Synthesis and Characterization of Na[*cis-mer*-$Mo(C_6F_5)(CO)_2\{P(OMe)_3\}_3$]†

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The complex $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$ can be reduced either chemically or electrochemically by one electron. Electrochemical studies suggest that the reduction is followed by a rapid but reversible structural change. The orange intermediate reduction product has not yet been isolated in pure form. Chemical reduction with sodium amalgam in tetrahydrofuran in the presence of trimethyl phosphite initially forms this orange product, but precipitation with hexane yields the pale yellow zerovalent σ-aryl molybdenum complex Na[*cis-mer*-$Mo(C_6F_5)(CO)_2\{P(OMe)_3\}_3$], in which the cycloheptatrienyl ligand has been displaced by three trimethyl phosphite groups. This complex has been fully characterized by IR, ^1H and ^{31}P NMR spectroscopy and X-ray crystallography.

No stable molybdenum(0) σ-alkyl or -aryl complexes have been reported. Whereas the other Group 6 transition metals form a variety of anionic $[MR(CO)_4L]^-$ complexes [M = Cr or W; L = CO, PPh_3, PMe_3, or $P(OMe)_3$; R = Me, Et, Ph, CH_2Ph, *etc.*],[1-3] the corresponding molybdenum complexes are apparently not stable. The only reported molybdenum(0) complexes containing organic σ-carbon-bound ligands are the anionic heptafluoro-1-methylpropenyl complex, $[Mo(CO)_5(C_4F_7)]^-$,[4] and the alkynyl complexes $[Mo(C{\equiv}CR)(CO)_4L]^-$ (L = CO or PPh_3, R = Me or Ph).[5] The only reported X-ray crystal structure of a zerovalent Group 6 σ-alkyl or -aryl complex is that of $[N(PPh_3)_2]$[*cis*-$WMe(CO)_4(PMe_3)$].[3]

We report here the synthesis, characterization and X-ray crystal structure determination of the zerovalent molybdenum σ-perfluoroaryl complex, Na[*cis-mer*-$Mo(C_6F_5)(CO)_2\{P(OMe)_3\}_3$] **2**. This compound was synthesised as part of an investigation of the redox chemistry of the cycloheptatrienylmolybdenum complex $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$ **1**. Isoelectronic cylopentadienyliron complexes are known to undergo both oxidatively- and reductively-induced migratory CO insertions.[6-8] An investigation of the oxidative electrochemistry of compound **1** revealed a reversible one-electron oxidation.[9] However, chemical oxidation in methanol produced an approximately 50% yield of methylpentafluorobenzoate, indicating that some CO insertion did occur after oxidation. This paper presents the results of the reductive electrochemistry of compound **1** and the characterization and X-ray structural analysis of the product resulting from the reaction of the reduced species $\mathbf{1}^-$ with trimethyl phosphite.

Results and Discussion

Electrochemical Reduction of $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$ **1**.—In a previous investigation it was found that complex **1** displayed a chemically and electrochemically reversible one-electron oxidation at +0.49 V *vs.* ferrocenium–ferrocene in CH_2Cl_2.[9] The reductive electrochemistry of this compound is substantially more complicated. In tetrahydrofuran (thf), cyclic voltammetry of compound **1** at a platinum electrode at a scan rate of 0.2 V s^{-1} displayed a cathodic peak at −2.04 V *vs.* ferrocenium–ferrocene coupled to a smaller anodic peak at −0.86 V. Similar electrochemistry was observed in other solvents. The large peak separation gives the reduction of **1** the appearance of electrochemical irreversibility (slow electron-transfer kinetics). However, this type of behaviour is also typical of structural changes coupled with electron-transfer processes.[10,11]

Our initial goal was to induce migratory insertion of a carbonyl ligand into the Mo–C bond of the pentafluorophenyl group. If this reaction were to occur the presence of electron-donating ligands might allow the insertion to proceed through an electron-transfer-catalysed mechanism, as in the case of the reduction of $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ in the presence of PPh_3.[8] However, the addition of electron-donating ligands such as phosphines, phosphites, and pyridines had no significant effect on the electrochemistry of **1**.

Once it was found that complex **1** underwent CO insertion following oxidation only on relatively long time-scales,[9] its controlled-potential electrolytic reduction in the presence of a nucleophile was examined. Controlled-potential electrolysis of a green 2 mmol dm^{-3} solution of **1** at −2.20 V *vs.* ferrocenium–ferrocene in thf in the presence of 20 mmol dm^{-3} trimethyl phosphite consumed 0.98 e^- and produced a dark orange product $\mathbf{1}^-$. Cyclic voltammetry after the reduction showed an anodic peak at −0.92 V coupled to a smaller cathodic peak at −1.98 V. Thus the product of the reduction was stable on this time-scale, even in the presence of trimethyl phosphite. The species $\mathbf{1}^-$ underwent an oxidation exactly the reverse of the starting compound's reduction. Controlled-potential re-oxidation at −0.60 V consumed 0.93 e^- and returned the green colour and cyclic voltammogram of **1**.

