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Thermally induced *endo* to *exo* isomerization in the *o*-xylylene complexes of zerovalent ruthenium and osmium, $M(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}o\text{-}(CH_2)_2C_6Me_4\}$ (M = Ru, Os)[1]

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Abstract

The *endo*-tetramethyl-*o*-xylylene complexes $M(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (M = Ru (*endo*-**1**), Os (*endo*-**2**)) isomerize to their *exo*-isomers on heating in the solid state at 400°C for 5 min. The osmium compound *exo*-**2** forms a 1:1 adduct with PMe_3, $Os(PMe_3)(\eta^6\text{-}C_6Me_6)[\kappa^2\text{-}o\text{-}(CH_2)_2C_6Me_4\}$ (**5**) in which the tetramethyl-*o*-xylylene is a bidentate σ-donor; the ruthenium compound *exo*-**1** is unreactive.

Keywords: Isomerization; Linkage isomers; Interconversions

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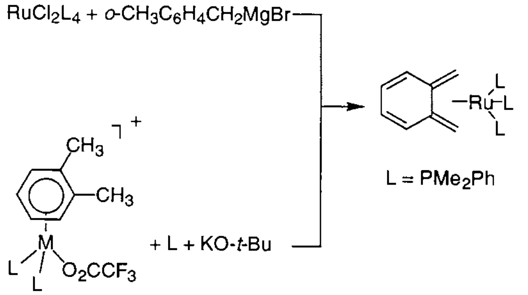
1. Introduction

Although they are generally incapable of existence in the free state at room temperature, *o*-xylylene (*o*-quinodimethane) and substituted *o*-xylylenes can be stabilized by coordination to transition metal centers. In their mononuclear complexes, they can bind as a η^4-conjugated diene via either the endocyclic (a) or exocyclic (b) pairs of double bonds, and they can also function as two-electron σ-donors via the exocyclic methylene groups (c) (Fig. 1). These coordination modes are exemplified by the compounds having M = $Fe(\eta^6\text{-}C_6Me_6)$ [1,2], $Ru(\eta^6\text{-}C_6Me_6)$ [3,4], $[Mn(CO)_3]^-$ [5] (Fig. 1a), M = $Fe(CO)_3$ [6,7] or $Co(\eta^5\text{-}C_5H_5)$ [8,9] (Fig. 1b), and M = Pt(1,5-COD) [10] or $M'(\eta^5\text{-}C_5H_5)_2$ (M′ = Ti, Zr, Hf) [11] (Fig. 1c). Despite the existence of these well-established compounds, however, there have been until recently no examples of linkage isomers of a and b or of interconversions between compounds of the various types. We have been interested in *o*-xylylene complexes with the d^8-metal fragment $Ru(PMe_2Ph)_3$ because linkage isomers *exo*- and *endo*-$Ru(PMe_2Ph)_3\{o\text{-}C_6H_4(CH_2)_2\}$ can be synthesized independently (Eqs. 1 and 2) [12–14].



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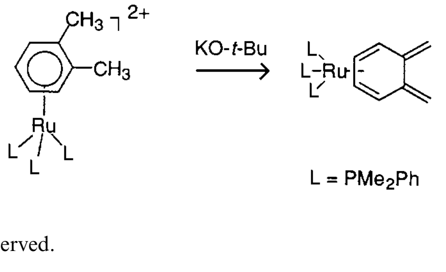

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[1] Dedicated to Professor Akira Nakamura on the occasion of his retirement from Osaka University.

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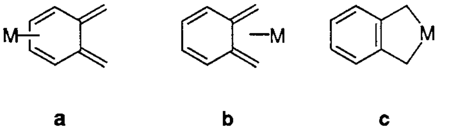
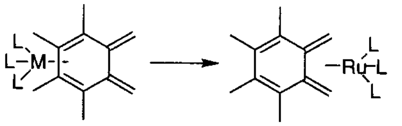


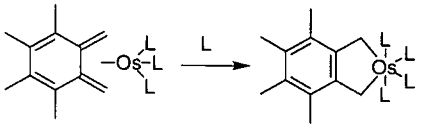
Fig. 1. Modes of *o*-xylylene coordination.

