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Studies on molybdenocene derivatives: reactions of $[Cp_2Mo(\eta^2\text{-NCMe})]$ and preparation of alkyl hydride complexes. Crystal structure of $[Cp_2Mo(PMe_3)]$

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Abstract

Reaction of $[Cp_2Mo(\eta^2\text{-NCMe})]$ (**1**) with PMe_3 affords $[Cp_2Mo(PMe_3)]$ (**2**), which is readily alkylated go give $[Cp_2MoR(PMe_3)]PF_6$(**3a**, R = Me; **3b**, R = Et). The crystal structure of **2** shows tricoordination around the Mo atom. Cyclic voltammetry of **3a** and **3b** and the analogues $[Cp_2MoR(CNMe)]I$, (**4a**, R = Me; **4b**, R = Et) and $[Cp_2MoMe(PPh_3)]PF_6$ (**7**) shows one reversible one-electron oxidation, but the potential is independent of R, in contrast to the complexes $[Cp_2MoR_2]$. Oxidative addition of Et_2S_2, Ph_2Se_2 or $(PhCOO)_2$ to **1** yields $[Cp_2Mo(ER)_2]$ (E = O, S or Se). The molybdenocene alkyl hydrides $[Cp_2Mo(H)Me]$ (**5**) and $[Cp_2MoH(CH_2PPh_3)]I \cdot THF$ (**6**) are prepared from $[Cp_2MoHI]$. Thermal decomposition of **6** as well as reaction of $[Cp_2MoMe_2]^+$ with $Ph_3C^\cdot$ provide evidence for transient formation of the methylidene complex $[Cp_2MoH(CH_2)]^+$.

1. Introduction

In previous publications on molybdenocene chemistry we have dealt with the preparation of both low oxidation state complexes, *e.g.* $[Cp_2MoL]$ (L = PPh_3 or CNR) [1], and alkyl derivatives, *e.g.* $[Cp_2MoR_2]$ (R = Et or Bu) [2] (Cp = η^5-C_5H_5 throughout the paper). The former electron-rich d^4 complexes readily add to electrophiles E (E = H^+, R^+ or ML_n) to give $[Cp_2Mo(E)L]^+$ complexes which retain the Mo–L bond. During these studies we found that $[Cp_2Mo(\eta^2\text{-NCMe})]$ (**1**) [3] is a very convenient starting material for preparation of the complexes $[Cp_2Mo(CNR)]$, which could not be reproducibly prepared by the use of reductive methods such as reduction of $[Cp_2MoX_2]$ [4] and $[Cp_2MoHL]^+$ [1,5]. In view of the ready preparation of **1**, the easy displacement of the NCMe ligand represents a simple and mild way of generating the Cp_2Mo fragment, which, apart from via the aforementioned reductive routes, has also been obtained by means of thermal and/or photochemical activation of $[Cp_3Mo(CO)]$ [6], $[Cp_2MoH_2]$ [7] or $[Cp_2Mo(PEt_3)]$ [7e] and by reductive alkane elimination from $[Cp_2Mo(H)R]$, as has been shown by Cooper *et al.* for $[Cp_2W(H)Me]$ [8]. Our method has provided us with a simple preparation of $[Cp_2Mo(PMe_3)]$ (**2**) and the possibility of testing oxidative additions of RE–ER bonds (E = O, S or Se) to Cp_2Mo. A single-crystal X-ray structure determination of **2** is presented together with an electrochemical study of several alkyl cations $[Cp_2Mo(R)L]^+$.

We describe here the complex $[Cp_2Mo(H)Me]$ and provide evidence for transient formation of the alkylidene complexes $[Cp_2Mo(CH_2)R]^+$ (R = H or Me).

