Organometallic Molybdenum(V) Complexes with Primary Phosphane Ligands – Syntheses, Spectroscopic Properties, and Crystal Structures of $[\mathrm{Cp'MoCl_4(PH_2R)}]$ ($\mathrm{R} = 2,4,6\text{-}\mathrm{Pr}^i_3\mathrm{C}_6\mathrm{H}_2$, Cyclohexyl, $\mathrm{Cp'} = \mathrm{C_5H_4Me}$)☆

Reinhard Felsberg, Steffen Blaurock, Svea Jelonek, Thomas Gelbrich, Reinhard Kirmse, Andreas Voigt, and Evamarie Hey-Hawkins*

Institut für Anorganische Chemie der Universität,
Talstraße 35, D-04103 Leipzig, Germany
Fax: (internat.) +49(0)341/9736151
E-mail: hey@server1.rz.uni-leipzig.de

Received December 4, 1996

Keywords: Methylcyclopentadienyl molybdenum(V) tetrachloride / Primary phosphane ligands / EPR spectroscopy / Molybdenum

$[\mathrm{Cp'MoCl_4(CH_3CN)}]$ ($\mathrm{Cp'} = \mathrm{C_5H_4Me}$) reacts with 2,4,6-triisopropylphenylphosphane or cyclohexylphosphane to give the phosphane complexes $[\mathrm{Cp'MoCl_4(PH_2R)}]$ [R = 2,4,6-$\mathrm{Pr}^i_3\mathrm{C}_6\mathrm{H}_2$ (**1**), Cy (**2**)]. **1** and **2** were characterized spectroscopically (IR, MS) and by crystal structure determinations. EPR investigations in liquid and frozen solution confirmed the presence of Mo(V) species and the data were used to analyze the spin-density distribution in the first coordination sphere.

Although organometallic trialkyl- and triarylphosphane complexes of early transition metals have been studied intensively, complexes derived from functionalized phosphanes that exhibit a reactive phosphorus-ligand bond have been largely neglected[1]. It has recently been shown that when Zr[2] and Ta[3] complexes react with primary phosphanes, oxidative addition (zirconocene) or formation of stable phosphane complexes [Ta(V)] occurs. The latter can be used as starting materials for the preparation of bridging[3a] and terminal[3b] tantalum phosphinidene complexes.

Various substituted cyclopentadienyl molybdenum(V) tetrachlorides are reduced on reaction with PH-functionalized lithium phosphanides to give the corresponding cyclopentadienyl molybdenum(III) dichloro complexes[4], which can then react with further lithium reagent, yielding terminal phosphanido, diphosphanyl, and diphosphene complexes[5]. We attempted to prevent the reduction of Mo(V) by employing a primary phosphane instead of the highly reducing lithium reagents for the introduction of a P-functionalized ligand.

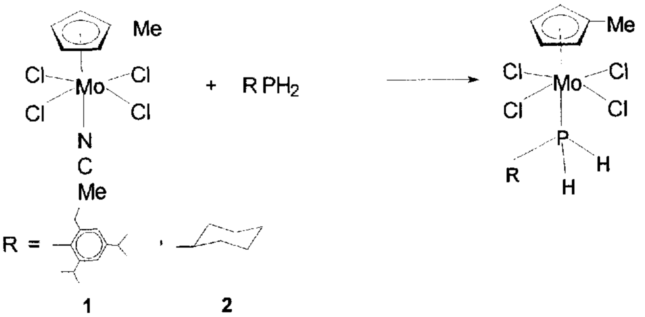
Here we report on the preparation, spectroscopic properties and molecular structures of the first organometallic molybdenum(V) complexes with *primary* phosphane ligands, $[\mathrm{Cp'MoCl_4(PH_2R)}]$ [$\mathrm{Cp'} = \mathrm{C_5H_4Me}$, R = 2,4,6-$\mathrm{Pr}^i_3\mathrm{C}_6\mathrm{H}_2$ (**1**), Cy (**2**)].

Results and Discussion

Synthesis and Properties of $[\mathrm{Cp'MoCl_4(PH_2R)}]$

When equimolar amounts of $\mathrm{PH_2R}$[6] [R = 2,4,6-$\mathrm{Pr}^i_3\mathrm{C}_6\mathrm{H}_2$, Cy] are added to a toluene suspension of $[\mathrm{Cp'MoCl_4(CH_3CN)}]$[7b], the solution turns red-brown with formation of the adducts $[\mathrm{Cp'MoCl_4(PH_2R)}]$ (Scheme 1). Due to the low basicity of primary phosphanes, no further reaction is observed with an excess of primary phosphane. This behaviour is in contrast to the reaction of $[\mathrm{Cp^*MCl_4}]$ (M = Mo, W; $\mathrm{Cp^*} = \mathrm{C_5Me_5}$) with *three* equivalents of the primary amine $\mathrm{NH_2Bu^t}$ which yields the imido complex $[\mathrm{Cp^*MCl_2(NBu^t)}]$ and $[\mathrm{NH_3Bu^t}]\mathrm{Cl}$[8].