Although density functional calculations on the model compound $Ru(PH_3)_3\{o\text{-}C_6H_4(CH_2)_2\}$ have shown the *exo*-isomer to be more stable thermodynamically than the *endo*-isomer by ca. 60 kJ mol^{-1} [15], the activation barrier to isomerization is high; the *endo*-isomer is stable in refluxing toluene and isomerizes to the *exo*-compound only in the molten state (ca. 300°C) [16]. However, methyl group substitution on the diene carbon atoms lowers the barrier to isomerization. Thus, the 3,4,5,6-tetramethyl-*o*-xylylene complexes $ML_3\{o\text{-}C_6Me_4(CH_2)_2\}$ (M = Ru, L = PMe_3; M = Os, L = PMe_3, PMe_2Ph) undergo *endo*- to *exo*-isomerization in solution above 65°C (Eq. 3); moreover, the *exo*-osmium complexes undergo addition of PMe_3 irreversibly, and PMe_2Ph reversibly, to form the κ^2-complexes $OsL_4\{\kappa^2\text{-}o\text{-}(CH_2)_2C_6Me_4\}$ (L = PMe_3, PMe_2Ph) (Eq. 4) [16,17].



(3)

M=Ru, L=PMe₃; M=Os, L=PMe₃, PMe₂Ph



(4)

L=PMe₃, PMe₂Ph

These findings led us to consider whether similar isomerizations might occur with the *endo*-tetramethyl-*o*-xylylene complexes that do not contain tertiary phosphines as co-ligands, e.g. $M(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (M = Fe, Ru, Os). The results of the investigation are the subject of this report.

2. Results

Gladfelter and coworkers [3,4] prepared $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (*endo*-**1**) by treatment of $[Ru(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ with an excess of potassium *t*-butoxide, KO-*t*-Bu, in THF. The previously unknown osmium(II) salt $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ (**3**) required for the corresponding preparation of $Os(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (*endo*-**2**) was made similarly to its ruthenium(II) analogue [18]. Treatment of $[OsCl_2(\eta^6\text{-}C_6Me_6)]_2$ [19,20] with $AgBF_4$ in acetone generated a labile cation, presumed to be $[Os(\eta^6\text{-}C_6Me_6)(OCMe_2)_3]^{2+}$ [21], which reacted with hexamethylbenzene in the presence of trifluoroacetic acid to give **3** almost quantitatively as a colourless solid. This procedure has been used previously to prepare a (η^6-benzene)(η^6-cyclophane)osmium dication [22].

Cyclic voltammetry of **3** showed that an irreversible reduction occurred when the potential reached -1.20 to -1.30 V (vs SCE) at scan rates of 100–2500 mV s^{-1}. The return scan revealed an equally irreversible and apparently directly related oxidation process at -0.69 to -0.54 V (vs SCE) (Fig. 2). This behaviour is in contrast with that reported for the corresponding iron(II) and ruthenium(II) cations, $[M(\eta^6\text{-}C_6Me_6)_2]^{2+}$ (M = Fe, Ru), which show two well-defined one-electron reductions [23–25]. For the iron compound, measured in 50% aqueous acetone with KCl as the supporting electrolyte, the two processes are well separated, the first ($E_{1/2} = -0.48$ V vs SCE) to the iron(I) cation $[Fe(\eta^6\text{-}C_6Me_6)_2]^+$ being reversible; the second ($E_{1/2} = -1.17$ V vs SCE) is irreversible and presumably generates the 20-electron species $[Fe(\eta^6\text{-}C_6Me_6)_2]$ [23]. For $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$ in acetonitrile with $[^nBu_4N][PF_6]$ as the supporting electrolyte, the two potentials are almost equal ($E_1^\circ = 1.021$ V, $E_2^\circ = -1.003$ V vs SCE) and give rise to an apparent two-electron, partially chemically reversible reduction to $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ [24,25]. We have not studied the chemical reduction of $[Os(\eta^6\text{-}C_6Me_6)_2]^{2+}$.

