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Intermolecular and intramolecular C–H activation reactions of (η-mesitylene)osmium complexes containing tertiary phosphines *

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Abstract

The preparations are described of the *hexahapto*-mesitylene complex $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$ (**1**) and of range of monomeric tertiary phosphine (L) derivatives containing halide, hydride, alkyl or aryl ligands of the general types $OsCl_2(\eta\text{-}C_6H_3Me_3)(L)$, $OsHCl(\eta\text{-}C_6H_3Me_3)(L)$, $OsCl(R)(\eta\text{-}C_6H_3Me_3)(L)$ ($R = CH_3$, C_6H_5), $OsH_2(\eta\text{-}C_6H_3Me_3)(L)$ and $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(L)$. Heating $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**2**) with propan-2-ol and Na_2CO_3 gives initially $OsHCl(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**7**) and finally the *ortho*-metallated complex $OsH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6H_3Me_3)$ (**12**). Similar treatment of $OsCl_2(\eta\text{-}C_6H_3Me_3)(P\text{-t-}BuPh_2)$ (**4**) gives $OsHCl(\eta\text{-}C_6H_3Me_3)(P\text{-t-}BuPh_2)$ (**9**) and the diastereomeric *ortho*-metallated complexes $OsX(o\text{-}C_6H_4P\text{-t-}BuPh)(\eta\text{-}C_6H_3Me_3)$ (X = H (**13a, 13b**), Cl (**14a, 14b**)). Reduction of $OsClR(\eta\text{-}C_6H_3Me_3)(L)$ with $NaBH_4$ in propan-2-ol gives thermally stable hydrido(alkyl) or hydrido(phenyl) complexes $OsH(R)(\eta\text{-}C_6H_3Me_3)(L)$ ($R = CH_3$, $L = PPh_3$ (**31**), PMe_3 (**32**); $R = C_6H_5$, $L = PPh_3$ (**33**), PMe_3 (**34**). Treatment of $OsCl_2(\eta\text{-}C_6H_3Me_3)(L)$ ($L = PPh_3$ (**2**), PMe_3 (**3**)) with neopentyllithium gives the osmacycles $Os(CH_2CMe_2CH_2)(\eta\text{-}C_6H_3Me_3)(L)$ ($L = PPh_3$ (**27**), PMe_3 (**28**)). Complex **28** reacts with HCl to give $OsCl(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**30**), which is reduced by $LiAlH_4$ to the thermally stable hydrido(neopentyl) complex $OsH(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**35**). Unlike their isoelectronic $(\eta\text{-}C_5Me_5)Ir$ counterparts, the hydrido(alkyl) complexes $OsH(R)(\eta\text{-}C_6H_3Me_3)(L)$ (**31, 32, 35**) do not undergo exchange with alkanes or arenes on heating, although some exchange, accompanied by loss of coordinated mesitylene, occurs on UV irradiation in the presence of arenes. The 16-electron fragments $Os(\eta\text{-}C_6H_3Me_3)(L)$ are, therefore, less accessible thermally than $Ir(\eta\text{-}C_5Me_5)(L)$. The alkanes RH are, however, eliminated quantitatively from **31**, **32**, and **35** at room

* Dedicated to Professor Gordon Stone on his 65th birthday with best wishes.