Scheme 1



Attempts to prepare adducts of Mo(V) complexes often result in reduction of the central metal atom to Mo(IV). Thus, $\mathrm{MoCl_5}$ is reduced to Mo(IV) by nitrogen-containing ligands (e.g., pyridine[9], or 2,2'-dipyridyl, nitriles[10], etc.)[11] or oxygen-containing ligands (e.g., DME)[12]. However, the acetonitrile adduct of $[\mathrm{Cp^RMoCl_4}]$ ($\mathrm{Cp^R}$ = Cp, Cp') is stable[7].

Up to now, to the best of our knowledge, only one phosphane complex of cyclopentadienyl molybdenum(V) [or tungsten(V)] tetrachloride is known, and this contains the *tertiary* phosphane ligand $\mathrm{PMe_3}$, i.e. $[\mathrm{Cp^*MCl_4(PMe_3)}]$ (M = Mo, W)[6]. However, several cyclopentadienyl molybdenum(IV)[13–16] or (III)[17–19] halide complexes with tertiary phosphane ligands are known. Only a small number

0009–2940/97/0606–0807 $ 17.50+.50/0

of molybdenum complexes with primary phosphanes are known and no crystal structure determination has been reported to date[20–23]. The majority are carbonyl complexes of molybdenum(0) with primary phosphanes, which are usually prepared by carbonyl displacement with primary phosphanes[21–23]. As far as we are aware, the only known primary phosphane complex of molybdenum in a higher oxidation state is [$Mo_2Cl_4(PH_2Ph)_4$][24]; theoretical calculations have been carried out on [$Mo_2Cl_4(PH_3)_4$][25].

For **1** and **2**, two isomers are possible, with the cyclopentadienyl ligand and the phosphane ligand in a *trans* or a *cis* arrangement. They can be distinguished by IR spectroscopy. For the *trans* arrangement, the idealized local symmetry of the $MoCl_4$ fragment in **1** and **2** is C_{4v}. Thus, 9 vibrations (2 A_1, 2 B_1, 1 B_2, 2 E) are expected, of which only A_1 (ν_sMoCl_4 and $\delta MoCl_4$) and E ($\nu_{as}MoCl_4$ and $\delta MoCl_2$) are infrared active[26]. For [$CpMoCl_4(CH_3CN)$], all four absorptions are observed (δMoCl 328 m, $\nu_{as}MoCl_4$ 293 vst, br, ν_sMoCl_4 245 m, δMoCl 224 vw, 202 w)[7a]. By comparison, the corresponding vibrations in **1** and **2** can be assigned (**1**: δMoCl 328 m-st, $\nu_{as}MoCl_4$ 313 vst, br, ν_sMoCl_4 282 st, δMoCl 247 w; **2**: δMoCl 329 m, $\nu_{as}MoCl_4$ 316 vst, br, ν_sMoCl_4 273 st).

The P–H stretching vibrations in **1** (2408 w, 2389 w, cm^{1}) and **2** (2430 w, 2388 w, cm^{1}) are shifted to higher wave numbers compared to the lithium phosphanides [$LiPH(2,4,6\text{-}Pr^{i}_{3}C_6H_2)$][27]: 2281, LiPHCy[28]: 2286 cm^{1}]. In [$Mo(CO)_3(PH_2Ph)_3$], νPH is observed at 2295 cm^{-1}[21], and the light-sensitive homoleptic complex [$Mo(PH_2Ph)_6$] exhibits several absorptions for νPH in the range 2100–2300 cm^{-1}[20].

Molecular ion peaks are observed in the mass spectra of **1** and **2**.

Molecular Structures of [$Cp'MoCl_4(PH_2R)$] [R = 2,4,6-$Pr^{i}_{3}C_6H_2$ (1), Cy (2)]

Single crystals of **1** and **2** were obtained from toluene solutions layered with hexane. **1** crystallizes in the triclinic space group $P\bar{1}$ and has two formula units per unit cell; **2** crystallizes in the monoclinic space group $P2_1/n$ and has four formula units per unit cell (Table 1).

The molecular structures of [$Cp'MoCl_4\{PH_2(2,4,6\text{-}Pr^{i}_{3}C_6H_2)\}$] (**1**) and [$Cp'MoCl_4(PH_2Cy)$] (**2**) are depicted in Figures 1 and 2. In both complexes, the Mo atom has a pseudo-octahedral geometry, with the phosphane ligand located trans to the Cp' ligand (regarded as unidentate), and the four chlorine ligands bent away from the Cp' ligand. Thus, the angles between P and the four chloro ligands lie between 70.35(4) and 78.38(4) (**1**) and 70.62(3) and 79.64(3)° (**2**). The Mo atoms is shifted towards the Cp' ligands and lies 0.61 Å (**1**) or 0.63 Å (**2**) above the plane defined by the four chloro ligands, which is parallel to the plane of the Cp' ring.