Treatment of a suspension of $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ (**3**) in THF with KO-*t*-Bu gave the *endo*-tetramethyl-*o*-xylylene complex $Os(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (*endo*-**2**) as an air-sensitive, pale yellow, crystalline solid in 94% yield, which was characterized by elemental analysis, mass spectrometry, infrared and NMR (^1H and ^{13}C) spectroscopy. The IR spectrum of *endo*-**2** exhibits a weak band due to ν(C=C) of the uncoordinated *exo*-methylene group at 1584 cm^{-1} (in a KBr disk) cf. 1590 cm^{-1} for *endo*-**1** [4]. The ^1H-NMR spectrum of *endo*-**2** shows a characteristic pair of doublets at δ 4.54 and 5.14 ($^2J_{HH} = 1.5$ Hz) due to the *exo*-methylene protons. Similar patterns have been observed in other *endo*-coordinated *o*-xylylene metal complexes [1,3–5,14,16]. In its $^{13}C\{^1H\}$-NMR spectrum, *endo*-**2** shows a resonance for the methylene carbon atoms at δ 91.21, which is comparable with the values of δ 89.04 and 88.0 for $M(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}(CH_2)_2C_6Me_4\}$ (M = Ru (*endo*-**2**) [3]; M = Fe (*endo*-4) [1,2]). The signal due to the uncoordinated pair of carbon atoms appears at δ 154.31; those due to the two pairs of coordinated ring carbon atoms appear at δ 84.11 and 50.34.

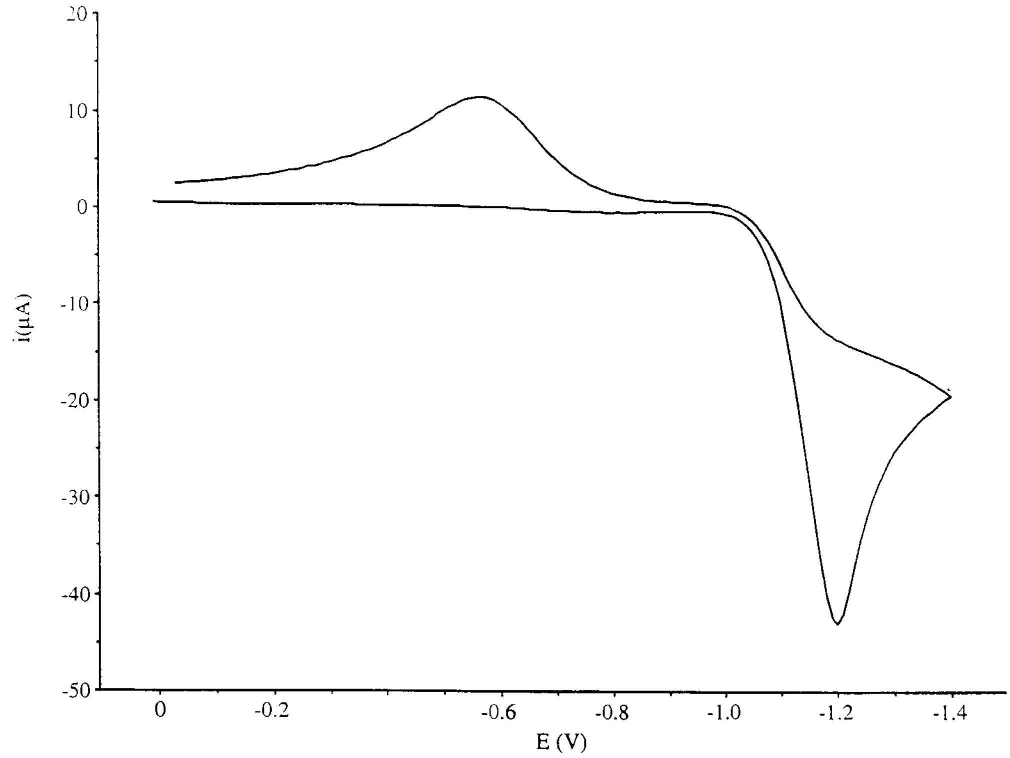
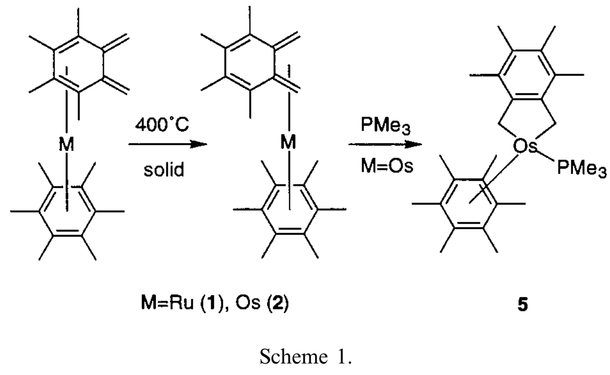


