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Rinaldo Poli, Malcolm Kelland. Synthesis, characterization, and reactivity of cyclopentadienyltrichloromolybdenum(IV). X-Ray structure of  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ). Journal of Organometallic Chemistry, 1991, 419 (1-2), pp.127-136. 10.1016/0022-328X(91)86169-Q. hal-03542741

**HAL Id: hal-03542741**

**<https://hal.science/hal-03542741>**

Submitted on 25 Jan 2022

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# Synthesis, characterization, and reactivity of cyclopentadienyltrichloromolybdenum(IV). X-Ray structure of $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$ ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ )

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(Received March 25th, 1991; in revised form June 3rd, 1991)

## Abstract

$\text{CpMoCl}_3$  has been generated by either oxidation of  $\text{CpMoCl}_2$  with  $\text{PhI}\cdot\text{Cl}_2$ , reduction of  $\text{CpMoCl}_4$  with  $\text{TiCl}_3$ , or valence comproportionation of  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$ . Low-energy IR spectroscopy and powder X-ray diffraction establish that this material is different from a 1:1 mixture of  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$ . The 18-electron adducts  $\text{CpMoCl}_3(\text{L-L})$  ( $\text{L-L} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) and  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  have been obtained by interaction with the appropriate free ligand, while the reaction with  $\text{PMe}_3$  leads to decomposition with formation of several different products. The crystal structure of the cage phosphite complex shows a pseudo-octahedral configuration with a facial arrangement of the three chloride ions.

## Introduction

We have recently investigated the chemistry of cyclopentadienylmolybdenum(III) complexes [1]. The starting material for the preparation of these compounds was  $\text{CpMoCl}_2$ , which was prepared by zinc reduction of  $\text{CpMoCl}_4$  [2]. While investigating the kinetics and mechanism of the halide exchange on the  $\text{CpMoX}_2(\text{PMe}_3)_2$  ( $\text{X} = \text{Cl, I}$ ) class of compounds [3], we have discovered that these substitutions are catalyzed by oxidation which produces complexes with the metal in the oxidation state +IV [4]. We were therefore interested in synthesizing cyclopentadienylmolybdenum(IV) complexes in order to probe their effectiveness as catalysts in the substitution reaction and to verify their viability as intermediates in the catalytic cycle. An attractive starting material for complexes of this kind was  $\text{CpMoCl}_3$ .

A careful survey of the literature [5] showed that this material had not yet been reported. Green [6] and Haines et al. [7] independently reported that oxidation of  $\text{CpMoCl}(\text{CO})_3$  with chlorine affords  $\text{CpMoCl}_3(\text{CO})_2$  and, according to the latter authors [7], this compound decomposes rapidly in solution with evolution of CO. They, however, did not investigate the product of this decomposition. We report here the preparation and characterization of  $\text{CpMoCl}_3$  and the formation of a few adducts, including the crystal structure of the bis-adduct with the cage phosphite,  $\text{P}(\text{OCH}_2)_3\text{CEt}$ .

## Experimental

All operations were conducted under an atmosphere of dinitrogen or argon by using standard Schlenk line and glove box techniques. Solvents were carefully dried by conventional methods and distilled under dinitrogen prior to use.

Instruments used were as follows: IR, Perkin–Elmer 1800; NMR, Bruker AF200, WP200, and AM400; X-ray powder diffraction, Phillips XRD 2000, operated by the MDI software. Elemental analyses were by M-H-W laboratories, Phoenix, Arizona.  $\text{CpMoCl}_4$  [1b] and  $\text{CpMoCl}_2$  [2a] were prepared as described previously. Dppe and dmpe were purchased from Strem Chemicals and used as received,  $\text{TiCl}_3$  (1 M solution in 2:1  $\text{CH}_2\text{Cl}_2$ /THF) was purchased from Aldrich and used as received, and  $\text{P}(\text{OCH}_2)_3\text{CEt}$  was prepared as described in the literature [8].

### Preparation of $\text{CpMoCl}_3$

(a) *By oxidation of  $\text{CpMoCl}_2$ .*  $\text{PhI} \cdot \text{Cl}_2$  (0.297 g, 1.08 mmol) was added to a stirred slurry of  $\text{CpMoCl}_2$  (0.50 g, 2.2 mmol) in  $\text{CH}_2\text{Cl}_2$ . The light brown precipitate darkened and dissolved to give an orange-brown solution and then a dark brown precipitate was deposited. After 10 min stirring at room temperature, the solution was filtered and the precipitate washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 5$  mL) and dried *in vacuo*. Yield 0.52 g, 90%.

