, all easily dissociate a PMe₃ ligand and proceed to products of intramolecular *ortho*-metallation. Half-sandwich complexes of molybdenum(II) constitute a well-represented class of organometallic complexes, by and large containing at least one CO ligand in the coordination sphere and obeying, with only few exceptions,^{6,7} the 18-electron rule. Loading the metal coordination sphere with better donor and poorer acceptor ligands such as phosphines should render the 16-electron product of ligand dissociation more accessible. This is especially true if the complex contains ligands that are capable of buffering the coordinative unsaturation via π-donation.⁸ A few years ago, we prepared the two complexes CpMoCl(PMe₃)₃ and Cp*MoCl(PMe₃)₃ and showed that they have a rich chemistry of ligand substitution.^{1,9} More recently, we have characterized the product of PMe₃ dissociation from the Cp* complex. The stable and reactive 16-electron Cp*MoCl(PMe₃)₂ complex,¹⁰

which is the first such complex to have a high spin ($S = 1$) ground state configuration. Surprisingly, this compound has no tendency to undergo *ortho*-metallation to lead to the hypothetical 18-electron molybdenum(IV) product $\text{Cp}^*\text{Mo}(\text{H})(\text{Cl})(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_2)(\text{PMe}_3)$,¹⁰ whereas the corresponding tungsten(IV) material has been described.¹¹ In this contribution, we report the synthesis and characterization of additional fully phosphine substituted Cp and Ind (Ind = indenyl, C_9H_7) molybdenum(II) chlorides containing the tridentate ligand $\text{Ph}_2\text{PCH}_2\text{PCH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ (triphos). On the basis of the previous results described above, we envisaged as possibilities the formation of either: (a) 18-electron systems with $\eta^5\text{-Cp}$ (or indenyl) and $\eta^3\text{-triphos}$ (**I**); (b) 16-electron systems with $\eta^5\text{-Cp}$ (or indenyl) and $\eta^2\text{-triphos}$ (**II**); (c) 16-electron systems with $\eta^3\text{-Cp}$ (or indenyl) and $\eta^3\text{-triphos}$ (**III**). The results reported here show that 18-electron compounds are obtained in each case.



EXPERIMENTAL

All operations were carried out under argon with standard Schlenk-line techniques. Toluene and heptane were refluxed over sodium at least 12 h before being distilled. Dichloromethane was refluxed over P_4O_{10} , under dinitrogen, distilled and then freeze-pump-thaw degassed (three cycles) under argon to remove any residual oxygen. Tetrahydrofuran (THF) was dried over type 4 Å molecular sieves (Fischer) and then refluxed over and distilled from Na/K/benzophenone ketyl under argon. Deuterated NMR solvents were degassed with the freeze-pump-thaw method (three cycles) under argon and stored over type 4 Å molecular sieves. NMR spectra were obtained using Bruker WP200 and AF200 spectrometers. The spectra were referenced with internal residual solvent peaks for ^1H and external 85% H_3PO_4 for ^{31}P . The H_3PO_4 standard solution was contained in a sealed capillary and immersed in the same solvent used for the measurement. Peaks are reported with

positive shifts at lower fields from TMS (^1H) and H_3PO_4 (^{31}P). EPR spectra were recorded on a Bruker ER200 spectrometer equipped with an X-band microwave generator. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software; the electrochemical cell was a modified Schlenk tube with a platinum counterelectrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with an Ag/AgCl reference electrode and a platinum working electrode. All measurements were carried out in CH_2Cl_2 solutions with Bu_4NPF_6 (ca 0.1 M) as supporting electrolyte. Potentials are reported vs the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple, which was introduced into the cell at the end of each measurement. Elemental analyses were obtained from MHW Laboratories (Phoenix, AZ, U.S.A.). Compounds $\{\text{CpMoCl}_2\}_n$,¹² and $\text{MoI}_3(\text{THF})_3$ ¹³ were prepared as described previously. $\text{MoCl}_3(\text{triphos})$ was prepared from $\text{MoCl}_3(\text{THF})_3$ and triphos as described previously;¹⁴ its ^1H NMR spectrum in CD_2Cl_2 showed that it consists of a mixture of isomers in solution (see Fig. 1a): δ 24, 22.5 and 21.0 (three very broad, overlapping resonances, overall $w_{1/2}$ ca. 1400 Hz), 17.7 (br, $w_{1/2}$ = 80 Hz), 17.2 (br, $w_{1/2}$ = 60 Hz), 16.6 (br, $w_{1/2}$ = 80 Hz), 15.8 (br, $w_{1/2}$ = 60 Hz), 11.4 (br, $w_{1/2}$ = 60 Hz), 10.8 (br, $w_{1/2}$ = 40 Hz), 10.2 (br, $w_{1/2}$ = 20 Hz), 9.0 (br, $w_{1/2}$ = 40 Hz), 8.7 (br, $w_{1/2}$ = 25 Hz), 8.3 (br, $w_{1/2}$ = 25 Hz), 6.5 (br, $w_{1/2}$ = 40 Hz), -16.4 (br, $w_{1/2}$ = 630 Hz), -23.2 (br, $w_{1/2}$ = 630 Hz), -35.5 (br, $w_{1/2}$ = 740 Hz), -41.1 (br, $w_{1/2}$ = 420 Hz), -70.4 (br, $w_{1/2}$ = 420 Hz). Solid $\text{CpNa}(\text{THF})_x$ was prepared by the standard reaction between sodium sand and freshly cracked CpH in THF at 0°C ; the solution was evaporated until the product started to crystallize and the precipitation was completed by addition of heptane, followed by filtration and drying under vacuum. An aliquot of the white $\text{CpNa}(\text{THF})_x$ solid was quenched in deoxygenated water and titrated with 0.1 N HCl, giving a value of 0.37 for x (effective molecular weight: 115). A THF solution of IndNa was prepared from IndH and sodium in refluxing THF and its concentration was determined by titration of an aliquot with 0.1 N HCl. AlCl_3 (Aldrich) was purified by sublimation under vacuum. Compound $\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (Strem) was used as received.