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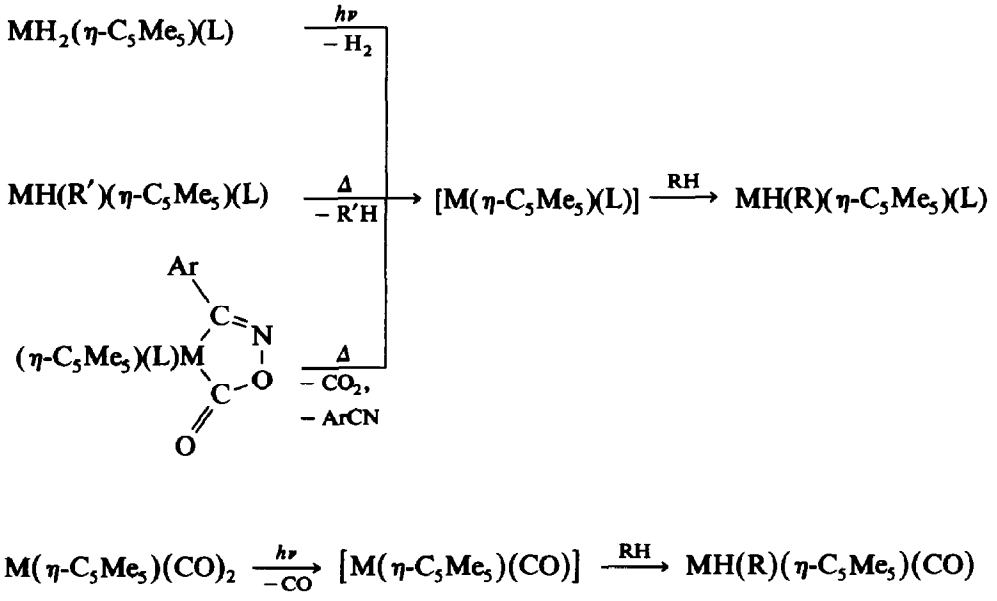
temperature in the presence of arenes (benzene, benzene-d_6, toluene, naphthalene) and of a trace of alumina or silica. Under these conditions, **32** and **35** give $OsH(aryl)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ and **31** gives a mixture (ca. 5/1) of **12** and $OsH(aryl)(\eta\text{-}C_6H_3Me_3)(PPh_3)$. There is no reaction with alkanes, ethylene, norbornene or CO. The fragments $Os(\eta\text{-}C_6H_3Me_3)(L)$ ($L = PPh_3$, PMe_3) can also be generated by reduction of **2** or **3** with $NaC_{10}H_8$ and detected either by formation of **12** ($L = PPh_3$) or by their reaction with arenes; there is, however, no reaction with cyclohexane. These observations suggest that the oxidative addition of alkanes to $Os(\eta\text{-}C_6H_3Me_3)(L)$ ($L = PPh_3$ (**2**), PMe_3 (**3**)) has a substantial kinetic barrier even though it should be thermodynamically favourable.

Introduction

The discovery that 16-electron fragments containing rhodium(I) or iridium(I) of the type $M(\eta\text{-}C_5Me_5)(L)$ ($M = Rh$, $L = PMe_3$; $M = Rh$, Ir; $L = PMe_3$, CO) can cleave the C–H bonds of alkanes and arenes to form hydrido(alkyls) or hydrido(aryls) by a process of oxidative addition has stimulated much activity in the field of C–H activation [1–3]. The reactions are generally carried out by photolysis of precursors such as $Ir(\eta\text{-}C_5Me_5)(CO)_2$ and $IrH_2(\eta\text{-}C_5Me_5)(PMe_3)$ ($M = Rh$, Ir) in the hydrocarbon or by thermal exchange of alkanes or arenes with labile hydrido(alkyls) such as $IrH(C_6H_{11})(\eta\text{-}C_5Me_5)(PMe_3)$ and $RhH(CH_2CMe_3)(\eta\text{-}C_5Me_5)(PMe_3)$ (Scheme 1). Recently, thermolysis or photolysis of 4-metallaisoxazolin-5-ones in alkanes or arenes has been shown to lead to the same complexes [4]. The rhodium system is considerably more reactive than the iridium, e.g. reductive elimination of



Scheme 1. M = Rh, Ir; L = CO, PMe_3.

alkanes from the hydrido(alkyl)iridium complexes occurs only at ca. 110 °C, or at room temperature in the presence of Lewis acids or oxidizing agents, whereas the corresponding rhodium compounds are unstable above −20 °C.

