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A reinvestigation of compound $CpMo(PMe_3)_2(CH_3)_2$: alkylation by single electron transfer and radical addition?

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The synthesis of the half-sandwich molybdenum(III) diphosphine dimethyl complex $CpMo(PMe_3)_2(CH_3)_2$ has been reinvestigated. The compound was obtained from the corresponding dichloro complex $CpMo(PMe_3)_2Cl_2$ and methyllithium at low temperatures and isolated as a crystalline product by conducting all operations at temperatures lower than −10 °C. The complex is thermally unstable at room temperature but has been fully characterised by EPR spectroscopy, cyclic voltammetry and X-ray diffraction. The formation reaction is retarded by excess phosphine. On the basis of this and other related observations, a mechanism involving phosphine pre-dissociation followed by single electron transfer and radical addition is proposed.

Introduction

A few years ago, the reaction of $CpMo(PMe_3)_2Cl_2$ with different alkylating reagents was investigated in our laboratory.[1] The formation of the desired dialkyl compound $CpMo(PMe_3)_2(CH_3)_2$ was only witnessed when using CH_3Li as the alkylating agent, while CH_3MgBr, $Al(CH_3)_3$ and CH_3ZnI reacted extremely slowly or not at all or gave different products (CH_3ZnI gave rise to a Cl/I exchange process). All attempts to isolate the product failed because of its thermal instability. Thus, the precise formulation of the compound was not proven unambiguously, as the spectroscopic characterisation in solution (limited to EPR spectroscopy) showed only the presence of two equivalent phosphorus atoms in the co-ordination sphere. Similar difficulties for the alkylation of phosphine-containing half-sandwich Mo(III) compounds were also encountered by Fryzuk *et al.* for the alkylation of $[\eta^5:P,P'\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i_2)_2]MoCl_2$[2] and by us for $CpMo(Ph_2PCH_2CH_2SMe)Cl_2$.[3]

More recently, we have reported the synthesis, characterisation and reactivity studies of the first example of stable paramagnetic molydenum(III) complexes containing alkyl ligands. These complexes have the general formula $CpMo(\eta^4\text{-diene})R_2$ (diene = buta-1,3-diene, 2-methylbuta-1,3-diene or 2,3-dimethylbuta-1,3-diene and R = methyl, benzyl or trimethylsilylmethyl).[4,5] Permethylated cyclopentadienyl analogues of these complexes have also been subsequently prepared and have shown activity in ethylene polymerisation.[6] All these alkyl compounds containing a diene ligand exhibit thermal stability in common organic solvents,[5] in remarkable contrast with the previously reported instability of $CpMo(PMe_3)_2(CH_3)_2$. In addition, the alkylation of $CpMo(\eta^4\text{-diene})Cl_2$ compounds works equally well with lithium and Grignard reagents, while the bis-phosphine analogue could only be alkylated with the lithium reagent. For these reasons, we have decided to reinvestigate the synthesis of this phosphine-containing alkyl compound. The successful isolation and full characterisation of this compound are reported in this contribution, and the mechanism of its formation reaction is discussed in comparison with the alkylation of the diene analogues.

Experimental

General procedures

All reactions involving air- and moisture-sensitive organometallic compounds were carried out in a Jacomex glove box or by the use of standard Schlenk techniques under an argon atmosphere. Toluene and diethyl ether were purified by distillation under argon after drying over sodium benzophenone ketyl. THF was dried over sodium benzophenone ketyl and then over Na/K alloy. Pentane was dried over sodium. EPR measurements were carried out at the X band microwave frequency on a Bruker ESP 300 spectrometer, equipped with an ER 4111 VT unit. The spectrometer was calibrated with diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$). EPR spectra simulations and fittings were carried out with WinSim.[7] Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software. The electrochemical cell is a locally modified Schlenk tube. The cell is fitted with a Pt counter-electrode, an Ag/AgCl reference electrode and a Pt working electrode. Bu_4NPF_6 was used as supporting electrolyte at a concentration of 0.1 M. All potentials are reported *vs.* the Cp_2Fe/Cp_2Fe^+ couple which was introduced under argon into the cell at the end of each measurement. Elemental analyses were performed with a Fisons EA 1108 apparatus. CH_3Li (1 M in THF–cumene 10/90) and CD_3Li (0.5 M in Et_2O) were used as received from commercial sources. The complex $CpMo(PMe_3)_2Cl_2$ was synthesised according to the literature procedure.[8]

