

Synthesis and X-Ray Crystal Structure of Tetra(2-methylphenyl)molybdenum(IV), $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$.† Redox Chemistry of $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ Compounds of Molybdenum, Rhenium, Ruthenium, and Osmium

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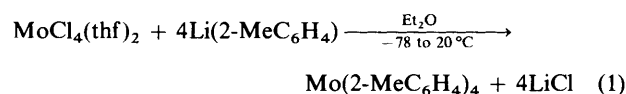
The reaction of $\text{MoCl}_4(\text{thf})_2$ (thf = tetrahydrofuran) with 4 equivalents of *o*-tolyl-lithium in diethyl ether yields $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ as air-sensitive purple crystals, characterized by X-ray crystallography. The redox chemistry of $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ (M = Mo, Re, Ru, or Os) has been studied by cyclic voltammetry and chemical methods. One-electron oxidation of the ruthenium and osmium derivatives gives tetra-aryl cations $[\text{M}(2\text{-MeC}_6\text{H}_4)_4]^+$; the osmium complex crystallizes from dichloromethane–diethyl ether as BF_4^- or CF_3SO_3^- salts which have been fully characterized.

We recently described the behaviour of homoleptic tetra *o*-tolyl derivatives of rhenium and osmium towards Lewis bases where, for rhenium,^{1a} addition of trimethylphosphine leads to η^2 -aryne derivatives via *ortho*-hydrogen abstraction; under analogous conditions $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$ undergoes reductive coupling and σ to π rearrangement to yield unusual osmium(II) η^6 -biaryl complexes.^{1b} To help delineate the factors responsible for influencing the course of these reactions, other homoleptic tetra-aryls are being studied. The synthesis of the 10-electron $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ was attempted since tetrahedral mesityl² and norbornyl³ analogues are known.

We also report the first redox studies of homoleptic tetrahedral aryls.^{3,4} These have led to the isolation of a rare⁵ osmium(V) complex, the unusual low-spin 11-electron tetrahedral cation $[\text{Os}(2\text{-MeC}_6\text{H}_4)_4]^+$.⁶

Results and Discussion

Synthesis and Crystal Structure of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$.—Addition of 4 equivalents of *o*-tolyl-lithium to $\text{MoCl}_4(\text{thf})_2$ (thf = tetrahydrofuran) in diethyl ether gives a dark brown solution from which deep purple $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ is obtained after extraction into hexane and crystallization [equation (1)].



The yield is poor (13%) and we have been unable to characterize other species present in the reaction mixture. The choice of reagents and conditions is important; repeating the reaction with *o*-tolylmagnesium bromide failed to yield any isolable product. Substituting MoCl_5 in equation (1) gave a reduced yield of the tetra-aryl. Attempts to prepare $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ by a route analogous to that reported for $\text{Mo}(\text{mes})_4$ ² (mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) were unsuccessful. Thus, reaction of $\text{MoCl}_3(\text{thf})_3$ with *o*-tolyl-lithium (or *o*-tolylmagnesium bromide) in diethyl ether or thf did not give the expected $[\text{Mo}(2\text{-MeC}_6\text{H}_4)_4]^-$ anion. The low reduction potential of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ (see below) may be responsible for this failure.

Under nitrogen or argon at 20 °C, $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ is stable indefinitely as a solid or in hydrocarbon solution; however, it decomposes rapidly when heated above ca. 70 °C. In the electron-impact mass spectrum at 70 eV the heaviest (ca. 1.12×10^{-17} J) observed ions were due to $\text{C}_{14}\text{H}_{14}^+$, C_7H_8^+ , and C_7H_7^+ ; no molybdenum-containing fragments were detected.

