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Contribution from the Department of Chemistry and Biochemistry,
University of Maryland, College Park, Maryland 20742

Syntheses and Properties of Paramagnetic Monocyclopentadienylmolybdenum(III) Compounds with a Four-Legged Piano-Stool Structure Containing the Bidentate Bis(diphenylphosphino)ethane Ligand

Steven T. Krueger, Beth E. Owens, and Rinaldo Poli*

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The MoCpX$_2$(dppe) derivatives [Cp = η^5-C$_5$H$_5$; X = Cl, Br, I; dppe = bis(diphenylphosphino)ethane] have been obtained by interaction of MoX$_3$(L-L)THF (THF = tetrahydrofuran) with TlCp and, for X = Cl, by reduction of MoCpCl$_4$ followed by treatment with dppe. The compounds have a low-spin (S = $^1/_2$) configuration, as shown by EPR spectroscopy, and display a reversible oxidation to the corresponding 16-electron [MoCpX$_2$(dppe)]$^+$ cations at $E_{1/2}$ = −0.33 V (X = Cl), −0.26 V (X = Br), and −0.20 V (X = I) with respect to the internal FeCp$_2$/FeCp$_2^+$ couple. The X-ray molecular structure of MoCpBr$_2$(dppe) shows a four-legged piano-stool geometry with a cis relative configuration of the two halide ligands. Crystal data: monoclinic, space group $P2_1/c$, a = 7.503 (1) Å, b = 20.188 (3) Å, c = 18.706 (2) Å, β = 94.02 (1)°, V = 2826 (1) Å^3, d_c = 1.69 g·cm^{-1}, μ(Cu Kα) = 88.76 cm^{-1}, Z = 4, R = 0.041, R_w = 0.047 for 1564 observations and 205 parameters with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Since the discovery of ferrocene,[1] there has been a tremendous growth in the studies of cyclopentadienyl (Cp) substituted transition-metal compounds.[2] Cyclopentadienyl-containing complexes are suitable model systems for studying the reactivity of the other metal–ligand bonds in homogeneous systems because of the inertness of the Cp ligand and its affinity for organic solvents. The vast majority of these studies, however, have dealt with systems where the transition metal has an even number of electrons (usually 18) in the valence shell. Derivatives with an odd number of electrons in the metal valence shell are typically short-lived, reactive intermediates.

The investigation of stable odd-electron coordination compounds is worthwhile, since new pathways for reactivity, notably electron transfer, might become dominant. These compounds might also be expected to be more labile toward ligand displacement chemistry[3] and therefore attractive for catalytic applications. For instance, a number of reactions occurring on even-electron systems have been found to be catalyzed by chemical[4] or electrochemical[5] redox processes, whereby more labile odd-electron species are produced.

We have started an investigation of molybdenum(III)–Cp complexes of formula MoCpX$_2$L$_2$ and MoCpX$_2$(L-L) (X = Cl, Br, I; L = monodentate phosphine; L-L = bidentate phosphine) of which the first examples were briefly described by Green.[6]

We have previously reported the derivatives with the monodentate phosphine PMe$_3$[7] and shown that (i) they are stable 17-electron mononuclear species with a four-legged piano-stool geometry, the phosphine ligands being trans to each other, (ii) they are low-spin complexes exhibiting sharp signals in the room-temperature EPR spectra, (iii) they have interesting electrochemical properties, being easily and reversibly oxidized to the stable 16-electron, paramagnetic (S = 1) Mo(IV) cations, [MoCpX$_2$(PMe$_3$)$_2$]$^+$, but not reduced to the hypothetical 18-electron Mo(II) anions, and (iv) there is substantial Mo–P π back-bonding and Mo–Cp δ back-bonding, and the electronically unsaturated configuration also allows halide-to-metal π donation.

We now wish to report synthetic and structural studies on similar derivatives containing the bidentate phosphine bis(diphenylphosphino)ethane (dppe).

Experimental Section

All operations were carried out under an atmosphere of dinitrogen by using standard glovebox and Schlenk-line techniques. Solvents were dehydrated by standard methods, deoxygenated, and distilled under dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC and Perkin-Elmer 1800; EPR, Brucker ER200; NMR, Brucker AF200; UV/vis, Shimadzu UV 240; scanning potentiostat, EG&G 362. Elemental analyses were by Galbraith Laboratories, Knoxville, TN, and by Midwest Microlab, Indianapolis, IN. The MoX$_3$(THF)$_3$ (X = Cl,[8] Br,[9] I[10]) materials were prepared by published procedures. MoCpCl$_4$, originally reported by Green,[11] has been prepared by adapting the procedure used by Schrock[12] to prepare the corresponding Cp*(η^5-C$_5$Me$_5$) derivative: Mo(CO)$_6$ (10.1 g, 38.3 mmol) and NaCp (3.601 g, 40.88 mmol) were refluxed in THF (50 mL) for 20 h, by which time the conversion to Na[MoCp(CO)$_3$] was complete as indicated by solution IR spectroscopy. To this solution was added MeI (2.70 mL, 43.4 mmol). After brief stirring, the mixture was evaporated to dryness and the residue was extracted with CH$_2$Cl$_2$ (50 mL). After filtration, the solid was washed with an additional 10 mL of CH$_2$Cl$_2$. The combined filtered

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solutions were transferred through a double-tip needle into a flask containing PCl_5 (20.2 g, 97.1 mmol) partially dissolved in 100 mL of CH_2Cl_2. A vigorous gas evolution took place, accompanied by the precipitation of a brown solid. The mixture was then refluxed for 10 h, during which time the precipitate turned red. The product was filtered out, washed thoroughly with CH_2Cl_2, and vacuum dried. Yield: 9.79 g (84.4%). Anal. Calcd (found) for $C_5H_5Cl_4Mo$: C, 19.8 (19.8); H, 1.7 (1.7). EPR (THF, room temperature): $g = 1.994$, $a_{Mo} = 38.2$ G (3.56 cm^{-1}). The ligand dppe was purchased from Strem Chemicals and used without further purification. The IR spectra of the new compounds are deposited as supplementary material.