The reduced species $\mathbf{1}^-$ is most likely not simply the $19e^-$ anion with the same structure as compound **1**. The large separation between the anodic and cathodic peak potentials of the $\mathbf{1}$–$\mathbf{1}^-$ couple suggests that significant structural changes accompany the electron transfer. However, the structure of compound $\mathbf{1}^-$ has not yet been established owing to its further reaction upon precipitation (see below). The IR and UV spectra of $\mathbf{1}^-$ were examined by reducing a 7 mmol dm^{-3} solution of **1** in thf containing 0.5 mol dm^{-3} $[NBu_4][PF_6]$ supporting electrolyte in a spectroelectrochemical cell similar to ones described in the literature.[12,13] Absorption maxima in the UV at 326 and 358 nm and carbonyl stretching bands in the IR at 1779 and 1866 cm^{-1} were observed.

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† Sodium *cis*-dicarbonyl-*mer*-(pentafluorophenyl)tris(trimethyl phosphite)molybdate(0).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Selected bond distances (Å) and angles (°) for Na[*cis-mer*-Mo(C_6F_5)$(CO)_2${($P(OMe)_3$}$_3$] **2** with estimated standard deviations (e.s.d.s) in parentheses

Mo–P(1)	2.434(1)	Mo–C(1)	2.384(3)
Mo–P(2)	2.410(1)	Mo–C(40)	1.904(4)
Mo–P(3)	2.421(1)	Mo–C(50)	1.982(4)
C(40)–O(40)	1.198(5)		
C(50)–O(50)	1.152(5)		
P(1)–O(11)	1.620(3)	O(11)–C(11)	1.388(6)
P(1)–O(12)	1.629(3)	O(12)–C(12)	1.438(6)
P(1)–O(13)	1.623(3)	O(13)–C(13)	1.454(5)
P(2)–O(21)	1.604(3)	O(21)–C(21)	1.411(8)
P(2)–O(22)	1.625(3)	O(22)–C(22)	1.441(6)
P(2)–O(23)	1.596(3)	O(23)–C(23)	1.404(6)
P(3)–O(31)	1.627(4)	O(31)–C(31)	1.381(8)
P(3)–O(32)	1.584(4)	O(32)–C(32)	1.371(7)
P(3)–O(33)	1.606(3)	O(33)–C(33)	1.455(6)
C(1)–C(2)	1.418(5)		
C(2)–C(3)	1.351(5)	C(2)–F(2)	1.313(4)
C(3)–C(4)	1.416(5)	C(3)–F(3)	1.338(4)
C(4)–C(5)	1.413(5)	C(4)–F(4)	1.326(5)
C(5)–C(6)	1.352(6)	C(5)–F(5)	1.336(5)
C(1)–C(6)	1.414(5)	C(6)–F(6)	1.312(4)
Na(1) ··· O(40)	2.357(3)	Na(2) ··· O(12)	2.355(3)
Na(1) ··· O(13)	2.525(3)	Na(2) ··· F(6)	2.432(3)
Na(1) ··· O(22)	2.560(3)	Na(2) ··· O(33)	2.774(4)
P(1)–Mo–P(2)	91.5(1)	P(1)–Mo–P(3)	94.5(1)
P(1)–Mo–C(1)	95.9(1)	P(2)–Mo–C(1)	91.5(1)
P(3)–Mo–C(1)	88.0(1)	P(1)–Mo–C(40)	85.1(1)
P(2)–Mo–C(40)	88.3(1)	P(3)–Mo–C(40)	92.1(1)
P(2)–Mo–C(50)	87.2(1)	P(3)–Mo–C(50)	86.8(1)
C(1)–Mo–C(50)	92.4(2)	C(40)–Mo–C(50)	86.7(2)
P(2)–Mo–P(3)	174.0(1)	C(1)–Mo–C(40)	179.0(1)
P(1)–Mo–C(50)	171.7(1)		
Mo–C(40)–O(40)	177.7(3)	Mo–C(50)–O(50)	173.6(4)
Mo–P(1)–O(11)	126.3(1)	Mo–P(1)–O(12)	120.7(1)
Mo–P(1)–O(13)	112.0(1)	Mo–P(2)–O(21)	121.2(1)
Mo–P(2)–O(22)	112.7(1)	Mo–P(2)–O(23)	118.5(1)
Mo–P(3)–O(31)	118.2(1)	Mo–P(3)–O(32)	120.4(2)
Mo–P(3)–O(33)	119.8(1)		
O(11)–P(1)–O(12)	90.8(2)	O(11)–P(1)–O(13)	102.0(2)
O(12)–P(1)–O(13)	100.4(1)	O(21)–P(2)–O(22)	100.2(2)
O(21)–P(2)–O(23)	96.5(2)	O(22)–P(2)–O(23)	104.9(2)
O(31)–P(3)–O(32)	97.3(3)	O(31)–P(3)–O(33)	94.2(2)
O(32)–P(3)–O(33)	101.8(2)		
P(1)–O(11)–C(11)	121.5(3)	P(1)–O(12)–C(12)	119.0(3)
P(1)–O(13)–C(13)	120.1(3)	P(2)–O(21)–C(21)	120.6(3)
P(2)–O(22)–C(22)	121.6(3)	P(2)–O(23)–C(23)	129.0(4)
P(3)–O(31)–C(31)	122.0(4)	P(3)–O(32)–C(32)	129.8(4)
P(3)–O(33)–C(33)	119.4(3)		
Mo–C(1)–C(2)	118.9(2)	Mo–C(1)–C(6)	124.5(2)
C(2)–C(1)–C(6)	116.0(3)	C(1)–C(2)–C(3)	122.1(3)
C(2)–C(3)–C(4)	121.5(3)	C(3)–C(4)–C(5)	116.6(3)
C(4)–C(5)–C(6)	121.6(3)	C(1)–C(6)–C(5)	122.1(3)
C(1)–C(6)–F(6)	121.5(3)	C(5)–C(6)–F(6)	116.4(3)
C(1)–C(2)–F(2)	121.7(3)	C(3)–C(2)–F(2)	116.2(3)
C(2)–C(3)–F(3)	121.6(3)	C(4)–C(3)–F(3)	116.8(3)
C(3)–C(4)–F(4)	121.4(3)	C(5)–C(4)–F(4)	122.0(3)
C(4)–C(5)–F(5)	116.1(4)	C(6)–C(5)–F(5)	122.3(4)