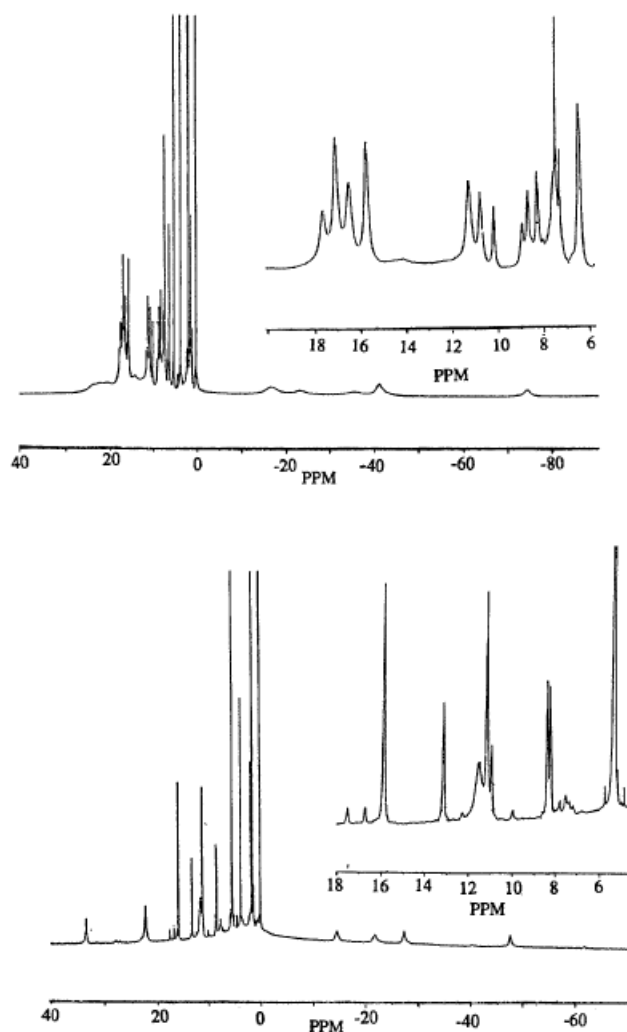


Fig. 1. Room temperature ^1H NMR spectra of compounds $\text{MoX}_3(\text{triphos})$ in CD_2Cl_2 . (a) $\text{X} = \text{Cl}$;
(b) $\text{X} = \text{I}$.

Preparation of $\text{CpMoCl}[\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$ (1)

From CpMoCl_2 , triphos and sodium. To 1.68 g (3.14 mmol) of bis(2-diphenylphosphinoethyl) phenylphosphine (triphos) in 50 cm^3 of THF was added 0.732 g (1.58 mmol) of $\{\text{CpMoCl}_2\}_n$ in a Schlenk flask. The solution was allowed to stir overnight and a bright red solution over a small amount of tan solid was formed. This solution was transferred by filter cannula into a Schlenk flask in which sodium amalgam had been prepared from 0.073 g (3.2 mmol) of sodium and 7 g of mercury. After stirring overnight, the solution remained red and a grey precipitate was present. The THF was removed *in vacuo* and the red solid redissolved in 30 cm^3 of CH_2Cl_2 . The red solution was filtered through Celite and the Celite was washed until the washings were colourless. The solution was concentrated to *ca* 7 cm^3 and layered with 20 cm^3 of *n*-heptane. Bright red crystals (1.6 g 67.9%)

were obtained upon diffusion at room temperature for 12 h. These were isolated by decanting off the mother liquor, washed with *n*-heptane and dried *in vacuo*. One of these crystals was used for the X-ray structural analysis. Found: C. 64.0; H. 5.9. Calc. for C₃₉H₃₈ClP₃Mo: C. 64.1; H, 5.2%. Although this material is analytically pure, its NMR characterization was hampered by minor amounts of oxidation impurity arising from the interaction with the chlorinated solvent. Prolonged standing in CH₂Cl₂ leads to a yellow material (see Results and Discussion). A product that was devoid of oxidation impurity was obtained as described above with the exception that toluene was used instead of CH₂Cl₂ to extract the product. ¹H NMR (C₂D₂, δ): 8.1, 7.4 and 7.1-6.9 (m, 20H, Ph), 4.2 (d, 5H, J_{HP} = 2.4 Hz, Cp), 3.1-2.1 (four br m, 8H, CH₂). ³¹P NMR (C₆D₆, δ): 133.5 (t, J_{PP} = 26.7 Hz), 84.8 (d, J_{PP} = 26.7 Hz).

From MoCl₃(triphos) and CpNa. MoCl₃(triphos) (155 mg, 0.21 mmol) and CpNa(THF)_{0.37} (52 mg, 0.45 mmol) were placed in a Schlenk tube, to which 20 cm³ of THF was added. The mixture was stirred for 1 h, resulting in the formation of a red solution, which was then evaporated to dryness. The residue was extracted with 25 cm³ of toluene. After filtration, the solution was concentrated to ca 5 cm³ and the product precipitated by the addition of heptane (20 cm³). The red solid was filtered off, washed with heptane and dried *in vacuo*. Yield 48 mg (31%). The NMR properties of this material match with those of the product obtained by the method above.

