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17-ELECTRON, FOUR-LEGGED PIANO STOOL $CpMoX_2L_2$ COMPLEXES (X = HALOGEN, L = TERTIARY PHOSPHINE). EPR EVIDENCE FOR THE EXISTENCE OF A SECOND ISOMER IN SOLUTION

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Abstract—Several 17-electron molybdenum(III) complexes of the type $CpMoCl_2L_2$ have been generated by either (1) reaction between $CpMoCl_2$ and the appropriate L, (2) reaction between $MoCl_3(THF)_3$, the appropriate L and CpTl, and (3) phosphine exchange from $CpMoCl_2(PPh_3)_2$. The iodide complexes $CpMoI_2L_2$ (L = $PMePh_2$, PPh_3) have been generated from the corresponding chloride and NaI. The complexes have been investigated by EPR (*X*-band and *Q*-band) and cyclic voltammetry. The four-legged piano stool structure is found by single crystal X-ray diffraction studies of the $PMePh_2$ and PPh_3 dichloride compounds. However, this structure equilibrates in solution with at least one other isomeric form which is observable for the PMe_2Ph complexes by *X*-band EPR and for other complexes, including the previously reported $CpMoCl_2(dppe)$, by *Q*-band EPR. Phosphine exchange equilibria show a thermodynamic stability trend that parallels the phosphine σ-donor strength.

We have recently been investigating 17-electron $CpMoX_2L_2$ (X = halogen, L = phosphine) compounds.[1–7] Structural studies, in combination with electrochemical and theoretical investigations, indicate the presence of X—Mo π-bonding and Mo—P π-back-bonding.[1,2] Replacement of the halide ligands with alkyl ligands induces spontaneous reduction with the production of four-legged piano stool molybdenum(II) derivatives, among which the *ortho*-metallated $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ has been structurally characterized.[5] Halide exchange reactivity studies show slow rates and do not proceed through an associative 19-electron intermediate.[6] In addition, this exchange reaction is catalysed by one-electron oxidation to provide the first example of an electron-transfer chain catalysed substitution, where a 17-electron system is accelerated by transformation to a 16-electron system.[7] Most of the above studies were carried out on the PMe_3 derivatives, with only the alkylation studies being extended to the PMe_2Ph dichloride derivative. In this contribution, we report the preparation, EPR and electrochemical properties, and phosphine exchange reactivity of a larger variety of phosphine derivatives, including the solid-state structure of the $CpMoCl_2L_2$ (L = $PMePh_2$, PPh_3) compounds.

EXPERIMENTAL

All operations were carried out under an atmosphere of dry dinitrogen. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. Cyclic voltammetric studies

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were carried out with an EG&G potentiostat connected to a Macintosh computer through MacLab hardware/software. *X*-band and *Q*-band EPR measurements were carried out with a Bruker ER200 spectrometer calibrated with diphenylpicrylhydrazyl radicals and equipped with a variable-temperature probe. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Midwest Microlab, Indianapolis, Indiana. $CpMoCl_2$[4] and $MoCl_3(THF)_3$[8] were prepared according to published methods.

Preparation of $CpMoCl_2(PPh_3)_2$

$CpMoCl_2$ (0.337 g, 1.45 mmol) and PPh_3 (0.829 g, 3.16 mmol) were placed in CH_2Cl_2 (20 cm^3) and the resulting mixture was stirred at room temperature. Most of the solid went into solution (deep green) within 2 h and stirring was continued overnight. Minor amounts of a grey insoluble material were eliminated by filtration, and the solution was reduced in volume to *ca* 10 cm^3 and placed at $-20°C$. The crystals that formed were isolated from the mother liquor, washed with heptanes and dried *in vacuo*. Yield: 0.523 g (48%). From the mother liquor, an additional crop of 47 mg was obtained by further cooling to $-20°C$ over a longer period of time (3 weeks). Total yield: 52%. Found: C, 65.0; H, 4.8. Calc. for $C_{41}H_{35}Cl_2MoP_2$: C, 65.1; H, 4.7%. A single crystal for the X-ray analysis was obtained by diffusion of n-heptane into a toluene solution.

Preparation of $CpMoCl_2(PMePh_2)_2$ *from* $CpMoCl_2$ *and* $PMePh_2$

To a slurry of $CpMoCl_2$ (138 mg, 0.595 mmol) in THF (15 cm^3) was added $PMePh_2$ (0.221 cm^3, 1.19 mmol). After 20 min almost all the molybdenum starting material had dissolved to produce a red–brown solution. The solution was evaporated to dryness and the residue taken up in toluene (5 cm^3), followed by filtration and layering with n-heptane (8 cm^3). Diffusion at room temperature gave 155 mg (41% yield) of analytically pure product. Found: C, 58.5; H, 4.8; Cl, 11.2; P, 9.9. Calc. for $C_{31}H_{31}Cl_2MoP_2$: C, 58.9; H, 4.9; Cl, 11.2; P, 9.8%. Crystals from this batch showed twinning problems when investigated by X-ray diffraction methods. An analogous preparation was repeated with $CpMoCl_2$ (370 mg, 1.60 mmol) and $PMePh_2$ (0.40 cm^3, 2.2 mmol) in CH_2Cl_2. After filtration, crystallization by diffusion of an n-heptane layer gave a CH_2Cl_2 mono-solvate form of the compound (yield 598 mg, 78% based on $PMePh_2$) in the form of single crystals which were suitable for the X-ray analysis. EPR studies showed that the compound is present in solution as a mixture of isomers (see Results).