2. Results and discussion

2.1. The complex $[Cp_2Mo(PMe_3)]$ and its derivatives

Treatment of a toluene solution of $[Cp_2Mo(\eta^2\text{-NCMe})]$ (**1**) with an excess of PMe_3 at room temperature followed by solvent evaporation and recrystallization from Et_2O gives $[Cp_2Mo(PMe_3)]$ (**2**) in high yield. This highly crystalline orange complex is very air sensitive but can be kept for long periods in solution at room temperature under an inert atmosphere without

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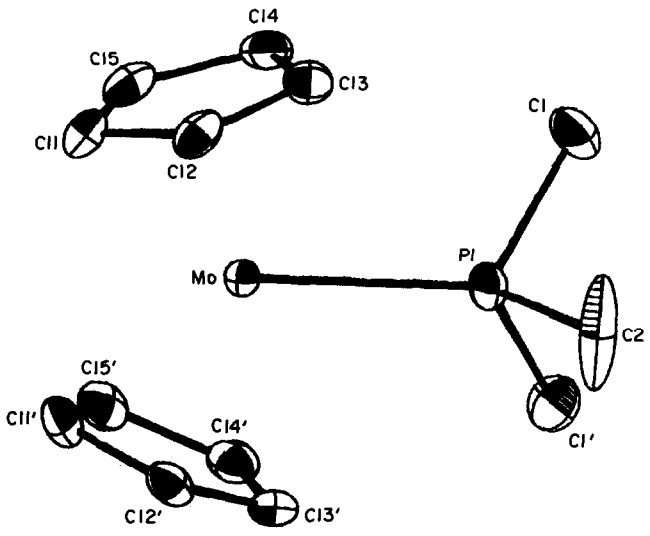


Fig. 1. Molecular structure of $[Cp_2Mo(PMe_3)]$ (2) with 50% probability thermal ellipsoids showing the atom-labelling scheme.

noticeable decomposition. This contrasts with the thermal (or photochemical) instability of $[Cp_2MoPPh_3]$ under similar conditions. The ^1H nuclear magnetic resonance (NMR) spectrum (Table 1) shows the expected doublets for both the η^5-C_5H_5 and CH_3 protons due to coupling with the ^{31}P nucleus. The coupling constant between the ligand and the ring protons, $^3J(^{31}P-^1H) = 4.9$ Hz, is much higher than that usually observed in many cationic complexes $[Cp_2MoX(PR_3)]^+$ [9], *i.e.* about 2 Hz, but is of the same order as the reported values for $[Cp_2Mo(PR_3)]$ (R = Et or Ph) [7b,c]. The chemical shift of the Cp protons of these PR_3 derivatives, 3.94 ppm, is one of the lowest found so far for $[Cp_2MoL]$ complexes (*e.g.* 4.36 ppm for L = CNR [1c] and 4.1 ppm for L = C_2H_4 [5b]). This certainly reflects the very high electron density around the metal due to the lack of extensive Mo → L back donation as found in other $[Cp_2MoL]$ complexes with unsaturated π-acidic ligands such as L = CO or CNR [1c,6].

The molecular structure of **2** is shown in Fig. 1 and selected bond lengths and bond angles are listed in Table 2. The crystal structure consists of discrete $[Cp_2Mo(PMe_3)]$ molecules with crystallographic mirror symmetry. The molybdenum is coordinated to two Cp rings and to the phosphorus atom of a trimethylphosphine. Mo–P bonds occur in a significant number of biscyclopentadienyl and in monocyclopentadienyl complexes in a variety of coordination geometries. The length of this bond is quite unaffected by the oxidation state of the metal or the type of coordination, as demonstrated by the examples given below. However, typical Mo–P double bonds as observed in $[Cp_2Mo\{=P(C_6H_2{}^tBu_3\text{-}2,4,6)\}]$ [10] (2.370(2) Å) and $[CpMo(CO)_2\{P(X)(NCMe_2(CH_2)_3CMe_2)\}]$ [11] (2.214(2) Å for X = Cl and 2.243(2) Å for X = NMe_2) are clearly shorter than single Mo–P bonds.

Examples of biscyclopentadienylmolybdenum(IV) complexes with Mo–P single bonds are $[Cp_2MoCH(CF_3)CH(CF_3)PPh_2]Cl \cdot H_2O$ [13] (2.487(1) Å), $[Cp_2MoMe(PPh_3)_3][PF_6]$[1a](2.526(4) Å) and $[Cp_2MoH(PPh_3)][PF_6]$ [1a] (2.501(4) Å). Related examples of monocyclopentadienylmolybdenum(II) complexes with Mo–P single bonds are $[CpMo(dppe)(\eta^2\text{-}MeC_2Me)]BF_4$ [14] (2.442(2) Å), $[CpMo\{CHMe(PPh_3)\}(CO)_2(PPh_3)]BF_4$ [15] (2.502(8) Å) and $[CpMo(\eta^3\text{-}CH_2CHC{=}O)(CO)(PPh_3)]$ [15] (2.509(10) Å).