Synthesis of $CpMo(PMe_3)_2(CH_3)_2$

All the steps of this procedure were carried out at a temperature lower or equal to −10 °C. To solid CH_3Li (1 mmol obtained after evaporation of 1 mL of the 1 M THF–cumene solution), $CpMo(PMe_3)_2Cl_2$ (155 mg, 0.45 mmol) was added. A THF–Et_2O (1 : 1) solution (30 mL) pre-cooled to −50 °C was transferred into the reaction flask. The resulting solution was stirred while the temperature was slowly raised. No reaction occurred until *ca.* −20 °C, when the solution started to change colour from dark red to orange within a few minutes. Stirring was continued at a temperature between −20 and −10 °C for 3 h (with no further colour change), to ensure complete conversion. After evaporation to dryness at −10 °C, the product was extracted with cold pentane (−10 °C, 15 mL). The mixture was filtered through Celite at −10 °C and the resulting solution was concentrated to *ca.* 3 mL and stored at −80 °C. This led to the crystallisation of the product $CpMo(PMe_3)_2(CH_3)_2$ (85 mg; 55%) within a few days. Anal. Calc. for $C_{13}H_{29}P_2Mo$: C, 45.49; H, 8.52. Found: C, 45.22, H, 8.47%. The compound

decomposes slowly in solution at room temperature, but is indefinitely stable as a solid if kept at −10 °C or below under an inert atmosphere. EPR (pentane, −80 °C): multiplet with Mo satellites, $g = 2.003$; $a_P = 25.81$ G; $a_H = 6.89$ G (6H); $a_H = 2.04$ (18H); $a_{Mo} = 29.81$ G.

Reaction of $CpMo(PMe_3)_2Cl_2$ with MeLi in presence of PMe_3

An alkylation reaction was carried out under similar conditions as in the previous section, from $CpMo(PMe_3)_2Cl_2$ (100 mg, 0.29 mmol) and MeLi (0.6 mmol) in a THF–Et_2O (1 : 1) mixture (20 mL) in presence of 1 equiv. of PMe_3 (0.3 mL, 1 M in THF). The alkylation was much slower as shown by the colour change and by EPR monitoring. After 9 h at a temperature between −20 and −10 °C, solvents were evaporated and the $CpMo(PMe_3)_3(CH_3)$ formation as the major product was attested by ^{1}H NMR spectroscopy after comparison with the previously reported spectrum.[1] The desired $CpMo(PMe_3)_2(CH_3)_2$ was found to be only the minor product by EPR (ratio 85 : 15).

Synthesis of $CpMo(PMe_3)_2(CD_3)_2$

By using a procedure identical to that described above for the dimethyl compound, $CpMo(PMe_3)_2(CD_3)_2$ was synthesised starting from $CpMo(PMe_3)_2Cl_2$ (195 mg, 0.57 mmol) and CD_3Li (1.25 mL, 0.5 M in Et_2O). Yield 100 mg (50%). Anal. Calc. for $C_{13}H_{23}D_6P_2Mo$: C, 44.70; H, 8.37. Found: C, 45.05, H, 8.51%. EPR (pentane, −80 °C): broad triplet with Mo satellites, $g = 2.003$; $a_P = 30.8$ G; $a_{Mo} = 21.0$ G.

Crystal structure determination of complex $CpMo(PMe_3)_2(CH_3)_2$

A dark red crystal of $CpMo(PMe_3)_2(CH_3)_2$ (0.4 × 0.4 × 0.4 mm) suitable for an X-ray analysis was obtained from a saturated pentane solution of $CpMo(PMe_3)_2(CH_3)_2$ at −80 °C. The crystal was rapidly mounted on an Enraf-Nonius Kappa CCD using Mo-Kα radiation under a cold nitrogen flux (110 K). 13262 reflections (3761 unique) were collected up to $\sin(\theta)/\lambda = 0.65$ Å^{-1} at 110 K. Absorption corrections were applied to the data during integration by the SCALEPACK[9] algorithm. The structure was solved *via* a Patterson search program[10] and refined (space group $P2_1/c$) with full-matrix least-squares methods[10] based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the complex were found in Fourier difference maps and freely refined with isotropic temperature factors. Final agreement indices are reported in Table 1.

CCDC reference number 159215.

See http://www.rsc.org/suppdata/dt/b1/b101441m/ for crystallographic data in CIF of other electronic format.

Table 1 Crystal data and structure refinement for $CpMo(PMe_3)_2(CH_3)_2$

Formula	$C_{13}H_{29}P_2Mo$
M	343.24
T/K	110(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.0760(4)
b/Å	10.0550(5)
c/Å	12.7220(4)
β/°	93.191(2)
V/Å^3	1670.08(11)
Z	4
F(000)	716
D/g cm^{-3}	1.365
Diffractometer	Enraf-Nonius KappaCCD
Scan type	Mixture of φ rotations and ω scans
λ/Å	0.71073
μ/mm^{-1}	0.955
Crystal size/mm	0.4 × 0.4 × 0.4
$\sin(\theta)/\lambda_{max}$/Å^{-1}	0.65
Index ranges, hkl	−16 to 16, 0–13, 0–16
Absorption correction	SCALEPACK
RC = Refl. collected	13262
IRC = Independent RC	3761 [R(int) = 0.025]
IRCGT = IRC with [$I > 2\sigma(I)$]	3475
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3761/0/261
R (for IRCGT)	$R1$[a] = 0.0239, $wR2$[b] = 0.0563
R (for IRC)	$R1$[a] = 0.0271, $wR2$[b] = 0.0583
Goodness-of-fit[c]	1.045
Largest diff. peak and hole/e Å^{-3}	0.52 and −0.65