(b) *By reduction of  $\text{CpMoCl}_4$ .*  $\text{TiCl}_3$  (0.4 mL of a 1.0 M solution in  $\text{CH}_2\text{Cl}_2$ /THF, 0.4 mmol) was added to a stirred slurry of  $\text{CpMoCl}_4$  (0.12 g, 0.40 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL). A dark orange-brown solution formed immediately which deposited a dark brown precipitate over 1–2 min. The pale orange-brown solution was filtered off and the precipitate was washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 3$  mL) and dried *in vacuo*. Yield 0.10 g, 95%. Anal. Found: C, 22.5; H, 1.7; Cl, 39.6.  $\text{C}_5\text{H}_5\text{Cl}_3\text{Mo}$  calcd.: C, 22.5; H, 1.9; Cl, 40.0. The low-energy IR spectrum (Nujol mull, CsI optics,  $\text{cm}^{-1}$ ) is reported in Fig. 1 in comparison with those of  $\text{CpMoCl}_4$  and  $\text{CpMoCl}_2$ :  $\text{CpMoCl}_4$ : 354.0s, 337.7s, 325.2s, 314.7s;  $\text{CpMoCl}_3$ : 386.1m, 339.4m, 318.5s, 299.3s, 293.0m, 266.0m;  $\text{CpMoCl}_2$ : 385.3w, 366.1w, 359.8w, 331.8m, 316.4m, 306.0s, 300.6s, 280.5w, 261.3w.

(c) *By conproportionation of  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$ .*  $\text{CpMoCl}_4$  (0.30 g, 1.0 mmol) and  $\text{CpMoCl}_2$  (0.23 g, 1.0 mmol) were stirred in  $\text{CH}_2\text{Cl}_2$  (10 mL). Immediately an orange-brown solution formed which deposited a dark-brown precipitate over a few minutes. The solution was filtered off and the precipitate was washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 5$  mL) and dried *in vacuo*. Yield 0.48 g, 91%.

The materials from the free above preparations have identical spectroscopic properties.

### Reactions of $\text{CpMoCl}_3$

(a) *With dppe: formation of  $\text{CpMoCl}_3(\text{dppe})$ .* Dppe (0.72 g, 1.81 mmol) was added to a stirred slurry of  $\text{CpMoCl}_3$  (0.48 g, 1.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). A green-brown solution formed which turned orange-brown within 5 min. The solution was reduced in volume to 3–4 mL and layered with 10 mL of n-heptane. After three days the brown-orange crystals were filtered off, washed with n-heptane, and dried *in vacuo*. Yield of  $\text{CpMoCl}_3(\text{dppe}) \cdot \text{CH}_2\text{Cl}_2$ , 1.09 g, 81%.  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 8.2–7.3 (20H,  $\text{C}_6\text{H}_5$ ); 5.35 (s, 2H,  $\text{CH}_2\text{Cl}_2$ ); 5.09 (d, 5H, Cp,  $J(\text{HP}) = 3$  Hz); 3.37 (m, 2H,  $\text{CH}_2$ ); 2.98 (m, 2H,  $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 59.8 (d, 1P,

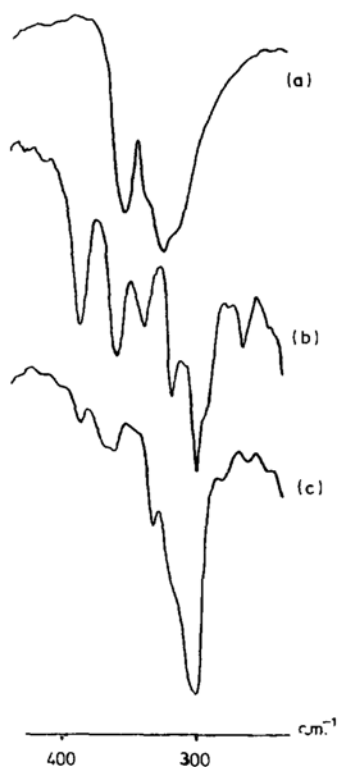


Fig. 1. Low-energy IR spectra of (a)  $\text{CpMoCl}_4$ ; (b)  $\text{CpMoCl}_3$ ; (c)  $\text{CpMoCl}_2$ .