The Cp ring in $[Cp_2Mo(PMe_3)]$ is planar (maximum deviation 0.0107 Å), with the Mo atom at a distance of 1.932(10) Å from this plane. The angle defined by the normals to the Cp planes is 142.8(3)°. A comparable angle of 144.6° is observed for $[Cp_2Mo\{=P(C_6H_2{}^tBu_3\text{-}2,4,6)\}]$ [10] and 147.7° for $[Cp_2Mo(CN{}^tBu)]$ [1c]. However, in tetracoordinated $[MoCp_2LL']$ complexes the Cp–Mo–Cp angle is normally smaller, ranging from 128.3(5)° to 139.2(3)° (see ref. 1c and references cited therein).

As mentioned above, electrophilic addition to the metal is the general reactivity pattern found for the

TABLE 1. ^1H NMR spectroscopic data

Complex	δ (ppm), multiplicity, relative area, $^nJ(AX)$ (Hz), assignment
$[Cp_2Mo(PMe_3)]$ (2) [a]	3.94 (d, 10, $^3J(^{31}P-^1H) = 4.9$, *Cp*; 0.97(d, 9, $^3J(^{31}P-^1H) = 8.1$, P*Me*$_3$)
$[Cp_2MoMe(PMe_3)]PF_6$ (3a) [b]	5.27(d, 10, $^3J(^{31}P-^1H) = 2.8$, *Cp*); 1.65(d, 9, $^3J(^{31}P-^1H) = 8.8$, P*Me*$_3$); −0.04(d, 3, $^3J(^{31}P-^1H) = 8.9$, Mo–*Me*)
$[Cp_2MoEt(PMe_3)]PF_4$ (3b) [b]	5.27 (d, 10, $^3J(^{31}P-^1H) = 2.8$, *Cp*); 1.65(d, 9, $^3J(^{31}P-^1H) = 10.9$, P*Me*$_3$); 1.21(t, 3, $^3J(^1H-^1H) = 7.2$, C*H*$_3$); 1.00(dq, 2, $^3J(^1H-^1H) = 7.2$, $^3J(^{31}P-^1H) = 7.2$, Mo–C*H*$_2$)
$[Cp_2Mo(H)Me]$ (5) [c]	4.32(s, 10, *Cp*); 0.32(s, 3, *Me*); −8.89(s, 1, *H*)
$[Cp_2Mo(H)CH_2PPh_3]ITHF$ (6) [d]	7.75–7.60(m, 15, *Ph*); 4.54(s, 10, *Cp*); 3.63(t, 4, $^3J(^1H-^1H) = 6.2$, OC*H*$_2$(CH$_2$)$_2$C*H*$_2$); 1.46(d, 2, $^2J(^{31}P-^1H) = 12.2$, C*H*$_2$–PPh$_3$); 1.19(t, 4, $^3J(^1H-^1H) = 6.2$, OCH$_2$(C*H*$_2$)$_2$CH$_2$); −8.05(d, 1, $^3J(^{31}P-^1H) = 7.9$, *H*)

[a] C_6D_6, 80 MHz, room temperature (Rt); [b] acetone-d_6, 300 MHz, Rt; [c] toluene-d_3, 100 MHz, −30°C; [d] CD_3CN, 100 MHz, RT. s, singlet; d, doublet; t, triplet; q, quartet.

TABLE 2. Selected bond lengths (Å) and bond angles (°) for $[Cp_2Mo(PMe_3)]$

Mo(1)–P(1)	2.468(3)	Mo(1)–Cp	1.932(6)
P(1)–C(1)	1.831(6)	P(1)–C(2)	1.818(10)
C(1)–P(1)–Mo(1)	118.8(2)	C(2)–P(1)–Mo(1)	118.0(3)
C(2)–P(1)–C(1)	99.0(4)	Cp–Mo(1)–Cp′	142.8(3)
P(1)–Mo(1)–Cp	108.6(2)		

electron-rich d^4 complexes $[Cp_2ML]$ (M = Mo or W) [1a,c,5b]:

$$[Cp_2ML] + E^+ \rightarrow [Cp_2Mo(E)L]^+ \quad (1)$$

Complex **2** exhibits similar reactivity and the alkyl derivatives $[Cp_2MoR(PMe_3)]PF_6$ (**3a**, R = Me; **3b**, R = Et) are isolated in high yields from reaction of **2** with RI followed by treatment with aqueous NH_4PF_6 and recrystallization.