Preparation of $MoCpCl_2$(dppe). Method A. $MoCl_3$(dppe)(THF) was obtained in situ from $MoCl_3(THF)_3$ (0.74 g, 1.77 mmol) and dppe (0.77 g, 1.93 mmol) as described in the literature.[9b] To this solution TlCp (0.52 g, 1.93 mmol) was added, and the resulting suspension was stirred at room temperature. The solution turned immediately a slightly darker red, and the EPR spectrum showed the presence of the product (Figure 1a). The mixture was filtered. The solid, which contained thallium chloride and the excess of TlCp, had a slight pink color, and its IR spectrum showed bands that are characteristic of the dppe ligand. This solid was discarded. The product was recovered from the solution by precipitation with *n*-heptane (yield 0.42 g, 34%). Once the compound is isolated, it dissolves only sparingly in THF, but it is soluble in CH_2Cl_2 and can be recrystallized from CH_2Cl_2/*n*-heptane. Its properties, notably the cyclic voltammogram (see Results section), show that the compound contains only minor amounts of impurities, but a completely satisfactory analysis could not be obtained.

Method B. $MoCpCl_4$ (0.60 g, 1.98 mmol) was suspended in 50 mL of THF and treated with 97 mg (4.2 mmol) of amalgamated (with ca. 10 g of Hg) sodium. The mixture was stirred at room temperature for a few hours. The red starting material rapidly dissolved to afford a brown solution, which eventually turned olive-green while a white solid precipitated. The EPR spectrum of the final solution showed only very weak lines, which were not attributable to a simple derivative, nor were they completely reproducible. We attribute these to small amounts of impurities. The mixture was filtered through Celite and treated with 0.791 g (1.8 mmol) at dppe at room temperature. The color immediately changed to red, and the EPR spectrum showed the desired product as the only EPR-active species. The solution was concentrated, and the light brown product was precipitated by addition of *n*-heptane. Yield: 0.39 g (31%). This product showed IR, EPR, and solubility properties identical with those of the material obtained by method A, but again, it could not be obtained in an analytically pure form.

Preparation of $MoCpX_2$(dppe) (X = Br, I). These compounds were prepared by procedures similar to that described above for the corresponding chloride species (method A), starting respectively from $MoBr_3(THF)_3$[9] (0.50 g, 0.90 mmol in 50 mL of THF) and $MoI_3(THF)_3$[10] (0.50 g, 0.72 mmol in 40 mL of THF). Yields of 70% (Br) and 88% (I) were obtained. Anal. Calcd (found) for $C_{31}H_{29}Br_2MoP_2$: C, 51.8 (51.3); H, 4.1 (4.1); Br, 22.3 (21.7). Calcd (found) for $C_{31}H_{29}I_2MoP_2$: C, 45.8 (45.7); H, 3.6 (3.2); I, 31.2 (30.5). These products exhibit the same solubility properties as those of $MoCpCl_2$(dppe). Diffusion of *n*-heptane into CH_2Cl_2 solutions produced mixtures of well-formed dark red-brown crystals and variable amounts of powder in each case. A single, parallelepiped-shaped crystal of the bromide compound for the X-ray analysis was selected from this diffusion experiment.

Reaction of $MoCpCl_2$(dppe) with PMe_3. A solution of $MoCpCl_2$(dppe) in CH_2Cl_2 was treated with an excess of PMe_3. Complete conversion to $MoCpCl_2(PMe_3)_2$ occurred within $^1/_2$ h, as shown by comparison of the EPR spectrum with that reported in the literature.[7]

X-ray Crystallography for $MoCpBr_2$(dppe). A single crystal was glued to the inside of a glass capillary, which was then sealed under dinitrogen and mounted on the diffractometer. The preliminary orientation matrix determination and the collection and reduction of data were performed in a routine manner. A semiempirical absorption correction was applied to the data.[13] The systematic absences from the data uniquely determined the space group as the monoclinic $P2_1/c$. Direct methods showed the positions of the molybdenum and bromine atoms, and the rest of the non-hydrogen atoms were located by alternate full-matrix least-squares cycles of refinement and difference Fourier maps by using the TEXSAN package of programs. Hydrogen atoms were included at calculated positions and used for structure factor calculations but not refined. Due to the limited amount of data, the carbon atoms of the phenyl rings were refined isotropically. Selected crystal data are reported in Table I, positional and equivalent isotropic displacement parameters are listed in Table II, and selected bond distances and angles are collected in Table III.