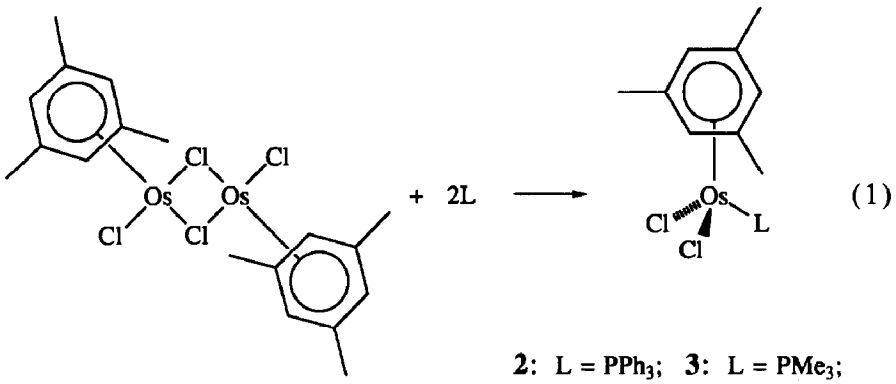
An obvious question is whether (η^6-arene)ruthenium(0) and (η^6-arene)osmium(0) fragments M(η-arene)(L) (M = Ru, Os) can be generated and whether they will behave like their isoelectronic counterparts M(η-C_5Me_5)(L) (M = Rh, Ir). Photolysis of $RuH_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ and $RuH_2(\eta\text{-}C_6H_6)(PMe_3)$ in arenes forms the corresponding hydrido(aryl) complexes RuH(aryl)(η-arene)(L), presumably by oxidative addition of an arene C–H bond to a transient Ru(η-arene)(L) species. In the absence of arene, however, the fragment $Ru(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ undergoes cyclometallation and there is no evidence for oxidative addition of cyclohexane to Ru(η-arene)(L) [5,6]. The fragments $Ru(\eta\text{-}C_6Me_6)(L)$ (L = various tertiary phosphines) can also be generated by treatment of $RuHCl(\eta\text{-}C_6Me_6)(L)$ with methyllithium. Under these conditions both cyclometallation and oxidative addition of external arenes occur, although the presumed intermediate hydrido(methyl) complex $RuH(CH_3)(\eta\text{-}C_6Me_6)(L)$ has not been detected [7]. Surprisingly, the dihydridoosmium complex $OsH_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ is photochemically inert, but reduction of $OsI_2(\eta\text{-}C_6H_6)(L)$ (L = PMe_3, P-i-Pr_3) with sodium naphthalene in the presence of benzene or toluene gives the corresponding hydrido(aryl) complexes OsH(R)(η-C_6H_6)(L), probably via intermediate osmium(0) fragments Os(η-C_6H_6)(L) [6,8]. Recently, the hydrido(methyl) complexes $OsH(CH_3)(\eta\text{-}C_6H_6)(L)$ (L = P-i-Pr_3, $P(OMe)_3$, $P(O\text{-}i\text{-}Pr)_3$) have been reported and unsuccessful attempts to eliminate methane from them by the action of heat, light or one-electron oxidants have been made [9].

Independently, we have been attempting to generate Os(η-arene)(L) in the expectation that these electron-rich, coordinatively unsaturated species would oxidatively add C–H bonds more readily than do the corresponding ruthenium systems. For the purposes of comparison with our work or ruthenium, the ideal arene would have been hexamethylbenzene, but our initial efforts to prepare the required precursor, $[OsCl_2(\eta\text{-}C_6Me_6)]_2$, by displacement of *p*-cymene from $[OsCl_2(\eta\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)]$ were unsuccessful [10*]. We therefore turned to mesitylene (1,3,5-trimethylbenzene) and report here the synthesis and C–H activation reactions of a range of (η-mesitylene)osmium complexes. While our work was in progress, Cabeza and Maitlis [11] reported some closely related osmium complexes of *p*-cymene, and after it was finished we learned that Werner and co-workers have also examined mesitylene-osmium chemistry [12].

Results

When an ethanolic solution of Na_2OsCl_6 is heated with 1,3,5-trimethyl-1,4-cyclohexadiene for 3–4 h, the *hexahapto*-mesitylene complex $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$ (1) precipitates as a yellow, microcrystalline solid in ca. 30% yield. As observed also in the preparation of the corresponding *p*-cymene complex [11], the yield can be increased to 65–70% by heating the mixture for ca. 120 h, but longer reaction times than this do not give more product. The complex is almost insoluble in most organic

* Reference number with asterisk indicates a note in the list of references.