The ^1H NMR spectra (Table 1) show the expected pattern, with ^{31}P–^1H) coupling being observed for all types of protons, *i.e.* η^5-C_5H_5, P–CH_3 and Mo–CH_3. The chemical shifts of the Cp protons and their coupling constants with ^{31}P are in the range normally found for this type of cationic complex.

In a previous paper we discussed the electrochemistry of the dialkyl complexes $[Cp_2MoR_2]$ (R = Me, Et or Bu) [2] and found an order of redox potentials with alkyl opposite to that due to inductive effects. In order to compare trends, we studied the electrochemistry of the cationic alkyl complexes **3a** and **3b** and their methylisocyanide analogues $[Cp_2MoR(CNMe)]PF_6$ (**4a**, R = Me; **4b**, R = Et) [1c]. The cyclic voltammograms are summarized in Table 3.

Within the solvent limits (−1.5 to 1.6 V; CH_3CN) only one reversible oxidation wave was observed for scans between 10 and 500 mV s^{-1}. This oxidation is assigned to the formation of the molybdenum(V) species $[Cp_2MoR(L)]^{2+}$. The order of the oxidation potentials is, however, the one expected on the basis of normal considerations of ligand σ donor capability. The PMe_3 complexes are easier to oxidize, reflecting a higher electronic density on the metal. The PPh_3 ligand is intermediate between PMe_3 and CNMe. On the other hand, no difference between the potentials of the Me and Et derivatives is observed unlike the complexes $[Cp_2MoR_2]$ where the difference in the oxidation potentials for R = Me and Et is about 60 mV [2]. The reason for this unexpected behaviour is not easy to identify. However, as noted elsewhere [1a], the complexes $[Cp_2MoR(L)]^+$ have a lower symmetry than $[Cp_2MoMe_2]$ owing to the distortions caused by the different ligands L. Since the anomalously low oxidation potential of the latter complex originates in an antibonding interaction between C–H bonds and the HOMO [2], it is likely that this distortion, affecting the orbital symmetry, relieves the antibonding situation, leading to normal values for the potentials. No significant difference between the oxidation potentials is observed for the diethyl and dibutyl derivatives, which do not suffer the anomalous destabilization observed for the dimethyl derivative. Accordingly, no such difference is observed for $[Cp_2MoR(L)]^+$ (R = Me or Et).

TABLE 3. Electrochemical data [a]

Compound	ΔE_p (mV)	$\frac{1}{2}(E_{p_a} + E_{p_c})$ (V)	i_c/i_a
$[Cp_2MoMe(PMe_3)]PF_6$ (**3a**)	50	0.68	1
$[Cp_2MoEt(PMe_3)]PF_6$ (**3b**)	50	0.67	1
$[Cp_2MoMe(PPh_3)]PF_6$ (**7**)	80	0.75	1.01
$[Cp_2MoMe(CNMe)]I$ (**4a**)	50	0.88	1
$[Cp_2MoEt'(CNMe)]I$ (**4b**)	50	0.86	1

[a] Cyclic voltammetry was performed at room temperature on 10^{-3} M solutions of the complex in MeCN and $[^nBu_4N]PF_6$ (0.10 M; the supporting electrolyte) at a scan rate of 100 mV s^{-1}.

2.2. *Oxidative additions to $[Cp_2Mo(\eta^2\text{-NCMe})]$ (1)*

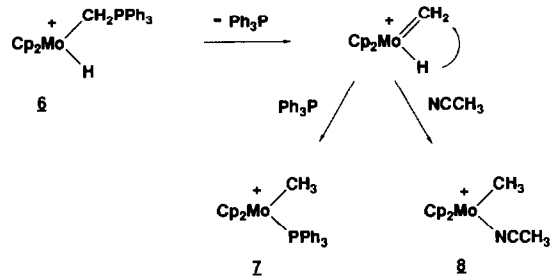
The easy preparation of **1** and the lability of the NCMe ligand in both the Cp_2Mo^{II} and Cp_2Mo^{IV} derivatives suggest that the oxidative addition of RE–ER should lead to NCMe replacement according to

$$[Cp_2Mo(\eta^2\text{-NCMe})] \rightarrow \{[Cp_2Mo]\} \rightarrow [Cp_2Mo(ER)_2] (E = O, S \text{ or } Se) \quad (2)$$