Table I. Crystal Data for $MoCpBr_2$(dppe)

formula	$C_{31}H_{29}Br_2MoP_2$
fw	719.27
space group	$P2_1/c$
a, Å	7.503 (1)
b, Å	20.188 (3)
c, Å	18.706 (2)
β, deg	94.02 (1)
V, Å^3	2826 (1)
Z	4
d_{calc}, g/cm^3	1.69
μ(Cu Kα), cm^{-1}	88.76
radiation (monochromated in incident beam)	Cu Kα (λ = 1.54178 Å)
temp, °C	20
transm factors: max, min	1.000, 0.464
R^a	0.041
$R_w{}^b$	0.047

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

Table II. Positional Parameters and *B*(eq) for $MoCpBr_2$(dppe)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo	0.3604 (1)	0.02478 (5)	0.31356 (6)	2.26 (5)
Br(1)	0.6230 (2)	0.05895 (7)	0.40568 (8)	3.47 (8)
Br(2)	0.6306 (2)	0.00002 (7)	0.23630 (8)	3.29 (7)
P(1)	0.2022 (5)	0.1264 (2)	0.3481 (2)	2.6 (2)
P(2)	0.2365 (5)	0.0705 (2)	0.1999 (2)	2.6 (2)
C(1)	0.105 (2)	−0.0320 (7)	0.3092 (7)	3.2 (7)
C(2)	0.150 (2)	−0.0230 (7)	0.3839 (8)	3.6 (8)
C(3)	0.308 (2)	−0.0591 (7)	0.3993 (7)	3.9 (8)
C(4)	0.359 (2)	−0.0895 (7)	0.3367 (8)	3.7 (8)
C(5)	0.232 (2)	−0.0721 (6)	0.2794 (7)	3.0 (7)
C(6)	0.023 (2)	0.1148 (6)	0.2111 (7)	3.2 (7)
C(7)	−0.006 (2)	0.1287 (6)	0.2897 (7)	2.6 (7)
C(10)	0.132 (2)	0.1405 (6)	0.4389 (6)	2.7 (3)
C(11)	0.212 (2)	0.1070 (6)	0.4966 (7)	2.7 (3)
C(12)	0.166 (2)	0.1195 (7)	0.5661 (7)	3.8 (3)
C(13)	0.044 (2)	0.1688 (7)	0.5774 (8)	4.1 (3)
C(14)	−0.036 (2)	0.2026 (7)	0.5201 (8)	4.7 (4)
C(15)	0.008 (2)	0.1885 (8)	0.4504 (8)	4.4 (4)
C(20)	0.306 (2)	0.2078 (7)	0.3335 (7)	3.0 (3)
C(21)	0.226 (2)	0.2563 (8)	0.2917 (8)	4.8 (4)
C(22)	0.303 (2)	0.3188 (9)	0.2885 (9)	5.4 (4)
C(23)	0.458 (2)	0.3318 (8)	0.3279 (8)	4.9 (4)
C(24)	0.546 (2)	0.2848 (8)	0.3698 (8)	4.8 (4)
C(25)	0.463 (2)	0.2216 (7)	0.3730 (8)	4.1 (3)
C(30)	0.368 (2)	0.1346 (7)	0.1573 (7)	3.0 (3)
C(31)	0.305 (2)	0.1577 (7)	0.0896 (7)	3.2 (3)
C(32)	0.385 (2)	0.2109 (8)	0.0569 (8)	4.7 (4)
C(33)	0.528 (2)	0.2390 (7)	0.0932 (8)	4.4 (4)
C(34)	0.599 (2)	0.2174 (7)	0.1567 (8)	4.6 (4)
C(35)	0.515 (2)	0.1621 (8)	0.1911 (8)	4.4 (4)
C(40)	0.187 (2)	0.0109 (7)	0.1285 (7)	3.3 (3)
C(41)	0.026 (2)	−0.0218 (7)	0.1183 (7)	3.9 (3)
C(42)	−0.005 (2)	−0.0734 (7)	0.0694 (8)	4.3 (3)
C(43)	0.129 (2)	−0.0905 (8)	0.0271 (8)	4.8 (4)
C(44)	0.289 (2)	−0.0585 (8)	0.0337 (8)	4.5 (4)
C(45)	0.320 (2)	−0.0076 (7)	0.0836 (7)	3.3 (3)

Results

(a) Syntheses. Two different synthetic routes have been investigated for the preparation of compounds $MoCpX_2$(dppe) [X = Cl (**1**), Br (**2**), I (**3**)]. The first is described in eq 1 and parallels

$$\mathrm{MoCpCl_4} \xrightarrow{(1)\ 2\mathrm{Na}} \xrightarrow{(2)\ \mathrm{dppe}} \underset{\mathbf{1}}{\mathrm{MoCpCl_2(dppe)}} \tag{1}$$

the strategy employed earlier by Green.[6] The latter consists of the interaction of the tetrachloro-bridged $[MoCp'Cl_2]_2$ (Cp′ = η^5-*i*-PrC_5H_4) material, obtained by oxidation of $MoCp'Cl(\eta^6\text{-}C_6H_6)$ with HCl,[6] with the phosphine ligand.