Preparation of [CpMoCl₁{PPh(CH₂CH₂PPh₂)₂}] [PF₆] ([I]PF₆)

To 0.426 g of **1** (0.583 mmol) in 30 cm³ of CH₂Cl₂ was added 0.15 g AgPF₆ (0.593 mmol). Overnight stirring produced a yellow-brown solution which was filtered through Celite to remove the grey Ag⁰ precipitate. The solvent was removed *in vacuo* to produce an oily yellow-brown product. The oil was redissolved in CH₂Cl₂, *n*-heptane was added and an oil was again produced. The colourless solvent was removed by cannula and the oil was dried *in vacuo*. This procedure was repeated until a brown powder was obtained. Yield: 0.385 g (75%). Found: C, 52.5; H, 4.7. Calc. for C_{39.25}H_{38.5}Cl_{1.5}F₆MoP₄ ([CpMo(triphos)][PF₆]·0.25CH₂Cl₂): C, 52.5; H, 4.3%. EPR (CH₂Cl₂): doublet of triplets, *g* = 2.23; *a*_{Mo} = 30.5 G, *a*_{P(d)} = 28.0 G, *a*_{P(t)} = 14.5 G (see Fig. 2).

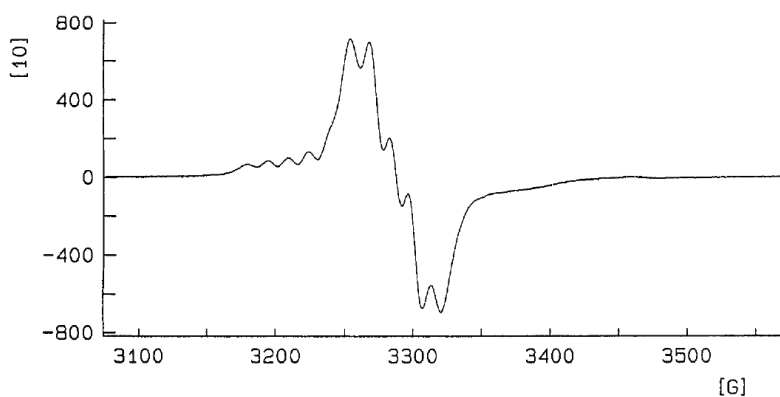


Fig. 2. EPR spectrum (X-band) of $[\text{CpMoCl}(\text{triphos})]^+$. Solvent CH_2Cl_2 .

Formation of $[\text{CpMoCl}\{\text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}] [\text{AlCl}_4]$, $[\text{I}]\text{AlCl}_4$

To 0.219 g of $\{\text{CpMoCl}_2\}_n$ (0.47 mmol) suspended in 30 cm^3 CH_2Cl_2 was added AlCl_3 (0.125 g, 0.94 mmol) and triphos (0.504, 0.94 mmol). After 15 min of stirring at room temperature, a red solution formed, which then turned yellow-brown after 1 h. The solvent was removed *in vacuo* resulting in a yellow brown oil. Repeated attempts at obtaining a solid from this oil were unsuccessful. The EPR spectrum is identical to that of isolated $[\text{I}]\text{PF}_6$.

Preparation of $(\eta^5\text{-C}_9\text{H}_7)\text{MoCl}(\text{triphos})$ (2)

$\text{MoCl}_3(\text{triphos})$ (250 mg, 0.33 mmol) was placed in a Schlenk tube and suspended in THF (25 cm^3). Addition of a THF solution of $\text{C}_9\text{H}_7\text{Na}$ (1.0 cm^3 , 0.73 M, 0.73 mmol) caused the immediate dissolution of the starting material and formation of a green solution, which was then evaporated to dryness. The residue was extracted in 30 cm^3 of toluene and the resulting solution was filtered and concentrated to ca 5 cm^3 . The green product was precipitated by addition of pentane (20 cm^3), filtered off and dried *in vacuo*. Yield 169 mg (63.7%). The crude material was purified by recrystallization from toluene-heptane. Found: C, 67.2; H, 5.4. Calc. for $\text{C}_{46.5}\text{H}_{44}\text{MoClP}_3$ [$\text{IndMoCl}(\text{triphos}) \cdot 1/2\text{C}_7\text{H}_8$]: C, 67.5; H, 5.4%. The compound decomposed upon dissolution in chlorinated hydrocarbons and in acetone, thus limiting the NMR spectroscopic characterization to C_6D_6 solutions. ^1H NMR (C_6D_6 , δ): 7.8, 7.3 and 7.1-7.0 [m, 21H, Ph and indenyl H(2)]. 6.9 and 6.7 [m, 4H, indenyl H(5)-H(8)], 4.01 [d, 2H, $J_{\text{HH}} = 3.7$ Hz, indenyl H(1), H(3)], 2.7-1.3 (four br m, 9H, CH_2). The methyl resonance of the toluene of crystallization was also observed in the ^1H NMR spectrum at δ 2.1, the aromatic resonance being obscured by the triphos resonances. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 134.3. 131.6. 129.1 (Ph), 128.5-

127.5 (region obscured by the C₆D₆ resonance), 126.6 (Ph), 115.6 [indenyl C(4), C(9)], 81.1 [indenyl C(2)], 79.0 [indenyl C(1), C(3)]. ³¹P {¹H} NMR (C₆D₆, δ): 133.2 (t. *J*_{PP} = 23.5 Hz), 83.8 (d. *J*_{PP} = 23.5 Hz).