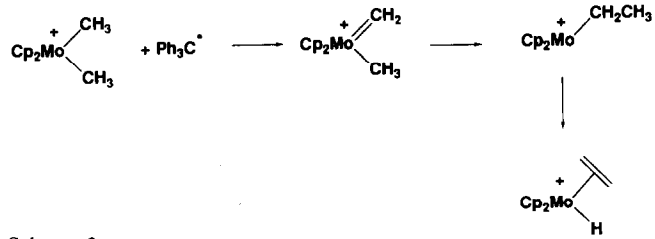
This is indeed the case, since reaction of $[Cp_2Mo(\eta^2$-NCMe)] in acetonitrile with Et_2S_2, Ph_2Se_2 or $(PhCOO)_2$ at about 50°C gives the corresponding $[Cp_2Mo(ER)_2]$ (ER = SEt, SePh or OOCPh) in very good yield. This process provides a synthetic route to $[Cp_2Mo(SePh)_2]$ much more attractive than the one previously reported from $[Cp_2MoCl_2]$ and RSeLi [16]. However, this type of oxidative addition is not always observed and the reaction of **1** with $PhSSiMe_3$ leads to the known $[Cp_2Mo(H)SPh]$ [17] as the only isolable product (85% yield). Similar hydride formation has also been observed in the reaction of $[Cp_2MoPPh_3]$ with Me_3SiCl [1a].

2.3. *Preparation of $[Cp_2MoHR]$ and related studies*

Reaction of $[Cp_2MoHI]$ with LiMe in tetrahydrofuran (THF) at −80°C followed by warming to −30°C and further work-up at or below this temperature gave yellow pentane-soluble $[Cp_2Mo(H)Me]$ (**5**) in good yield. In contrast, reaction of $[Cp_2MoXMe]$ (X = Cl or Br) [2] with Red-Al gave only $[Cp_2MoH_2]$. The alkyl hydride **5** is rather thermally sensitive, particularly in solution. Its ^1H NMR spectrum at −30°C in toluene-



Scheme 1.

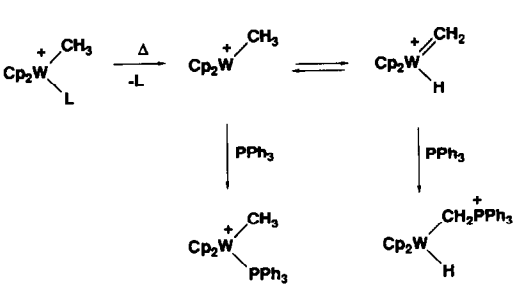


Scheme 3.

d_8 (Table 1) shows the expected singlet resonances at 0.32 ppm (Mo–CH_3) and −8.89 ppm (Mo–H). Above −20°C decomposition is observed and at −10°C these resonances disappear, but no definite product could be identified. In the solid state the stability was just enough to get a reproducible C, H analysis from freshly purified samples. In view of its instability and difficult preparation, no further attempts were made to study its reactivity and/or decomposition. Nevertheless, the three compounds $[Cp_2MoH_2]$ (decomposition above 200°C), $[Cp_2MoMe_2]$ (decomposition at 180°C) and $[Cp_2MoH(Me)]$ are another demonstration of the enhanced instability of *cis* H–alkyl fragments compared with their *cis* dihydride and dialkyl analogues.

The reaction of $[Cp_2MoHI]$ and H_2CPPh_3 affords $[Cp_2Mo(H)CH_2PPh_3]I$ (**6**) isolated as the THF solvate in 91% yield. In contrast with $[Cp_2MoHMe]$, **6** is stable at room temperature and the ^1H NMR spectrum shows the expected Mo–CH_2–P doublet and Mo–H resonances (Table 1).