We have produced our Mo(III) intermediate in situ by sodium reduction of $MoCpCl_4$. It was not possible to isolate "$MoCpCl_2$", or a derivative of it, in pure form by this procedure. At the end of the reduction step all the molybdenum is in solution, presumably

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Table III. Selected Intramolecular Distances (Å) and Angles (deg) and Estimated Standard Deviations for $MoCpBr_2(dppe)$

	Distances		
Mo–Br(1)	2.617 (2)	P(1)–C(20)	1.85 (1)
Mo–Br(2)	2.620 (2)	P(2)–C(6)	1.86 (1)
Mo–P(1)	2.479 (4)	P(2)–C(30)	1.84 (1)
Mo–P(2)	2.441 (4)	P(2)–C(40)	1.82 (1)
Mo–C(1)	2.23 (1)	C(1)–C(2)	1.43 (2)
Mo–C(2)	2.33 (1)	C(1)–C(5)	1.39 (2)
Mo–C(3)	2.38 (1)	C(2)–C(3)	1.40 (2)
Mo–C(4)	2.35 (1)	C(3)–C(4)	1.40 (2)
Mo–C(5)	2.25 (1)	C(4)–C(5)	1.43 (2)
P(1)–C(7)	1.84 (1)	C(6)–C(7)	1.53 (2)
P(1)–C(10)	1.84 (1)		
	Angles		
Br(1)–Mo–Br(2)	80.64 (6)	Mo–P(2)–C(30)	117.4 (5)
Br(1)–Mo–P(1)	87.8 (1)	Mo–P(2)–C(40)	115.8 (4)
Br(1)–Mo–P(2)	134.2 (1)	C(6)–P(2)–C(30)	101.7 (6)
Br(2)–Mo–P(1)	134.8 (1)	C(6)–P(2)–C(40)	105.6 (6)
Br(2)–Mo–P(2)	81.58 (9)	C(30)–P(2)–C(40)	103.7 (6)
P(1)–Mo–P(2)	75.8 (1)	C(2)–C(1)–C(5)	110 (1)
Mo–P(1)–C(7)	105.5 (4)	C(1)–C(2)–C(3)	106 (1)
Mo–P(1)–C(10)	123.0 (4)	C(2)–C(3)–C(4)	109 (1)
Mo–P(1)–C(20)	118.9 (4)	C(3)–C(4)–C(5)	108 (1)
C(7)–P(1)–C(10)	105.0 (6)	C(1)–C(5)–C(4)	106 (1)
C(7)–P(1)–C(20)	103.7 (6)	P(2)–C(6)–C(7)	112 (1)
C(10)–P(1)–C(20)	98.7 (6)	P(1)–C(7)–C(6)	113 (1)
Mo–P(2)–C(6)	111.2 (4)		

as a salt of $[MoCpCl_{2+n}]^{n-}$, and subsequent workup generates an insoluble powder, probably a mixture of $MoCpCl_2$ and NaCl. In fact, we now know that the previously unreported $MoCpCl_2$ is completely insoluble in THF. A convenient synthesis of pure $MoCpCl_2$ and a study of its reactivity with Cl^- will be reported separately.[14] In any event, the intermediate obtained in situ by sodium reduction of $MoCpCl_4$ reacts with dppe to produce the desired product (see eq 1). The $MoCp^*Cl_2(PMe_3)_2$ (Cp^* = η^5-C_5H_5) derivative has also been prepared in two steps from $MoCp^*Cl_4$ by sodium reduction followed by interaction with PMe_3. The intermediate Mo(III)–Cp* complex was not isolated.[15] The synthetic method illustrated in eq 1 has not been extended to the other halide systems, although $MoCpBr_4$ is known,[16] because of the convenience and generality of the second method described below.

The known[9] $MoX_3(dppe)(THF)$ (X = Cl, Br, I) compounds react rapidly with 1 equiv of TlCp in THF at room temperature to generate solutions of compounds **1**–**3** according to eq 2. The

$$MoX_3(dppe)(THF) + TlCp \rightarrow MoCpX_2(dppe) + TlX + THF \quad (2)$$
$$X = Cl\ (\mathbf{1}),\ Br\ (\mathbf{2}),\ I\ (\mathbf{3})$$

syntheses are best carried out by preparing the $MoX_3(dppe)(THF)$ compounds in situ from $MoX_3(THF)_3$ as described in the literature.[9] This eliminates the need to isolate the $MoX_3(dppe)(THF)$ intermediates.

Figure 1. EPR spectra of compounds $MoCpX_2(dppe)$ at room temperature with CH_2Cl_2 as solvent: (a) X = Cl; (b) X = Br; (c) X = I.

Compounds **1**–**3** are soluble in CH_2Cl_2. Crystallization from CH_2Cl_2 by slow diffusion of *n*-heptane produces, in each case, a mixture of well-formed crystals and variable amounts of powder. One of the crystals obtained for the bromide system has been investigated crystallographically and shown to be mononuclear (vide infra). Perhaps the powder is of an oligonuclear isomer where the diphosphine ligand serves as a bridging unit instead of chelating to the same metal center. A similar situation has been reported for the phosphido-bridged compounds $[Co(\mu\text{-}PPh_2)(CO)_3]_n$.[17] We have not investigated further the nature of this powder, except for verifying in the case of X = Cl that the powder and the crystalline material have identical IR spectra in the 4000–150-cm^{-1} region.

(b) EPR Studies. Compounds **1**–**3** are paramagnetic. The EPR spectra at room temperature are reported in Figure 1. The *g* values show the same trend already observed for the compounds $MoCpX_2(PMe_3)_2$.[7] The position of the isotropic *g* value (**1**, 1.986; **2**, 2.014; **3**, 2.054) seems to depend strongly on the nature of the halide ligands whereas it is almost insensitive to the nature of the phosphine [values for $MoCpX_2(PMe_3)_2$ are 1.982 (X = Cl), 2.006 (X = Br), and 2.046 (X = I)][7] and to the relative geometry of

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the ligands in the complexes (e.g. trans for the PMe_3 compounds, cis for the dppe).