Formation of $CpMoCl_2(PMePh_2)_2$ *from* $MoCl_3(THF)_3$, $PMePh_2$ *and* CpTl

$MoCl_3(THF)_3$ (93 mg, 0.22 mmol) and $PMePh_2$ (0.08 cm^3, 0.41 mmol) were placed in THF (30 cm^3) and the resulting suspension was stirred overnight at room temperature. To the resulting yellow solution CpTl (60 mg, 0.22 mmol) was added and stirring was continued at room temperature. The solution darkened and the precipitation of an off-white solid was noted. An EPR investigation of this solution showed an identical spectrum as observed for the analytically pure $CpMoCl_2(PMe_2Ph)_2$, which was obtained as described above.

Preparation of $CpMoCl_2(PEt_3)_2$

To a slurry of $CpMoCl_2$ (0.295 mg, 1.27 mmol) in toluene (30 cm^3) was added PEt_3 (0.45 cm^3, 3.08 mmol). After 2 days of stirring at room temperature, the solution was filtered through Celite and the solvent completely removed by evaporation under reduced pressure. The residue was recrystallized from 20 cm^3 of hot n-heptane to afford well-formed crystals of the product, which were separated from the mother liquor, rapidly washed with n-heptane and dried *in vacuo*. Yield: 193 mg (32%). The mother solution gave another crop of product after evaporation to *ca* 10 cm^3 and cooling to $-20°C$ (total yield: 0.241 g, 40%). Several attempts to obtain analytical data on this material always gave low C, H, P contents and a slightly high Cl content, indicating the possible facile loss of phosphine.

Formation of $CpMoCl_2L_2$ *derivatives in solution from* $CpMoCl_2(PPh_3)_2$ *and* L [L = $P(^nPr)_3$, $P(^nBu)_3$]

Since the phosphine exchange reactions from $CpMoCl_2(PPh_3)_2$ proceed quantitatively (see Results), we generated solutions of these materials by mixing the bis-PPh_3 complex and a slight excess of the desired phosphine in CH_2Cl_2. These solutions were used directly for the EPR characterization, and, after addition of the $(^nBu)_4NPF_6$ supporting electrolyte, for the electrochemical characterization by cyclic voltammetry (the results are collected in Table 1).

Table 1. Electrochemical and EPR spectroscopic properties of $CpMoX_2L_2$ complexes[a]

Compound	$E_{1/2}$ (V)[b]	g	a_P (G)[c]	a_{Mo} (G)[c]	Ref.
1. Monodentate phosphine complexes					
$CpMoCl_2(PMe_3)_2$	−0.52	1.982	15.0	41.0	1
$CpMoBr_2(PMe_3)_2$	−0.46	2.006	17.5	39.5	1
$CpMoI_2(PMe_3)_2$	−0.42	2.046	18.0	35.0	1
$CpMoICl(PMe_3)_2$	−0.48	2.015	17.9	39.3	4, 7
$CpMoCl_2(PEt_3)_2$	−0.62	1.978	13.4	39.4	This work
$CpMoCl_2(PPr^n{}_3)_2$	−0.63	1.979	13.4	38.8	This work
$CpMoCl_2(PBu^n{}_3)_2$	−0.62	1.981	13.3	39.8	This work
$CpMoCl_2(PMe_2Ph)_2$	−0.55	1.994	15.7	42.6	This work[d]
$CpMoCl_2(PMePh_2)_2$	−0.43	1.978[e]	9	40	This work
$CpMoCl_2(PPh_3)_2$	−0.38	1.978	10.7	41.6	This work
$CpMoI_2(PMePh_2)_2$		2.042[e]	15	34	This work
$CpMoI_2(PPh_3)_2$		2.056	14		This work
2. Bidentate phosphine complexes					
$CpMoCl_2(dppe)$	−0.33	1.986	26	29	2
$CpMoBr_2(dppe)$	−0.26	2.014	23		2
$CpMoI_2(dppe)$	−0.20	2.054			2
$CpMoCl_2(dmpe)$[f]		1.993	28	33	3
$CpMoBr_2(dmpe)$[f]		2.009	27		3
$CpMoI_2(dmpe)$[f]		2.043			3

[a] Solvent = CH_2Cl_2 unless otherwise stated.

[b] Half-wave potential for the first reversible one-electron oxidation process. Values are reported versus the internal ferrocene/ferricinium standard, which was added to the solution at the end of each experiment.

[c] X-band spectra; values in cm^{-1} can be obtained by the formula: $a\ (cm^{-1}) = a\ (G) \times g \times \beta$ ($\beta = 4.6686 \times 10^{-5}\ cm^{-1}\ G^{-1}$).

[d] EPR data in THF solution are from ref. 5.

[e] Value for the four-legged piano stool isomer (see the Results).

[f] THF solvent.

Phosphine exchange equilibrium studies

These investigations were carried out by mixing a given $CpMoCl_2L_2$ complex and a given L′ free phosphine in a determined stoichiometric ratio (see Table 2) in a determined amount of solvent (concentration of the Mo complex $\leqslant 2 \times 10^{-2}$ M). The reaction was monitored by EPR spectroscopy. Most of the reactions involving phosphine ligands that are sensitive to chlorinated hydrocarbons were carried out in THF or toluene as a solvent. CH_2Cl_2 was used for the exchange reactions involving the dppe complex as a starting material or product, since this compound is insufficiently soluble in toluene and THF.

Formation of $CpMoI_2L_2$ (L = $PMePh_2$, PPh_3)

These compounds were generated in solution by halide exchange from the corresponding CpMo Cl_2L_2 and anhydrous NaI in THF, by analogy with the preparation of $CpMoI_2(PMe_3)_2$ from $CpMoCl_2(PMe_3)_2$.[4] The exchange took only a few minutes to occur in each case. The products were only characterized in solution by EPR (see Table 1) and not isolated.