Heating a solution of **6** in NCMe for 6 h under reflux followed by work-up with NH_4PF_6 gives a crude precipitate. The ^1H NMR spectrum shows that it is a mixture of $[Cp_2MoMe(PPh_3)]^+$ (**7**) and $[Cp_2MoMe(NCMe)]^+$ (**8**), both of which are already known [18]. The formation of **7** and **8** in good yields excludes reductive elimination of $[CH_3PPh_3]^+$ as the dominant pathway and no salt of this cation could be isolated from the reaction mixture. The alternative decomposition mode can be understood from the mechanism shown in Scheme 1, which is initiated by PPh_3 dissociation and H migration to the adjacent methylidene. The external ligand, either PPh_3 or NCMe, occupies the vacant coordination site to give **7** or **8** respectively.



Scheme 2.

In essence, this mechanism is the reverse reaction of α elimination from $[Cp_2WMe(L)]^+$ where L is a labile ligand (Scheme 2) [19].

Given the general similarities between molybdenocene and tungstenocene, this result is rather predictable, but to our knowledge no evidence for (CH_2) derivatives of molybdenocene has yet been produced. Indeed, similar α elimination has been observed on irradiation of $[Cp_2WMe_2]^+$ in NCMe + PPh_3 to give $[Cp_2W(H)(CH_2PPh_3)]^+$ after initial loss of $CH_3^{\cdot}$ radicals [20], but the same reaction with $[Cp_2MoMe_2]^+$ gave **8** without any evidence of a methylidene complex [18].

Further proof of the transient existence of $[Cp_2Mo{=}CH_2]^+$ is given by the reaction of $[Cp_2MoMe_2]PF_6$ with $Ph_3C^{\cdot}$, which leads to $[Cp_2MoH(C_2H_4)]^+$ in high yield as depicted in Scheme 3. The analogous experiment with W was reported by Hayes *et al.* [21].

3. Experimental details

3.1. Syntheses

All experiments were carried out under an atmosphere of argon using Schlenk techniques. Solvents (diethyl ether, toluene and THF) were dried by distillation from Na + benzophenone. Acetonitrile was dried over CaH_2 and distilled after refluxing for several hours over P_2O_5. Acetone was distilled and kept over 4 Å molecular sieves. $[Cp_2Mo(\eta^2\text{-NCMe})]$ [3], $[Cp_2MoR(CNMe)]I$ (R = Me or Et) [1c], $[Cp_2Mo(PPh_3)]$ and $[Cp_2MoMe(PPh_3)]PF_6$ [1a] were prepared as described in the literature.

3.2. Analytical procedures

Microanalyses were performed by Dornis and Kolbe Microanalytical Laboratory, Mülheim/Ruhr, Germany and in our laboratories.

^1H NMR spectra were obtained with JEOL JN-PS-100 (100 MHz), Bruker SY 80 FT (80 MHz) and Bruker CXP 300 (300 MHz) spectrometers. IR spectra

were recorded on a Perkin–Elmer 457 spectrophotometer using KBr pellets.

3.3. Crystal structure determination

Crystal data: $C_{13}H_{19}MoP$, $M_r = 302.21$, orthorhombic, space group $Cmc2_1$, $a = 12.750(4)$, $b = 10.504(2)$, $c = 9.293(6)$ Å, $V = 1244.6$ Å^3, $Z = 4$, $D_c = 1.61$ g cm^{-3}, μ(Mo Kα) = 10.32 cm^{-1}.

Data collection: All X-ray measurements were made at room temperature using an Enraf–Nonius CAD4 diffractometer and graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The intensities of 1831 unique reflections in the range $1.5° \leq \theta \leq 30.0°$ were measured in the ω–2θ scan mode with ω scan widths of $0.80 + 0.35 \tan\theta$. The data were empirically corrected for absorption using the Enraf–Nonius CAD4 software (minimum and maximum transmission factors of 0.8592 and 0.9967 respectively).

Structure determination and refinement: 1726 reflections satisfied the criterion $F \geq 3\sigma(F)$ and were used for structure solution and refinement. The molybdenum position was located on a mirror plane from a Patterson map and the positions of the other non-hydrogen atoms from subsequent difference Fourier syntheses. The phosphorus atom and carbon C(2) also lie on the same plane as Mo. The hydrogen atoms were calculated and inserted in idealized positions. All non-hydrogen atoms were refined anisotropically. The weighting scheme $w = (1.208/\sigma^2)\,|F| + 0.000416F^2$ was found to give acceptable agreement analysis. Six low angle and strong reflections thought to be affected by extinction were removed from the data. The final refinement converged at $R = 0.0285$ and $R_w = 0.0290$. The maximum shift/e.s.d. ratio in the final refinement cycle was 0.007. A peak of 1.62 e Å^{-3} in the vicinity of the molybdenum atom remained in the final electron density difference map. A comparative refinement with all atoms in the molecule in the $(-x, -y, -z)$ positions converged to $R = 0.0303$ and $R_w = 0.0310$, thereby confirming the initial absolute configuration for the molecule now reported. Final atomic positional parameters for the refined atoms are presented in Table 4.