Although the EPR spectra of the PMe_3 compounds with different halide ligands show similar line broadenings,[7] the EPR lines of the compounds reported here are sharper for X = Cl and they broaden markedly on going to the heavier halides (all spectra were taken on ca. 10^{-4} M solutions). This effect may be due to a faster spin relaxation for the compounds with the heavier halide (halide atomic orbitals have been shown to participate extensively to the singly occupied MO), although it is not clear why the effect would be more pronounced for the *cis*-dppe derivatives than for the *trans*-$(PMe_3)_2$ derivatives. An alternative possibility is that a fast chemical exchange process occurs at a rate in the order **1** < **2** < **3**. This exchange might involve either dissociation of a halide ligand [to generate $[MoCpX(dppe)]^+X^-$] or of one end of the diphosphine [to generate $MoCpX_2(\eta^1\text{-dppe})$] or ring slippage of the Cp ring [for instance, to generate $Mo(\eta^3\text{-}C_5H_5)X_2(dppe)$]. A dissociation process is in accord with an increased rate for heavier (bulkier) halide derivatives, whereas the absence of this broadening effect for the PMe_3 derivatives might be consistent with a stronger Mo–PMe_3 interaction with respect to the Mo–dppe interaction if phosphine dissociation is the chemical exchange process involved. Both the facile dissociation of the Mo–dppe bond and the higher stability of the PMe_3 complexes seem to be consistent with the observed fast and quantitative phosphine exchange reaction illustrated in eq 3.

$$MoCpCl_2(dppe) + 2PMe_3 \rightarrow MoCpCl_2(PMe_3)_2 + dppe \quad (3)$$

Hyperfine splitting parameters for compound **1** from the room-temperature spectrum are a_{Mo} = 29 G (3.0 × 10^{-3} cm^{-1}) and a_P = 26 G (2.7 × 10^{-3} cm^{-1}). For the bromide compound, **2**, no phosphorus coupling was observed at room temperature in THF. The resonance sharpened to a distinguishable triplet upon cooling to about −30 °C (a_P = 23 G, 2.4 × 10^{-3} cm^{-1}), but the splitting is evident at room temperature in CH_2Cl_2 (Figure 1b). Compound **3** starts to exhibit the central triplet feature (a_P = 18 G, 1.8 × 10^{-3} cm^{-1}) at −50 °C in THF. Interestingly, the a_P value decreases on going from to Cl to Br to I for the *cis*-dppe derivatives, whereas it has the opposite trend for the *trans*-$(PMe_3)_2$ derivatives.[7] Compound **2** shows also additional hyperfine coupling when dissolved in CH_2Cl_2, which may be attributed to the two equivalent bromine nuclei (^{79}Br and ^{81}Br, both with $I = {}^3/_2$ and similar nuclear magnetic moment, total abundance 100%). An analogous coupling to the chlorine nuclei is not observed for compound **1** (see Figure 1a) nor is coupling to the iodine nuclei observed for compound **3** (Figure 1c).

(c) **Structural Study.** The structure of compound **2** has been determined by single-crystal X-ray diffraction methods. Two ORTEP drawings are shown in Figure 2. The molecule resides on a general position and contains neither crystallographic nor ideal symmetry elements. The local $MoBr_2(dppe)$ moiety has an ideal mirror plane passing through the Mo atom and bisecting the Br(1)–Mo–Br(2) and P(1)–Mo–P(2) angles, but this symmetry is destroyed by the orientation of the Cp ring, as can be visualized in the top view of the molecule (Figure 2b). The molecule has a typical four-legged piano-stool geometry, similar to that reported earlier for the $MoCpX_2(PMe_3)_2$ (X = Cl, I) molecules,[7] the only major difference being that the relative configuration of the four "legs" is trans in the PMe_3 complexes, whereas it is forced to cis in compound **2** by the chelating ligand. The angles between trans bonds [Br(1)–Mo–P(2) = 134.2 (1)°; Br(2)–Mo–P(1) = 134.8°] in the dppe structure are larger than the X–Mo–X angles found in the PMe_3 compounds mentioned above (125.14 (7)° for X = Cl; 125.6 (1)° for X = I) but similar or smaller than the P–Mo–P angles of the same compounds (133.66 (6)° for X = Cl; 141.2 (1)° for X = I).[7] These differences are probably the result of a combination of steric interactions between the halide and phosphorus atoms and the presence of the chelate ring in the dppe structure. The diphosphine bite angle at the molybdenum atom is 75.8 (1)°. Strangely, there is asymmetry in the Br(*n*)–Mo–P(*n*) angles (*n* = 1, 87.8 (1)°; *n* = 2, 81.58 (9)°).