Synthesis and Characterization of Na[*cis-mer*-Mo(C_6F_5)-$(CO)_2${$P(OMe)_3$}$_3$] **2**.—Compound **1** was also reduced chemically with sodium amalgam, producing what appeared to be the same orange product as observed upon electrolytic reduction. The absorption maxima in the UV were the same as those of the electrochemically produced species, but the carbonyl stretching bands in the IR were located at 1758 and 1872 cm^{-1}. However, the addition of 0.5 mol dm^{-3} [NBu_4][PF_6] caused these bands to shift to 1782 and 1867 cm^{-1}, essentially identical to those of the electrochemically produced $\mathbf{1}^-$. A precipitate, presumably $NaPF_6$, was also observed to form. The difference in the CO stretching frequencies between the Na^+ and NBu_4^+ salts of $\mathbf{1}^-$ most likely arises from contact ion pairing with the Na^+ cation.

Attempts to isolate $\mathbf{1}^-$ after chemical reduction of **1** have not been successful as yet. However, by layering hexane over thf solutions of $\mathbf{1}^-$ containing trimethyl phosphite, large single crystals of an air-sensitive pale yellow product **2** were obtained. The infrared spectrum of compound **2** in acetonitrile displayed carbonyl stretching bands at 1763 and 1859 cm^{-1}, suggesting that the two carbonyl ligands remained and that the desired insertion reaction had not taken place.

The ^1H NMR spectrum of compound **2** in [$^2H_8$]tetrahydrofuran showed an apparent triplet at δ 3.43 and a doublet at δ 3.51 with integrals in a 2:1 ratio. The triplet is typical of the $X_nAA'X_n'$ type where $J(AA') \gg |J(AX) - J(AX')|$.[14] In this limiting case, the two X resonances produce an apparent triplet in which the distance between the two outer peaks is equal to the sum of J(AX) and J(AX′). In the compound **2** X would represent the protons of two magnetically equivalent trimethyl phosphite ligands and A their phosphorus nuclei. The observed 10.1 Hz splitting between the two outer peaks of the apparent triplet would then be equal to $^3J(PH) + {}^5J(PH)$. An additional trimethyl phosphite ligand displays a normal doublet with ^3J(PH) also equal to 10.1 Hz. This type of ^1H NMR spectrum has been observed with other phosphine and phosphite complexes.[15,16]