Fig. 2. Cyclic voltammogram of $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ (**3**) in CH_3CN/0.15 M $[^nBu_4N][PF_6]$ at 25°C, scan rate 500 mV s^{-1}, concentration = 3.19×10^{-3} M.

In contrast to the *tris*(tertiary phosphine)-ruthenium(0) and -osmium(0) *endo*-tetramethyl-*o*-xylylene complexes $ML_3\{\eta^4\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (M = Ru, L = PMe_3; M = Os, L = PMe_3, PMe_2Ph) [16,17], the η^6-hexamethylbenzene analogues *endo*-**1** and *endo*-**2** appear to be stable in solution to either decomposition or to isomerization to the corresponding *exo*-compounds at elevated temperatures, even over prolonged periods (36 h at 110°C in toluene-d_8). The remarkable thermal stability of these ruthenium(0) and osmium(0) complexes is in marked contrast to the lability of the analogous iron(0) complex $Fe(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4(CH_2)_2\}$ (*endo*-**4**), which decomposes in solution above − 20°C [1,2]. However, thermolysis of solid *endo*-**1** and **2** at 400°C under an atmosphere of argon for 5 min yields the new *exo*-tetramethyl-*o*-xylylene complexes [M = Ru (*exo*-**1**), Os (*exo*-**2**)], in 66 and 33% yields, respectively (Scheme 1). Thermolysis of solid *endo*-**4** under similar conditions resulted only in complete decomposition to metallic iron. *Exo*-**1** and -**2** have been characterized by elemental analysis, mass spectrometry and NMR (^{1}H and ^{13}C) spectroscopy. The ^{1}H-NMR spectra each show two characteristic doublets associated with the methylene groups of the η^4-diene fragment at δ 2.12 (H_{syn}) and 0.08 ($^2J_{HH} = 3.0$ Hz, H_{anti}) for *exo*-**1**, and at δ 2.70 (H_{syn}) and 0.53 ($^2J_{HH} = 4.0$ Hz, H_{anti}) for *exo*-**2**. Correspondingly, the $^{13}C\{^1H\}$-NMR spectra each show a resonance, at δ 30.70 and 21.66 for *exo*-**1** and -**2**, respectively, assigned to the *exo*-methylene carbon atoms, which are shifted by ca. 60–70 ppm to low frequency of the corresponding resonances in *endo*-**1** and -**2**. The inner carbon atoms of the coordinated *exo*-1,3-diene resonate in the region of δ 90, ca. 60 ppm to low frequency of their chemical shift in the uncoordinated *exo*-1,3-diene in the *endo*-complexes.

Like the analogous osmium tris(trimethylphosphine) complex [16,17], *exo*-**2** reacts irreversibly with trimethylphosphine to form a pale yellow 1:1 adduct **5** containing κ^2-tetramethyl-*o*-xylylene (hexamethylbenzene-1,2-diyl) as a chelate σ-bonded ligand (Scheme 1). The methylene proton resonances of **5** appear as an AB quartet at ca. δ 2.7, cf. δ 2.3 in $Os(PMe_3)_4\{\kappa^2\text{-}o\text{-}$



Scheme 1.