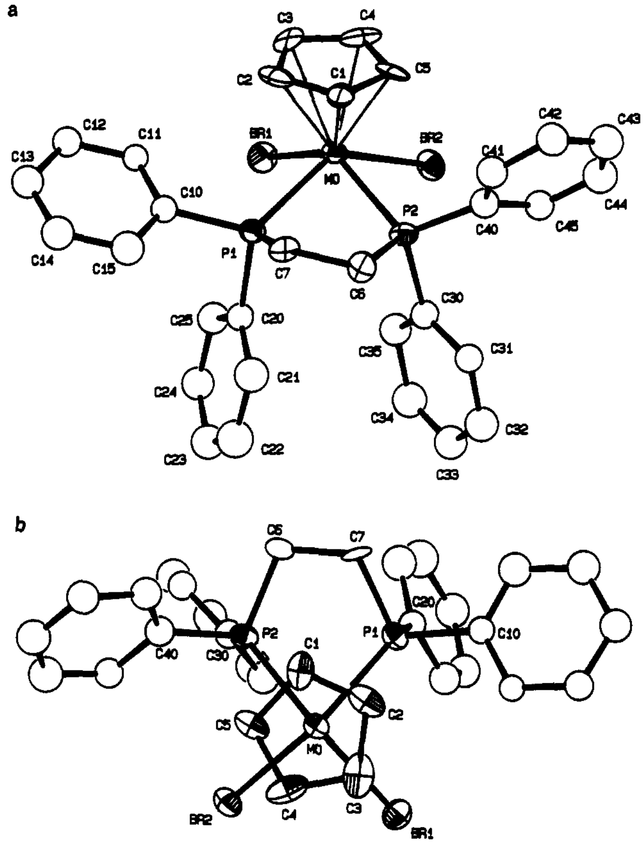

Figure 2. (a) ORTEP view of the $MoCpBr_2(dppe)$ molecule, showing the atomic numbering scheme employed. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 40% probability level. (b) View of the $MoCpBr_2(dppe)$ molecule along an axis approximately perpendicular to the Cp ring plane. The ORTEP plot files were modified with the program PLOTMD[32] for label position optimization.

Other structural features of compound **2** are similar to those of the previously reported PMe_3 adducts.[7] In particular, the Cp ring experiences the same type of distorsion from a η^5 to a η^3,η^2 arrangement, the "η^2" part of the ring [C(1) and C(5)] being closer to the Mo center [2.23 (1) and 2.25 (1) Å, respectively] than the "η^3" portion [2.33 (1), 2.38 (1), and 2.35 (1) Å]. This type of distorsion is consistent with the presence of Mo–Cp δ back-donation, as discussed by Hoffmann et al.[18] The Mo–Br distances [average 2.618 (2) Å] are longer than other terminal Mo(III)–Br distances found in the literature. Examples are values in the 2.561–2.593-Å range for $[MoBr_4(dppe)]^-$,[19] 2.544 (3) Å for the terminal Mo–Br bonds in $[Mo_2Br_9]^{3-}$,[20] 2.56 (1) Å (average) for $MoBr_3(4\text{-}MeNC_5H_4)_3$,[21] and 2.60 (1) Å (average) and 2.54 (3) Å (average) in $Mo_4Br_3(O\text{-}i\text{-}Pr)_9$ and $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$, respectively.[22] On the other hand, the Mo–P distances are shorter than any other Mo(III)–P distance reported in the literature, which are in the range 2.54–2.59 Å for the complexes $Mo_2Cl_6(PEt_3)_4$,[23] $Mo_2Cl_6(dppm)_2$,[24] $Mo_2Cl_6(dppe)_2$,[25] $Mo_2(\mu\text{-}SEt)_2Cl_4(dmpe)_2$,[26] $[Mo_2I_7(PMe_3)_2]^-$,[27] and *mer*-$MoI_3(PMe_3)_3$.[9b] These trends parallel those reported by us for the $MoCpX_2(PMe_3)_2$ (X = Cl, I) com-

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pounds,[7] where longer Mo–Cl and Mo–I distances and shorter Mo–P distances, with respect to similar bonds in other literature compounds, were observed. The Mo–P distances of $MoCpX_2(PMe_3)_2$ complexes are 2.482 (2) Å (X = Cl) and 2.501 (2) Å (X = I). The Mo–C(Cp) distances are scattered in the 2.23–2.38-Å range (average 2.31 Å). These are slightly longer than the corresponding distances in $MoCpX_2(PMe_3)_2$ (X = Cl, I) (ranges and average values are 2.21–2.35, 2.27 Å for X = Cl and 2.24–2.35, 2.29 Å for X = I) and are in better agreement with the values found for other Mo(III)–Cp compounds (in the range 2.30–2.32 Å).[28]

(d) Electrochemical Studies. Compounds **1**–**3** have been studied electrochemically by cyclic voltammetry in CH_2Cl_2 solutions by using a platinum working electrode, $n\text{-}Bu_4N^+PF_6^-$ as the supporting electrolyte and a Ag/AgCl reference electrode. All half-wave potentials were measured and are reported with respect to the ferrocene/ferrocenium couple. The ferrocene was added to the solutions at the end of each measurement as an internal standard, and potentials are *IR* uncorrected.

All three compounds exhibit the same one-electron reversible oxidation (ΔE_p = 100 mV for X = Cl, 80 mV for X = Br, 88 mV for I; the reversible $FeCp_2/FeCp_2^+$ couple shows ΔE_p of 145, 88, and 87 mV, respectively, in the three experiments) at the following $E_{1/2}$ values: −0.33 V (X = Cl), −0.26 V (X = Br), −0.20 V (X = I). These values follow the same trend observed before for the $MoCpX_2(PMe_3)_2$ compounds [$E_{1/2}$ = −0.52 V (Cl), −0.46 V (Br), and −0.42 V (I) with respect to internal $FeCp_2/FeCp_2^+$],[7] the chloride compound being the most easily oxidized. The absolute $E_{1/2}$ value for each $MoCpX_2(dppe)$ compound is ca. 0.2 V more positive than that of the corresponding $MoCpX_2(PMe_3)_2$ compound. That is, the dppe complexes are less easily oxidized than the corresponding PMe_3 complexes. The products of these electron-transfer processes are presumably the Mo(IV) 16-electron cations $[MoCpX_2(dppe)]^+$. We have not coulometrically determined the number of electrons involved in these electron-transfer processes. However, for the similar processes of the $MoCpX_2(PMe_3)_2$ complexes, the nature of the oxidation product as the $[MoCpX_2(PMe_3)_2]^+$ cation was established by independent chemical synthesis for X = Cl, followed by crystallographic and cyclic voltammetric analysis of the product.[7] Furthermore, the Mo(IV) 16-electron $[MoCpCl_2(dppe)]^+$ cation has been reported as the BF_4^- salt,[29] synthesized by interaction of $MoCpCl_3(dppe)$ with $AgBF_4$.