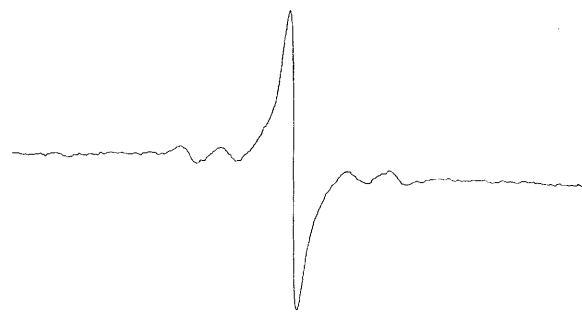


Figure 1. E.s.r. spectrum (X-band) of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ in toluene at 293 K. The field width is 400 G (4×10^{-2} T)

The complex is exceedingly sensitive to oxygen and to moisture: hydrocarbon solutions decompose rapidly to an intractable mixture of products; the solid decomposes to a black tar within several minutes. These results should be compared with those reported for analogous rhenium,⁷ ruthenium,⁷ and osmium⁸ compounds: the compounds of Ru and Os are air stable, whereas the rhenium derivative cleanly gives the oxo-aryl $\text{ReO}(2\text{-MeC}_6\text{H}_4)_4$ on exposure to air or dry oxygen.⁷ We also note that $\text{Mo}(\text{mes})_4$ is reported to be air-stable.²

The i.r. spectrum (Nujol mull) of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ is similar to those of related derivatives, comprising mainly peaks attributable to the *o*-tolyl ligands.^{7,8} However, an additional medium intensity C–H stretch is observed at 2361 cm^{-1} . Although this absorption is in the region expected for ‘agostic’ interactions,^{9,†} X-ray crystallography provides no evidence for such interaction.

The solution magnetic moment of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ [$\mu_{\text{eff.}} = 2.9(1)$] is close to the spin-only value for two unpaired electrons ($\mu = 2.83$) and is similar to those reported for related mesityl² and norbornyl³ MR_4 species. Figure 1 shows the e.s.r. spectrum of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ in toluene at 293 K ($g_{\text{iso}} = 1.983$, $A_{\text{iso}} =$

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

‡ There are now several examples of complexes displaying low C–H stretches that do not contain agostic interactions; see for example B. Hessen, J. H. Teuben, T. H. Lemmon, J. C. Huffman, and K. G. Caulton, *Organometallics*, 1985, 4, 946.

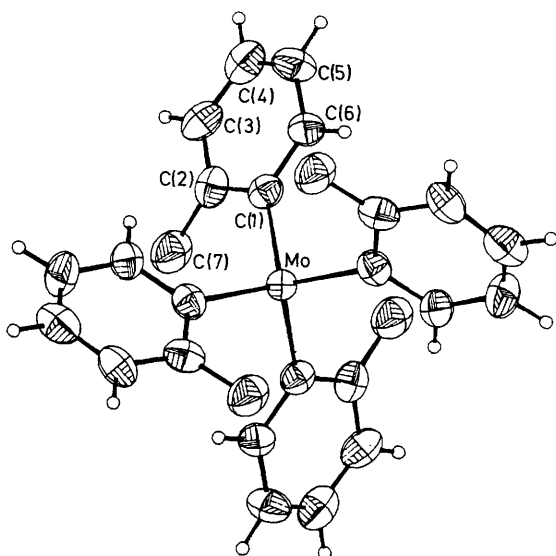


Figure 2. Molecular structure of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ showing the atom labelling scheme. Methyl hydrogens omitted for clarity; ellipsoids at 50% probability

Table 1. Bond lengths (Å) and angles ($^\circ$) for $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$

C(1)–Mo	2.086(9)	C(2)–C(1)	1.416(12)
C(6)–C(1)	1.389(11)	C(3)–C(2)	1.410(14)
C(7)–C(2)	1.449(14)	C(4)–C(3)	1.370(13)
C(5)–C(4)	1.324(14)	C(6)–C(5)	1.378(13)
C(1)–Mo–C(1A)	108.4(3)	C(1)–Mo–C(1B)	111.5(5)
C(2)–C(1)–Mo	122.7(7)	C(6)–C(1)–Mo	119.1(7)
C(6)–C(1)–C(2)	117.9(9)	C(3)–C(2)–C(1)	117.7(10)
C(7)–C(2)–C(1)	120.4(9)	C(7)–C(2)–C(3)	121.8(9)
C(4)–C(3)–C(2)	120.9(10)	C(5)–C(4)–C(3)	121.5(10)
C(6)–C(5)–C(4)	119.6(9)	C(5)–C(6)–C(1)	122.2(10)