$J = 47 \text{ Hz}$ ); 35.9 (d, 1P,  $J = 47 \text{ Hz}$ ). The NMR spectra are similar to that reported before for  $\text{CpMoCl}_3(\text{dppe}) \cdot \text{MeOH}$  in  $\text{CD}_3\text{CN}$  and for  $\text{CpMoCl}_3(\text{dppe}) \cdot \text{Me}_2\text{CO}$  in  $\text{CD}_2\text{Cl}_2$  [9].

(b) *With dmpe: formation of  $\text{CpMoCl}_3(\text{dmpe})$ .*  $\text{CpMoCl}_3$  (99 mg, 0.37 mmol) was suspended in 5 mL of THF and treated with dmpe (60  $\mu\text{L}$ , 0.40 mmol). The immediate formation of a flocculent grey precipitate was observed. The solvent was completely removed under vacuum and the residue was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ . After removal of small amounts of insoluble material by filtration, the volume of the solution was reduced to ca. 2 mL by evaporation and the product was crystallized by diffusion of 5 mL of *n*-heptane. Yield 81 mg, 52%. The  $^1\text{H}$  and  $^{31}\text{P}$ -NMR properties of this material are identical to those reported for  $\text{CpMoCl}_3(\text{dmpe})$  [10].

(c) *With  $\text{P}(\text{OCH}_2)_3\text{CEt}$ : formation of  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$ .*  $\text{CpMoCl}_3$  (137 mg, 0.51 mmol) was suspended in 10 mL of  $\text{CH}_2\text{Cl}_2$  and treated with  $\text{P}(\text{OCH}_2)_3\text{CEt}$  (175 mg, 1.08 mmol). Within 5 min stirring at room temperature, the brown molybdenum complex reacted to give a clear orange solution. The product was crystallized by cooling to  $-80^\circ\text{C}$ , filtered, and dried *in vacuo*. Yield 114 mg, 38%. Anal. Found: C, 33.9; H, 5.0.  $\text{C}_{17}\text{H}_{27}\text{Cl}_3\text{MoO}_6\text{P}_2$  calcd.: C, 34.5; H, 4.6%.  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 5.69 (t, 5H, Cp,  $J(\text{HP}) = 4.2 \text{ Hz}$ ); 4.34 (t, 12H,  $\text{CH}_2$ ,  $J(\text{HP}) = 2.4 \text{ Hz}$ ); 1.26 (q, 4H,  $\text{CH}_2$ ,  $J = 7.6 \text{ Hz}$ ); 0.83 (t, 6H,  $\text{CH}_3$ ,  $J = 7.6 \text{ Hz}$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 128.9. The mother solution was layered with *n*-heptane (10 mL) to give

58 additional mg of product in the form of large crystals. The  $^1\text{H-NMR}$  of this material is identical with that of the product crystallized at low temperature, with the additional presence of a peak at  $5.33 \delta$  due to  $\text{CH}_2\text{Cl}_2$  of crystallization (3 moles per mole).

The compound is soluble in  $\text{CH}_2\text{Cl}_2$  and insoluble in  $\text{CHCl}_3$  and toluene. The crystal used for the X-ray analysis was obtained from a  $\text{CH}_2\text{Cl}_2$ /n-heptane recrystallization of the residue from the interaction of  $\text{CpMoCl}_2$  and the phosphite ligand, which was carried out in an attempt to prepare the 17-electron  $\text{CpMoCl}_2[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  complex. The first crystals obtained from the n-heptane diffusion were orange and displayed identical NMR properties to those listed above for the trichloride bis-phosphite complex. Relayering the resulting solution with additional n-heptane produced an inseparable mixture of orange crystals and a green waxy material, which was not further characterized.

*NMR investigation of the reaction between  $\text{CpMoCl}_3$  and  $\text{PMe}_3$  (1 : 2 molar ratio)*

53 mg of  $\text{CpMoCl}_3$  (0.20 mmol) were introduced in a Schlenk tube and suspended in 1 mL of  $\text{CD}_2\text{Cl}_2$ . The tube and its contents were cooled to  $-78^\circ\text{C}$  and  $\text{PMe}_3$  (40  $\mu\text{L}$ , 0.40 mmol) was introduced through a microsyringe. The temperature was raised gently resulting in the formation of a dark violet solution, which was then transferred at low temperature into an NMR tube. The NMR tube was cooled further to the liquid nitrogen temperature, flame sealed under vacuum, and thawed back to  $-78^\circ\text{C}$  until it was introduced in the precooled NMR probe (see Results).