X-ray crystallography

(a) $CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$. Crystals suitable for X-ray structural determination were mounted on a glass fibre with epoxy cement. Table 3 lists crystal parameters, data collection and refinement parameters. The unit cell parameters were obtained from the least-squares fit of 25 reflections ($20° \leqslant 2\theta \leqslant 25°$). Systematic absences in the diffraction data uniquely established the space group as $P2_1/c$. No correction for absorption was required (low μ, well-shaped crystal, T_{max}/T_{min} = 1.063).

The structure was solved by heavy-atom methods

Table 2. Phosphine exchange equilibrium studies

Starting material	Free phosphine					
	PPh_3	$PMePh_2$	dppe	PEt_3	PMe_2Ph	PMe_3
$CpMoCl_2(PPh_3)_2$		2.2 : 1/toluene equilibrium (favours $PMePh_2$)	xs/THF quantitative 1 : 1/CH_2Cl_2 quantitative	2.5 : 1/CH_2Cl_2 quantitative	2.8 : 1/CH_2Cl_2 quantitative	2.6 : 1/CH_2Cl_2 quantitative
$CpMoCl_2(PMePh_2)_2$	2.2 : 1/toluene equilibrium (favours $PMePh_2$)		1.1 : 1/CH_2Cl_2 quantitative	2.0 : 1/toluene quantitative	2.0 : 1/toluene quantitative	2.1 : 1/toluene quantitative
$CpMoCl_2(dppe)$		2.3 : 1/CH_2Cl_2 no reaction		3.7 : 1/CH_2Cl_2 almost quantitative 2.1 : 1/CH_2Cl_2[a] equilibrium (favours dppe)	2.2 : 1/CH_2Cl_2 equilibrium	2.3 : 1/CH_2Cl_2 quantitative
$CpMoCl_2(PEt_3)_2$			1 : 1/CH_2Cl_2 dppe complex forms[b]		2.0 : 1/toluene equilibrium	4.5 : 1/CH_2Cl_2 and 2.1 : 1/toluene both quantitative
$CpMoCl_2(PMe_2Ph)_2$				2.0 : 1/toluene equilibrium		2.2 : 1/toluene quantitative
$CpMoCl_2(PMe_3)_2$				4.5 : 1/toluene no exchange	20 : 1/toluene equilibrium	

[a] After 24 h, the equilibrium starts to shift back towards the starting dppe complex.
[b] Minor exchange after 3 h; >90% exchange after 5 days at room temperature.

Table 3. Crystal data for compounds $CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$ and $CpMoCl_2(PPh_3)_2$

Compound	$CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$	$CpMoCl_2(PPh_3)_2$
Formula	$C_{32}H_{33}Cl_4MoP_2$	$C_{41}H_{35}Cl_2MoP_2$
fw	717.26	756.52
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pccn*
a (Å)	10.076(2)	48.208(6)
b (Å)	19.375(4)	9.169(2)
c (Å)	16.799(4)	15.925(2)
β (°)	104.12(2)	
V (Å^3)	3180.6(14)	7039(3)
Z	4	8
Crystal dimensions (mm)	$0.32 \times 0.41 \times 0.51$	$0.1 \times 0.3 \times 0.4$
Crystal colour	Cherry red	Deep red
d_{calc} (g cm^{-3})	1.498	1.43
μ (cm^{-1})	8.61 (Mo-K_α)	56.47 (Cu-K_α)
Temperature (K)	297	296
T_{max}/T_{min}	1.063	2.012
Diffractometer	Nicolet R3m	Enraf–Nonius CAD4
Monochromator	Graphite	Graphite
Radiation	Mo-K_α (λ = 0.71073 Å)	Cu-K_α (λ = 1.54178 Å)
2θ scan range (°)	4–51	4–110
Data collected (h, k, l)	± 13, $+24$, $+21$	$+51$, $+9$, $+16$
Collected, independent, observed ($F_o \geqslant n\sigma(F_o)$) reflections	6331, 5918, 4050 (n = 5)	5035, 5035, 2076 (n = 6)
R (merg) (%)	1.92	
Standard reflections	3 standard/197 reflections	3 standard/197 reflections
Variations in standards (%)	<1	3.2
$R(F)^a$ (%)	3.95	4.8
$R(wF)^b$ (%)	4.31	6.0
Δ/σ (max)	0.040	0.07
$\Delta(\rho)$ (e Å^{-3})	0.329	0.42
N_o/N_v	13.3	8.8
GOF^c	1.060	1.17

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

which located the molybdenum atom. The remaining non-hydrogen atoms were located through subsequent difference-Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions [d(CH) = 0.960 Å, $U = 1.2U$ for attached C] and the phenyl rings were constrained as rigid, planar hexagons [d(CC) = 1.396 Å]. All non-hydrogen atoms were refined with anisotropic thermal parameters. For each molecule of $CpMoCl_2(PMePh_2)_2$ there is a molecule of methylene chloride located in the lattice. All software and the sources of the scattering factors are contained in the SHELXTL program library.[9]*

(b) $CpMoCl_2(PPh_3)_2$. A suitable single crystal was mounted in a thin-walled glass capillary which was flame-sealed under a dinitrogen atmosphere. Crystal parameters, data collection and structure refinement parameters are collected in Table 3. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° $\leqslant 2\theta \leqslant$ 45°). Systematic absences in the diffraction data uniquely established the space group as *Pccn*. The data were corrected for Lorentz and polarization factors, and also for absorption.[10]

The method of solution and treatment of hydrogen atoms is the same as was used above; however, only the Mo, Cl, P and C atoms of the Cp ring were refined anisotropically. The carbon atoms of the phenyl groups were refined freely as isotropic contributors. All software and the sources of the

* Full tables of bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates and F_oF_c data for compounds $CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$ and $CpMoCl_2(PPh_3)_2$ have been deposited with the Editor as supplementary material. The atomic positional parameters have been deposited with the Cambridge Crystallographic Data Centre.