A second irreversible oxidation takes place at higher potentials [$E_{p,a}$ = +0.95 V (Cl), +0.83 V (Br), +0.93 V (I)]. A comparison of the peak heights suggests that these are also one-electron processes. Figure 3a shows a representative voltammogram obtained for the iodide complex.

Contrary to predictions based on the 18-electron rule, reversible one-electron reduction processes to afford the hypothetical Mo(II) anions $[MoCpX_2(dppe)_2]^-$ are not observed for any halide derivative. Irreversible reduction processes are observed instead, and these are further complicated by an apparent subsequent chemical process involving the neutral molecules that continue to flow toward the working electrode, as shown by the effect of scanning the potential through the irreversible reduction process on the reversible first oxidation wave (see Figure 3b for X = I). Identical behavior was displayed by the other halide derivatives. We have not further investigated this electrochemical reduction.

Discussion

The mononuclear compounds **1**–**3** show properties similar to those observed for the PMe_3 derivatives described earlier.[7] Experimental evidence obtained for the $MoCpX_2(PMe_3)_2$ compounds and their oxidation products, supported by Fenske–Hall MO calculations carried out on *trans*-$MoCpX_2(PH_3)_2$ model molecules,[7] suggest the following: (i) the molecules have a low-spin ($S = {}^1/_2$) electronic configuration; (ii) there is significant Mo(III)–P π back-bonding; (iii) there is significant Mo(III)–Cp δ back-bonding; (iv) these two back-bonding mechanisms decrease substantially in importance upon oxidation of the materials to the 16-electron $[MoCpX_2(PMe_3)_2]^+$ cations. The EPR properties of the dppe compounds (Figure 1) suggest that they also have a low-spin electronic configuration.

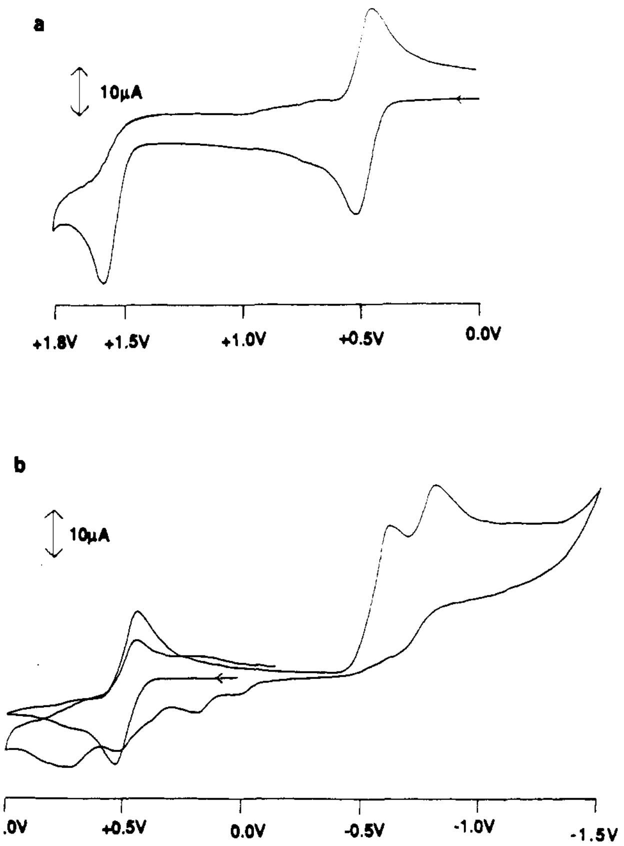

Figure 3. Cyclic voltammograms of $MoCpBr_2(dppe)$ in CH_2Cl_2 (scan speed = 200 $mV{\cdot}s^{-1}$): (a) showing the two oxidation processes; (b) showing the reduction processes and the effect of these on the quasi-reversible first oxidation process.

The structural parameters of compound **2** indicate that Mo(III)–P π back-bonding and Mo(III)–Cp δ back-bonding are also present in this compound. In fact, the shorter Mo–P distances in compound **2** with respect to those found for $MoCpX_2(PMe_3)_2$ (X = Cl, I) would seem to indicate that there is more π back-donation in the dppe compound, in accord with the expected lower energy of the phosphorus accepting orbitals in the aryl-substituted phosphine ligand.