Table 1
Metal to diene–carbon bond lengths (Å) in *endo*-*o*-xylylene complexes of ruthenium(0) and osmium(0)

	M–C(outer)	M–C(inner)	Ref.
Ru(η^6-C_6Me_6) {$C_6Me_4(CH_2)_2$}	2.204(6), 2.208(5)	2.119(6), 2.137(5)	[3]
Os($PMe_2Ph)_3$ {$C_6Me_4(CH_2)_2$}	2.281(8), 2.276(8)	2.226(8), 2.234(8)	[16]
Os($PMe_2Ph)_3$ {$C_6H_4(CH_2)_2$}	2.259(3), 2.257(3)	2.177(3), 2.172(3)	[14]
Ru($PMe_2Ph)_3$ {$C_6H_4(CH_2)_2$}	2.261(5), 2.256(5)	2.160(4), 2.141(4)	[14]

$(CH_2)_2C_6Me_4$}, and the methylene carbon atoms appear as a doublet at δ 8.75 ($J_{PC} = 10.3$ Hz), cf. δ 9.37 in $Os(PMe_3)_4$\{κ^2-*o*-$(CH_2)_2C_6Me_4$\} [16], i.e. about 13 ppm to low frequency of their chemical shift in *exo*-**2**. Correspondingly, the carbon atoms to which the methylene groups are attached shift from δ 88.44 in *exo*-**2** to δ 150.76 in **5** as a consequence of the removal of the aromatic C–C bond from the coordination sphere. Unfortunately, the carbon analysis of **5** remained ca. 3% high even after repeated recrystallizations of the sample, for reasons that are not clear. However, the identity of the product was established unequivocally by accurate mass measurement of the parent ion peak and by the characteristic changes in the NMR spectroscopic features of the ligand resulting from the change in bonding mode.

The ruthenium compound *exo*-**1** does not react with trimethylphosphine, even on prolonged heating.

3. Discussion

The results provide further confirmation of the predicted greater stability of η^4-*exo* over η^4-*endo*-coordination in ML_3(*o*-xylylene) complexes of ruthenium and osmium [15] and establish that this is valid for $L_3 = \eta^6$-C_6Me_6 as well as for $L_3 = (PMe_3)_3$ or $(PMe_2Ph)_3$. The barrier to isomerization is clearly greater for the C_6Me_6 complexes, which, unlike their tris(tertiary phosphine) counterparts, do not isomerize in refluxing toluene. This difference may be attributed to the weaker binding of *endo*-*o*-$C_6Me_4(CH_2)_2$ in the tris(tertiary phosphine) complexes that is implied by a comparison of the metal–carbon bond lengths in the metal–diene unit (Table 1). Thus, the distances to the outer and inner diene carbon atoms of Ru(η^6-C_6Me_6)\{η^4-*o*-$C_6Me_4(CH_2)_2$\} [3] are, respectively, ca. 0.06 and 0.10 Å less than the corresponding distances in $Os(PMe_2Ph)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} [16]. These differences are far greater than any attributable to the change from ruthenium to osmium, as is evident from the very similar M–C(diene) distances observed in the pair $M(PMe_2Ph)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} (M = Ru, Os) [14], and they presumably reflect the higher *trans*-bond weakening influence of three dimethylphenylphosphine ligands relative to that of the arene.

Clearly the *endo*-*o*-xylylene unit must be partially detached from the metal atom during the process of isomerization, but we have no definitive information about the mechanism. In the *endo*- to *exo*-isomerization of $Ru(PMe_3)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} there is evidence for two pathways, one of which requires dissociation of PMe_3 in the initial step, presumably in order to provide a site for the coordination of an *exo*-double bond [16]. Although such dissociation is not possible for *endo*-**1** and *endo*-**2**, one could envisage reversible η^6- to η^4- to η^2-processes in the coordinated C_6Me_6 that would have the same effect. Alternatively, as in the case of $M(PMe_3)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} (M = Ru, Os), isomerization may also be possible without prior dissociation of the auxiliary ligand.

The irreversible addition of PMe_3 to *exo*-**2** forming the κ^2-complex **5**, and the failure of *exo*-**1** to react similarly, parallel the behaviour of the corresponding $M(PMe_3)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} (M = Ru, Os) complexes. The lack of reactivity of *exo*-**1** is somewhat surprising in view of the prediction, based on density functional theory (DFT) calculations, that $M(PH_3)_4$\{κ^2-*o*-$(CH_2)_2C_6H_4$\} is more stable than $M(PH_3)_3$\{η^4-*o*-$C_6Me_4(CH_2)_2$\} for both ruthenium and osmium (though more so for the latter) [15].