Table 1. Crystal data and structure refinement for **1** and **2**

	1	**2**
Formula	$C_{21}H_{32}Cl_4MoP$	$C_{12}H_{20}Cl_4MoP$
Molecular weight	553.18	432.99
Temperature (K)	210(2)	230(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
Cell constants:		
a (Å)	6.6005(4)	6.9355(5)
b (Å)	10.1533(7)	20.052(2)
c (Å)	19.095(1)	12.1651(9)
α (°)	96.854(1)	90
β (°)	99.074(1)	106.542(1)
γ (°)	101.872(1)	90
V ($Å^3$)	1221.3(1)	1621.8(2)
Z	2	4
Crystal size (mm)	0.4 x 0.4 x 0.3	0.4 x 0.4 x 0.3
Number of frames	1271	1271
Exposure time/frame (s)	20	20
d_{calcd} (g/cm^3)	1.504	1.773
2Θ range (°)	2-54	4-52
h (min., max.)	-8/7	-8/7
k (min., max.)	-13/7	-24/12
l (min., max.)	-24/24	-12/14
Total reflections	7219	7266
Independent reflections	5132 [*R*(int.) = 0.0719]	2909 [*R*(int.) = 0.0562]
F(000)	566	868
Parameters	328	233
Abs. coeff. (μ/mm^{-1})	1.045	1.547
Largest difference peak/hole (e/$Å^3$)	1.274/-1.000	0.707/-0.831
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0470	*R*1 = 0.0308
	*wR*2 = 0.1432	*wR*2 = 0.0871
R indices (all data)	*R*1 = 0.0666	*R*1 = 0.0367
	*wR*2 = 0.1802	*wR*2 = 0.0950
Goodness-of-fit (F^2)	1.038	1.189

The average Mo–C(Cp') distance is 2.371(6) Å in **1** and 2.370(4) Å in **2** and does not differ significantly from Mo–C(Cp) distances in related complexes[13–16]. The Mo–Cl bond lengths [**1**: Mo–Cl 2.399(1) to 2.426(1) Å; **2**: Mo–Cl 2.4054(9) to 2.4285(9) Å] are slightly shorter than those observed in related compounds (cf., [$CpMoCl_3L_2$]: L_2 = dmpe: av. 2.493 Å[13]; L_2 = dppe: av. 2.476(3) Å[14]; L = $P(OCH_2)_3CEt$: av. 2.46(1) Å[15]; L = PMe_2Ph: av. 2.554(1) Å[16]).

While the Mo–P bond lengths of molybdenum(0) carbonyl phosphane adducts are in the range of 2.45 to 2.60 Å (bulky ligands have longer Mo–P bonds)[29,30], and those of Mo(II) phosphane complexes range from ca. 2.53 to 2.56 Å[31], the Mo–P bond lengths of 18-electron molybdenum cyclopentadienyl complexes in which one phosphane adopts a position *trans* to the cyclopentadienyl ring are generally longer {2.688(4) Å in [$CpMoCl_3(dppe)$][14]}. The 17-electron complexes **1** and **2** show shorter Mo(1)–P(1) bond lengths of 2.617(1) (**1**) and 2.554(1) Å (**2**). In the structurally related 16-electron complex [$Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^{i}_{3}C_6H_2)\}$] [Ta–P 2.710(2) Å] lengthening of the metal–P bond was observed[3a].

EPR Studies of [$Cp'MoCl_4(PH_2R)$] [R = 2,4,6-$Pr^{i}_{3}C_6H_2$ (1), Cy (2)]

1 and **2** are stable organometallic radicals (17-electron species). As far as we know the only related Mo(V) complexes which have been studied by EPR spectroscopy are [Cp^*MoCl_4][32], [$Cp^*MoCl_4(PMe_3)$][32] and [$CpMoX_4(CH_3CN)$] (with X = Cl, Br)[7a]. However, these studies were conducted in liquid solution without any interpretation of the data obtained.

Figure 1. Molecular structure of [Cp'MoCl$_4${PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$)}] (**1**) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP)[41]; hydrogen atoms (other than P–H) are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mo(1)–P(1) 2.617(1), Mo(1)–Cl(1) 2.415(1), Mo(1)–Cl(2) 2.399(1), Mo(1)–Cl(3) 2.426(1), Mo(1)–Cl(4) 2.416(1), Mo–C(Cp) 2.343(5) to 2.400(6), P(1)–C(7) 1.822(5), Mo–centre 2.050, Cl(1)–Mo(1)–Cl(2) 86.62(6), Cl(3)–Mo(1)–Cl(2) 86.60(5), Cl(3)–Mo(1)–Cl(4) 86.04(5), Cl(1)–Mo(1)–Cl(4) 86.14(5), P(1)–Mo(1)–Cl(1) 75.83(5), P(1)–Mo(1)–Cl(2) 78.38(4), P(1)–Mo(1)–Cl(3) 76.88(4), P(1)–Mo(1)–Cl(4) 70.35(4), Mo(1)–P(1)–C(7) 126.6(2), centre–Mo(1)–P(1) 175.5