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0190P)^2 + 1.66P]$, $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. [c] Goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

Results and discussion

(a) Synthesis

As our previous study[1] showed that only CH_3Li is able to convert $CpMo(PMe_3)_2Cl_2$ to the dimethyl species [eqn. (1)], we have

$$CpMo(PMe_3)_2Cl_2 + 2\ CH_3Li \rightarrow CpMo(PMe_3)_2(CH_3)_2 + 2\ LiCl \quad (1)$$

continued our investigations with this reagent. In addition, it was previously shown that the use of THF as solvent leads to a lower conversion to the paramagnetic product relative to toluene, this being tentatively attributed to a competition between substitution and single electron transfer pathways. With the idea in mind of limiting competing redox processes and facilitating solvent removal at low temperature, while maintaining convenient conversion rates and substrate solubility, we used a 1 : 1 mixture of THF and diethyl ether as solvent.

A smooth reaction occurs in the temperature range −20 to −10 °C. By carrying out all manipulations at or below −10 °C (see Experimental section), the product was obtained by crystallisation from cold pentane as orange crystals in 50% yield. All attempts to work at a temperature higher than −10 °C invariably failed due to the thermal instability of $CpMo(PMe_3)_2(CH_3)_2$.[1] An EPR spectroscopic monitoring of the reaction gave no evidence for the presence, at any time, of an intermediate mixed compound, $CpMo(PMe_3)_2(CH_3)Cl$. The characteristic triplet of $CpMo(PMe_3)_2Cl_2$ is replaced by a new triplet due to the dialkyl species (Fig. 1).

The formation reaction was found to be strongly hindered by the presence of free PMe_3. When the synthetic procedure was carried out in the presence of 1 equivalent of PMe_3, the EPR monitoring showed a much slower disappearance of the starting dichloride compound. On the other hand, this reaction affords another compound as the major product, namely the reduced $CpMo(PMe_3)_3(CH_3)$ compound, in agreement with the previous report.[1] This retardation effect will be discussed later, together with the reaction mechanism, in section (e).

(b) EPR spectroscopic study

As shown in Fig. 1(b), the EPR spectrum exhibits a discernible coupling only to the Mo and the two P nuclei at 0 °C. The availability of the isolated, crystalline product has now allowed a more detailed spectroscopic study in a dilute pentane solution and at lower temperatures. The resulting spectrum at −80 °C shows additional superhyperfine splitting [Fig. 1(c)]. By analogy with the $CpMo(\eta^4\text{-diene})R_2$ complexes,[4,5] we considered that the unpaired electron could couple with the six methyl hydrogen atoms. However, the observed pattern contains many more lines than expected for a triplet of septets. Therefore, we considered also the possible coupling to the remote PMe_3 hydrogen nuclei. Simulations and analytical fittings[7] permitted the full interpretation of the observed spectrum as the result of coupling with the two equivalent

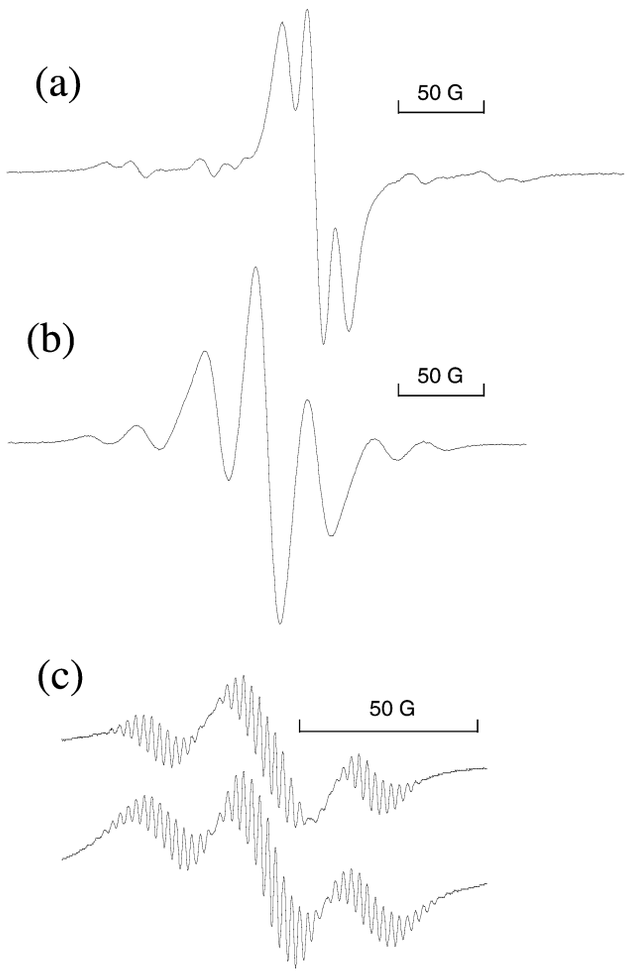


Fig. 1 EPR spectra of (a) $CpMo(PMe_3)_2Cl_2$ at 0 °C in THF; (b) $CpMo(PMe_3)_2(CH_3)_2$ at 0 °C in THF and (c) $CpMo(PMe_3)_2(CH_3)_2$ at −80 °C in pentane: experimental (above) and best fitting (below).