Finally, we note the remarkable thermal stability of complexes **1** and **2**, even though they contain the zerovalent metal atom and neutral ligands that could be readily lost. In this respect, the complexes seem to be exceeded only by ruthenocene and substituted ruthenocenes [26–28].

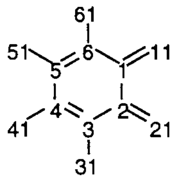
4. Experimental

4.1. General Procedures

The following instruments were used: Varian Inova 600 (^1H, 2D [^1H-^{13}C]-GHMQC, ^{13}C-NMR at 150.86 MHz), VXR Inova 500 (^1H-NMR, ^{31}P at 202.404 MHz), and Varian VXR-300S and Varian Gemini 300 (^1H-NMR, ^{13}C-NMR at 75.43 MHz), VG AutoSpec and VG ZAB-2SEQ (EI mass spectra at 70 eV), and VG Quattro II (electrospray triple quadrupole), and Perkin-Elmer 683 (infrared). NMR spectra were recorded at 293 K, unless otherwise stated. The compounds Ru(η^6-C_6Me_6)\{η^4-*o*-$C_6Me_4(CH_2)_2$\}(*endo*-**1**) [3,4], Fe(η^6-C_6Me_6)\{η^4-*o*-$C_6Me_4(CH_2)_2$\}(*endo*-**4**) [1,2], and $[OsCl_2(\eta^6$-$C_6Me_6)]_2$ [19,20] were prepared by reported procedures. Organic solvents of reagent grade were dried by published procedures [29] and distilled under nitrogen. All reactions were carried out under argon by standard Schlenk techniques. Elemental analyses were carried out in-house. Solid samples were heated in argon-filled Schlenk tubes of ca. 250 ml volume placed inside a Heraeus ROK/A 6/60 tube furnace.

Electrochemical measurements were performed using an AD Instruments MacLab/400 potentiostat and a Cyress Systems EE014 mini electrochemical cell fitted with a platinum-disk working electrode (1.0 mm diameter) a platinum auxiliary electrode, and a Ag | AgCl reference electrode (against which ferrocene was oxidized at + 0.40 V vs SCE) isolated by a fritted salt bridge; typical scan rates were 100–2500 mV s^{-1}. Electrolyte solutions contained 0.15 mol dm^{-3} $[^{n}Bu_4N][PF_6]$ in freshly distilled acetonitrile. The solutions were purged and maintained under an atmosphere of N_2.

Carbon atoms in tetramethyl-*o*-xylylene are numbered as shown below:



4.2. Preparation of $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$, **3**

A vigorously stirred suspension of $[OsCl_2(\eta^6\text{-}o\text{-}C_6Me_6)]_2$ (200 mg, 0.236 mmol) in degassed acetone (5 ml) was treated with $AgBF_4$ (184 mg, 0.944 mmol) for 1 h. The solution was filtered through Celite to remove precipitated silver chloride and the solvent was removed under reduced pressure to give a yellow oil. The residue was treated with an excess of hexamethylbenzene (300 mg, 1.85 mmol) and trifluoroacetic acid (5 ml) and the solution was heated to 90°C for 10 min. Solvent was removed under reduced pressure and the oily residue was triturated with ether. The resulting off-white solid was washed with ether and recrystallized from DMSO/methanol/ether to give white crystals of $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ (301 mg, 93%). ^{1}H-NMR (DMSO-d_6, 300 MHz): δ 2.15 (s, C_6Me_6). $^{13}C\{^1H\}$-NMR (DMSO-d_6, 75.43 MHz): δ 100.31 (s, C_6Me_6), 15.15 (s, $C_6\mathit{Me}_6$). MS, electrospay (MeOH), *m*/*z* 603, $[M-BF_4]^+$. Anal. Calc. for $C_{24}H_{36}B_2F_8Os$: C, 41.88; H, 5.27. Found: C, 41.19; H, 5.38.