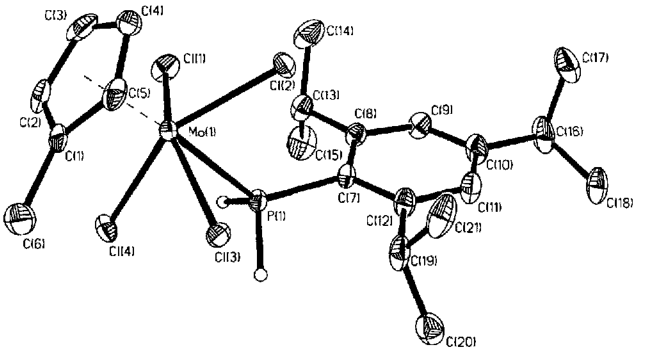


Figure 2. Molecular structure of [Cp'MoCl$_4$(PH$_2$Cy)] (**2**) showing the atom numbering scheme employed (ORTEP, 50% probability, SHELXTL PLUS; XP)[41]; hydrogen atoms (other than P–H) are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Mo(1)–P(1) 2.554(1), Mo(1)–Cl(1) 2.4285(9), Mo(1)–Cl(2) 2.426(1), Mo(1)–Cl(3) 2.4054(9), Mo(1)–Cl(4) 2.4206(9), Mo–C(Cp) 2.338(4) to 2.396(4), P(1)–C(7) 1.826(4), Mo–centre 2.048, Cl(1)–Mo(1)–Cl(2) 86.38(4), Cl(3)–Mo(1)–Cl(2) 83.66(3), Cl(3)–Mo(1)–Cl(4) 85.91(3), Cl(1)–Mo(1)–Cl(4) 88.68(4), P(1)–Mo(1)–Cl(1) 70.62(3), P(1)–Mo(1)–Cl(2) 75.23(3), P(1)–Mo(1)–Cl(3) 79.64(3), P(1)–Mo(1)–Cl(4) 74.84(3), Mo(1)–P(1)–C(7) 124.77(12), centre–Mo(1)–P(1) 175.2

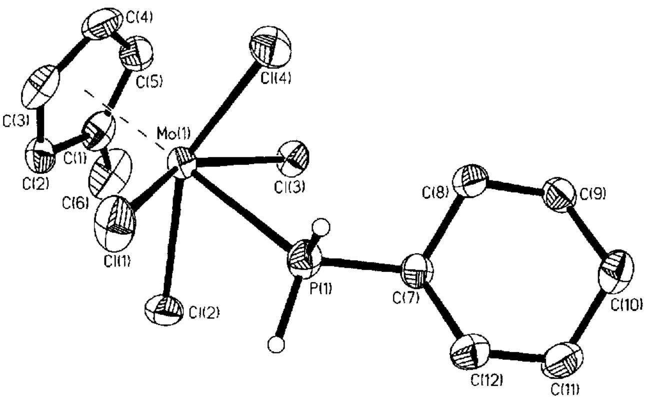
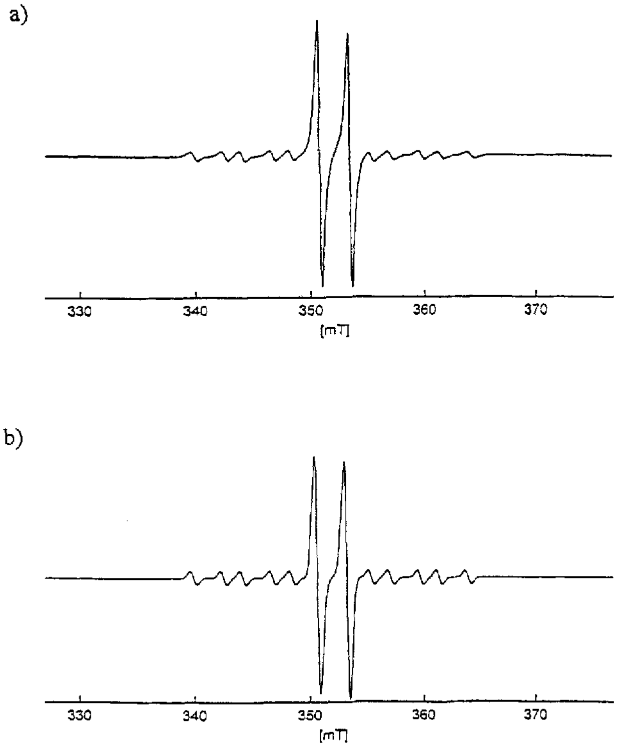


Figure 3. Experimental (a) and simulated (b) X-band EPR spectrum of **2** in toluene at 295 K



[Cp'MoCl$_4${PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$)}] (**1**) and [Cp'MoCl$_4$(PH$_2$Cy)] (**2**) show EPR spectra which are consistent with Mo(V) (4d^1, $S = 1/2$). Figure 3 shows the liquid-solution EPR spectrum of **2**, together with its simulation. It consists of a 12-line multiplet symmetrically arranged around an intense central doublet. The doublet arises from species which contain molybdenum isotopes with a nuclear spin $I = 0$ (total natural abundance 74.5%); the doublet splitting is due to hyperfine interaction with the ^{31}P nucleus ($I = 1/2$). The weaker multiplet comes from the complexes, which contain the molybdenum nuclei ^{95}Mo ($I = 5/2$, natural abundance 15.9%) and ^{97}Mo ($I = 5/2$, natural abundance 9.6%). These result in a sextet which is split by the ^{31}P nucleus into twelve lines. Two of these lines appear to be overlapped by the central doublet. An isotropic splitting of the hyperfine lines due to the two isotopes ^{95}Mo and ^{97}Mo is not observed because of the small differences in their nuclear properties.

In contrast, the room-temperature EPR spectrum of **1** consists of an intense single line whose line width of $\Delta B_{pp} = 4.5$ mT is a factor of 7 broader than that observed for **2**. This prevents the observation of hyperfine interactions. The derived isotropic parameters are given in Table 2.