Table 4. Selected bond distances (Å) and angles (°) for compounds $CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$ and $CpMoCl_2(PPh_3)_2$

$CpMoCl_2(PMePh_2)_2 \cdot CH_2Cl_2$		$CpMoCl_2(PPh_3)_2$	
Mo—P(1)	2.534(1)		2.546(3)
Mo—P(2)	2.528(1)		2.547(3)
Mo—Cl(1)	2.466(1)		2.457(3)
Mo—Cl(2)	2.477(1)		2.451(3)
Mo—CNT*	1.943(5)		1.96(1)
P(1)—C(16)	1.837(3)	P(1)—C(10)	1.86(1)
P(1)—C(26)	1.838(3)	P(1)—C(20)	1.81(1)
P(1)—C(27)	1.811(5)	P(1)—C(30)	1.85(1)
P(2)—C(36)	1.833(3)	P(2)—C(40)	1.83(1)
P(2)—C(46)	1.833(3)	P(2)—C(50)	1.84(1)
P(2)—C(47)	1.826(5)	P(2)—C(60)	1.85(1)
P(1)—Mo—P(2)	145.8(1)		141.7(1)
P(1)—Mo—Cl(1)	80.6(1)		81.5(1)
P(1)—Mo—Cl(2)	79.8(1)		77.7(1)
P(1)—Mo—CNT	107.1(2)		109.4(4)
P(2)—Mo—Cl(1)	80.0(1)		80.7(1)
P(2)—Mo—Cl(2)	78.7(1)		80.1(1)
P(2)—Mo—CNT	107.1(2)		109.1(3)
Cl(1)—Mo—Cl(2)	105.6(1)		115.9(1)
Cl(1)—Mo—CNT	123.0(2)		122.2(4)
Cl(2)—Mo—CNT	131.4(2)		121.8(3)

scattering factors are contained in the TEXSAN program library.[11] Selected bond distances and angles for both compounds are collected in Table 4. Additional crystallographic data are available as supplementary material.

RESULTS

Syntheses

The $CpMoCl_2L_2$ complexes described in this report were prepared or generated in solution by one or more of three different methods (see Experimental for details): (1) from $CpMoCl_2$ and two equivalents of the desired phosphine [eq. (1)], by analogy to the reported preparation of $CpMoCl_2(PMe_3)_2$;[4] (2) from $MoCl_3(THF)_3$, two equivalents of phosphine and CpTl [eq. (2)], by analogy to the reported preparation of $CpMoCl_2(PMe_3)_2$[1] and $CpMoCl_2(dppe)$;[2] and (3) by phosphine exchange from the bis-PPh_3 complex $CpMoCl_2(PPh_3)_2$ [eq. (3)].

$$CpMoCl_2 + 2L \longrightarrow CpMoCl_2L_2 \quad (1)$$

$$MoCl_3(THF)_3 + 2L + CpTl \longrightarrow CpMoCl_2L_2 + 3THF + TlCl \quad (2)$$

$$CpMoCl_2(PPh_3)_2 + 2L \longrightarrow CpMoCl_2L_2 + 2PPh_3 \quad (3)$$

Equation (3) is very practical for generating the desired complexes in solution because the PPh_3 complex is easily prepared as an analyically pure, crystalline solid, and because all other phosphines replace PPh_3 quantitatively (*vide infra*). We have not isolated the products obtained through this phosphine exchange procedure, since we were only interested in investigating their EPR and electrochemical properties in solution. Both EPR and cyclic voltammetric investigations of these solutions showed no evidence for the formation of compounds other than the desired products of phosphine exchange.

The iodide complexes $CpMoI_2L_2$ ($L = PMePh_2$, PPh_3) were generated in solution by the halide exchange reaction starting from the corresponding dichloride complexes [eq. (4)], by analogy to the reported preparation of $CpMoI_2(PMe_3)_2$ from $CpMoCl_2(PMe_3)_2$.[4] Again, as we were only interested in the solution properties of these materials, they were not isolated. These reactions are much faster than the corresponding exchange in the PMe_3 case where the intermediate mixed-halide compound $CpMoICl(PMe_3)_2$ could be selectively generated and isolated.[4]

$$CpMoCl_2L_2 + 2NaI \longrightarrow CpMoI_2L_2 + 2NaCl \quad (4)$$

EPR characterization

It has been observed before that the EPR signals of complexes in the series $CpMoX_2(PMe_3)_2$,[1] $CpMoX_2(dppe)$[2] and $CpMoX_2(dmpe)$[3] experience a shift to higher g values on going from X = Cl to X = I, whereas the position of the signal is not greatly affected by the nature of the phosphorus donors. The results reported here confirm this general trend (see Table 1). The dichloride complexes exhibit g values in the 1.978–1.994 range, while the g value observed for the diiodide complexes is in the 2.042–2.056 range. The a_P and a_{Mo} constants also seem to correlate to a certain extent with the nature of X, although the variations in these cases are small compared to the experimental error. There also seems to be a dependence of a_P and a_{Mo} on the nature of the neutral donor. The most significant changes are observed on going from bis-(monodentate phosphine) to diphosphine complexes (the geometry changing from *trans* to *cis* in this series, *vide infra*), where an increase of the a_P value from 9–16 to 23–28 G is observed and, correspondingly, the a_{Mo} parameter slightly decreases from 38–41 to 29–33 G. The smallest a_P values are observed for the $PMePh_2$ and PPh_3 dichloride complexes which, as the X-ray structural results show (*vide infra*), have longer Mo—P distances compared to the previously reported PMe_3 and dppe analogues.[1,2] As for most of the complexes of this class published previously,[1–4] we have not been able to discern any hyperfine splitting due to coupling to the halogen nuclear spins in any of the spectra reported here.