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z) : (a) $-y, x, -1.0 + z$; (b) $-x, -y, 1.0 - z$.

Table 2. Geometries of $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ species

Metal	Electronic configuration	C–M–C Angles ($^\circ$)	Ligand twist*	Ref.
Mo^{IV}	d^2 (10 e)	108.4–111.5	54.9	This work
Re^{IV}	d^3 (11 e)	105.6–113.4	55.1–59.6	7
Os^{V}	d^3 (11 e)	101.1–114.3	16.5–24.8	6
Ru^{IV}	d^4 (12 e)	106.3–114.9	44.6–45.2	7
Os^{IV}	d^4 (12 e)	106.9–117.1	44.1–44.9	8

* Represented by the torsion angle $\text{P1-M-C}_\alpha\text{-C}_\beta$ where P1 is a point on the $\bar{4}$ axis (or two-fold in the case of Os^{V}) and C_α and C_β are the metal- and methyl-bonded carbons of the *o*-tolyl groups.

$2.5 \times 10^{-3} \text{ cm}^{-1}$). Our e.s.r. data are similar to those reported by Schrock and co-workers³ for tetranorbornylmolybdenum.

Chemical reactions of $\text{Mo}(2\text{-C}_6\text{H}_4)_4$ will be described separately but it may be noted that in common with its rhenium analogue^{1a} the complex undergoes ligand-induced *ortho*-hydrogen abstraction on treatment with trimethylphosphine, to give the diamagnetic aryne derivative $\text{Mo}(\eta^2\text{-}2\text{-MeC}_6\text{H}_3\text{)}(2\text{-MeC}_6\text{H}_4)_2(\text{PMe}_3)_2$ whose structure is similar to that of the rhenium aryne.^{1a}

A diagram of the tetra-aryl molecule, which has crystallographic $\bar{4}$ symmetry, is shown in Figure 2, with bond lengths

and angles in Table 1. The molecule has a geometry very close to tetrahedral, with the two unique C–Mo–C angles of 108.4(3) and 111.5(5) $^\circ$. The Mo–C bond length is similar to those in the Mo_2R_6 dimer, $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$,¹⁰ 2.131 Å. In many respects the geometry is similar to that of the homoleptic dialkylamide, $\text{Mo}(\text{NMe}_2)_4$, which, however, is diamagnetic, due probably to the lifting of the *d*-orbital degeneracy by $\text{N}_{\text{amide}}\text{-Mo } \pi$ bonding.¹¹ Here the L–Mo–L (L = N) angles also differ only slightly (107.3–112.5 $^\circ$) in spite of the presence of a ‘lone pair.’ Clearly, steric factors play a significant part in determining the spatial arrangement of the ligands.

Of more immediate interest is to compare the geometry, especially the distribution of angles, with those of the directly analogous species $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ (M = Re, Os, or Ru) and $[\text{Os}(2\text{-MeC}_6\text{H}_4)_4]^+$. It is surprising to note that although all of the neutral species $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ have essentially the same configuration and distribution of *o*-tolyl methyl groups, giving structures with effect $\bar{4}$ symmetry, they occur with several different crystal structures. Only $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ (M = Ru or Os) are isostructural. We presume this occurs because of small differences in structure which affect the exact metal geometry in terms of C–M–C angles and orientation of *o*-tolyl rings and therefore the crystal packing. For convenience we present the comparative data in Table 2, from which the following facts emerge: first, the distortion from ideal tetrahedral geometry (C–M–C 109.5 $^\circ$) is minimal for the d^2 high-spin molybdenum(IV) complex, is significant for the d^4 , diamagnetic complexes of Ru^{IV} and Os^{IV} , and is largest for the d^3 , paramagnetic low-spin compounds of Re^{IV} and Os^{V} . This is to be expected from Jahn-Teller effects. It should be noted also that the structure of $[\text{Os}(2\text{-MeC}_6\text{H}_4)_4]^+$ is unique. The arrangement of the *o*-tolyl groups is such as to give the ion approximate two-fold symmetry, but not $\bar{4}$.