Anisotropic displacement factors, coefficients and positional parameters for idealized hydrogen as well as lists of observed and calculated structure factors are available as supplementary data from the authors and deposited. All computations required to solve and refine the structure were done using SHELX86 [22] and SHELX76 [23]; the drawing was done using ORTEP [24].

TABLE 4. Positional parameters

	x	y	z
Mo	0	8121.3(3)	10000
P(1)	0	6645(1)	7932(2)
C(11)	1152(3)	9284(4)	11316(4)
C(12)	1394(3)	9480(4)	9820(6)
C(13)	1705(3)	8292(4)	9284(5)
C(14)	1652(3)	7348(4)	10404(5)
C(15)	1287(3)	7962(4)	11663(5)
C(1)	−1093(4)	5529(5)	7730(7)
C(2)	0	7324(8)	6133(7)

3.4. Electrochemistry

The electrochemical instrumentation consisted of a PAR 173 potentiometer, a PAR 175 voltage programmer and a Houston Instruments Omnigraphic 2000 X–T. Potentials were referred to a calomel electrode (SCE) containing a saturated solution of KCl. The experimental set-up was checked against a 10^{-3} M solution of ferrocene and $LiClO_4$ (0.10 M) in acetonitrile. The ferrocenium/ferrocene potential was in agreement with the literature value [25].

The working electrodes were a 2 mm piece of Pt wire and the auxiliary electrode a Pt wire coil. The experiments were performed in a PAR polarographic cell at room temperature. The solutions used were 1 mM in solute and 0.1 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate.

Solvents were dried as described above. Solutions were degassed with dry N_2 before each experiment and an N_2 atmosphere was maintained over the solution during the experiments.

Preparation of [$Cp_2Mo(PMe_3)$] (2)

PMe_3 (1 ml) was added to a solution of [$Cp_2Mo(\eta^2$-NCMe)] (0.160 g, 0.60 mmol) in toluene. The reaction mixture was stirred for 6 h at 60°C, the solvent evaporated in vacuum and the residue extracted with diethyl ether at 40°C. The compound was obtained as red crystals by cooling the extract. Yield 60%. Anal. Found: C, 51.57; H, 6.32; Mo, 31.70; P,10.16. $C_{13}H_{19}MoP$ calc.: C, 51.62; H, 6.34; Mo, 31.74; P, 10.26.

Preparation of [$Cp_2MoMe(PMe_3)$]PF_6 (3a)

Addition of MeI (40 μl) to a solution of [$Cp_2Mo(PMe_3)$] (0.158 g, 0.53 mmol) in 20 ml toluene caused immediate precipitation of a yellow solid. This was filtered off, washed with Et_2O (3 × 5 ml), taken up in 30 ml H_2O and treated with aqueous NH_4PF_6. The resulting precipitate was filtered, washed with H_2O and recrystallized from acetone + Et_2O to give orange crystals in 70% yield. Anal. Found: C, 36.22; H, 4.71; P, 12.70. $C_{14}H_{22}F_6MoP_2$ calc.: C, 36.34; H, 4.80; P 13.41. IR, ν_{max} (KBr): 3110, 2980, 2900, 2810, 1440, 1320 and 830 cm^{-1}.

Preparation of $[Cp_2MoEt(PMe_3)]PF_6$ (**3b**)

Treatment of a solution of $[Cp_2Mo(PMe_3)]$ (0.444 g, 1.47 mmol) in 40 ml toluene with EtI (130 μl) caused immediate precipitation of a yellow solid. This was filtered off, washed with Et_2O (2 × 3 ml), taken up in 30 ml H_2O and treated with aqueous NH_4PF_6. The resulting precipitate was filtered, washed with H_2O and recrystallized from acetone + Et_2O to give orange crystals in 70% yield. Anal. Found: C, 37.80; H, 5.06; Mo, 20.10; P, 12.99. $C_{14}H_{24}F_6MoP_2$ calc.: C, 37.83; H, 5.08; Mo, 20.14; P, 13.02. IR, ν_{max} (KBr): 3110, 2980, 2880, 1440, 1320 and 830 cm^{-1}.