The ^{31}P-{^1H} NMR spectrum of compound **2** showed an apparent septet at δ 169 and a doublet of triplets at δ 179, integrating in a 1:2 ratio. This result agrees with the ^1H NMR spectrum in indicating the presence of three trimethyl phosphite ligands, two of which are equivalent. The apparent septet at δ 169 is interpreted as a partially overlapping triplet of triplets arising from coupling of one trimethyl phosphite phosphorus nucleus to the other two equivalent phosphorus nuclei and to two of the fluorines on the C_6F_5 ligand (presumably the two equivalent *ortho* fluorines). The coupling constants for this trimethyl phosphite ligand would then be $^2J(PP) = 47.5$ Hz and $^4J(FP) = 23.1$ Hz. Likewise, the doublet of triplets observed for the two equivalent phosphites gives coupling constants of $^2J(PP) = 47.4$ Hz and $^4J(FP) = 8.5$ Hz.

Thus, IR and NMR spectroscopy suggested a structure for compound **2** consisting of two terminal carbonyls, three trimethyl phosphite ligands (two of which are magnetically equivalent), and a pentafluorophenyl ligand. This composition could not be confirmed by elemental analysis. Replicate analyses of spectroscopically pure crystalline material were reproducible, but grossly in error, failing to account for a significant portion of the sample. Since the results of the analyses were so far out of range and since incorporation of likely impurities, even though not seen by NMR spectroscopy, could not bring the analyses into compliance, it was concluded that it would not be possible to obtain a satisfactory elemental analysis. However, an X-ray structural analysis confirmed the identity of compound **2**.

Structure of Na[*cis-mer*-Mo(C_6F_5)$(CO)_2${$P(OMe)_3$}$_3$] **2**.—The molecular structure of compound **2** and the atom labelling scheme are illustrated in Fig. 1. Selected bond distances and angles are summarized in Table 1. The central zerovalent molybdenum atom is six-co-ordinate in an octahedral arrangement. While the average ligand–Mo–ligand bond angle is 90(3)°, slight distortions within individual bond angles are apparent. The two *cis* carbonyl ligands have a C–Mo–C bond angle of 86.7(2)°, due to steric repulsion from the bulkier pentafluorophenyl and trimethyl phosphite ligands. Likewise, the bond angle between the two *trans* trimethyl phosphite groups is slightly distorted, bending away from the pentafluorophenyl ligand [P(2)–Mo–P(3) 174.0(1)°]. The orientations of the two carbonyl groups are also affected by the pentafluorophenyl group and the trimethyl phosphite groups. The carbonyl *trans* to the pentafluorophenyl ligand has only a slight deviation from ideality; Mo–C(40)≡O(4) 177.7(3)° in