Figure 4 shows the frozen-solution EPR spectrum of **2** in toluene (together with its simulation). The spectrum is axially symmetric and can be described by the spin Hamiltonian[33] (eq. 1),

$$\mathrm{H_{sp}} = \mu_B \cdot [g_\parallel \cdot \mathbf{B}_z \cdot \mathbf{S}_z + g_\perp(\mathbf{B}_x \cdot \mathbf{S}_x + \mathbf{B}_y \cdot \mathbf{S}_y)] + \mathbf{A}_\parallel^{\mathrm{Mo}} \cdot \mathbf{S}_z \cdot \mathbf{I}_z + \mathbf{A}_\perp^{\mathrm{Mo}}(\mathbf{S}_x \cdot \mathbf{I}_x + \mathbf{S}_y \cdot \mathbf{I}_y) + \mathbf{A}_\parallel^{\mathrm{P}}\mathbf{S}_z \cdot \mathbf{I}_z + \mathbf{A}_\perp^{\mathrm{P}}(\mathbf{S}_x \cdot \mathbf{I}_x + \mathbf{S}_y \cdot \mathbf{I}_y), \qquad \text{(eq. 1)}$$

where all symbols given have their usual meaning. Interestingly, in contrast to the poorly resolved room-temperature spectrum, the resolution of the 130 K spectrum of **1** is comparable to that of **2**. In Table 2 the principal values obtained for the **g**-tensors and the ^{95,97}Mo and ^{31}P hyperfine structure tensors $\mathbf{A}^{\mathrm{Mo}}$ and $\mathbf{A}^{\mathrm{P}}$ are listed and compared to those determined for [Cp*MoCl$_4$][32], [Cp*MoCl$_4$(PMe$_3$)][32], [CpMoCl$_4$(CH$_3$CN)][7a] and [CpMoBr$_4$(CH$_3$CN)][7a]. Unfortunately, for the cited complexes, EPR studies have been made only at 295 K. Furthermore, the accuracy of the parameters determined is low and the g_o values for [Cp*-

Table 2. EPR parameters for **1**[a], **2**[a], $[Cp^*MoCl_4]$[32] (**I**), $[Cp^*MoCl_4(PMe_3)]$[32] (**II**), $[CpMoCl_4(CH_3CN)]$[7a] (**III**) and $[CpMoBr_4(CH_3CN)]$[7a] (**IV**). Hyperfine constants are given in $[10^{-4}\ cm^{-1}]$

	1	2	I	II	III	IV
$g_{\parallel}$	1.975	1.968				
$g_{\perp}$	1.990[c]	1.995				
g_{av}[b]	1.985	1.986				
g_o	1.985	1.986	1.99	1.97	1.94	1.99
$A_{\parallel}^{Mo}$	62.6	64.9				
$A_{\perp}^{Mo}$	27.9	28.8				
a_{av}^{Mo}[b]	39.5	40.8				
a_0^{Mo}	[c]	39.9	36.2	41.4	45.3	41.8
$A_{\parallel}^{P}$	28.9	28.8				
$A_{\perp}^{P}$	21.8	21.8				
a_{av}^{P}[b]	24.1	24.1				
a_0^{P}	[d]	24.1		24.8		
solvent:	toluene	toluene	THF	THF	acetone	acetone

[a] Experimental error: g_0, $g_{\parallel}$, $g_{\perp}$ ± 0.002; a_o^{Mo}, $A_{\parallel}^{Mo}$, $A_{\perp}^{Mo}$ ± 0.5; a_o^{P}, $A_{\parallel}^{P}$, $A_{\perp}^{P}$ ± 0.5. – [b] $g_{av} = (g_{\parallel} + 2g_{\perp})/3$ and $a_{av} = (A_{\parallel} + 2A_{\perp})/3$. – [c] Not resolved. – [d] Perpendicular part poorly resolved – values obtained with $g_{av} = g_0$ and $g_{\perp} = (3g_o - g_{\parallel})/2$.

$MoCl_4]$[32] and $[Cp^*MoCl_4(PMe_3)]$[32] (see Table 2) are questionable.

The hyperfine parameters can be used to estimate the spin density on the nuclei, and, therefore, allow conclusions to be made about the nature of the M–L bonds, in particular the hybridisation of the orbitals[34,35]. For this, the complete parameters of the hyperfine tensors are needed. The spin densities ($c_{s,p,d}^{(X)}$) can then be obtained by using eq. 2a,b,

$$(c_s^X)^2 = a_{o,exp.}^X / a_{o,th.}^X \qquad \text{(eq. 2a)}$$

$$(c_{p,d}^X)^2 = b_{exp.}^X / b_{th.}^X\,, \qquad \text{(eq. 2b)}$$

where s, p, and d represent atomic orbitals, X is the nucleus under discussion, a_0 the isotropic hyperfine interaction and b^X the dipolar part of the hyperfine tensor.