From these results, it seems that in these $d^2 - d^4$ $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ complexes with purely σ bonding, the electronic configuration of the MC_4 system is best described as close to that for T_d symmetry, with all electrons in the *e* orbitals. The least distortion occurs for the ‘spherically’ symmetrical d^2 ($d_{x^2-y^2}, d_{z^2}$) and d^4 ($d_{x^2-y^2}, d_{z^2}$) systems, the most for the d^3 systems. It is also worth noting, however, that for the complexes of Re, Ru, and Os the M–C bonds are always shorter than the Mo–C bonds and we have already highlighted the steric interactions between the *o*-tolyl methyls related by two-fold axes in the $\text{M}(2\text{-MeC}_6\text{H}_4)_4$ structures.^{7,8}

Finally, it must be noted that in the symmetrical $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ complex there is no evidence of $\text{Mo} \cdots \text{H}$ agostic interactions. Indeed, the *o*-tolyl methyls are seen to be under pressure since the molybdenum–aryl bonding is slightly asymmetric, with the Mo–C–C angle on the side of the methyl substituent larger than that on the other side (123 vs. 119 $^\circ$).

Redox Chemistry of Homoleptic Tetrahedral Aryls.—The cyclic voltammetry (c.v.) data on homoleptic tetra-*o*-tolyls of molybdenum, rhenium, ruthenium, and osmium are collected in Table 3.

(a) **Molybdenum.** Attempts to oxidize $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ to the molybdenum(V) cation $[\text{Mo}(2\text{-MeC}_6\text{H}_4)_4]^+$ by a procedure analogous to that used to prepare $[\text{Mo}(\text{mes})_4]\text{I}_3$ ² were unsuccessful. Thus, addition of iodine to $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ in thf resulted in decomposition to an intractable mixture; oxidations with AgBF_4 or $\text{Ag}[\text{O}_3\text{SCF}_3]$ in thf also failed. C.v. data suggest a possible explanation for these results: the oxidation of $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$ (which occurs at +0.63 V in thf) was found to be irreversible up to scan rates of 200 mV s^{-1} . A reversible reduction wave was observed at –1.82 V. This is a rather low potential and it is not surprising that preparative attempts to synthesize the putative $[\text{Mo}(2\text{-MeC}_6\text{H}_4)_4]^-$ anion have not been successful (e.g. Na–Hg amalgam or Na–K alloy in

Table 3. Cyclic voltammetry of homoleptic aryls, $M(2\text{-MeC}_6\text{H}_4)_4$

M	Solvent ^a	$E_{1/2}^a/V$	
		$M^{IV}-M^V$	$M^{IV}-M^{III}$
Mo	thf	(+0.63)	-1.82
Re	thf	(+0.40)	-1.46
Ru	thf	(+0.64)	(-1.96)
Ru	CH ₂ Cl ₂	+0.51	-1.88
Os	thf	+0.41	-1.89
Os	CH ₂ Cl ₂	+0.33	-1.96

^a With 0.2 mol dm⁻³ NBu₄PF₆ as supporting electrolyte. ^b Values in parentheses indicate irreversible redox couples.

dimethoxyethane). These electrochemical data should be compared with those for tetranorbornylmolybdenum³ which show two oxidation waves at -0.15 and +1.25 V (relative to Ag-Ag⁺); only the former process was reversible.