The most interesting observation is the complex shape of the EPR spectrum for the compound $CpMoCl_2(PMePh_2)_2$ [see Fig. 1(a)]. This is at variance with the spectra observed for the other members of the $CpMoCl_2(PMe_xPh_{3-x})_2$ series, which show a simple binomial triplet with molybdenum satellites. The high-field part of the complex pattern shown in Fig. 1(a) resembles the high-field half of a binomial triplet, which would have $g = 1.978$ in good agreement with the value observed for other dichloride complexes, whereas the other signals are located in a region around an approximate g value of 2.00.

The possibility that the other resonances are due to by-products or products of decomposition due to reaction with the solvent or adventitious air and/or moisture is excluded based on the following observations: (1) an identical pattern is obtained by generating the compound *in situ* by two different synthetic pathways [eqs (1) and (2)], or by redissolving the analytically pure crystalline solid; (2) an identical pattern within experimental error is observed in CH_2Cl_2 and THF; and (3) the deliberate exposure of the solution to air leads to a decrease of *all the resonances* shown in Fig. 1(a) and to the appearance of new resonances. Further observations suggest that the additional signals are due to one or more different isomers in equilibrium with the main isomer, whose signal is a triplet centred at $g = 1.978$. These are: (1) a homogeneous sample (by microscopic inspection) of large crystals of the mono-CH_2Cl_2 solvate (found to have a four-legged piano stool structure by X-ray crystallography, *vide infra*) was dissolved in CH_2Cl_2 at low temperature and investigated immediately by EPR: the first spectrum showed a slightly different pattern than shown in Fig. 1(a), with a predominant triplet at $g = 1.978$ and smaller resonances at higher g, but subsequent recordings once again gave a pattern identical to that shown in Fig. 1(a); and (2) quantitative phosphine exchange reactions (described in more detail below) of $CpMoCl_2(PMePh_2)_2$ with dppe, PEt_3, PMe_2Ph and PMe_3 generate EPR spectra attributable to the pure products of exchange as the only observable species.

A possible alternative hypothesis to account for additional resonances would be an equilibrium with a different compound resulting from dissociation of phosphine ligands, e.g. a 15-electron $CpMoCl_2(PMePh_2)$ complex. This is ruled out by the observation of unchanged EPR spectral properties upon the addition of a large excess of free PMe_2Ph.

Variable-temperature EPR investigations did not help establish which isomeric form has the lowest energy, because the Boltzmann factor in the temperature range that can be investigated by isotropic techniques is not significantly altered. For instance, assuming that a 60:40 mixture of two isomers is present at 298 K (which corresponds to a 1.00 KJ energy difference between the two ground states), this would merely change to *ca* 64:36 upon cooling to 210 K. The broadening of the EPR lines observed during this temperature change causes more dramatic effects on the individual peak heights than would such a small variation of isomer distribution.

A complex pattern was also observed for the diiodide analogues of the $PMePh_2$ complex, $CpMoI_2(PMePh_2)_2$ [see Fig. 1(g)], but not for the corresponding PPh_3 complex. The approximate appearance of this spectrum is that of a quintet, but the observed relative intensities do not match with those expected (computer simulation) for a binomial quintet. In addition, the observed pattern in Fig. 1(g) does not show a perfect inversion symmetry which would be expected for the spectrum of a single compound. A possible alternative involves