Preparation of MoI₃(triphos)

MoI₃(THF)₃ (950 mg, 1.37 mmol), triphos (735 mg, 1.37 mmol) and THF (12 cm³) were placed in a Schlenk tube equipped with a magnetic stirrer bar. The resulting mixture was stirred overnight, resulting in the formation of a red precipitate. This was isolated by decanting off the mother liquor, washed with cold THF and dried *in vacuo*. Yield 988 mg (71%). Found: C, 41.7; H, 3.4. Calc. for C₃₆H₃₇I₃MoO_{0.5}P₃ [MoI₃(triphos)·0.5THF]: C, 41.3; H, 3.6%. ¹H NMR (CD₂Cl₂, δ, room temperature): 33.4 (br s, *w*_{1/2} = 41 Hz, 2H, *o*-Ph), 22.5 (br s, *w*_{1/2} = 73 Hz, 4H, *o*-Ph), 11.4 (br s, *w*_{1/2} = 80 Hz, 4H, *o*-Ph); 15.9 (4H), 12.3 (2H) and 11.2 (4H) (all br s, *w*_{1/2} = 15 Hz, *m*-Ph); 10.8 (1H), 8.5 (2H) and 8.3 (2H) (all br s, *w*_{1/2} = 15 Hz, *p*-Ph); -14.7 (br s, *w*_{1/2} = 120 Hz, 2H, CH₂), -21.8 (br s, *w*_{1/2} = 150 Hz, 2H, CH₂), -27.8 (br s, *w*_{1/2} = 100 Hz, 2H, CH₂), -47.5 (br s, *w*_{1/2} = 110 Hz, 2H, CH₂). This NMR spectrum is illustrated in Fig. 1b (see also Results section). Resonances due to THF of crystallization were also observed at δ 3.7 (s) and 1.8 (s).

Preparation of (η⁵-C₉H₇)MoI₃(triphos) (3)

In a Schlenk tube equipped with a magnetic stirrer bar was placed MoI₃(triphos) (140 mg, 0.14 mmol) and THF (20 cm³). To the resulting suspension was added a THF solution of C₉H₇Na (0.60 cm³, 0.73 M, 0.44 mmol) while stirring at room temperature, causing an immediate dissolution of the starting solid and the formation of a green solution. This solution was evaporated to dryness and the residue was extracted with 20 cm³ of toluene. The resulting solution was filtered, concentrated to ca 5 cm³ by evaporation under reduced pressure and treated with heptane (20 cm³) to cause the precipitation of the green microcrystalline product, which was filtered off and dried *in vacuo*. Yield 65 mg (53%). Recrystallization was carried out from toluene-heptane. Found: C, 58.9; H, 4.4. Calc. for C₄₃H₄₀IMoP₃: C, 59.2; H, 4.6%. The compound decomposed upon dissolution in chlorinated hydrocarbons and in acetone, thus limiting the NMR spectroscopic characterization to C₆D₆ solutions. ¹H NMR (C₆D₆, δ): 8.0, 7.4-6.9 [m, 21H, Ph and indenyl H(2)], 6.8 and 6.6 [m, 4H, indenyl H(5)-

H(8)], 3.9 [d, 2H, $J_{\text{HH}} = 4.3$ Hz, indenyl H(1), H(3)], 2.8, 2.6, 2.3 and 1.3 (br m, 8H, CH₂). ¹³C{¹H} NMR (C₆D₆, δ): 134.5, 132.4, 129.3 (Ph), 128.5-127.8 (region obscured by the C₆D₆ resonance), 126.8 (Ph), 113.6 [indenyl C(4),C(9)], 79.6 [indenyl C(2)], 78.5 [indenyl C(1), C(3)], 35.5 (m, CH₂), 31.5 (m, CH₂). ³¹P NMR (C₆D₆, δ): 132.7 (t, $J_{\text{PP}} = 24.9$ Hz), 80.2 (d, $J_{\text{PP}} = 24.9$ Hz).

X-ray crystallography

A single crystal of compound **1** was glued to the inside of a thin-walled glass capillary, which was then flame sealed under dinitrogen and mounted on the diffractometer. The determination of the unit cell and the orientation matrix was based on the least-squares fit of the setting angles of 25 well-centred reflections. Data collection and reduction and structure solution (MITHRIL) and refinement (alternating full-matrix least-squares/difference Fourier cycles) were routine. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included as idealized isotropic contributions ($d_{\text{CH}} = 0.960$ Å, $B = 1.2B$ for attached carbon) and used for structure factor calculations, but not refined. The data were corrected for absorption by the ψ scan method.¹⁵ Crystal data are reported in Table 1 and selected bond distances and angles are collected in Table 2. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

Table 1. Crystal and refinement parameters for compound Tp*MoOI₂·C₇H₈

Formula	C ₃₉ H ₃₈ ClMoP ₃
Formula weight	731.4
Space group	P2 ₁ /n
<i>a</i> (Å)	14.334(4)
<i>c</i> (Å)	17.208(4)
<i>c</i> (Å)	13.904(3)
β (°)	105.53(2)
<i>V</i> (Å ³)	3304 (3)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.47

$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	6.45
Radiation (monochromated in incident beam)	Mo-K α ($\lambda = 0.71072$ Å)
Temp. (°C)	23
F(000)	1460
Transmission factors: max, min.	1.00, 0.698
R^a	0.044
R_w^b	0.053

^a $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. ^b $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Intermolecular distances (Å) and angles (°) for compound **1**

Mo-Cl	2.526(2)
Mo-P(1)	2.414(2)
Mo-P(2)	2.391(2)
Mo-P(3)	2.459(2)
Mo-CNT ^a	1.976(9)
Cl-Mo-P(1)	89.87(7)
Cl-Mo-P(2)	138.10(8)
Cl-Mo-P(3)	83.84(7)
Cl-Mo-CNT ^a	108.2(3)
P(1)-Mo-P(2)	77.67(7)
P(1)-Mo-P(3)	118.32(7)
P(1)-Mo-CNT ^a	121.7(3)
P(2)-Mo-P(3)	77.90(7)
P(2)-Mo-CNT ^a	113.7(4)
P(3)-Mo-CNT ^a	119.9(3)

^a CNT is the centre of gravity of atoms C(61)-C(65).