(b) *Rhenium*. Initial attempts to prepare $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ ⁷ by treating $\text{ReCl}_4(\text{thf})_2$ with 4 equivalents of *o*-tolylmagnesium bromide in thf or diethyl ether gave deep blue, air-sensitive solutions from which no pure product could be isolated; the tetra-aryl was formed only when a deficiency of Grignard reagent was used (*ca.* 2 equivalents), giving a moderate 29% yield.⁷ We propose that the blue solution contains the rhenium(III) anion $[\text{Re}(2\text{-MeC}_6\text{H}_4)_4]^-$ based on the following observations: (i) addition of *o*-tolylmagnesium bromide or Na-Hg amalgam (1 equivalent) to pure $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ in thf also gives the blue solution; (ii) treatment of the blue solution with anhydrous copper(I) chloride, followed by work-up in the usual manner,⁷ gives $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ in moderate yield; (iii) bulk electrolysis of $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ at *ca.* -2.0 V at a platinum gauze electrode in thf also gave the blue solution; reduction under these conditions was reversible; and (iv) c.v. experiments showed that $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ undergoes a reversible reduction at -1.46 V in thf.

Attempts to isolate the rhenium(III) anion by addition of various counter ions $[\text{NEt}_4^+, \text{NBu}_4^+, \text{N}(\text{PPh}_3)_2, \text{etc.}]$ failed to give a pure product. Reduction of $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ with alkali metals in the presence of crown ethers also failed. No reaction was detected between $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ and $\text{Co}(\eta\text{-C}_5\text{H}_5)_2$ in hexane, thf, or acetonitrile.

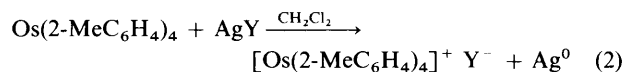
The reduced species was unaffected by addition of phosphines (PMe_3 or PMe_2Ph). This contrasts with the behaviour of neutral $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ which reacts to give $\text{Re}(2\text{-MeC}_6\text{H}_4)_4(\text{PR}_3)$ at -80 °C, then, on warming the η^2 -aryne $\text{Re}(\eta^2\text{-}2\text{-MeC}_6\text{H}_3)(2\text{-MeC}_6\text{H}_4)_2(\text{PR}_3)_2$.^{1a} The reactivity of $[\text{Re}(2\text{-MeC}_6\text{H}_4)_4]^-$ towards dry oxygen or moist air also differs from that of the neutral complex. Thus, the reduced species when treated rapidly with either reagent in thf forms dark orange-brown mixtures from which no pure products could be isolated.

Electrochemical oxidation of $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$ at +0.40 V is irreversible (see Table 3). On a preparative scale, no reaction was observed between the tetra-aryl and $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ in thf or dichloromethane; treatment with stronger oxidants (*e.g.* Ag⁺) resulted in decomposition.

(c) *Ruthenium*. C.v. data for $\text{Ru}(2\text{-MeC}_6\text{H}_4)_4$ ⁷ in thf at 20 °C show two irreversible redox waves at +0.64 and -1.96 V. In dichloromethane, however, these processes became reversible at scan rates as low as 20 mV s⁻¹. Both waves were shifted slightly: oxidation of Ru^{IV} to Ru^V occurred at +0.51 V; reduction to Ru^{III} took place at -1.88 V. Chemical oxidation of $\text{Ru}(2\text{-MeC}_6\text{H}_4)_4$ with silver salts ($\text{BF}_4^-, \text{PF}_6^-,$ or CF_3SO_3^-) in dichloromethane gave deep purple solutions stable for days at 20 °C; however, repeated attempts to isolate a solid

ruthenium(V) complex have failed. Addition of hexane or diethyl ether to concentrated dichloromethane solutions of the oxidized species resulted in reduction back to maroon $\text{Ru}(2\text{-MeC}_6\text{H}_4)_4$.