4.3. Preparation of $Os(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4\text{-}(CH_2)_2\}$, *endo*-**2**

A stirred suspension of $[Os(\eta^6\text{-}C_6Me_6)_2](BF_4)_2$ (100 mg, 0.145 mmol) in THF (20ml) was treated with an excess of KO-*t*-Bu (65 mg, 0.58 mmol) for 18 h. The THF was removed under reduced pressure and the resulting yellow residue was extracted with *n*-hexane (2 × 30 ml). The solution was filtered through celite and the solvent was removed under reduced pressure to give the product (70 mg, 94%) as a pale yellow crystalline solid. ^{1}H-NMR (C_6D_6, 300 MHz): δ 5.14 (d, $^2J_{HH} = 1.5$ Hz, $=CH_2$), 4.54 (d, $^2J_{HH} = 1.5$ Hz, $=CH_2$), 1.70 (s, $Me_{41,51}$), 1.68 (s, C_6Me_6), 1.48 (s, $Me_{31,61}$). $^{13}C\{^1H\}$-NMR (C_6D_6, 75.43 MHz): δ 154.31 (s, $C_{1,2}$), 91.21 (s, $C_{11,21}$), 84.11 (s, $C_{4,5}$), 79.77 (s, C_6Me_6), 50.34 (s, $C_{3,6}$), 21.09 (s, $Me_{31,61}$), 15.57 (s, $Me_{41,51}$), 14.42 (s, $C_6\mathit{Me}_6$). IR (KBr disk) 1584 cm^{-1} [ν(free C=C)]. MS (EI), *m*/*z* (parent ion), Anal. Calc. $^{12}C_{24}{}^1H_{34}{}^{192}Os$: 514.2275. Found: 514.2276. Anal. Calc. $C_{24}H_{34}Os$: C, 56.22; H, 6.68. Found: C, 56.11; H, 6.80.

4.4. Preparation of $Ru(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}exo\text{-}o\text{-}C_6Me_4\text{-}(CH_2)_2\}$, *exo*-**1**

A sample of *endo*-**1** (173 mg, 0.408 mmol) was heated at 400°C for 5 min during which time its colour changed from yellow to deep brown. The residue was extracted with ether (40 ml) and the extracts were filtered through neutral alumina (activity 1). Evaporation of ether gave a yellow solid, which on recrystallization from *n*-hexane gave *exo*-1 as yellow crystals (114 mg, 66%). ^{1}H-NMR (toluene-d_8, 300 MHz): δ 2.12 (d, $J_{HH} = 3.0$ Hz, H_{syn}), 2.11 (s, C_6Me_6), 2.04 (s, $Me_{31,61\ \text{and}\ 41,51}$), 0.08 (d, $J_{HH} = 3.0$ Hz, H_{anti}). $^{13}C\{^1H\}$-NMR (toluene-d_8, 75.43MHz): δ 133.44 (s, $C_{3,6\ \text{or}\ 4,5}$), 131.65 (s, $C_{4,5\ \text{or}\ 3}$), 92.27 (s, $C_{1,2}$), 90.33 (s, C_6Me_6), 30.70 (s, $C_{11,21}$), 17.24 (s, $C_{41,51\ \text{or}\ 31}$), 17.15 (s, $C_{31,61\ \text{or}\ 41,51}$), 16.27 (s, $C_6\mathit{Me}_6$). MS (EI), *m*/*z* (parent ion), Anal. Calc. $^{12}C_{24}{}^1H_{34}{}^{102}Ru$: 424.1704. Found: 424.1704. Anal. Calc. $C_{24}H_{34}Ru$: C, 68.05; H, 8.09. Found: C, 67.42; H, 7.62.

4.5. Preparation of $Os(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}exo\text{-}o\text{-}(CH_2)_2\text{-}C_6Me_4\}$, *exo*-**2**