RESULTS

Syntheses and spectroscopic characterization

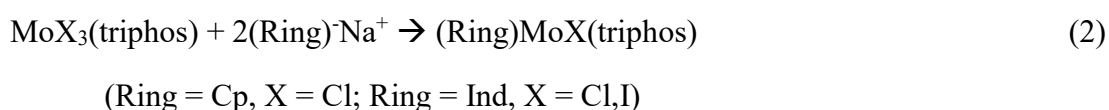
Two methods have been employed for the preparation of the molybdenum(II) complexes described in this contribution. The first is the standard protocol that we have described previously for the related compound $\text{CpMoCl}(\text{PMe}_3)_3$,⁹ *i.e.* interaction of $\{\text{CpMoCl}_2\}_n$ with the required amount of the phosphine, in this case triphos, followed by reduction by amalgamated sodium in THF [eq. (1)] to form compound **1**. This method could not be applied to the synthesis of the corresponding indenyl derivatives, because we have not yet developed a convenient synthetic strategy to the precursor $\{\text{IndMoCl}_2\}_n$. Our attempts to synthesize the latter material have been based on the same strategy which is successful for the preparation of $\{\text{CpMoCl}_2\}_n$, *i.e.* reduction of CpMoCl_4 ,¹² which is in turn conveniently obtained by PCl_5 or PhICl_2 oxidation of $\text{CpMo}(\text{CH}_3)(\text{CO})_3$ or $[\text{CpMo}(\text{CO})_3]_2$.^{16,17} However, the corresponding IndMoCl_4 , could not be obtained as a pure material by mild PCl_5 oxidation of $\text{IndMo}(\text{CH}_3)(\text{CO})_3$. The material that is obtained from this treatment shows the expected EPR properties for the desired product (EPR: $g = 2.002$, $a_{\text{Mo}} = 37.3$ G; *cf.* CpMoCl_4 : $g = 1.994$, $a_{\text{Mo}} = 38.2$ G¹⁸), but the isolated product has variable IR properties and colour depending on the reaction time and temperature, indicating that it is a mixture of different compounds. These and other observations lead us to believe that IndMoCl_4 is unstable with respect to ring loss and that the decomposition starts to occur before the formation reaction is complete.



The second method involves a transmetallation reaction starting from molybdenum(III) precursors. The precursor $\text{MoCl}_3(\text{triphos})$ has been reported earlier,¹⁴ but its intimate stereochemistry was not established either by X-ray crystallographic or NMR spectroscopic methods. We find that, in solution, the compound prepared as reported in the literature¹⁴ exists as a mixture of more than one isomer, presumably *fac* and *mer*. Both isomers display paramagnetically shifted ¹H NMR resonances falling in the characteristic regions for alkyl- and aryl-substituted phosphines coordinated to octahedral molybdenum(III) (see Fig. 1a).^{19,20} The backbone aliphatic protons are observed upfield, in the δ -15 to -75 region, while the phenyl protons are found downfield (δ +8 to +30 region), the *ortho*

protons being the broadest and most shifted. Each possible isomer (*fac* or *mer*) has C_s symmetry, thereby giving rise to four methylene resonances (2:2:2:2) and five resonances for each type of phenyl proton (4:4:4:4:2 for *ortho* and *meta*, 2:2:2:2:1 for *para*). On the other hand, more resonances than expected for a single isomer are observed. The general broadness of these resonances does not allow a detailed peak assignment and a measurement of the relative isomer ratio. Compound MoI₃(triphos) has been synthesized by ligand substitution from MoI₃(THF)₃, and it also shows paramagnetically shifted ¹H NMR resonances (Fig. 1b). These resonances are sharper than those of the corresponding chloro complex, and the number of major peaks is consistent with the pattern expected for a single isomer (see Experimental for peak assignments). Also in this case, however, there are other similarly shifted resonances, albeit with very small intensity, that are assigned to a second isomer. This result indicates that one isomer is prevalent in solution for the triiodo compound, although the symmetry equivalence of the two possible isomers (both C_s) does not allow the establishment of which this is.

The addition of two equivalents of transmetallating agent CpNa or IndNa (Ind = indenyl, η^5 -C₉H₇) to MoX₃(triphos) results in the formation of the desired half-sandwich molybdenum(II) derivatives [see eq. (2)], including the indenyl compounds (Ind)MoX(triphos) [X = Cl (**2**); I (**3**)] that could not be accessed through the synthetic strategy illustrated in eq. (1). One equivalent exchanges one halide ligand and the other equivalent serves as the reducing agent. The overall transformation is slow at room temperature and the sparingly soluble MoX₃(triphos) is not completely consumed when only one equivalent of CpNa or IndNa is used. From this we conclude that exchange and metal reduction (in either order) follow each other in rapid succession after the first initial slow step. We have some indirect evidence for an exchange process preceding the reduction process (see Discussion). The fate of the reducing equivalent has not been investigated. While our studies were in progress, we have learned that compound **1** can also be obtained by an alternative method, *i.e.* reaction of CpMoH(triphos) with CDCl₃.²¹