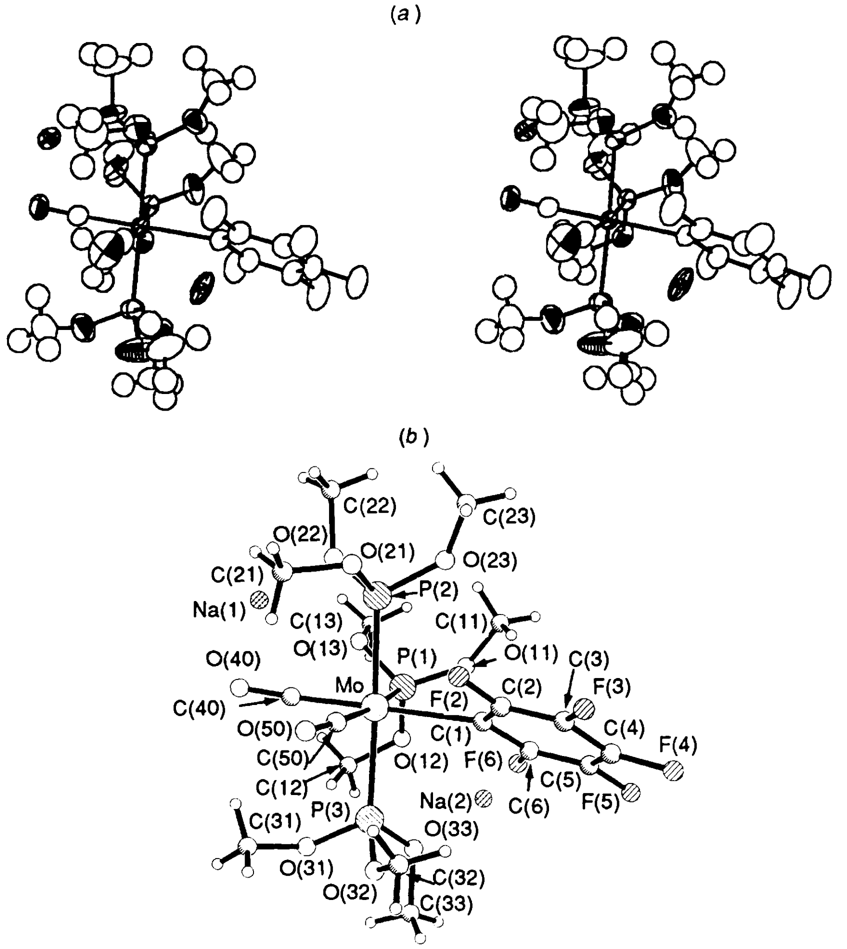


Fig. 1 Stereoview (*a*) and atom labelling scheme (*b*) of Na[*cis-mer*-Mo(C_6F_5)(CO)$_2${P(OMe)$_3$}$_3$] **2**

the direction of the *cis* carbonyl group [C(50)≡O(50)]. The angle Mo–C(50)≡O(50) is more non-linear, 173.6(4)°. A shorter Mo–C bond length is observed in the *trans* carbonyl [1.904(4) Å] as compared to the *cis* [1.982(4) Å] carbonyl. Subsequently, the *trans* carbonyl shows an elongation of the C≡O bond [1.198(5) Å] while the *cis* carbonyl triple bond of 1.152(5) Å is reasonable when considering the summation of the radii found in the work of Pauling[17] (1.153 Å) and when comparing it to the work of Bueno and Churchill.[18]

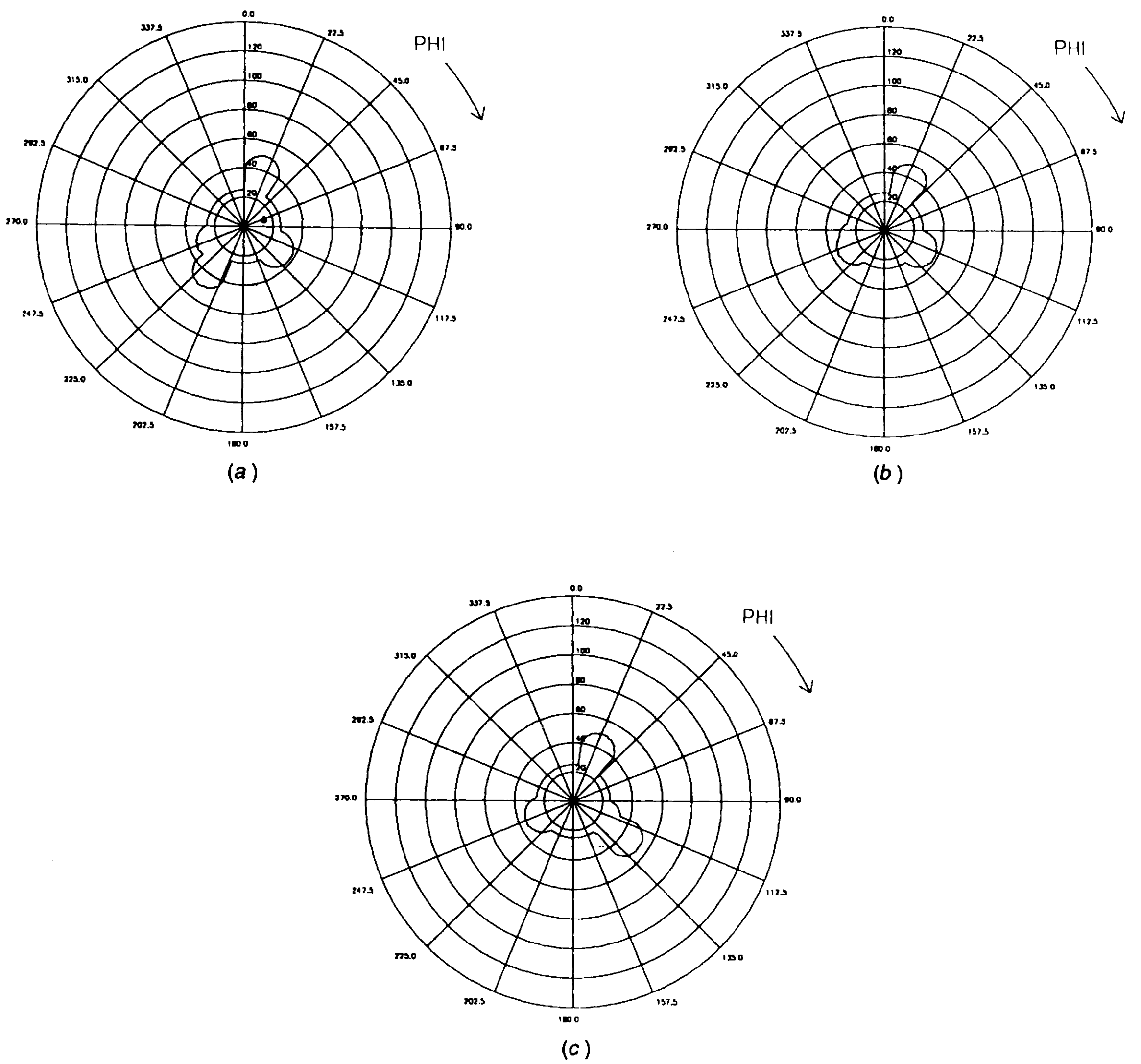
The trimethyl phosphite ligands show no unusual distortions. The respective average Mo–P, P–O, and O–C bond distances of 2.42(1), 1.61(1), and 1.42(3) Å are internally consistent and in good agreement with other experimental values found in the Cambridge Structural Database.[19] The phosphorus atoms are tetrahedrally co-ordinated with an average Mo–P–O bond angle (118°) above ideality and an average O–P–O bond angle slightly less, 99(4)°. However, the average of all involved bond angles is 109°. The mean P–O–C bond angle of 123(5)° is quite normal. The orientation and the relative steric bulk of the three trimethyl phosphite ligands can be represented in terms of cone angles θ,[20] by looking down the molybdenum–phosphorus bonds. Ligand profiles have been generated with the program CONE[20e] and are displayed in Fig. 2. They are calculated silhouettes of the trimethyl phosphite ligands. The outlines of these ligands are clearly observed. The average maximum half-cone angle, $(\theta/2)_{max}$, is approximately 52°, making $\theta \approx 104°$. These silhouette profiles and their representative numerical values can be used to predict conformations and reaction rates and mechanisms.[20]