(d) *Osmium*. Cyclic voltammograms of $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$ ⁸ in dichloromethane and thf with $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ as internal standard are shown in Figure 1 of ref. 6. Three reversible redox waves are seen in thf, one corresponding to oxidation of Os^{IV} to Os^V (+0.41 V), the second to reduction of Os^{IV} to Os^{III} (-1.89 V), and a further reduction (-2.47 V) that may be metal- (Os^{III} to Os^{II}) or ligand-based. The first two waves shift to lower potential in dichloromethane; the second reduction wave was not observed due to reduction of the solvent. Bulk electrolysis of $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$ at +0.7 V in thf or dichloromethane gave dark purple solutions of the osmium(V) cation. Only the latter solutions were stable; in thf on removing the applied potential the maroon colour of the starting material quickly reappeared due to reduction by the solvent. Accordingly, preparative scale oxidations with AgBF_4 or $\text{Ag}[\text{O}_3\text{SCF}_3]$ in thf failed to yield the desired $[\text{Os}(2\text{-MeC}_6\text{H}_4)_4]^+$ cation. In dichloromethane, however, the same reactions immediately gave deposits of metallic silver and deep purple solutions from which crystals of the osmium(V) salts [equation (2), $\text{Y} = \text{BF}_4^-$ or CF_3SO_3^-] were isolated in high yield on work-up.



The X-ray crystal structure of the trifluoromethanesulphonate (triflate) salt has been described.⁶

The compounds are air-stable for prolonged periods as solids or in dichloromethane or acetonitrile solution; their molar conductivities correspond to 1:1 electrolytes.¹² Dissolution in thf, however, results in immediate reduction back to $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$, no doubt the reason preparative scale reactions in this solvent failed.

I.r. spectra show bands characteristic of the *o*-tolyl ligands, and additional strong peaks due to either BF_4^- (1 055 cm⁻¹) or CF_3SO_3^- (1 270 and 636 cm⁻¹) counter ions.

The e.s.r. spectrum of the triflate salt in frozen dichloromethane at 77 K consists of a single broad line at *ca.* $g = 2$. Magnetic susceptibilities, determined by the Evans method¹³ in acetonitrile at 30 °C, accord with a single unpaired electron, *i.e.* low-spin Os^V , d^3 [*cf.* the isoelectronic, 11-electron $\text{Re}(2\text{-MeC}_6\text{H}_4)_4$]. Examples of low-spin tetrahedral complexes are rare.⁵ In 1972 Bower and Tennent¹⁴ reported low-spin tetranorbornyls of Fe and Co; Theopold and co-workers recently examined the structure¹⁵ and redox properties⁴ of the cobalt derivative in detail. Results from our laboratories have shown that tetrahedral MR_4 complexes of rhenium ($\text{R} = 2\text{-MeC}_6\text{H}_4$),⁷ ruthenium ($\text{R} = 2\text{-MeC}_6\text{H}_4$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$, 4- $\text{Bu}^t\text{C}_6\text{H}_4$, or C_6H_{11}),⁷ and osmium ($\text{R} = \text{C}_6\text{H}_5$, 2- MeC_6H_4 , or C_6H_{11})⁸ all have low-spin electronic configurations.

One-electron reduction of the osmium(V) cations back to neutral $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$ appears to be the predominant reaction pathway. The reaction with thf has already been noted above; similar reductions occur when the salts are treated with NaBPh₄, PMe_2Ph , TEMPO, LiMe, or MgCl (CH_2SiMe_3).

Experimental

All manipulations were performed under an atmosphere of argon using dry, oxygen-free solvents. Microanalyses were by Pascher or Imperial College Laboratories. Spectrometers: i.r., Perkin-Elmer 1720 (Nujol mulls, values in cm⁻¹); n.m.r., JEOL FX 90Q; mass, VG 7070 at 70 eV; e.s.r., Varian E-12 (*X*-band).