All compounds **1-3** are fairly soluble in aromatic hydrocarbons and decompose upon standing in CH₂Cl₂. This decomposition involves oxidation to molybdenum(III) species (see below), as had been shown previously for the analogous CpMoCl(PMe₃)₃.⁹ The oxidation of **1** has been investigated in detail, both chemically and electrochemically, and is described later. The spectroscopic properties of compounds **1-3** are all consistent with a diamagnetic, 18-electron compound (type **I**) and do not show any evidence for an equilibrium with a 16-electron species of type **II** or **III**. The 16-electron complex Cp*MoCl(PMe₃)₂ is paramagnetic (spin triplet),¹⁰ and we have evidence that the analogous Cp system, CpMoCl(PMe₂Ph)₃, is in equilibrium with a paramagnetic 16-electron CpMoCl(PMe₂Ph)₂ complex, the chemical exchange between 18-electron and 16-electron compounds being frozen on the NMR time scale.²² We therefore believe that a hypothetical isomer of type **II** or **III** for compounds **1-3** would also be paramagnetic, but no shifted resonances in the expected regions for these 16-electron species were observed. The Cp resonance for **1** is found in the typical region (δ 4.2), with observable coupling only to the unique phosphorus nucleus. The same situation had been found previously for CpMoCl(PMe₃)₃.⁹ For the indenyl complexes, the most diagnostic resonance is that of the carbon nuclei connecting the two rings together [‘hinge’ carbon atoms, C(4) and C(9)]. This resonance is typically found in the δ 110-130 range for η^5 -bound indenyl rings²³⁻²⁵ and at much higher values for η^3 -bound ones [for instance: δ 157.3 for [IndFe(CO)₃]⁻, 156.7 for IndIr(PMe₃)₃ and 156.4 for IndIr(PMe₂Ph)₃].^{26,27} For **2** and **3**, these resonances are found at δ 115.6 and 113.6, well within the range observed for η^5 compounds. The tridentate configuration of the triphos ligand is clearly demonstrated by the 1:2 triplet-doublet sets of ³¹P NMR resonances found for each compound, with J_{PP} in the 23-27 Hz range.

Crystallographic characterization

The structure of compound **1** has been confirmed by X-ray crystallography (see Fig. 3). The molecular geometry is based on the “four-legged piano stool”, which is ubiquitous for compounds of the CpML₄ type,^{28,29} and is the first one for fully phosphine-substituted CpMoXL₃ complexes (X = any one-electron donor). The most interesting angular parameters are the angles between the Mo-CNT bonds (CNT is the centre of gravity of the Cp ring) and the other bonds. The two relative *trans* donors C(1) and P(2) have smaller angles than the other donors P(1) and P(3). This follows the

established pattern of angular *trans* influence,²⁹ which places the pair of ligands with overall stronger σ -bonding ability at smaller angles in order to maximize the interaction with the more favourable metal orbitals.³⁰ The Mo-Cl distance [2.526(2) Å] is longer than for the molybdenum(III) complex [CpMoCl(PMe₃)₃]⁺ [2.427(9) Å in the PF₆ salt⁹ and 2.509(3) Å in the BF₄ salt³¹], as expected. Other relevant four-legged piano stool molybdenum(II) complexes also show a longer distance [*e.g.* 2.541(5) Å in CpMoCl(CO)(dppe)³² and 2.542(9) Å in CpMoCl(CO)₃³³]. A comparison of the Mo-P distances [av. 2.42(3) Å] with other literature values [*e.g.* 2.388(8) Å in (C₅H₄Me)MoI(CO)₂[P(OMe₃)₃],³⁴ 2.50(1) Å in CpMoI(CO)₂(PBu₃),³⁵ 2.532(6) Å in CpMoBr(CO)₂(PPh₃),³⁶ 2.473(3) Å in CpMo(COCH₃)(CO)₂(PPh₃)³⁷ and 2.47(3) Å in CpMoCl(dppe)³²] suggests that the Mo-P bonds tend to shorten when more phosphine and less CO ligands are present in the coordination sphere (consistent with diminished π -competition) and a further shortening effect is also due to the presence of chelate rings.

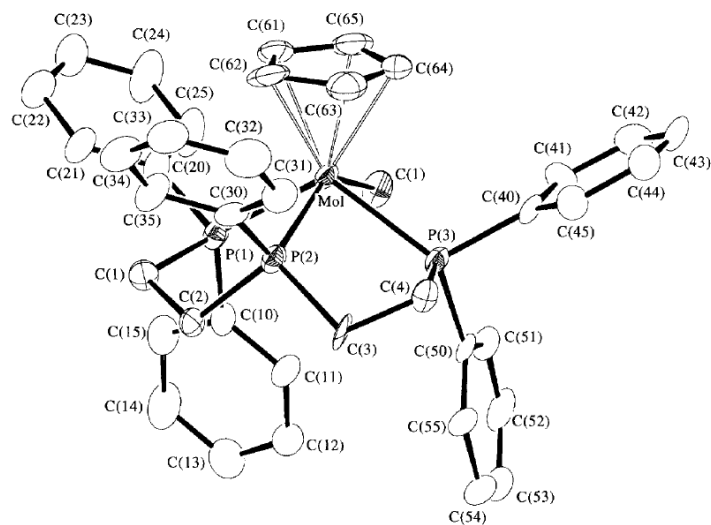


Fig. 3. An ORTEP view of compound CpMoCl(triphos). Ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity.

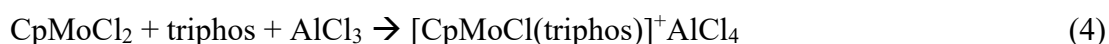
Chemical and electrochemical oxidation

As mentioned above, compound **1** slowly decomposes when standing in CH₂Cl₂ to afford yellow solutions and, for this reason, its NMR spectrum could not be observed when the isolation of the material involved extraction into CH₂Cl₂. As will be shown later, CH₂Cl₂ induces the oxidation of **1** to [**1**]⁺ and the 1/[**1**]⁺ redox couple is reversible. Therefore, contamination of **1** by even a trace

amount of paramagnetic $[1]^+$ is likely to be the cause of line broadening in the NMR spectrum of **1**. It has also been reported that the similar compound $\text{CpMoCl}(\text{PMe}_3)_3$, decomposes in CH_2Cl_2 and that this decomposition involves oxidation to the corresponding 17-electron molybdenum(III) cation. These observations prompted us to investigate more closely the oxidative chemistry of both the Cp and the indenyl compounds.