Since the $[MoCpX_2(dppe)]^+$ oxidation products have not been structurally characterized, we cannot say whether the Mo–P π back-donation mechanism involves mainly the P 3d orbitals, as suggested for $[MoCpCl_2(PMe_3)_2]^{n+}$ (n = 0, 1),[7] or rather the combination of P–C σ* orbitals of appropriate symmetry, as suggested by Trogler, Ellis, and co-workers[30] and experimentally confirmed in a number of cases by Orpen and Connelly.[31] For pairs of compounds of formula $M(PR_3)L_n^{m+}$ (m = 0, 1), the π back-donation into P–C σ* orbitals is indicated by an increase of the P–C bond lengths, which is concomitant with the decrease of M–P bond length on going from m = 1 to m = 0.[31] However, a slightly less significant comparison can be made by comparing the P–C bond distances in compound **2** [where the Mo–P distances are 2.46 (3) Å] with those of the 18-electron Mo(IV) compound $MoCpCl_3(dppe)$, for which the reported Mo–P bond lengths are

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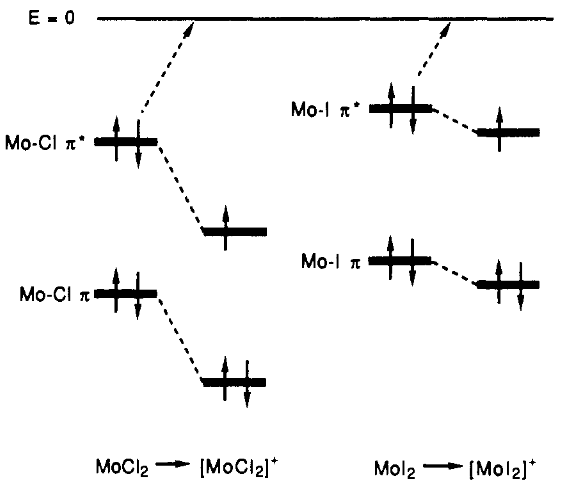
Scheme I



2.521 (2) Å (equatorial) and 2.688 (2) Å (axial).[29] These P–C bond lengths are 1.85 (1) Å for compound **2** and (average) 1.843 (9) Å for $MoCpCl_3$(dppe). The increase of Mo–P bond length on going from Mo(III) to Mo(IV) is an indication of reduced Mo-to-P π back-donation. This increase, however, is not paralleled by a significant decrease of P–C bond lengths. This situation is analogous to that observed for the $[MoCpCl_2(PMe_3)_2]^{n+}$ (n = 0, 1) pair of complexes[7] and is consistent with little participation of the P–C σ^* orbitals in the π bonding. In cases where the P–C bond distances *have* been observed to shorten upon metal-based one-electron oxidation, the bond length shortening amounts to as much as 0.03 Å.[31] Concerning the Mo–Cp δ back-bonding, this is mainly suggested by the asymmetry of the Cp ring, which distorts toward a η^3,η^2 conformation with the η^2 portion *closer* to the metal, as discussed by Hoffmann.[18]

An interesting point of note is the correlation between the oxidation potential and the nature of the halogen atoms. The oxidation potential becomes more positive (i.e. oxidation is more difficult) in the order Cl < Br < I, both for the $MoCpX_2(PMe_3)_2$ series[7] and for the $MoCpX_2$(dppe) series reported in this paper. The orbital that furnishes the electron in the oxidation process has been established to be the SHOMO for the PMe_3 complexes,[7] i.e. the MO whose main contribution comes from the Mo d_{xy} atomic orbital and which has Mo–X π^* character. The reported calculations show that it is lower in energy for X = Cl than for X = I (see Figure 3 of ref 7). Thus, a higher oxidation potential for X = Cl would be expected. However, we have to consider how the energy changes on going from the Mo(III) to the Mo(IV) system. Since the Mo(IV) product is electronically less saturated (16-electron), the better π-donor Cl will be able to stabilize it more than the heavier halogen atoms. This is illustrated in Scheme I (Cp and phosphine ligands have been omitted in the formulas).

Another question concerns the correlation between the oxidation potential and the nature of the phosphine. The orbital that furnishes the electron in the oxidation process has also a weak Mo–P π character. Qualitative considerations suggest that this orbital will be stabilized (that is, its energy will be lowered) by a more efficient π back-donation mechanism to the phosphine ligands. Therefore, the more Mo–P back-donation, the more stabilized the MO that furnishes the electron, the higher the oxidation potential. This seems in agreement with the observed data: the Mo–P bond lengths suggest greater π back-donation in the dppe complexes, and the oxidation potential for these complexes is higher.

These conclusions are based on three approximations. First, the orbital that furnishes the electron in the oxidation process is the same for the trans and the cis structures. Simple considerations suggest that the electronic structures of the cis and trans isomers are identical. Second, the energy of the SHOMO *in the Mo(IV) species* does not depend strongly on the nature of the phosphine ligand for compounds with the same halide ligand. This is a reasonable approximation because the π back-donation in this oxidized material is strongly reduced (we also recall here that this orbital does not contain Mo–P σ character).[7] Third, solvation effects are roughly constant for compounds with different phosphine ligands.

It is interesting to observe at this point that, although the Mo–P bonds are shorter in the $MoCpX_2$(dppe) derivatives than in the $MoCpX_2(PMe_3)_2$ derivatives (vide supra), the phosphine exchange study of eq 3 seems to suggest that the bond strength is in the order Mo–PMe_3 > Mo–dppe. Notice also that reaction 3 is endoentropic. However, we cannot exclude that the energetic preference for the PMe_3 derivatives is due to the cis to trans reorganization energy or to steric effects. To understand the role of each of these factors, we are planning to prepare other selected phosphine derivatives and to investigate them structurally, electrochemically, and by phosphine exchange equilibrium studies.

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Supplementary Material Available: Tables of FTIR data (Nujol mull) for $MoCpX_2$(dppe) (X = Cl, Br, I) and crystal data, complete bond distances and angles, hydrogen positions, and anisotropoic thermal parameters for $MoCpBr_2$(dppe) (7 pages). A listing of calculated and observed structure factors for $MoCpBr_2$(dppe) (20 pages). Ordering information is given on any current masthead page.