The atoms in the pentafluorophenyl ring are planar with an absolute mean deviation of 0.012(6) Å. The ring leans slightly toward the C(5) carbonyl group placing the molybdenum atom 0.34 Å from the least-squares plane. The Mo–C(1) bond length is 2.384(3) Å which is considerably longer than the Mo–C bond length of 2.244(9) Å found in the pseudo-octahedrally co-ordinated structure [Mo(C_6F_5)(CO)$_2$(η-C_7H_7)].[21a] The carbon-to-carbon bond distances within the pentafluorophenyl ring range from 1.351(5) to 1.418(5) Å with a mean of 1.39(3) Å. This averaged value is in excellent agreement with the work of Churchill and O'Brien[21a] [1.38(1) Å] and with the electron diffraction investigation by Almenningen *et al.*[22] for hexafluorobenzene [1.394(7) Å]. The C–F bond lengths [range 1.312(4)–1.338(4), mean 1.33(1) Å] are also in good agreement with the previous work.[21a,22] The C–C–C bond angles within the ring range from 116.0(3) to 122.1(3)° with a mean of 120(2)° and C–C–F bond angles range from 116.1(4) to 122.3(4)° with a mean of 120(3)°.

The four sodium ions in the unit cell are located at two non-equivalent special sites (2c and 2d). Both sites are located in channels that traverse along the *Y* axis of the unit cell. The first sodium ion, Na(1), is nestled between two trimethyl phosphite ligands and one carbonyl ligand with oxygen to sodium contact distances between 2.357(3) and 2.560(3) Å. The second sodium ion, Na(2), is positioned in line with the C(6)–F(6) bond and lies close to O(12) of one of the trimethyl phosphite groups. The contact distances Na(2)···O(12) and Na(2)···F(6) are 2.355(3) and 2.432(3) Å, respectively. The orientation of the sodium cation to the organometallic anion can clearly be seen in the packing diagram in Fig. 3.

Conclusion

Cyclic voltammetry of complex **1** results in an apparently irreversible one-electron reduction at −2.04 V *vs.* ferrocenium–



(*a*) (*b*) (*c*)

Fig. 2 Ligand profiles ($\theta/2$ *vs.* φ) for complex **2** looking down (*a*) the Mo–P(1), (*b*) the Mo–P(2), and (*c*) the Mo–P(3) bond. PHI (φ) is the angle of rotation about the metal–phosphorus bond[20c]