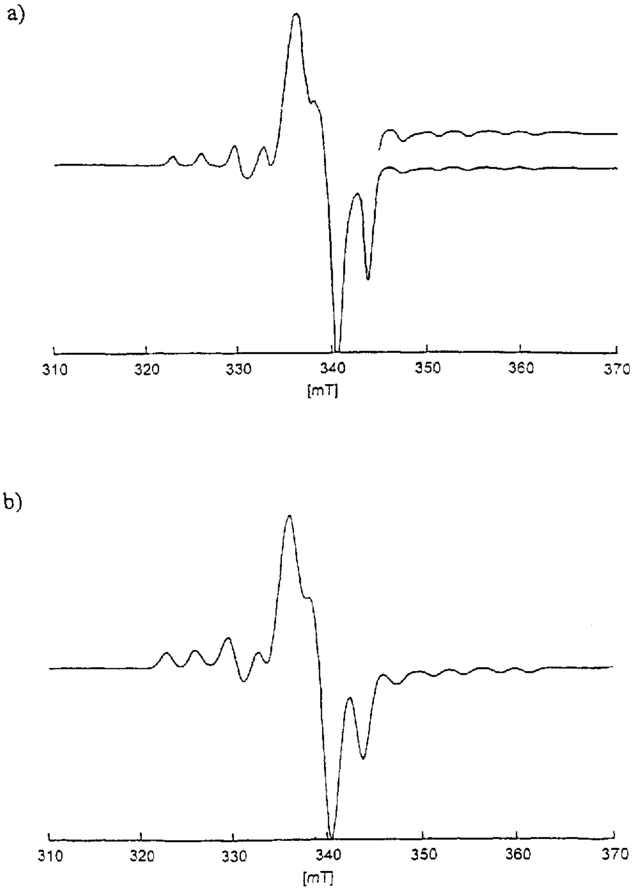
Using the values for the parameters $a_{o,th.}^X$ and $b_{th.}^X$ calculated by Morton and Preston[35] and eq. 2a,b, gave the following spin densities for these atoms in **2** whose nuclei gave rise to observable hyperfine interactions: $(c_d^{Mo})^2 = 0.84$, $(c_s^{Mo})^2 = 0.06$, $(c_p^P)^2 = 0.02$ and $(c_s^P)^2 = 0.005$. Thus, 84% of the spin density is located in the Mo 4d orbitals, and 6% was estimated to be in the Mo 5s orbital. The latter value appears to be questionable because of spin-polarisation effects, which are known to yield large discrepancies in the ns contributions, especially for heavier transition metal ions[36,37].

The 3s and 3p spin densities determined for the ^{31}P nucleus can be used to estimate the 3s,3p-hybridisation of the P atom (eq. 3).

$$(c_s^P)^2 = \alpha_P^2 (1 - n^2) \qquad (c_p^P)^2 = \alpha_P^2 n^2 \qquad \text{(eq. 3)}$$

where α_P^2 is the overall spin density on the P atom and amounts to $\alpha_P^2 = 2.5\%$.

Figure 4. Experimental (a) and simulated (b) X-band EPR spectrum of **2** in toluene at 130 K; the high-field part is additionally increased in intensity by a factor of 5



This gives a degree of hybridisation n^2 of 0.8, close to that expected for a tetrahedrally coordinated P atom (n^2 = 0.75). This result is consistent with the molecular structure (see Figure 2), which shows nearly tetrahedral coordination of the P atom. After summation of the spin densities estimated for Mo (contribution neglected) and P and consideration of the fact that, due to overlap contributions, some terms with a negative sign are contained in the normalization condition of the molecular orbital of the unpaired electron, about 15–25% spin density remains. This is expected to be located on the four Cl and the Cp′ ligands in the first coordination sphere. Unfortunately, hyperfine interactions with nuclei of these ligands were not observed; therefore, the spin densities on these nuclei remain an open question. The interpretation of the EPR spectra of the Mo(V) complex **1** yields, within error limits, the same results.

Conclusions

The first organometallic molybdenum(V) complexes with *primary* phosphane ligands, $[Cp'MoCl_4(PH_2R)]$ [R = 2,4,6-$Pr^i_3C_6H_2$ (**1**), Cy (**2**)], show a *trans* arrangement of the Cp′ and phosphane ligands. EPR investigations in liquid and frozen solution confirmed the presence of Mo(V) species, and the data were used to analyze the spin-density distribution in the first coordination sphere.

As deprotonation of primary phosphanes in molybdenum carbonyl complexes can be achieved with alkyl lithium reagents or DBU[21–23], we are presently investigating the reactivity of **1** and **2**, with the preparation of posphinidene complexes (with elimination of HCl, analogous to the preparation of Ta phosphinidene complexes[3]) being one of our major goals.

We gratefully acknowledge support of this work by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft*. We thank the company *Chemetall* for a generous donation of lithium alkyls, *H. C. Starck GmbH & Co. KG* for a generous donation of $MoCl_5$, and *Hoechst AG* for a generous donation of chemicals.

Experimental Section

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The IR spectra were recorded on a FT-IR spectrometer Perkin-Elmer Spectrum 2000 in the range 200–400 (CsI) and 400–4000 (KBr) cm^{-1}; MS: VG 12-250. X-ray structural analyses: Siemens SMART CCD diffractometer. EPR spectra of ca. 10^{-3} M solutions of **1** and **2** in toluene were recorded with a BRUKER ESP 300E at X-band frequency ($\nu \approx 9.5$ GHz) at T = 295 K and 130 K. The simulated spectra were generated by using the simulation program "powder"[38]. The melting points were determined in sealed capillaries under argon and are uncorrected. $[Cp'MoCl_4(CH_3CN)]$[7b], PH_2Cy[6b] and $PH_2(2,4,6\text{-}Pr^i_3C_6H_2)$[6a] were prepared by literature procedures.