*X-Ray crystallography for  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2 \cdot 3\text{CH}_2\text{Cl}_2$*

As the crystals of this compound become opaque upon applying reduced pressure, the crystal chosen for the X-ray analysis was mounted in a capillary under mother liquor and sealed with wax. Orientation, crystal system determination, and data collection and reduction were carried out in a routine manner. No decay of intensity was observed for three periodically monitored standard reflections. A semi-empirical absorption correction [11] was applied to the data.

The position of the Mo atom was obtained from the Patterson map. All computations were carried out by using the TEXSAN package [12]. After the Mo position was refined, the structure was expanded with DIRDIF, which revealed most of the atoms of the molybdenum complex. Subsequent alternate cycles of full-matrix least-squares refinement and difference Fourier maps revealed the rest of the molecule and the three interstitial dichloromethane molecules. Of these, two were partially disordered. Isotropic refinement converged to  $R = 0.13$ . The Mo, P, O, and Cl atoms (including some Cl atoms of the dichloromethane molecules) were then refined with anisotropic thermal parameters. Hydrogen atoms for the Mo complex only were included at calculated positions and used for structure factor calculations but not refined. Final convergence was achieved at  $R = 0.099$ . The relatively high final agreement figures may be ascribed to several factors, among which a non-completely satisfactory absorption correction (transmission factors vary between 1.0 and 0.29) and the high thermal activity and partial disorder of the interstitial dichloromethane molecules. Although the disorder was apparently modelled satisfactorily, several peaks around  $1 \text{ e}/\text{\AA}^3$  remained in the final difference Fourier map in close proximity to the three dichloromethane molecules. They could be due to other minor and unresolved disorder.

Table 1

Selected crystal data for  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2 \cdot 3\text{CH}_2\text{Cl}_2$ 

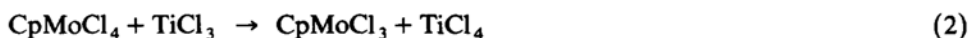
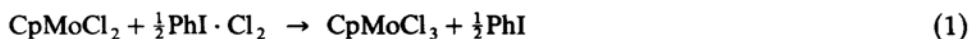
Formula	$\text{C}_{20}\text{H}_{33}\text{Cl}_9\text{MoO}_6\text{P}_2$
F.W.	846.44
space group	$\text{P}\bar{1}$
$a$ , Å	11.096(6)
$b$ , Å	11.917(3)
$c$ , Å	15.415(4)
$\alpha$ , deg	68.90(2)
$\beta$ , deg	89.23(3)
$\gamma$ , deg	64.78(3)
$V$ , Å <sup>3</sup>	1697(2)
$Z$	2
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.66
$\mu(\text{Cu-K}\alpha)$ , cm <sup>-1</sup>	109.96
radiation (monochromated in incident beam)	Cu-K $\alpha$ ( $\lambda = 1.54178$ Å)
Temp., °C	23
transmission factors: max, min	1.000, 0.289
$R^a$	0.099
$R_w^b$	0.120

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

Selected crystal data are listed in Table 1, fractional atomic coordinates for the  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  molecule are reported in Table 2, and selected bond distances and angles are in Table 3.

## Results and discussion

The  $\text{CpMoCl}_3$  material has been prepared by three different methods, which are outlined in eq. 1–3. The oxidation of  $\text{CpMoCl}_2$  must be carried out with the stoichiometric amount of chloride, because an excess results in the conversion to  $\text{CpMoCl}_4$ . For this reason the stoichiometric reagent  $\text{PhI} \cdot \text{Cl}_2$  has been used rather than chlorine itself. The reduction of  $\text{CpMoCl}_4$  had already been investigated. Reduction with the equimolar amount of zinc or with two equivalents of amalgamated sodium affords  $\text{Mo}^{\text{III}}$  materials,  $\text{CpMoCl}_2$  and  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^-$ , respectively [2]. We have now found that the trichloride  $\text{Mo}^{\text{IV}}$  material can be produced selectively by using the equimolar amount of the one-electron reducing agent  $\text{TiCl}_3$ . Finally, conproportionation of equimolar amounts of  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$  also produces  $\text{CpMoCl}_3$ . This last method shows that the  $\text{Mo}^{\text{IV}}$  material is thermodynamically stable with respect to valence disproportionation.