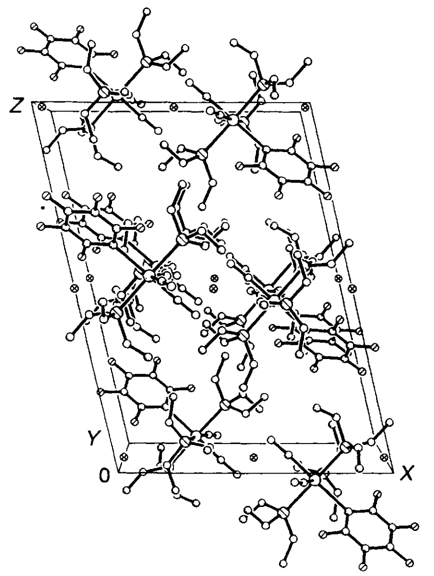


Fig. 3 Packing diagram for complex **2**

ferrocene in thf. The appearance of electrochemical irreversibility most likely arises from structural changes which follow the electron transfer. The one-electron reduction and the accompanying structural changes produce a stable orange product $\mathbf{1}^-$ which displays an apparently irreversible oxidation at −0.92 V. Reoxidation of $\mathbf{1}^-$ regenerates compound **1**, indicating that the proposed structural changes following reduction of **1** are reversible.

Compound **1** can also be reduced chemically with sodium amalgam. When this reduction is carried out in the presence of trimethyl phosphite, precipitation with hexane yields **2**. So far as we are aware this is the first stable zerovalent molybdenum σ-aryl complex. The structure of **2** has been determined by X-ray crystallography.

Experimental

General.—Complex **1** was prepared according to the literature procedure.[21] Solvents were distilled under nitrogen before use: CH_2Cl_2 (Fisher Optima) from CaH_2 and thf (Fisher Optima) from sodium–benzophenone. All other chemicals were reagent grade or better. All reactions were carried out under an atmosphere of nitrogen or argon. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Instruments.—Infrared spectra were obtained using a

Table 2 Atomic coordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	7 125(1)	2 496(1)	4 586(1)
P(1)	7 521(1)	261(1)	4 576(1)
O(11)	7 930(2)	−476(3)	3 961(2)
C(11)	7 557(5)	−234(5)	3 243(3)
O(12)	8 399(2)	−342(3)	5 191(2)
C(12)	8 303(3)	−317(4)	5 921(2)
O(13)	6 597(2)	−619(2)	4 664(2)
C(13)	6 674(3)	−1 984(4)	4 632(3)
P(2)	5 681(1)	2 220(1)	3 639(1)
O(21)	4 910(2)	3 349(3)	3 398(2)
C(21)	4 378(4)	3 861(6)	3 878(4)
O(22)	4 940(2)	1 137(3)	3 816(2)
C(22)	4 064(4)	769(6)	3 303(3)
O(23)	5 832(2)	1 883(3)	2 860(2)
C(23)	5 237(5)	2 199(8)	2 193(3)
P(3)	8 530(1)	3 004(1)	5 538(1)
O(31)	8 435(3)	2 758(4)	6 356(2)
C(31)	7 778(4)	3 424(6)	6 662(3)
O(32)	8 929(3)	4 407(3)	5 664(3)
C(32)	8 775(4)	5 404(5)	5 178(3)
O(33)	9 538(2)	2 216(3)	5 622(2)
C(33)	10 379(4)	2 529(5)	6 195(4)
C(1)	8 093(2)	3 116(3)	3 761(2)
C(2)	7 799(2)	4 188(3)	3 325(2)
C(3)	8 372(3)	4 684(3)	2 909(2)
C(4)	9 309(2)	4 167(3)	2 894(2)
C(5)	9 595(2)	3 081(4)	3 314(2)
C(6)	9 022(3)	2 594(3)	3 733(2)
F(2)	6 950(2)	4 753(3)	3 302(2)
F(3)	8 105(2)	5 727(3)	2 522(1)
F(4)	9 883(2)	4 677(3)	2 501(2)
F(5)	10 477(2)	2 596(3)	3 292(2)
F(6)	9 365(2)	1 588(2)	4 104(1)
C(40)	6 343(3)	2 029(3)	5 246(2)
O(40)	5 825(2)	1 726(3)	5 640(2)
C(50)	6 665(3)	4 244(3)	4 680(2)
O(50)	6 345(3)	5 214(3)	4 775(3)
Na(1)*	5 000	0 000	5 000
Na(2)*	10 000	0 000	5 000

* Site multiplicity = ½.