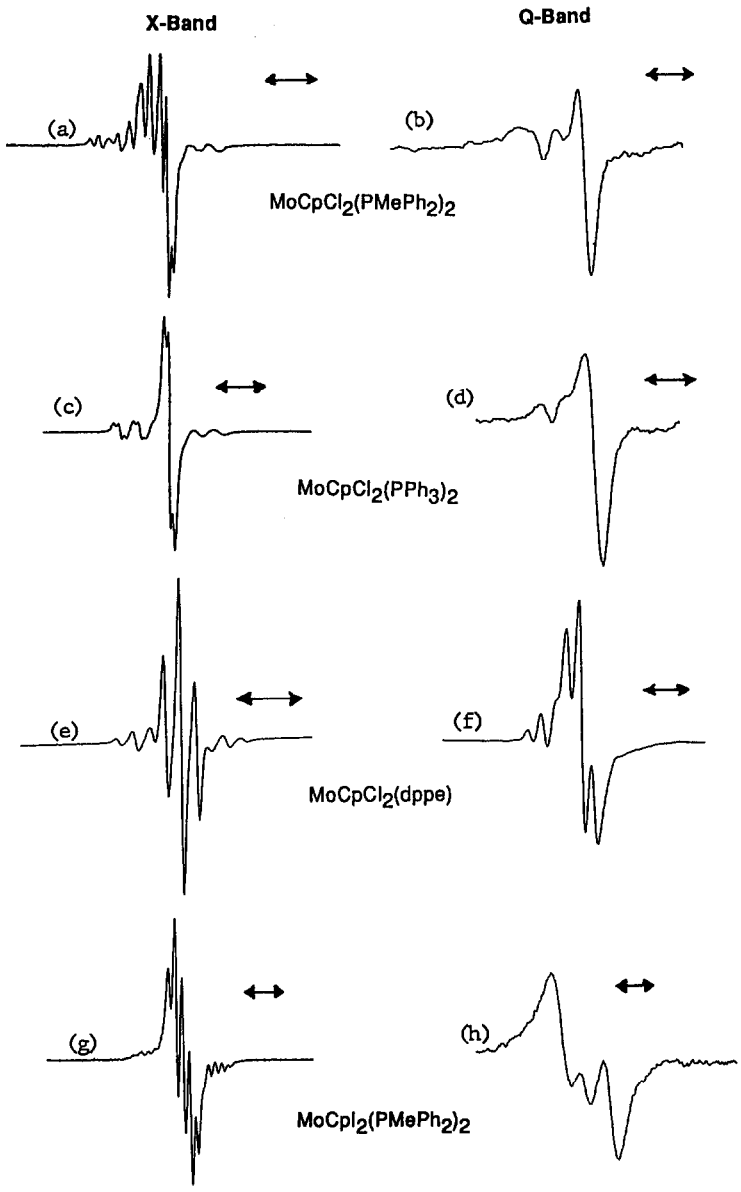


Fig. 1. Room-temperature EPR spectra of $CpMoX_2L_2$ complexes in CH_2Cl_2: (a) and (b) X = Cl, L = $PMePh_2$; (c) and (d) X = Cl, L = PPh_3; (e) and (f) X = Cl, L_2 = dppe; (g) and (h) X = I, L = $PMePh_2$. (a), (c), (e) and (g) are *X*-band spectra; (b), (d), (f) and (h) are *Q*-band spectra. Spectra are not shown on the same *g* scale. Refer to Table 1 for *g* values and hyperfine splitting parameters. The double-pointed arrow markers indicate a 100 G range.

the accidental overlap of two triplets. If we assign, by analogy to the dichloride complex of Fig. 1(a), the high-field portion of the spectrum to a binomial triplet which is due to the four-legged piano stool structure, the measured *g* value of 2.042 for this triplet is in the correct range found for other diiodide four-legged piano stool complexes (see Table 1). Thus, we believe that we have again an equilibrium of isomers.

With the hope of spreading out the partially overlapping resonances of the $CpMoX_2(PMePh_2)_2$ isomers (X = Cl, I), we have obtained *Q*-band EPR spectra for these complexes [see Fig. 1(b) and (h)]. Unfortunately, there is a general line broadening on going from X-band to *Q*-band spectra, which does not permit to observe phosphorus couplings and thus to draw conclusions on the number of isomers present and their symmetry. We were, however, surprised to find that compounds that show symmetrical *X*-band EPR spectra [e.g. $CpMoCl_2(PPh_3)_2$ and the previously reported[2] $CpMoCl_2$(dppe)] also show asymmetric EPR spectra at the

Q-band frequency, suggesting the freezing-out of isomer equilibria also in these cases [see Fig. (1)]. For the $CpMoX_2(PMe_3)_2$ (X = Cl, I) compounds, the spectra (not shown) are symmetric at both X- and Q-band frequencies.

Qualitative phosphine exchange studies

Table 2 illustrates the exchange studies that have been carried out [eq. (5)]. The equilibrium position can be determined only qualitatively because of the minor changes of g and hyperfine splitting parameters. The data in Table 2 indicate a relative stability of the $CpMoCl_2L_2$ system in the order $PPh_3 < PMePh_2 \ll$ dppe $\approx PEt_3 \approx PMe_2Ph \ll PMe_3$.

$$CpMoCl_2L_2 + 2L' \rightleftharpoons CpMoCl_2L'_2 + 2L \quad (5)$$

The free phosphines PMe_3, PMe_2Ph and PEt_3 are known to slowly react with CH_2Cl_2 to give phosphonium products.[12] This reactivity does not present complications when equilibrium (5) is investigated in CH_2Cl_2, as long as the exchange is quantitative in either direction. However, if an equilibrium position is attained, then the reaction of the free phosphine with the solvent is expected to slowly shift the equilibrium towards the formation of the complex with the less sensitive phosphine. This is the case for the reaction of $CpMoCl_2$(dppe) with PEt_3, or for the corresponding reverse reaction of $CpMoCl_2(PEt_3)_2$ with dppe (see footnotes [b] and [c] of Table 2). CH_2Cl_2 must be used in the reactions that involve the dppe complex, since this complex is not sufficiently soluble in any other solvent. In all other cases, equilibrium reactions involving phosphines that are sensitive to chlorinated hydrocarbons were conducted in toluene or THF.

X-ray structures

The general structural features of the $CpMoCl_2(PMePh_2)_2$ and $CpMoCl_2(PPh_3)_2$ molecules, drawings of which are shown respectively in Figs 2 and 3, are similar to those already described and discussed for the analogous compounds $CpMoX_2(PMe_3)_2$ (X = Cl, I)[1] and $CpMoICl(PMe_3)_2$.[4] We shall limit our discussion here to the differences encountered on going from the $CpMoCl_2(PMe_3)_2$ compound to the $PMePh_2$ and PPh_3 analogues.

While the average Mo—Cl distances are similar in the three compounds [2.471(3), 2.472(5) and 2.454(3) Å for the PMe_3, $PMePh_2$ and PPh_3 complexes, respectively], the average Mo—P distance substantially increases along with the size of the phosphine [2.482(2), 2.531(3) and 2.546(3) Å, respectively]. The Mo—P distance in the PMe_3 complex was described as exceptionally short compared to other typical Mo^{III}—PR_3 distances[1] and a rationalization was given based on a substantial π-back-bonding contribution to the Mo—P bond. This effect is apparently counterbalanced by the increase of steric bulk for the larger $PMePh_2$ and PPh_3 ligands. The back-bonding capability of the molybdenum centre in the $PMePh_2$ and PPh_3 complexes is evidenced by the asymmetry of the Mo—Cp moiety, which is comparable in each case to that observed for the PMe_3 complex[1] and which can be attributed, according to a published theoretical analysis,[13] to the Mo—Cp δ interaction.