phosphorus nuclei ($a_P = 25.81$ G), the six equivalent hydrogen atoms of the methyl groups ($a_H = 6.89$ G), and the eighteen equivalent hydrogen atoms of the phosphine ligands ($a_H = 2.04$ G). Any other coupling model (for instance including a coupling to the five equivalent Cp protons) did not match the experimental spectrum. Examples of hyperfine coupling to Cp protons are known, for instance for compounds $CpCr(NO)(PPh_3)(CH_2SiMe_3)$[11,12] or $Cp_2Zr(allyl)$.[13] However, this kind of coupling was not observed for compounds $CpMo(\eta^4\text{-diene})R_2$.[4,5] In order to further confirm our spectral interpretation, the analogous compound $CpMo(PMe_3)_2(CD_3)_2$ was also prepared by using a CD_3Li solution. EPR spectra were recorded in diluted solutions under the same conditions used for the homologous bis-CH_3 complex. However, the larger broadness of the spectrum caused by the smaller a_D hyperfine coupling and by the larger number of lines allowed only the visual observation of the phosphorus coupling. Even by working at low temperature in pentane, the spectrum of the deuterated compound is broader than that observed for the bis-CH_3 compound at room temperature and shown in Fig. 1(b). No reliable information on the values of the a_D and a_H hyperfine coupling could be obtained from the digital fitting procedure.[14]

(c) Molecular structure

On the basis of this EPR spectrum and literature precedents,[15] the "four-legged piano stool" geometry appears most likely for the complex. The EPR spectrum does not permit us, however, to distinguish between the *cis* and *trans* configurations, both being characterised by equivalent PMe_3 and equivalent CH_3 ligands. Suitable crystals for an X-ray analysis were obtained from a saturated pentane solution at −80 °C. The structural determination shows that the molecule adopts in fact the *trans* four-legged piano stool geometry, as shown in Fig 2. Table 2 collects the relevant bond distances and angles.

Table 2 Selected bond distances (Å) and angles (°) for $CpMo(PMe_3)_2(CH_3)_2$[a]

Mo–CNT	1.964(3)	Mo–C(6)	2.271(2)
Mo–P(1)	2.4465(5)	Mo–C(7)	2.268(2)
Mo–P(2)	2.4445(5)		
CNT–Mo–P(1)	115.0(2)	C(6)–Mo–C(7)	128.23(8)
CNT–Mo–P(2)	115.0(2)	P(1)–Mo–C(6)	79.54(6)
CNT–Mo–C(6)	115.7(3)	P(1)–Mo–C(7)	79.01(6)
CNT–Mo–C(7)	116.1(3)	P(2)–Mo–C(6)	79.98(6)
P(1)–Mo–P(2)	130.03(2)	P(2)–Mo–C(7)	78.98(6)

[a] CNT is the cyclopentadienyl ring centroid [atoms C(1)–C(5)].

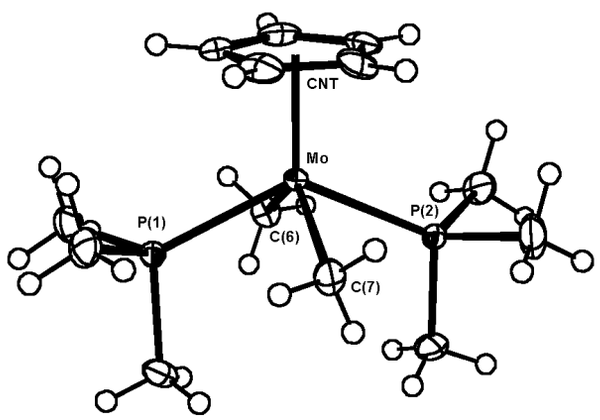


Fig. 2 An ORTEP[58] view of compound $CpMo(PMe_3)_2(CH_3)_2$ with thermal ellipsoids drawn at the 30% probability level.