(Methylcyclopentadienyl)[(2,4,6-triisopropylphenyl)phosphane]molybdenum Tetrachloride (**1**): $PH_2(2,4,6\text{-}Pr^i_3C_6H_2)$ (1.3 ml, ca. 1.2 g, 52 mmol) was added with a pipette to a suspension of $[Cp'MoCl_4(CH_3CN)]$ (1.87 g, 52 mmol) in 25 ml of toluene. The mixture was stirred at room temperature for 10 min, after which a brown solution and a brown solid had formed. After stirring for 2 d, the solvent was removed in vacuum, giving a red-brown slimy residue. Washing with hexane (20 ml) gave a powdery solid, which was isolated by filtration and dried in vacuum. Toluene (10 ml) was then added to the solid to separate the soluble product **1** from the insoluble unreacted $[Cp'MoCl_4(CH_3CN)]$. **1** was precipitated as brown crystals from the yellow-brown toluene solution by addition of hexane (10 ml). Yield: 1.8 g (62%), dec. 139°C. – IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2408 w, 2389 w (νPH). – FIR (CsI), $\tilde{\nu}$ (cm^{-1}) = 328 m-st (δMoCl), 313 vst, br ($\nu_{as}MoCl_4$), 282 st (ν_sMoCl_4), 247 w (δMoCl). – MS; *m/z* (%): 553 (1) $[M^+]$, 236 (55) $[PH_2(2,4,6\text{-}Pr^i_3C_6H_2)^+]$, 44 (100) $[(Pr^i)^+]$, and fragmentation products thereof are observed. – $C_{21}H_{32}Cl_4PMo$ (553.19): calcd. C 45.59, H 5.83, Cl 25.63; found C 44.43, H 5.81, Cl 25.36.

(Cyclohexylphosphane)(methylcyclopentadienyl)molybdenum Tetrachloride (**2**): PH_2Cy (0.7 ml, ca. 0.7 g, 60 mmol) was added with a pipette to a suspension of $[Cp'MoCl_4(CH_3CN)]$ (1.64 g, 46 mmol) in toluene (25 ml). The mixture was stirred at room temperature for 10 min, after which a brown solution and brown solid had formed. After stirring for 2 d, the solvent was removed in vacuum giving a dark-brown slimy residue. Washing with hexane (20 ml) gave a powdery solid, which was isolated by filtration and dried in vacuum. Toluene (20 ml) was then added to the light-brown solid to separate the soluble product **2** from the insoluble unreacted $[Cp'MoCl_4(CH_3CN)]$. **2** was precipitated as brown crystals from the yellow-brown toluene solution by addition of hexane (20 ml). Yield: 1.9 g (98%), dec. 134.5°C. – IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2430 w, 2388 w (νPH). – FIR (CsI): $\tilde{\nu}$ (cm^{-1}) = 329 m (δMoCl), 316 vst, br ($\nu_{as}MoCl_4$), 273 st (ν_sMoCl_4). – MS; *m/z* (%): 432 (0.5) $[M^+]$, 115 (55) $[PH_2Cy^+]$, and fragmentation products thereof are observed. – $C_{12}H_{20}Cl_4PMo$ (432.99): calcd. C 33.28, H 4.66, Cl 32.75; found C 33.38, H 4.88, Cl 32.78.

X-ray Crystal Structure Determination of **1** *and* **2**[39]: Data (Mo-K_α = 0.71073 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections for **1** and **2** were used for refinement (SAINT) of the unit cell parameters. Empirical absorption correction with SADABS[40]. The structures were solved by direct methods (SHELXTL PLUS)[41]. Mo, P, Cl and C atoms anisotropic, H atoms located by difference maps and refined isotropically. For **1**, the P–H protons were refined isotropically in calculated positions. Table 1 lists crystallographic details.

☆ Dedicated to Professor Dr. *Joachim Strähle* on the occasion of his 60th birthday.

[1] *Comprehensive Organometallic Chemistry II*, Eds. E. W. Abel, F. G. A. Stone, G. Wilkinson, Volumes 4 and 5, Pergamon Press **1995**.

[2] [2a] E. Hey-Hawkins, *Chem. Rev.* **1994**, *94*, 1661; [2b] J. Ho, R. Rousseau, D. W. Stephan, *Organometallics* **1994**, *13*, 1918; (and references therein).

[3] [3a] G. A. A. Hadi, K. Fromm, S. Blaurock, S. Jelonek, E. Hey-Hawkins, *Polyhedron* **1997**, *16*, 721; [3b] G. A. A. Hadi, E. Hey-Hawkins, et al. (in preparation).

[4] K. Fromm, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **1993**, *619*, 261.

[5] E. Hey-Hawkins, K. Fromm, *Polyhedron* **1995**, *14*, 2825.

[6] [6a] R = $2,4,6\text{-}Pr^i_3C_6H_2$: H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, *J. Organomet. Chem.* **1991**, *415*, 327; Y. van den Winkel, H. M. M. Bastiaans, F. Bickelhaupt, *J. Organomet. Chem.* **1991**, *405*, 183; P. Kölle, G. Linti, H. Nöth, G. L. Wood, C. K. Narula, R. T. Paine, *Chem. Ber.* **1988**, *121*, 871; [6b] R = Cy: G. Becker, O. Mundt, M. Rössler, E. Schneider, *Z. anorg. allg. Chem.* **1978**, *443*, 41; H. Schindlbauer, E. Steininger, *Monatsh. Chem.* **1961**, *92*, 868; F. Pan, E. Steininger, E. Zorn, *Monatsh. Chem.* **1962**, *93*, 230.