The angular distortions around the $MCl_2(PR_3)_2$

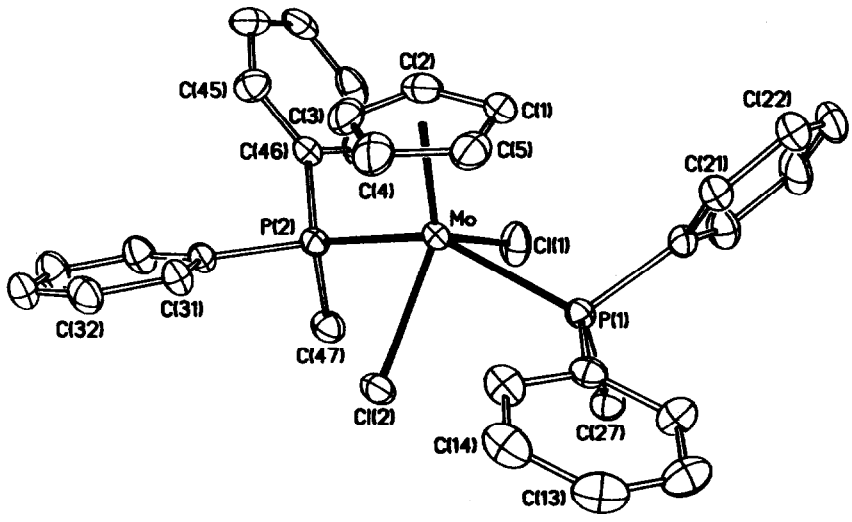


Fig. 2. An ORTEP view of the $CpMoCl_2(PMePh_2)_2$ molecule showing the atomic numbering scheme employed. Ellipsoids are drawn at the 40% level.

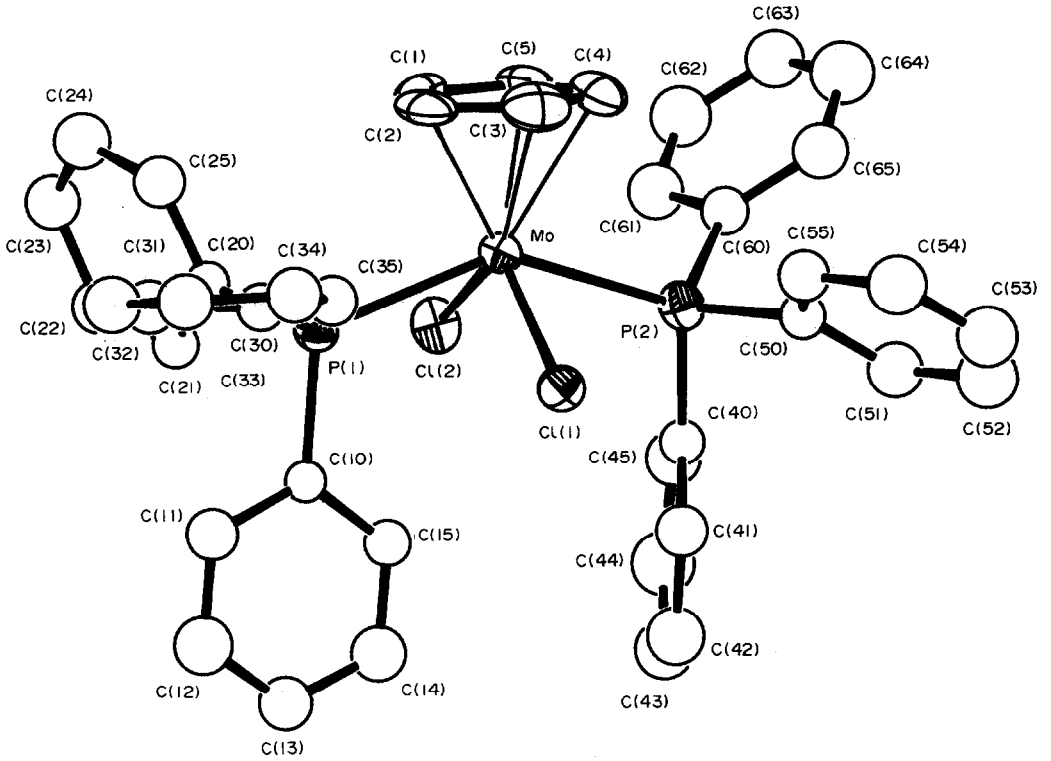


Fig. 3. An ORTEP view of the $CpMoCl_2(PPh_3)_2$ molecule showing the atomic numbering scheme employed. Ellipsoids are drawn at the 40% level.

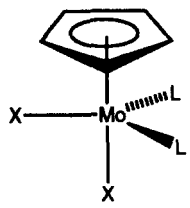
base of the structure, as expressed by the Cp (centre)—Mo—L angles, θ_L,[14] are somewhat interesting. The average θ_P angles are similar in the PMe_3, $PMePh_2$ and PPh_3 compounds, i.e. 113.1,[1] 107.1 and 109.2°, respectively. However, whereas the θ_{Cl} angles average 117.4 for the PMe_3 complex and 122.0 for the PPh_3 complex, with both individual parameters in close proximity of the average value for both complexes, the $PMePh_2$ structure shows two very different θ_{Cl} angles for the two chloride ligands, i.e. 123.0(2) and 131.4(2)° for Cl(1) and Cl(2), respectively. We do not see an obvious reason for this asymmetry. There is no apparent steric compression on the position occupied by Cl(2) because the two phosphine ligands remain firmly located along the directions of the corner of a square in a projection down the Mo—Cp(centre) vector. In addition, the corresponding PPh_3 complex has even bulkier phosphine ligands, but nevertheless the two chloride ligands display similar θ angles.