The complex crystallised in the monoclinic space group $P2_1/c$ with the entire molecule in the asymmetric unit. The geometry is similar to that of its precursor $CpMo(PMe_3)_2Cl_2$.[16] The two structures are in fact isomorphous. The Cp ligand is oriented in such a way that one C atom is eclipsed with atom C(6). Thus, the molecule is pseudo-C_s-symmetric, the mirror plane passing through atoms Mo, C(6) and C(7). Like in the dichloride precursor, the two phosphine ligands are related by this pseudo-symmetry operation. The Mo–C(alkyl) distances are significantly longer than in $CpMo(\eta^4\text{-}C_4H_4Me_2\text{-}2,3)(CH_3)_2$ [average 2.224(9) Å],[5] which is the only other structurally characterised alkylmolybdenum(III) compound with a 17-electron configuration. In turn, those distances were found to be longer than all previously determined Mo(III)–alkyl distances. This trend can be related to the electron donating properties of the neutral ligands ($2PMe_3 > \eta^4\text{-}C_4H_4Me_2\text{-}2,3$), thereby affecting the atomic radius of the molybdenum centre. The Mo–P distances, on the other hand, are significantly *shorter* than those in the parent $CpMo(PMe_3)_2Cl_2$ structure [average 2.484(2) Å].[16] The two methyl ligands are stronger σ-donors than the two chloride ligands and make the Mo(III) centre more electron rich (this is confirmed by the electrochemical study, *vide infra*), thus an *increase* of metal radius is expected on going from the dichloride to the dimethyl compound. The Mo–P bond shortening can therefore be interpreted as a sign of an increased Mo–P π-back bonding caused by the greater metal electron richness. Significant Mo(III)–P π-back bonding is in fact already present in the dichloride compound.[16] The Mo–CNT (Cp ring centroid) distance is intermediate between those of the above mentioned compounds [1.939(2) Å for $CpMo(PMe_3)_2Cl_2$ and 2.020(5) Å for $CpMo(\eta^4\text{-}C_4H_4Me_2\text{-}2,3)Me_2$]. Parameters of interest for discussion are also the angles between the "basal" Mo–L bonds and the Mo–CNT bond. These angular distortions have been interpreted on the basis of π and σ interaction schemes.[17,18] The

Table 3 Cyclic voltammetric data for $CpMo(PMe_3)_2(CH_3)_2$ and comparison with $CpMo(PMe_3)_2Cl_2$,[a] $CpMo(\eta^4\text{-}C_4H_6)(CH_3)_2$ and $CpMo(\eta^4\text{-}C_4H_6)Cl_2$

	Mo(II)/Mo(III)	Mo(III)/Mo(IV)	Mo(IV)/Mo(V)	Ref.
$CpMo(PMe_3)_2(CH_3)_2$[b]	−2.51 reversible	−1.27 reversible	−0.05 reversible	This work
$CpMo(PMe_3)_2Cl_2$[c]	−2.15 irreversible	−0.52 reversible	+0.68 irreversible	16
$CpMo(\eta^4\text{-}C_4H_6)(CH_3)_2$[d]	−2.09 reversible	−0.17 irreversible	— —	19
$CpMo(\eta^4\text{-}C_4H_6)Cl_2$[d]	−1.11 reversible	0.73 irreversible	— —	19

[a] Values are potentials in volts *versus* Cp_2Fe–Cp_2Fe^+: $E_{1/2}$ for reversible processes, $E_{p,a}$ or $E_{p,c}$ for irreversible oxidation or reduction processes, respectively, measured at 200 mV s^{-1}. [b] In THF at −20 °C. [c] In CH_2Cl_2 at room temperature. [d] In THF at room temperature.

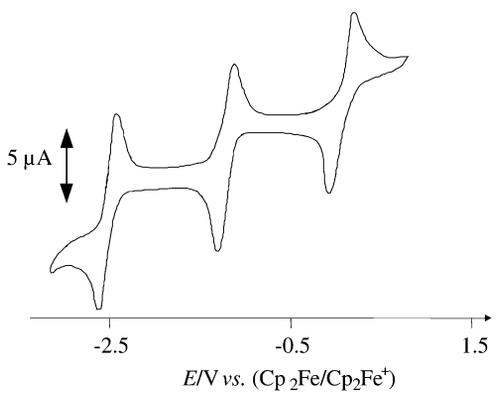


Fig. 3 Cyclic voltammogram of $CpMo(PMe_3)_2(CH_3)_2$: solvent = THF; T = −20 °C; v = 200 mV s^{-1}.

angle related to the X-type donors decreases slightly from X = Cl (average 117.4°)[16] to X = CH_3 [average 115.9(4)°], while the angle related to the L-type donors (PMe_3) increases on going from the dichloride (average 113.2°) to the dimethyl compound [average 115.0(2)°]. This trend is consistent with both the σ scheme (the *trans* pair of ligands with stronger σ-donor properties yields lower angles; CH_3 is a stronger σ donor than Cl)[18] and with the π scheme (better π acceptors tend to give greater angles in 17-electron compounds; PMe_3 is a better π acceptor in the dimethyl compound).[17]

(d) Electrochemical study

Compound $CpMo(PMe_3)_2(CH_3)_2$ was investigated by cyclic voltammetry since half-sandwich molybdenum(III) complexes usually display a rich electrochemical behaviour.[15] The study was carried out at −20 °C due to the thermal instability of $CpMo(PMe_3)_2(CH_3)_2$. The voltammogram is shown in Fig. 3 and potentials are given in Table 3 in comparison with those of the parent $CpMo(PMe_3)_2Cl_2$ compound and the analogous $CpMo(\eta^4\text{-}C_4H_6)X_2$ (X = Cl, CH_3).