[7] [7a] M. Scheer, T. T. Nam, K. Schenzel, E. Herrmann, P. G. Jones, V. P. Fedin, V. N. Ikorski, V. E. Fedorov, *Z. anorg. allg. Chem.* **1990**, *591*, 221; [7b] K. Fromm, E. Hey-Hawkins, *Z. anorg. allg. Chem.* **1993**, *619*, 261.

[8] K. Köhler, H. W. Roesky, A. Herzog, H. Gornitzka, A. Steiner, I. Usón, *Inorg. Chem.* **1996**, *35*, 1773.

[9] E. A. Allen, B. J. Brisdon, G. W. A. Fowles, *J. Chem. Soc.* **1964**, 4531.

[10] J. R. Dilworth, R. L. Richards, *Inorg. Syn.* **1980**, *20*, 121.

[11] *Comprehensive Inorganic Chemistry*, 1. Aufl., Vol. 3, Pergamon Press, **1973**, p. 721 ff.

[12] E. Hey- Hawkins, H. G. von Schnering, *Z. Naturforsch.* **1991**, *46B*, 307.

[13] B. E. Owens, R. Poli, *Inorg. Chim. Acta* **1991**, *179*, 229.

[14] K. Stärker, M. D. Curtis, *Inorg. Chem.* **1985**, *24*, 3006.

[15] R. Poli, M. A. Kelland, *J. Organomet. Chem.* **1991**, *419*, 127.

[16] F. Abugideiri, J. C. Gordon, R. Poli, B. E. Owens-Waltermire, A. L. Rheingold, *Organometallics* **1993**, *12*, 1575.

[17] S. T. Krueger, B. E. Owens, R. Poli, *Inorg. Chem.* **1990**, *29*, 2001.

[18] M. L. H. Green, A. Izguierdo, J. J. Martin-Polo, V. S. B. Mtetwa, K. Prout, *J. Chem. Soc., Chem. Commun.* **1983**, 538.

[19] J. C. Fettinger, D. W. Keogh, R. Poli, *J. Am. Chem. Soc.* **1996**, *118*, 3617.

[20] M. W. Anker, J. Chatt, G. J. Leigh, A. G. Wedd, *J. Chem. Soc. Dalton Trans.* **1975**, 2639.

[21] P. M. Treichel, W. K. Dean, W. M. Douglas, *J. Organomet. Chem.* **1972**, *42*, 145.

[22] A. J. Deeming, S. Doherty, *Polyhedron* **1996**, *15*, 1175 (and references therein).

[23] G. Johannsen, O. Stelzer, *Chem. Ber.* **1977**, *110*, 3438.

[24] F. A. Cotton, L. M. Daniels, G. L. Powell, A. J. Kahaian, T. J. Smith, E. F. Vogel, *Inorg. Chim. Acta* **1988**, *144*, 109.

[25] B. E. Bursten, W. F. Schneider, *Inorg. Chem.* **1989**, *28*, 3292.

[26] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, G. Thieme Verlag, 2. Aufl., Stuttgart, **1988**.

[27] E. Hey-Hawkins, S. Kurz, G. Baum, *Z. Naturforsch.* **1995**, *50B*, 239.

[28] E. Hey-Hawkins, S. Kurz, *Phosphorus, Sulfur* **1994**, *90*, 281.

[29] E. C. Alyea, G. Ferguson, S. Kannan, *Acta Cryst.* **1996**, *52C*, 765 (and references therein).

[30] G. Hogarth, T. Norman, *J. Chem. Soc. Dalton Trans.* **1996**, 1077.

[31] F. A. Cotton, L. M. Daniels, S. C. Haefner, E. N. Walke, *Inorg. Chim. Acta* **1996**, *247*, 105 (and references therein).

[32] R. C. Murray, L. Blum, A. H. Liu, R. R. Schrock, *Organometallics* **1985**, *4*, 953.

[33] A. Abragam, M. H. L. Pryce, *Proc. Roy. Soc. London*, **1951**, *205A*, 135.

[34] R. Kirmse, J. Stach, *ESR-Spektroskopie-Anwendungen in der Chemie*, Akademie-Verlag Berlin **1985**, p. 86–95.

[35] J. R. Morton, K. F. Preston, *J. Magn. Reson.* **1978**, *30*, 577.

[36] C. P. Keijzers, E. de Boer, *J. Chem. Phys.* **1972**, *57*, 1277.

[37] C. P. Keijzers, E. de Boer, *Molec. Phys.* **1975**, *29*, 1007.

[38] L. K. White, R. L. Belford, *J. Am. Chem. Soc.* **1976**, *98*, 4428; A modified version by K. Köhler and R. Böttcher (University Leipzig, **1991**) was used for the simulation.

[39] Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, giving reference to the depository numbers CSD 406296 (for **1**) and CSD 406350 (for **2**), and citing the authors and this paper.

[40] R. H. Blessing, *Acta Cryst.* **1995**, *51A*, 33.

[41] SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., **1990**, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactiv Molecular Graphics.

[96266]