$\text{CpMoCl}_3$  is a brown solid, whereas the tetrachloride is red/purple and the dichloride is golden yellow. When powdery  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$  are mixed in the solid state in a 1 : 1 molar ratio, the resulting material has the same appearance as  $\text{CpMoCl}_3$ . It is therefore imperative to verify that the trichloride product that we

Table 2

Positional parameters and  $B_{\text{eq}}$  for  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CET}]_2 \cdot 3\text{CH}_2\text{Cl}_2$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
Mo	0.0613(3)	0.2275(3)	-0.1597(2)	3.2(3)
Cl(1)	-0.128(1)	0.2996(9)	-0.0716(6)	5(1)
Cl(2)	-0.041(1)	0.0924(8)	-0.1878(6)	4(1)
Cl(3)	-0.122(1)	0.3995(9)	-0.2888(6)	5(1)
P(1)	0.081(1)	0.433(1)	-0.1802(7)	4(1)
P(2)	0.153(1)	0.233(1)	-0.3070(7)	4(1)
O(1)	0.009(3)	0.567(2)	-0.279(2)	6(3)
O(2)	0.234(3)	0.415(2)	-0.176(2)	6(3)
O(3)	0.025(3)	0.497(2)	-0.103(2)	8(4)
O(4)	0.156(3)	0.367(2)	-0.370(2)	6(3)
O(5)	0.302(3)	0.121(3)	-0.293(2)	8(3)
O(6)	0.082(3)	0.200(2)	-0.377(2)	5(3)
C(1)	0.262(4)	0.026(3)	-0.111(2)	4.2(8)
C(2)	0.282(3)	0.134(3)	-0.105(2)	3.2(7)
C(3)	0.219(4)	0.181(4)	-0.036(3)	5(1)
C(4)	0.154(4)	0.103(4)	0.004(3)	5(1)
C(5)	0.177(4)	0.006(3)	-0.039(3)	5.0(9)
C(6)	0.027(4)	0.677(4)	-0.282(3)	6(1)
C(7)	0.249(4)	0.525(4)	-0.176(3)	7(1)
C(8)	0.035(5)	0.614(4)	-0.115(3)	7(1)
C(9)	0.107(4)	0.654(3)	-0.193(2)	4.1(8)
C(10)	0.121(4)	0.784(3)	-0.205(2)	4.0(8)
C(11)	0.195(4)	0.826(4)	-0.278(3)	7(1)
C(12)	0.212(4)	0.375(4)	-0.454(3)	6(1)
C(13)	0.359(4)	0.119(4)	-0.377(3)	7(1)
C(14)	0.133(5)	0.217(4)	-0.465(3)	7(1)
C(15)	0.253(4)	0.237(4)	-0.464(3)	5(1)
C(16)	0.308(5)	0.241(4)	-0.561(3)	8(1)
C(17)	0.432(6)	0.270(5)	-0.569(4)	12(2)

obtain is not in fact simply a dichloride and tetrachloride mixture. That this is not the case is already indicated by the behavior of the conproportionation reaction (the two insoluble dichloride and tetrachloride solids generate an orange-brown solution before the dark brown product reprecipitates), but definite proof is provided by low-energy IR and powder X-ray diffraction analyses, the results of which are shown in Figs. 1 and 2. The materials obtained by the three different routes (eq. 1–3) exhibit identical properties. The X-ray powder diffraction pattern of the  $\text{CpMoCl}_3$  material (Fig. 2b) shows that this phase does not contain any  $\text{CpMoCl}_4$ . The quality of the X-ray data does not make it possible to rule out the presence of a minor amount (< 10%) of  $\text{CpMoCl}_2$  in the trichloride compound, although the material used for the X-ray experiment analyzed correctly for  $\text{CpMoCl}_3$ . The low energy IR spectra, on the other hand, indicate that minor amounts of  $\text{CpMoCl}_3$  might contaminate the dichloride sample, whereas they do not give indication of the presence of  $\text{CpMoCl}_2$  in the trichloride material (see Fig. 1).