A sample of *endo*-**2** (60 mg, 0.117 mmol) was heated at 400°C for 5 min during which time its colour changed from yellow to deep brown. The residue was extracted with *n*-hexane (50 ml). Evaporation of the extract gave a yellow solid, which, after sublimation (ca. 300°C, 0.05 Torr) and recrystallization from hot benzene to remove free hexamethylbenzene, gave *exo*-2 as yellow crystals (20 mg, 33%). ^{1}H-NMR (C_6D_6, 300MHz): δ 2.70 (d, $J_{HH} = 4.0$ Hz, H_{syn}), 2.12 (s, C_6Me_6), 1.75 (s, $Me_{31,61\ \text{and}\ 41,51}$), 0.53 (d, $J_{HH} = 4.0$ Hz, H_{anti}). $^{13}C\{^1H\}$-NMR (toluene-d_8, 363K, 75.43MHz): δ 130.72 (s, $C_{3,6\ \text{or}\ 4,5}$), 129.84 (s, $C_{4,5\ \text{or}\ 3,6}$), 88.44 (s, $C_{1,2}$), 81.93 (s, C_6Me_6), 21.66 (s, $C_{11,21}$), 17.36 (s, $C_{41,51\ \text{or}\ 31,61}$), 17.10 (s, $C_{31,61\ \text{or}\ 41,51}$), 16.63 (s, C_6Me_6). MS (EI), *m*/*z* (parent ion), Anal. Calc. $^{12}C_{24}{}^1H_{34}{}^{192}Os$: 514.2275.

Found: 514.2279. Anal. Calc. $C_{24}H_{34}Os$: C, 56.22; H, 6.68. Found: C, 55.87; H, 6.61.

4.6. *Attempted isomerization of* $Fe(\eta^6\text{-}C_6Me_6)\{\eta^4\text{-}endo\text{-}o\text{-}C_6Me_4(CH_2)_2\}$, *endo*-**4**

A sample of *endo*-**4** (200 mg, 0.529 mmol) was heated at 400°C for 5 min during which time its colour changed from red to black. The residue was extracted with *n*-hexane (50 ml). Evaporation of the extract gave a colourless crystalline solid, which was shown by ^{1}H-NMR spectroscopy to be hexamethylbenzene.

4.7. *Preparation of* $Os(PMe_3)(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}o\text{-}(CH_2)_2\text{-}C_6Me_4\}$, **5**

A sample of *exo*-**2** (25 mg, 0.049 mmol) in toluene (2 ml) was treated with PMe_3 (5.5 µl, 0.053 mmol). The solution was heated under reflux for 5 min. Removal of the volatile materials under reduced pressure gave **5** as a pale yellow crystalline solid (28 mg, 98%). ^{1}H-NMR (toluene-d_8, 600 MHz): δ 2.71 (dd, $J_{HH} = 16.6$ Hz, $J_{PH} = 5.2$ Hz, $=CH_2$), 2.67(d, $J_{HH} = 16.6$ Hz, $=CH_2$), 2.57 (s, $Me_{31,61\ \mathrm{or}\ 41,51}$), 2.25 (s, $Me_{41,51\ \mathrm{or}\ 31,61}$), 1.77 (s, C_6Me_6), 0.92 (d, $J_{PH} = 8.3$ Hz, PMe_3). ^{13}C-NMR (toluene-d_8, 150.86 MHz): δ 150.76 (s, $C_{1,2}$), 130.64 (s, $C_{3,6\ \mathrm{or}\ 4,5}$), 129.16 (s, $C_{4,5\ \mathrm{or}\ 3,6}$), 87.53 (d, $J_{PC} = 3.3$ Hz, C_6Me$_6$), 16.66 (s, $C_{31,61\ \mathrm{or}\ 41,51}$), 16.53 (s, $C_{41,51\ \mathrm{or}\ 31,61}$), 15.74 (d, $J_{PC} = 32.5$ Hz, PMe_3), 15.35 (s, C_6Me_6), 8.75 (d, $J_{PC} = 10.3$ Hz, $C_{11,21}$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 202.404 MHz): δ -36.50 (s). MS (EI), *m/z* (parent ion), Anal. Calc. $^{12}C_{27}{}^{1}H_{43}{}^{192}Os^{31}P$: 590.2717. Found: 590.2732. The spectroscopic data establish the identity of the compound beyond doubt, although the carbon analysis was consistently high. Anal. Calc. $C_{27}H_{43}OsP$: C, 55.08; H, 7.36. Found: C, 58.31, 58.51; H, 7.26, 7.49.

Under the same conditions, *exo*-**1** did not react with PMe_3.

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