Table 4. Electronic spectra of $M(2\text{-MeC}_6\text{H}_4)_4$ species

Metal	$\lambda/\text{nm} (\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$			
Mo ^a	650 (2 000), 560 (2 000), 496 (2 200), 397 (7 700)			
Re ^a	590 (2 600), 550 (2 800), 440 (4 700), 380 (4 000)			
Ru ^b	580 (3 000), 510 (2 900), 430 (3 000)			
Os ^b	659 (3 600), 576 (6 400), 500 (5 600), 450 (5 200)			
Os ^v ^b	670 (5 300), 560 (5 980), 493 (9 650)			

^a Hexane solution. ^b Acetonitrile solution.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for $\text{Mo}(2\text{-MeC}_6\text{H}_4)_4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0	0	0
C(1)	-1 419(6)	269(5)	-8 549(10)
C(2)	-1 471(9)	1 109(7)	-7 316(12)
C(3)	-2 506(9)	1 281(8)	-6 515(13)
C(4)	-3 425(9)	647(8)	-6 908(13)
C(5)	-3 388(7)	-117(9)	-8 094(11)
C(6)	-2 389(7)	-332(7)	-8 887(13)
C(7)	-470(9)	1 715(9)	-6 837(13)

Cyclic voltammetry: OE-PP2 instrument with 0.2 mol dm^{-3} NBu_4PF_6 as supporting electrolyte at 20°C with platinum working, tungsten auxiliary, and silver pseudo-reference electrodes. Scan rates of $20\text{--}200 \text{ mV s}^{-1}$ were employed in all studies. All potentials are referenced to the $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$ redox couple of $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ at 0.00 V .¹⁶ Relative to our silver pseudo-reference electrode, $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ was oxidized at $+0.85 \text{ V}$ with $\Delta E_p = 90 \text{ mV}$. This rather high value (theoretical = 59 mV) is presumably due to uncompensated resistance in solution.¹⁷ Melting points were determined in sealed capillaries under argon and are uncorrected. Conductivities were measured on a Data Scientific PTI-18 (0.01 mol dm^{-3} solutions in MeCN). Magnetic moments were measured at 30°C on the FX 90Q by the Evans method¹³ in toluene or MeCN. The electronic spectra (Perkin-Elmer 551) are given in Table 4.

The compounds $\text{MoCl}_4(\text{thf})_2$,¹⁸ $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$,⁸ and $\text{Ru}(2\text{-MeC}_6\text{H}_4)_4$,⁷ were prepared by literature methods; $\text{Li}(2\text{-MeC}_6\text{H}_4)$ was prepared by reaction of $2\text{-MeC}_6\text{H}_4\text{Br}$ with LiBu^n in hexane.

Tetra(2-methylphenyl)molybdenum(IV).—A solution of $\text{Li}(2\text{-MeC}_6\text{H}_4)$ (1.02 g , 10.4 mmol) in diethyl ether (20 cm^3) was added to a suspension of $\text{MoCl}_4(\text{thf})_2$ (1.00 g , 2.60 mmol) in diethyl ether (20 cm^3) at -78°C . The brown mixture was allowed to warm to room temperature and stirred overnight. After removal of volatiles *in vacuo*, the residue was extracted with hexane ($2 \times 30 \text{ cm}^3$) and filtered. The purple solution was concentrated to *ca.* 5 cm^3 and cooled to -15°C for 8 h. Deep purple crystals were collected by filtration. Yield: 13% , 0.15 g ; m.p. $70\text{--}75^\circ\text{C}$ (decomp.) (Found: C, 73.3 ; H, 6.2 . $\text{C}_{28}\text{H}_{28}\text{Mo}$ requires C, 73.0 ; H, 6.1%). I.r.: $3 045\text{w}$, $2 361\text{m}$, $1 566\text{m}$, $1 248\text{m}$, $1 191\text{m}$, $1 162\text{w}$, $1 108\text{m}$, $1 027\text{w}$, 859w , 793m , 740s , 537w , 436m , 380w , and 275m cm^{-1} , $\mu_{\text{eff.}} = 2.9(1)$.