$\text{CpMoCl}_3$  reacts with selected donors to form 18-electron adducts. The bidentate ligands *dmpe* and *dppe* generate the already known [9,10] monoadducts (eq. 4). The identity of these material is established by comparison of the NMR spectra with those already available in the literature. Stärker and Curtis report that the *dppe*

Table 3

Selected bond distances (Å) and angles (deg.) for  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2 \cdot 3\text{CH}_2\text{Cl}_2$ 

Mo-Cl(1)	2.50(1)	Mo-C(4)	2.39(4)	P(2)-O(6)	1.59(2)
Mo-Cl(2)	2.48(1)	Mo-C(5)	2.39(3)	C(1)-C(2)	1.43(4)
Mo-Cl(3)	2.43(1)	P(1)-O(1)	1.64(2)	C(1)-C(5)	1.47(4)
Mo-P(1)	2.46(1)	P(1)-O(2)	1.61(3)	C(2)-C(3)	1.42(4)
Mo-P(2)	2.47(1)	P(1)-O(3)	1.62(2)	C(3)-C(4)	1.38(5)
Mo-C(1)	2.34(3)	P(2)-O(4)	1.55(2)	C(4)-C(5)	1.46(4)
Mo-C(2)	2.24(3)	P(2)-O(5)	1.57(3)	Mo-Cp <sup>a</sup>	2.00
Mo-C(3)	2.35(4)				
Cl(1)-Mo-Cl(2)	85.0(3)	Mo-P(2)-O(6)	116(1)		
Cl(1)-Mo-Cl(3)	79.0(3)	Mo-P(2)-O(5)	116(1)		
Cl(1)-Mo-P(1)	88.0(4)	Mo-P(2)-O(6)	116(1)		
Cl(1)-Mo-P(2)	152.2(4)	C(2)-C(1)-C(5)	102(3)		
Cl(2)-Mo-Cl(3)	79.0(3)	C(1)-C(2)-C(3)	115(3)		
Cl(2)-Mo-P(1)	156.5(4)	C(2)-C(3)-C(4)	105(3)		
Cl(2)-Mo-P(2)	87.0(3)	C(3)-C(4)-C(5)	108(3)		
Cl(3)-Mo-P(1)	77.6(4)	C(1)-C(5)-C(4)	108(3)		
Cl(3)-Mo-P(2)	73.3(3)	Cp <sup>a</sup> -Mo-Cl(1)	103.4		
P(1)-Mo-P(2)	88.6(4)	Cp <sup>a</sup> -Mo-Cl(2)	103.2		
Mo-P(1)-O(1)	120(1)	Cp <sup>a</sup> -Mo-Cl(3)	176.8		
Mo-P(1)-O(2)	114(1)	Cp <sup>a</sup> -Mo-P(1)	100.3		
Mo-P(1)-O(3)	116(1)	Cp <sup>a</sup> -Mo-P(2)	104.3		

<sup>a</sup> Cp = center of gravity of the cyclopentadienyl ring.

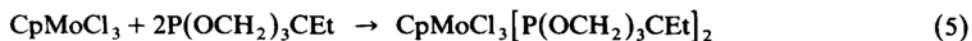
complex is present in solution as a mixture of isomers, one corresponding to the crystallographically characterized molecule having one axial (*trans* to Cp) and one equatorial (*cis* to Cp) phosphorus donor, and the other one having two equivalent phosphorus donors [9b]. We observe that the only species present in solution initially is the structurally characterized isomer, and the isomerization reaction takes place over several days at room temperature.



(L-L = dmpe, dppe)

Contrary to dppe and dmpe,  $\text{PMe}_3$  fails to afford a stable adduct. Interaction of  $\text{CpMoCl}_3$  with two equivalents of  $\text{PMe}_3$  in  $\text{CH}_2\text{Cl}_2$  at low temperature rapidly affords a dark violet solution. Upon warming, however, the color changes to purple and eventually to orange while a flocculent solid precipitates.  $^1\text{H}$  and  $^{31}\text{P}$ -NMR monitoring of this reaction reveals that several diamagnetic and paramagnetic species are formed. Among the latter,  $\text{MoCl}_3(\text{PMe}_3)_3$  was identified by the typical  $^1\text{H}$ -NMR resonances at ca.  $-15$  and  $-33$   $\delta$  (1:2 ratio) at room temperature [13].

Unlike  $\text{PMe}_3$ , the cage phosphite  $\text{P}(\text{OCH}_2)_3\text{CEt}$  reacted cleanly with  $\text{CpMoCl}_3$  to form a bis adduct (eq. 5).