A preliminary cyclic voltammetric study of **1** in CH_2Cl_2 (during the entire experiment. *e.g.* within *ca* 1 h, no extensive decomposition occurred) confirmed that the compound undergoes a reversible one-electron oxidation process at -0.82 V ($\Delta E_p = 70$ mV) vs the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ standard ($\Delta E_p = 107$ mV). At higher potentials, this is followed by a second one-electron oxidation ($E_{1/2} = +0.82$ V, $\Delta E_p = 90$ mV). The assignment of these as one-electron processes is confirmed by the isolation and electrochemical characterization of the 17-electron molybdenum(III) cation (see below). The similar compound $\text{CpMoCl}(\text{PMe}_3)_3$ had previously been investigated electrochemically and was reported to undergo a reversible one-electron oxidation process at -1.46 V and a second oxidative process at -0.18 V. The product of the first oxidation process, *i.e.* the cation $[\text{CpMoCl}(\text{PMe}_3)_3]^+$, was isolated and characterized by EPR and X-ray crystallography.⁹ Therefore, both oxidative processes shift considerably to higher potentials upon substituting three PMe_3 ligands with the triphos ligand, in accord with the decreased electron-releasing ability of triphos. It is also interesting to compare these potentials with that reported for the oxidation of $\text{CpMoCl}(\text{CO})_3$ (irreversible wave with $E_{p,a} = +0.63$ V).³⁸ There is therefore a potential shift of $+0.64$ V on going from $(\text{PMe}_3)_3$ to triphos and a further shift of $+1.45$ V on going from triphos to $(\text{CO})_3$.

The PF_6 salt of $[1]^+$ has been obtained by treatment of **1** with a CH_2Cl_2 solution of AgPF_6 , [eq. (3)] and the corresponding AlCl_4 salt has been obtained by a different synthetic strategy, namely interaction of $[\text{CpMoCl}_2]_n$ with triphos in the presence of AlCl_3 [eq. (4)]. Both salts are yellow-brown and give yellow solutions when dissolved in CH_2Cl_2 , in which they are very soluble. They are both isolated from solution as oily materials, and only with difficulty could the PF_6 be converted into a sufficiently pure solid material. The AlCl_4 salt could not be isolated as an analytically pure solid.



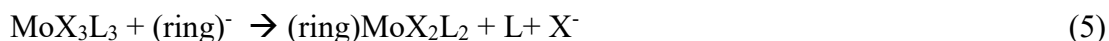
The cyclic voltammogram of $[1]^+PF_6^-$ exhibits a reversible reduction ($E_{1/2} = -0.80$ V, $\Delta E_p = 54$ mV) and a reversible oxidation ($E_{1/2} = 0.83$ V, $\Delta E_p = 55$ mV) vs the ferrocene/ferricinium standard ($\Delta E_p = 70$ mV), in good agreement with the two oxidative processes observed for the precursor **1**. The 17-electron configuration of the molybdenum(III) salts is demonstrated by the EPR spectrum which is illustrated in Fig. 2. The spectrum consists of a doublet of triplets, as expected for a compound having two types of phosphorus nuclei in a 1:2 ratio, flanked by satellites due to the low abundance (ca 25%) molybdenum isotopes (^{95}Mo and ^{97}Mo , both with $I = 5/2$), at $g = 2.030$. A satisfactory simulation of the spectrum gave the hyperfine parameters $a_{Mo} = 30.5$ G, $a_{P(d)} = 28.0$ G and $a_{P(t)} = 14.5$ G. A similarly shaped spectrum was obtained for $[CpMoCl(PMe_3)_3]^+$ ($g = 2.006$, $a_{Mo} = 36.5$ G, $a_{P(d)} = 26.0$ G, $a_{P(t)} = 19.5$ G).⁹ When red **1** is left in a CH_2Cl_2 solution at room temperature for several hours, the colour turns yellow. The resulting solution showed an EPR spectrum identical with that illustrated in Fig. 2, demonstrating the oxidative decomposition of **1** in this solvent.

The oxidative behaviour of the indenyl compounds **2** and **3** has also been briefly investigated. Qualitatively, both compounds behave in the same way as the cyclopentadienyl analogue **1**. The cyclic voltammogram of either compound shows a reversible oxidation process ($E_{1/2} = -0.82$ V for **2**, -0.74 V for **3**, vs Cp_2Fe/Cp_2Fe^+), but no reversible second oxidation process is observed in either case. Instead, complex and irreversible oxidative processes follow at higher potentials, indicating that the product of double oxidation is not sufficiently stable for the indenyl systems on the time scale of a cyclic voltammetric run. The measured oxidation potentials show that the change of ligand from chlorine to iodine has a more pronounced effect than the change of ligand from Cp to indenyl. The chloride compounds are more easily oxidized than the iodide compounds, a feature that has been observed before for the oxidation of other molybdenum(II) derivatives.^{38,39} The products of one-electron oxidation for compounds **2** and **3** were not isolated. The EPR spectra for solutions of **2**⁺ and **3**⁺, as obtained by addition of Ag^+ to the respective neutral complexes, are identical to the spectra obtained when the neutral precursors are left in CH_2Cl_2 for an extended period of time (several hours at room temperature). These spectra, however, did not compare with that of **1**⁺, indicating that further chemical or stereochemical transformations occur after oxidation of **2** and **3**. The nature of these oxidation products has not been further investigated.