Mattson Instruments Cygnus 100 FTIR, ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra on a Bruker AMX 360 NMR spectrometer. Chemical shifts were assigned relative to $SiMe_4$ as internal standard for ^1H and 85% H_3PO_4 as external standard for ^{31}P. Cyclic voltammetry and controlled-potential electrolyses were performed using a Bioanalytical Systems BAS 100A electrochemical analyser. Cyclic voltammetry was done using a 0.5 mm platinum-disc working electrode, a platinum-wire auxiliary electrode, and a Ag–AgCl reference electrode. Controlled-potential electrolyses were performed using 25 × 25 mm platinum-foil working and auxiliary electrodes and a silver-wire quasi-reference electrode. Spectroelectrochemical measurements were made in a cell similar to ones described in the literature[12,13] having calcium fluoride windows and a 100-mesh platinum-gauze working electrode. All potentials are expressed relative to the formal potential of the ferrocenium–ferrocene couple, which we measure as approximately +0.45 V *vs.* Ag–AgCl.

Synthesis of Na[*cis-mer*-Mo(C_6F_5)$(CO)_2${P$(OMe)_3$}$_3$] **2**.—Complex **1** (0.100 g, 0.244 mmol) and trimethyl phosphite (300 μl, 2.54 mmol) were dissolved in thf (3 cm^3), and 0.1% Na(Hg) (11.2 g, 0.487 mmol) was added. After the solution had changed from green to orange it was stirred for 5 min and then filtered through a medium-porosity Büchner funnel into a Schlenk tube. This solution was carefully layered with hexane (30 cm^3) and allowed to stand overnight. The product, **2**, formed as large pale yellow *crystals* (0.124 g, 71%) (Found: C, 22.0; H, 4.3; F, 7.65; P, 12.4. $C_{17}H_{27}F_5MoNaO_{11}P_3$ requires C, 28.6; H, 3.8; F, 13.3; P, 13.0%). IR: ν_{max}/cm^{-1} (CO) 1885s, 1732s (Nujol); 1859s, 1763s (acetonitrile). NMR (C_4D_8O): δ_H 3.43 [18 H, t, ^3J(PH) + ^5J(PH) = 10.1, P$(OMe)_3$] and 3.51 [9 H, d, ^3J(PH) 10.1, P$(OMe)_3$]; δ_P 169 [1 P, tt, ^2J(PP) 47.5, ^4J(FP) 23.1, P$(OMe)_3$] and 179 [2 P, dt, ^2J(PP) 47.4, ^4J(FP) 8.5 Hz, P$(OMe)_3$].

X-Ray Structural Analysis of Na[*cis-mer*-Mo(C_6F_5)$(CO)_2$-{P$(OMe)_3$}$_3$] **2**.—*Crystal Data.* $C_{17}H_{27}F_5MoNaO_{11}P_3$, M_r = 714.2, monoclinic, space group $P2_1/c$ (No. 14, C^5_{2h}), a = 13.861(1), b = 10.6067(8), c = 19.214(1) Å, β = 102.68(1)°, U = 2755.8(3) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), T = 292 K, Mo-K$\bar{\alpha}$ (λ = 0.710 73 Å), D_c = 1.721 Mg m^{-3}, Z = 4, F(000) = 1440, μ = 0.733 mm^{-1}.

Data collection and processing. Owing to the air sensitivity of the compound, a single crystal of high optical quality was chosen and mounted in a sealed capillary under an atmosphere of dry nitrogen. The crystal data were collected on an Enraf–Nonius CAD-4F diffractometer using graphite-monochromatized radiation (ω–2θ mode with an ω scan width = 1.25 + 0.35 tan θ). Of the 5664 measured reflections (3.0 ⩽ 2θ ⩽ 50.0°; h 0–16, k −5 to 12, l −22 to 22), 4318 were unique having $I > 3\sigma(I)$ (R_{int} = 0.041). Three standard reflections ($\bar{2}54$, $51\bar{1}$, $15\bar{4}$) showed no significant deviation in intensity. Polarization, Lorentz, and empirical absorption (maximum, minimum transmission factors = 0.9998, 0.9562) corrections were made. Systematic absences ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$) yielded the space-group assignment.

Structure analysis and refinement. Direct methods (SHELXTL-PC)[23] were used to obtain a structural solution. The model was refined employing the block full-matrix least-squares method. A total of 347 parameters were refined which constituted a data-to-parameter ratio of 12.4:1. Positions for hydrogen atoms were calculated and not refined; all other atoms were refined anisotropically. The residual electron-density map showed the highest peak density to be 1.29 e $Å^{-3}$ in the region of the molybdenum atom which is quite normal for heavy atoms. Elsewhere, only random fluctuations were observed. Anomalous dispersion correction factors and atomic scattering factors were taken from ref. 24. The weighting scheme was $w = 1/[\sigma^2(F) + 9.7 \times 10^{-5} F^2]$. After applying a secondary extinction correction [$g = 2.9(9) \times 10^{-4}$], final reliability values were obtained, R = 0.040 and R' = 0.056. Final atomic coordinates are summarized in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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