The complex displays one reductive and two oxidative one-electron, reversible processes at −2.51, −1.27 and −0.05 V, respectively. The reversibility of all processes (i_a/i_c = 1) is maintained at scan rates as low as 100 mV s^{-1}. This is rather remarkable in view of the fact that the analogous dichloride system shows only one reversible oxidation, while the reduction (at a less extreme potential) and the second oxidation give no sign of chemical reversibility even at much higher scan rates.[16] Compound $CpMo(\eta^4\text{-}C_4H_6)(CH_3)_2$, as well as analogues with different diene and alkyl groups, displays a reversible reduction, while the first oxidation is completely irreversible even at 1000 V s^{-1} and a second oxidation is not observed[19] (see Table 3). Therefore, no rapid chemical process seems to occur after conversion to the 18-electron complex $[CpMo(PMe_3)_2(CH_3)_2]^-$ or to the 16-electron complex $[CpMo(PMe_3)_2(CH_3)_2]^+$ and even to the 15-electron complex $[CpMo(PMe_3)_2(CH_3)_2]^{2+}$. It can be observed from Table 3 that all electrochemical processes are shifted towards more negative potentials relative to both $CpMo(PMe_3)_2Cl_2$ and $CpMo(\eta^4\text{-}C_4H_6)(CH_3)_2$, attesting to the greater electron-releasing power of CH_3 *vs.* Cl and $2PMe_3$ *vs.* η^4-diene. The negative shift on going from the dichloro to the dimethyl system is smaller for the bis-phosphine system (−0.36 V) than for the butadiene system (−0.98 V). This may be attributed to an electronic "saturation" phenomenon: while the diene ligand can buffer the excess electron density received from the methyl ligands by a more effective Mo-diene π-back bonding interaction, the less π-acidic and more strongly σ-donating phosphine ligands are less capable of establishing an equally efficient buffering effect.

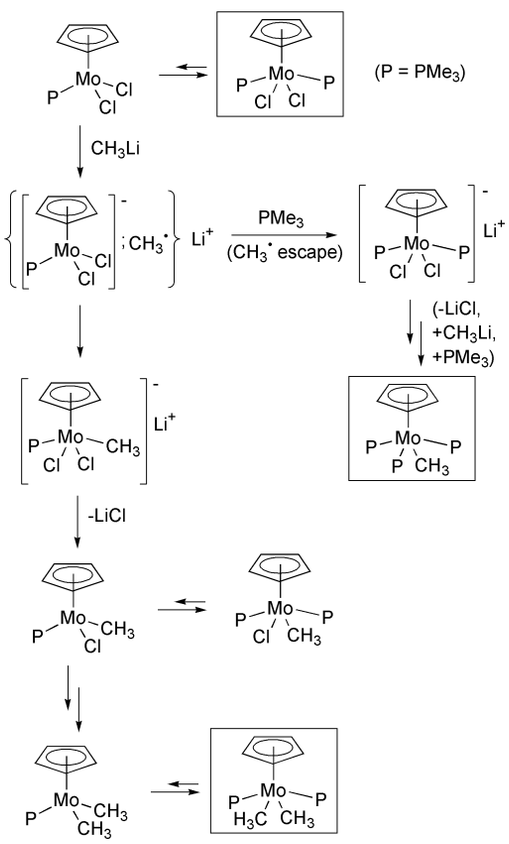
The different chemical reversibility of the reductive processes for the different compounds in Table 3 can be tentatively interpreted on the basis of the possible loss of a chloride ligand, resulting from unfavourable filled–filled repulsions in the reduced 18-electron complex $[CpMo(PMe_3)_2Cl_2]^-$. These repulsions are related to the π-donor nature of the chloride ligand and are therefore absent in the dimethyl systems. In addition, Cl^- is a much better leaving group than CH_3^-. Conversely, the 16-electron complex formed by oxidation should be stabilised to a greater extent by π-donation in the case of the dichloride ligand and this process is indeed reversible. On the other hand, the oxidation of the dimethyl complex still produces a stable species, in spite of the lack of π-stabilisation. Previous studies by us[20–25] and others[26–30] have shown that 16-electron complexes may be stabilised by adopting a triplet ground state. This phenomenon may prevent co-ordination of donor molecules including solvents such as THF, since this necessitates an expensive electron pairing process to vacate the necessary orbital for co-ordination.[20] Although we have made no attempt to isolate this oxidation product, we believe that it probably adopts a triplet ground state. Previous examples of triplet 16-electron half-sandwich Mo(IV) compounds are known,[16,31–33] although none contains alkyl ligands. Even more remarkable is the relative stability (on the CV time scale) of the 15-electron $[CpMo(PMe_3)_2(CH_3)_2]^{2+}$ species. This is a d^1 species and possesses a vacant orbital which can be used to accommodate an additional two-electron donor. It is isoelectronic with the stable $CpMoCl_4$ and its Cp* analogue, which also resist co-ordination of THF but do in fact add stronger donors such as phosphine ligands.[31,34,35] Compound $Cp^*Mo(CH_3)_4$ is also a stable 15-electron compound.[36] The lack of reversibility for the second oxidation of $CpMo(PMe_3)_2Cl_2$ could indeed be ascribed to solvent co-ordination to the highly unsaturated $[CpMo(PMe_3)_2Cl_2]^{2+}$ species, while the analogous dimethyl complex may resist or undergo a slower solvent co-ordination process for steric and/or electronic reasons.