DISCUSSION

Several points are worthy of discussion. The first one relates to the solution structure of octahedral molybdenum(III) complexes, as exemplified in this paper by the $\text{MoX}_3(\text{triphos})$ ($X = \text{Cl}, \text{I}$) starting materials. These classes of complexes are characterized by a pseudo- t_{2g}^3 configuration with three unpaired electrons and their spectroscopic characterization in solution has traditionally been difficult. Structural studies have generally been limited to solid state, single-crystal X-ray diffractometry. Recently, however, it has become clear that sufficiently sharp, paramagnetically shifted ^1H NMR resonances can be observed which can provide important structural information for these complexes.^{19,40} Complexes $\text{MoX}_3(\text{PR}_3)_3$, ($X = \text{Cl}, \text{Br}, \text{I}$; $\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}$) have been shown to adopt exclusively the meridional geometry in solution. For the complexes reported here, however, ^1H NMR spectroscopy shows (see Fig. 1) that at least two isomers (presumably *mer* and *fac*) are present. One isomer is dominant for the triiodide complex, whereas both isomers are present in substantial amounts for the trichloride complex.

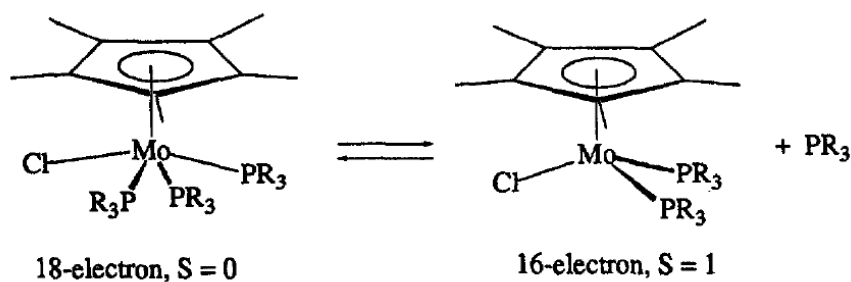
The second point concerns the synthetic procedure utilized to obtain ring-substituted (ring = Cp or indenyl) molybdenum(II) materials starting from molybdenum(III) coordination complexes. We have for some time attempted to use this procedure to access ring-substituted molybdenum(III) complexes by simple transmetallation reactions, *e.g.* eq. (5).



We were particularly interested in synthesizing indenyl derivatives such as $(\text{Ind})\text{MoX}_2(\text{PMe}_3)_2$ in order to investigate the halide and phosphine exchange kinetics for a comparison with the corresponding published studies on the cyclopentadienyl derivatives.^{41,42} However, the reaction between $\text{MoX}_3(\text{PMe}_3)_3$ and $(\text{Ind})^-\text{Na}^+$ in stoichiometric amounts invariably left a large part of the molybdenum(III) material unreacted. This indicates that more than one equivalent of the indenyl reagent react with the molybdenum material, a possibility being that the second equivalent acts as a reducing agent to afford molybdenum(II) products, which were, however, never isolated. This reaction did show the formation of small amounts of the desired indenylmolybdenum(III) complexes,

(Ind)MoX₂(PMe₃)₂ (weak EPR signals identical in shape to those reported for CpMoX₂(PMe₃)₂),⁴³ but only the less soluble unreacted MoX₃(PMe₃)₃ could be recovered from the reaction mixtures. For the triphos system reported in this work, we have proven by isolation and characterization of the final molybdenum(II) product, that the second equivalent of the transmetallating agent (either Cp⁻ or Ind⁻) indeed induces a reduction of the molybdenum centre.

The real purpose of this work was to gain further insight into the factors affecting the equilibrium between standard (18-electron) and electronically unsaturated (paramagnetic, spin triplet 16-electron) phosphine substituted molybdenum(II) complexes. We have established, for instance, that the 18-electron compound Cp*MoCl(PMe₃)₃ is kinetically inert but, upon warming above room temperature, it establishes an equilibrium with the paramagnetic (*S* = 1), stable 16-electron species Cp*MoCl(PMe₃)₂ and that the latter is the major species at equilibrium (e.g. see Scheme 1). Although the steric compression of three PMe₃ ligands and the bulky Cp* ring can favour ligand dissociation by energetically destabilizing the saturated structure, and the high donor power of the ligand set (including the chlorine lone pairs) undoubtedly provides stabilization to the unsaturated structure, there is also the possibility of an extra electronic stabilization for the unsaturated species, which is related to the change of spin state from *S* = 0 to *S* = 1 upon ligand dissociation. All these factors could balance the energetic loss due to the rupture of the Mo-P bond.⁴⁴ An analogous spin state change could stabilize a hypothetical unsaturated structure with a slipped ring (e.g. **II**) with respect to the saturated one (**I**) with two additional Mo—C bonds. The magnitude of this spin-change-related energetic stabilization is the subject of current theoretical investigations which will be reported in due course. The current experimental study has shown that the steric/electronic requirements of the (Ring)MoX(triphos) system are such that a saturated structure with η⁵-ring and tridentate triphos ligand is always observed, even for the indenyl derivatives, for which the ring has an extra thermodynamic stabilization in the ring-slipped η³ form. Further experimental studies are in progress.



Scheme 1

Supplementary material available

Crystal data, full tables of bond distances and angles, anisotropic thermal parameters, and hydrogen-atom coordinates for compound **1** (12 pp.); calculated and observed structure factors for compound **1** (19 pp.). Ordering information is given on any current masthead page.

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