The  $^1\text{H}$ -NMR spectrum of compound  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  shows a fairly large coupling (4.2 Hz) between the Cp protons and the two equivalent phosphorus nuclei. The oxygen-bound methylene protons exhibit a triplet at 4.34  $\delta$  which is due to long range coupling to the phosphorus atoms. Saturation of the phosphorus



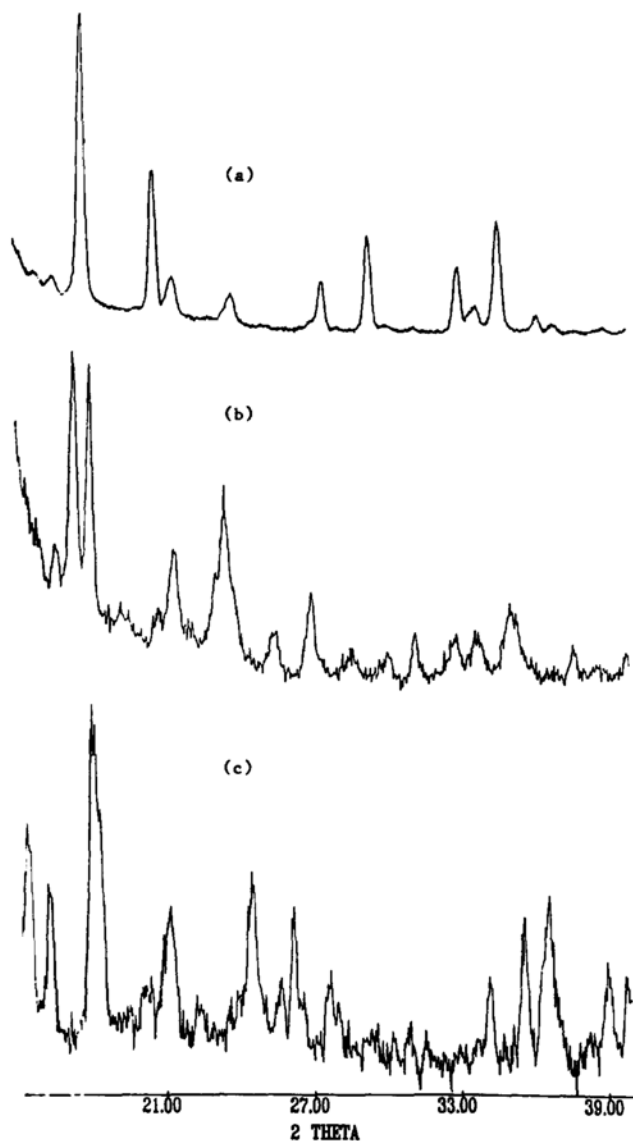


Fig. 2. Powder X-ray diffraction pattern of (a)  $\text{CpMoCl}_4$ ; (b)  $\text{CpMoCl}_3$ ; (c)  $\text{CpMoCl}_2$ .

absorption transforms the triplet into a singlet. The triplet pattern, instead of the expected doublet of doublets, indicates virtual coupling. As shown below, the solid state structure of the complex exhibits a *cis* arrangement of the two equivalent phosphites (structure Ib, *vide infra*). Four different crystals were investigated and found to have the same unit cell parameters. It is possible, however, that the solution structure is *trans* (Ia). Virtual coupling is a phenomenon that is usually observed for the  $^1\text{H-NMR}$  resonances of phosphine protons in compounds with phosphine ligands in a *trans* relative geometry, but no case is reported, to the best of our knowledge, of virtual coupling for phosphite protons when the relative