(e) Formation mechanism

The retardation effect of free PMe_3 on the alkylation reaction clearly indicates the intervention of a phosphine dissociation pre-equilibrium, leading to the reactive species. Another example of an alkylation reaction retarded by free phosphine

has been previously reported.[37] Thus, CH_3Li does not react with the 17-electron $CpMo(PMe_3)_2Cl_2$ compound directly or at least not at a significant rate. This observation is rather enlightening when compared with the following additional observations available from previous studies: (i) compound $CpMo(PMe_3)_2Cl_2$ is not alkylated by Grignard reagents;[1] (ii) compounds of type $CpMo(\eta^4\text{-diene})Cl_2$ are alkylated equally effectively by both lithium and Grignard reagents;[5] (iii) compounds $CpMo(\eta^4\text{-diene})Cl_2$ are more easily reducible than $CpMo(PMe_3)_2Cl_2$ (see Table 3);[5] (iv) alkyllithium reagents are stronger reductants than the corresponding Grignard reagents.

On the basis of the above observations, we propose an alkylation mechanism for the $CpMo(PMe_3)_2Cl_2$ species as shown in Scheme 1. This starts with phosphine dissociation to generate



Scheme 1

the 15-electron $CpMo(PMe_3)Cl_2$ intermediate. Methyllithium undergoes a single electron transfer (SET) process with this intermediate to produce the 16-electron complex $[CpMo(PMe_3)Cl_2]^-$ and a methyl radical. The 16-electron complex most likely adopts a spin triplet configuration, by analogy with the previously described $Cp^*Mo(PMe_3)_2Cl$ and $Cp^*Mo(dppe)Cl$ complexes.[38,39] Now, two competing reactions may take place. Co-ordination of PMe_3 affords an 18-electron complex $[CpMo(PMe_3)_2Cl_2]^-$ while the methyl radical diffuses away from the metal centre and decays. Subsequently, the resulting Mo(II) complex continues its path to afford the observed reduction product, $CpMo(PMe_3)_3(CH_3)$. Alternatively, trapping of the methyl radical by the 16-electron Mo(II) intermediate affords again a Mo(III) species, $[CpMo(PMe_3)Cl_2(CH_3)]^-$, with a 17-electron configuration. Subsequent ligand exchange processes complete a formal Cl/CH_3 exchange process and a second exchange may subsequently take place by the same succession of events. This course of actions would be determined by the following circumstances.

(i) Alkylating agents are not able to attack the 17-electron $CpMo(PMe_3)_2Cl_2$ species by nucleophilic addition. In fact, this species was shown previously to resist the addition of nucleophiles, because the singly occupied orbital is engaged in a 2c–3e π interaction with the chloride lone pairs which raises the orbital energy. Compounds of type $CpMoX_2L_2$ have been shown to undergo dissociative ligand exchanges *via* 15-electron intermediates[40,41] rather than the typical associative exchanges for organometallic 17-electron compounds.[42–44]

(ii) Neither CH_3MgBr nor the stronger reductant methyllithium is able to transfer an electron to $CpMo(PMe_3)_2Cl_2$, because of the large negative reduction potential of this species (see Table 3). However, phosphine dissociation renders the metal less electron rich and therefore more easily reducible. We are not aware of electrochemical studies on pairs of stable complexes that are related by a phosphine association/dissociation process, thus we cannot estimate the potential shift caused by the PMe_3 dissociation. A Cl^- dissociation was shown to shift the potential by *ca.* +1.2 V for the $[Cp^*Mo^{IV/V}Cl_n(PMe_3)]$ ($n = 3$ *vs.* 4) system.[45] Evidently, the reduction potential of the $CpMo(PMe_3)Cl_2$ 15-electron intermediate must be accessible only to the more strongly reducing lithium reagent.

(iii) Phosphine dissociation from $CpMo(PMe_3)_2Cl_2$ is a relatively facile process as shown by both experimental[41] and theoretical studies.[46–48] A reason for this favourable dissociation is a spin change, the 15-electron intermediate adopting a spin quartet ground state configuration. According to the DFT calculations of the spin crossover point,[48] the activation energy for this dissociation process would be of the order of 12 kcal mol^{-1}, corresponding to a dissociation rate of *ca.* 10^4 s^{-1} at room temperature.