Reaction of $[Cp_2Mo(\eta^2\text{-NCMe})]$ with Et_2S_2

A solution of $[Cp_2Mo(\eta^2\text{-NCMe})]$ (0.145 g, 0.54 mmol) in MeCN was treated with Et_2S_2 (2 ml) for 2 h at 45°C. The solution was evaporated to dryness and the orange residue washed with Et_2O (3 × 5 ml) and shown to be $[Cp_2Mo(SEt_2)]$ (80% yield) by comparison of its IR and ^1H NMR spectra with those of an authentic sample [26].

Reaction of $[Cp_2Mo(\eta^2\text{-NCMe})]$ with Ph_2Se_2

$[Cp_2Mo(\eta^2\text{-NCMe})]$ (0.145 g, 0.54 mmol) was dissolved in MeCN and treated with Ph_2Se_2 (0.175 mg, 0.56 mmol). The reaction mixture was stirred for 2 h. The resulting precipitate was filtered off, washed with Et_2O (3 × 7 ml) and shown to be $[Cp_2Mo(SePh)_2]$ [16] (60% yield). Anal. Found: C, 49.80; H, 3.73; Mo, 17.80. $C_{22}H_{20}MoSe_2$ calc.: C, 49.10; H, 3.75; Mo, 17.82. IR, KBr): 3100, 1570, 1475, 1440, 750 and 700 cm^{-1}.

Reaction of $[Cp_2Mo(\eta^2\text{-NCMe})]$ with $(PhCOO)_2$

$(PhCOO)_2$ (0.102 g, 0.42 mmol) was added to a solution of $[Cp_2Mo(\eta^2\text{-NCMe})]$ (0.110 g, 0.41 mmol) in MeCN and stirred for 1 h. A grey precipitate separated and the solution became brown. The precipitate was filtered off and the solution evaporated. The oily residue was washed with diethyl ether. Recrystallization from CH_2Cl_2 + Et_2O afforded $[Cp_2Mo(OCOPh)_2]$ as a brown powder in 60% yield by comparison of its IR and ^1H NMR spectra with those of an authentic sample [26].

Preparation of $[Cp_2Mo(H)Me]$ (**5**)

$[Cp_2Mo(H)I]$ (0.30 g, 0.86 mmol) was dissolved in THF at −80°C and LiMe in Et_2O (2.0 ml, 3.6 mmol) was added. The reaction mixture was allowed to warm to −30°C and unreacted LiMe destroyed with a few drops of ethanol. The solvent was removed in vacuum at −30°C and the residue extracted with pentane. Cooling the concentrated extract at −80°C for 40 h gave the product as a yellow powder in 40% yield. Anal. Found: C, 54.38; H, 5.84. $C_{11}H_{14}Mo$ calc.: C, 54.56; H, 5.83.

Preparation of $[Cp_2Mo(H)CH_2PPh_3]I$ (**6**)

A solution of $[Cp_2Mo(H)I]$ (0.30 g, 0.87 mmol) in THF was treated with a solution of CH_2PPh_3 (0.24 g, 0.87 mmol) in the same solvent. The resulting yellow precipitate was filtered off and washed with Et_2O (3 × 5 ml). Yield 91%. Anal. Found: C, 56.38; H, 5.42. $C_{33}H_{36}IMoOP$ calc.: C, 56.40; H, 5.20. IR, ν_{max} (KBr): 3060, 2980, 2890, 1430, 1110, 750, 715 and 690 cm^{-1}.

4. Conclusions

The complex $[Cp_2Mo(\eta^2\text{-NCMe})]$ is a very convenient starting material for the preparation of other $[Cp_2MoL]$ derivatives, both in the 2 +, $[Cp_2MoL]$, and 4 +, $[Cp_2Mo(ER)_2]$, oxidation states. The possibility of extending this addition to N–N and P–P bonds is being tested. With regard to the chemistry of alkyl hydrides and alkylidenes, the Cp_2Mo fragment behaves in a manner entirely analogous to its W analogue, although intramolecular migrations of H and R to the adjacent CH_2 are much faster, as expected.

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