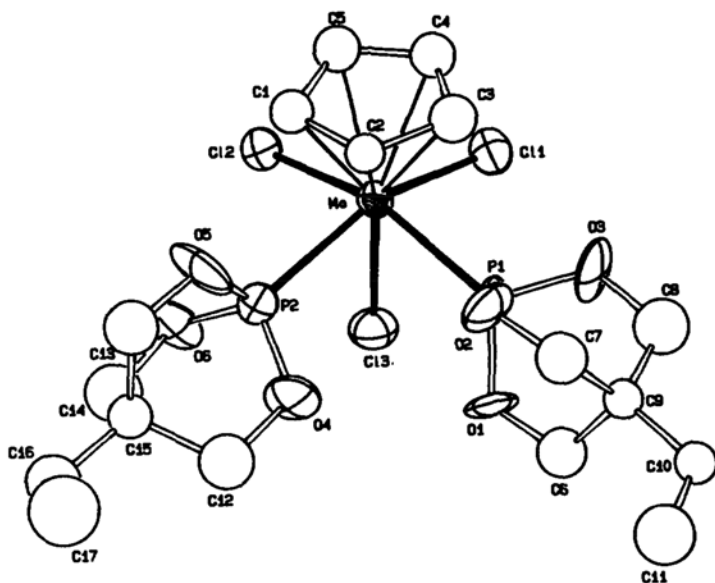
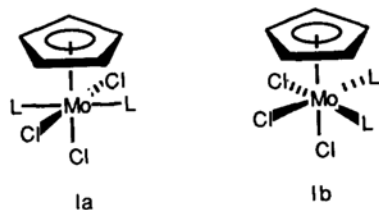


Fig. 3. An ORTEP view of the  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$  molecule.

geometry is either *cis* or *trans*. It is also possible that the *cis* and *trans* isomers interconvert rapidly on the NMR time scale, although no major change of the NMR line shape is observed upon cooling the sample to 250 K. It is worth noting that the NMR spectra show no evidence for the presence of an isomer with a phosphite ligand *trans* to the Cp ring, which would be isostructural with the crystallographically characterized *dmpe* and *dppe* molecules.



The structure of the bis-phosphite complex has been determined by X-ray diffraction methods. A drawing of the molecule is illustrated in Fig. 3. Given the poor quality of the structure, only the geometrical features of the molecule will be considered and the bond distances and angles, listed in Table 3, will not be discussed. The most interesting aspect of this structure is the disposition of the ligands in a pseudo-octahedral configuration (considering the Cp ligand as occupying a single coordination position) with the three chloride ligands in a *facial* arrangement. This is at variance with both structurally characterized  $\text{CpMoCl}_3(\text{L}-\text{L})$  analogues ( $\text{L}-\text{L} = \text{dppe}$  [9], *dmpe* [10]), which exhibit a *meridional* arrangement of the chlorides and one of the two phosphorus atom donors *trans* to the Cp ring.

It is possible that the *facial* structure would be electronically preferred in all instances but the *dppe* and *dmpe* ligand cannot adopt such a configuration because of unfavorable interactions with the Cp ring. The cage phosphite ligand has very small steric requirements. Another possibility for the observed difference is that, due

to the bending of the four equatorial ligands away from the Cp ring (see Cp-Mo-*cis*-ligand angles in Table 3), the small bite of the chelating diphosphines is best adjusted in a *cis-trans* arrangement (*cis* and *trans* refer here to the position occupied by the Cp ligand) with respect to a *cis-cis* arrangement whereas the two monodentate phosphite ligands prefer to stay further away from each other and thus occupy two *cis* positions. In this case, the two ligands should prefer to be located *trans* relative to each other (structure Ia) rather than *cis* (structure Ib). It is relevant to observe, however, that structure Ib is adopted in solution by the analogous compounds  $\text{CpMoX}_3(\text{CO})_2(\text{X} = \text{Cl, Br, I})$  [6,7].

In conclusion, we have reported the new material  $\text{CpMoCl}_3$ , we have shown that it is distinct from  $\text{CpMoCl}_2$  and  $\text{CpMoCl}_4$ , and we have described the formation of a few adducts with neutral phosphine and phosphite ligands.

*Supplementary material available.* Full tables of bond distances and angles, anisotropic thermal parameters, hydrogen atom and solvent molecule coordinates (6 pages), a listing of calculated and observed structure factors (25 pages) for compound  $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CET}]_2 \cdot 3\text{CH}_2\text{Cl}_2$ , and listings of the X-ray powder diffraction data for compounds  $\text{CpMoCl}_n$  ( $n = 2-4$ ) (3 pages) are available from R. Poli.

## Acknowledgements

We are grateful to the Camille and Henry Dreyfus Foundation (New Faculty Award) and to the National Science Foundation (Presidential Young Investigator Award, CHE-9058375) for support of this work. We thank Dr. B.W. Eichhorn and Mr. G. Szabo for the powder X-ray analyses, Dr. R.K. Khanna and Ms. M. Ngoh for assistance with the low-energy IR measurements, and Dr. B.E. Owens for preliminary investigations.

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