(iv) Nucleophilic addition of the alkylating agent to the 15-electron intermediate, although possible, does not compete with the SET process for the methyllithium reagent. It is not excluded that the less reducing Grignard reagent could in fact slowly alkylate $CpMoCl_2(PMe_3)$. However, this process is not synthetically useful because of the thermal instability of the product.

(v) A small concentration of free PMe_3 leads to a preferential recombination of the methyl radical with the 16-electron $[CpMo(PMe_3)Cl_2]^-$ intermediate, whereas the co-ordination of PMe_3 favourably competes when this is present in larger concentrations. This scheme is in perfect agreement with the observed outcome of the alkylation process as a function of free PMe_3.

(vi) The one-electron reduction of a spin *quartet* $CpMo(PMe_3)Cl_2$ species leads directly to the 16-electron product in the *triplet* spin state, *i.e.* the expected ground state for this species. Under these circumstances, the recombination between 16-electron $[CpMo(PMe_3)Cl_2]^-$ and spin doublet $CH_3^\bullet$ should be essentially barrierless. Phosphine co-ordination, on the other hand, requires a spin pairing and could be kinetically retarded by the need to attain a higher-energy crossover point.[21,23] These may be favourable circumstances leading to a preference for this radical recombination pathway.

It should be remarked that the reduction of transition metal halides by organolithium and magnesium reagents is a well known occurrence, often representing a nuisance to the synthetic organometallic chemist. However, the subsequent fast recombination of the organic radical with the metal centre leading to the formal substitution product has not been previously established to the best of our knowledge. On the other hand, an analogous mechanism has been demonstrated for the conversion of $[Cp^*Mo(CO)_3(PR_3)]^+$ to $Cp^*Mo(CO)(PR_3)_2H$ by the action of $LiAlH_4$.[49] Furthermore, SET processes followed by radical recombination are quite well established for Wurtz coupling reactions involving easily reducible halide substrates and organolithium or magnesium reagents.[50] These mechanisms have been evidenced by EPR[51] and CIDNP[52–56] techniques. In our case, it would be impossible to use these techniques, because the starting Mo(III) compound is itself paramagnetic.

On the basis of the above mechanistic proposal, we are led to reconsider the recently reported alkylation process for the analogous $CpMo(\eta^4\text{-diene})Cl_2$ compounds.[5] As shown in Table 3, the diene ligands make the metal more easily reducible relative to two PMe_3 ligands. The reduction potential of $CpMo(\eta^4\text{-}C_4H_6)Cl_2$ is about 1 V less negative than that of $CpMo(PMe_3)_2Cl_2$. It is therefore possible that both CH_3Li and CH_3MgBr are able to reduce the diene compound directly or, even more favourably, after partial deco-ordination of the diene ligand to afford a 15-electron $CpMo(\eta^2\text{-}C_4H_6)Cl_2$.

There are additional considerations leading to a proposal of an SET-radical addition mechanism for the alkylation of $CpMo(\eta^4\text{-diene})Cl_2$ complexes. While all alkylation reactions gave good yields for the desired substitution product without the observation of reduction by-products by using either lithium or Grignard reagents, the corresponding arylations with arylmagnesium bromide gave mixtures of substitution and reduction (yielding $[CpMo(\eta^4\text{-diene})Br]_2$), while the allylation reaction with allylmagnesium bromide gave reduction exclusively.[57] Thus, counterintuitively, the more weakly reducing allyl Grignard gives exclusively reduction while the more strongly reducing alkyllithium gives exclusively substitution. This observation would in fact be rationalised if a mechanism analogous to that shown in Scheme 1 also operates for the reaction of the diene complexes with alkylating agents (both lithium and Grignards). Following the SET step, the fate of the reduction products is determined by the reactivity and stability of the radical. The radical addition reaction prevails for the more reactive alkyl radicals, whereas the stabilised and less reactive allyl radical escapes the "radical cage" leading to reduction. The aryl radicals have an intermediate reactivity and lead to both pathways.

Conclusion

The alkylation product from the reaction between $CpMo(PMe_3)_2Cl_2$ and CH_3Li has been isolated and fully characterised. Its formation reaction necessitates phosphine dissociation and appears to proceed by a SET process followed by radical addition. Transition metal reduction by organolithium and magnesium reagents is a well known process, but cases where recombination of the organic radical with the metal fragment to afford the product of formal alkyl/halide exchange have apparently not been described previously. This is, on the other hand, a well established reaction sequence in organic Wurtz coupling reactions. In the presence of excess phosphine, the rate of alkylation decreases and the reaction is diverted toward the formation of reduction products. The EPR spectrum of $CpMo(PMe_3)_2(CH_3)_2$ shows an unusual multiplicity due to four kinds of atoms, including the remote PMe_3 protons. The cyclic voltammetry exhibits three reversible one electron processes at more negative potentials than the corresponding waves of the parent dichloro complex. The mechanism of decomposition of this thermally unstable compound and the nature of its decomposition products will be the topics of further investigations.

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