Tetra(2-methylphenyl)osmium(V) Salts.—(a) *Tetrafluoroborate*. Dichloromethane (10 cm^3) was added to a mixture of $\text{Os}(2\text{-MeC}_6\text{H}_4)_4$ (0.10 g , 0.18 mmol) and AgBF_4 (0.21 g , 1.1 mmol). After stirring for 1 h, the purple solution was filtered, concentrated to 10 cm^3 , and layered with diethyl ether (10 cm^3). Dark purple crystals were collected by filtration after 1 d. Yield: 0.11 g , 95% ; m.p. $201\text{--}202^\circ\text{C}$ (Found: C, 52.7 ; H, 4.4 . $\text{C}_{28}\text{H}_{28}\text{BF}_4\text{Os}$ requires C, 52.4 ; H, 4.4%), $\mu_{\text{eff.}} = 1.1(2)$. I.r.: $1 563\text{m}$, $1 538\text{m}$, $1 432\text{s}$, $1 279\text{m}$, $1 186\text{m}$, $1 164\text{m}$, $1 055\text{s}$ br,

789w , 754s , 695m , 656w , 520w , 440m , 391w , and 257w cm^{-1} . Conductivity: $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($10^{-3} \text{ mol dm}^{-3}$ in MeCN, 20°C).

(b) *Trifluoromethanesulphonate*. The above procedure was repeated using $\text{Ag}[\text{O}_3\text{SCF}_3]$ in place of AgBF_4 . Yield: 71% ; m.p. $173\text{--}174^\circ\text{C}$ (Found: C, 49.6 ; H, 4.0 . $\text{C}_{29}\text{H}_{28}\text{F}_3\text{O}_3\text{OsS}$ requires C, 49.5 ; H, 4.0%), $\mu_{\text{eff.}} = 1.6(3)$. I.r.: $1 563\text{m}$, $1 538\text{m}$, $1 270\text{s}$, $1 223\text{w}$, $1 188\text{m}$, $1 150\text{m}$, $1 112\text{w}$, $1 032\text{s}$, $1 012\text{w}$, 790w , 750s , 723w , 636s , 571w , and 517m cm^{-1} . Conductivity: $117 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($10^{-3} \text{ mol dm}^{-3}$ in MeCN, 20°C).

X-Ray Crystallography.—All X-ray measurements were made on a crystal, of dimensions $0.24 \times 0.20 \times 0.18 \text{ mm}^3$, sealed under argon in a thin-walled glass capillary using a CAD4 diffractometer, graphite-monochromated X-radiation ($\lambda = 0.710 69 \text{ \AA}$) and previously detailed procedures.¹⁹ The structure was solved *via* the heavy-atom method and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogens were included in idealized positions with a common, fixed U_{iso} of 0.1 \AA^2 . Experimental and refinement details are as follows.

Crystal data. $\text{C}_{28}\text{H}_{28}\text{Mo}$, $M = 460.44$, tetragonal, space group $P4_2/c$, $a = b = 11.936(1)$, $c = 8.088(2) \text{ \AA}$, $U = 1 152.4 \text{ \AA}^3$, $Z = 2$, $D_c = 1.327 \text{ g cm}^{-3}$, $\mu = 5.08 \text{ cm}^{-1}$, $F(000) = 456$.

Data collection. $1.5 \leq \theta \leq 35^\circ$, $0 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 9$. 1 202 Reflections measured, 596 unique, 444 observed [$I > 1.5\sigma(I)$].

Refinement. Number of parameters 69, weight $w = [\sigma^2(F) + 0.002F_o^2]^{-1}$, $R = 0.0397$, $R' = 0.0372$. Final atomic fractional co-ordinates of the non-hydrogen atoms are given in Table 5.

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