DISCUSSION

This paper extends the class of 17-electron $CpMoX_2L_2$ compounds (X = halogen; L = tertiary phosphine). Previously reported complexes had L = PMe_3[1,4] or L_2 = dppe[2] and dmpe.[3] The new derivatives have similar EPR spectroscopic properties to those reported for the above-mentioned compounds, showing in most cases a binomial triplet with molybdenum satellites for the *X*-band spectra. However, the spectrum is more complex for the compounds $CpMoX_2(PMePh_2)_2$ (X = Cl, I) [see Fig. 1(a) and (g)]. Detailed studies described in the Results for the chloride complex indicate an equilibrium between a four-legged piano stool structure and one or more additional isomers in solution. The equilibrium, slow on the *X*-band EPR time-scale, is rapidly established from the crystalline solid, which has the four-legged piano stool structure. EPR studies at the *Q*-band frequency show that whereas the PMe_3 derivative still gives a symmetric feature, the more encumbered PPh_3 derivative gives a feature similar to that of the $PMePh_2$ derivative, indicating that we again have isomers.

Detailed information on the number and type of isomers could not be obtained because of the extensive overlap or fluxionality in the *X*-band spectra, and because of line-broadening in the *Q*-band spectra. According to a theoretical analysis,[13] the four-legged piano stool structure is of the lowest energy, followed by a pseudo-trigonal bipyramidal structure where the Cp ring and another ligand

occupy the two axial positions. According to these calculations, π-acceptor ligands should prefer to be located in the trigonal plane, whereas π-donor ligands should occupy preferentially the axial position *trans* to the Cp ring. For the compounds $CpMoX_2(PMePh_2)_2$ (X = Cl, I), then, a pseudo-trigonal bipyramidal structure with X *trans* to Cp would seem most likely (see **I**). In this regard, it is



I

interesting to note that the structure of $CpMoCl_2(PMePh_2)_2$ (Fig. 2), although clearly of the four-legged piano stool type, shows a significant distortion of the Mo—Cl(2) bond. This bond is bent further down by *ca* 10° with respect to the Mo—Cl(1) bond, towards the pseudo-axial position of the hypothetical structure **I**.

We point out that for the previously reported[2] dppe complex, which equally shows freezing out of an isomer equilibrium on the *Q*-band EPR time-scale [Fig. 1(f)], crystallographic evidence (on the corresponding dibromide complex)[2] indicates a four-legged piano stool structure with a *cis* rather than *trans* arrangement within the four "leg" positions. However, the dppe chelate should not prevent the molecule from assuming alternate geometries based on the trigonal bipyramid. An alternative possibility is that the minor isomer is *cis*-$CpMoX_2L_2$ for the compounds with monodentate phosphines, where the major isomer adopts the *trans* geometry, and vice versa for the complexes with bidentate phosphines. A *trans* arrangement for four-legged piano stool compounds containing chelating diphosphines is well established.[15] This hypothesis, however, does not appear to easily reconcile with the similarity of the *Q*-band spectra of $CpMoCl_2L_2$ (L = $PMePh_2$, PPh_3) (*trans* geometry in the solid state) and $CpMoCl_2$(dppe) (*cis* geometry in the solid state for the dibromide analogue). The observed behaviour could be consistent with this hypothesis only if the dppe complex affords a *trans* major isomer in solution.

Worthy of note here is the reported fluxional behaviour of the related 18-electron compounds $CpMX(CO)L_2$ [M = Mo, W; X = Cl, Br, I; L = $PMePh_2$, $P(OMe)Ph_2$], which show as many as five different isomers at low temperature.[16] These isomers have been assigned to the two *cis* and *trans* piano stool structures and to the three possible pseudo-trigonal bipyramidal structures. To the best of our knowledge, the present report is the first one containing evidence for the existence of isomers other than the four-legged piano stool for 17-electron systems of the (η-ring)ML_4 type.

To summarize the isomer equilibrium story, we can conclude that equilibria between different isomers are established for all these 17-electron $CpMoX_2L_2$ complexes, but in most cases these are too rapid in the *X*-band EPR time-scale and only an average symmetric spectrum is observed. In the case of the PMe_3 complexes (X = Cl and I), if an equilibrium exists to give observable Boltzmann populations of other isomers, this is fast even in the *Q*-band EPR time-scale.

One of the original interests of this study was the qualitative investigation of the relationship between the oxidation potential, the EPR properties and the thermodynamic stability of the compound. According to the results of Fenske–Hall calculations on the model compound $CpMoCl_2(PH_3)_2$,[1] the HOMO and SHOMO have Mo—P π and Mo—Cl π^* contributions. Thus, keeping constant the nature of the halogen, the introduction of a more π-acidic phosphine should lower the energy of HOMO and SHOMO and increase the oxidation potential. This is indeed observed within the series of PMe_xPh_{3-x} compounds with the PMe_2Ph complex as the only exception.

In spite of the suggested (by the electrochemical data) higher π-acidity of $PMePh_2$ and PPh_3, the derivatives with these phosphines have *longer* Mo—P bonds in the solid state with respect to the PMe_3 derivative. Two factors could be held responsible for this effect: the first is a greater importance of σ contributions for the determination of the Mo—P distance. However, we observe that metal–phosphorus distances are notoriously more sensitive to π than to σ effects.[17] The second factor is the increased steric congestion around the metal on going from the PMe_3 complex to the compounds with the bulkier phosphines. The importance of σ effects is usually strongly reflected in the thermodynamic strength of the M—P bond.[18] Consistent with these expectations, phosphine exchange equilibria always favour the complex with the stronger σ-donor phosphine ligand, with the exception of the dppe complex which enjoys the additional thermodynamic stabilization of the chelate effect (see Table 2).

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