(1)

1

2: L = PPh_3; **3**: L = PMe_3;

4: L = P-t-$BuPh_2$; **5**: L = PCy_3;

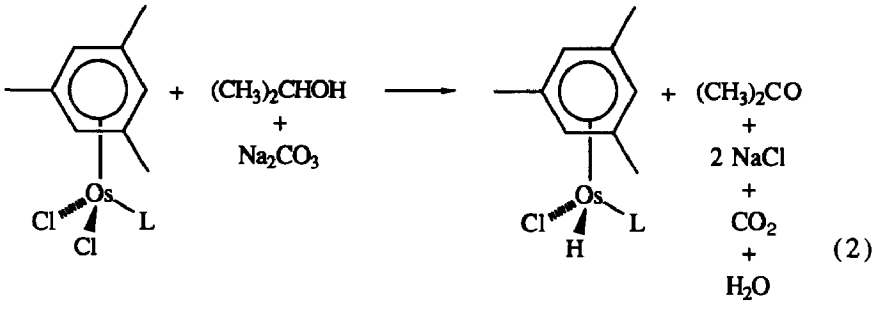
6: L = P-i-Pr_3

solvents, but it is slightly soluble in dimethylsulphoxide (DMSO) and acetonitrile, probably owing to the formation of monomeric species $OsCl_2(\eta\text{-}C_6H_3Me_3)$(solvent). The far IR spectrum shows two strong bands at 309 and 268 cm^{-1} due to terminal and bridging ν(OsCl) modes. In DMSO-d_6 the ^1H NMR spectrum shows two singlets due to the aromatic and methyl protons of coordinated mesitylene at δ 5.75 and 2.20 ppm, the former being shifted by about 1 ppm to low frequency relative to free mesitylene. In the solid state, the complex is probably dimeric, with bridging chlorine atoms, like its *p*-cymene analogue [13].

The chlorine bridges of **1** are cleaved on reaction with a variety of tertiary phosphines to give air-stable, orange or yellow, monomeric complexes $OsCl_2(\eta\text{-}C_6H_3Me_3)$(L) (**2–6**) in good yield (eq. 1).

The IR spectra of **2–6** show two strong bands due to ν(OsCl) in the region 300–260 cm^{-1} and the ^1H NMR spectra show two singlets in the regions δ 5.40–4.80 and 2.30–1.70 ppm due to the aromatic and methyl protons, respectively, of coordinated mesitylene. The compounds are assigned half-sandwich structures similar to those established by X-ray crystallography for the areneruthenium(II) complexes $RuCl_2(\eta\text{-}C_6H_6)(PMePh_2)$ [14], $[RuCl_2(\eta\text{-1-Me-4-}Me_2CHC_6H_4)(PMePh_2)$ [14] and $RuCl_2(\eta\text{-1-Me-2-}CO_2MeC_6H_4)[PPh_2$(neomenthyl)] [15]. The ease of preparation of the tricyclohexylphosphine complex **5** is noteworthy, because the ruthenium complex $RuCl_2(\eta\text{-}C_6Me_6)(PCy_3)$ cannot be obtained by heating $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ with an excess of PCy_3 [7].

Although the elemental analyses for the triisopropylphosphine derivative **6** were in agreement with the expected values, the ^1H NMR spectrum of this compound showed two sets of resonances due to coordinated mesitylene in addition to the resonances due to P-i-Pr_3, and the $^{31}P\{^1H\}$ NMR spectrum showed two singlets in ca. 3/1 ratio at δ −5.54 and −9.27 ppm; complexes **2–5** show only one ^{31}P resonance. Neither of these resonances is due to free P-i-Pr_3. Similar spectra have been observed for the ruthenium complexes $RuCl_2(\eta$-arene)(P-i-$Pr_3)$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$) [7]. The two species in solution may be rotamers arising from restricted rotation about the Os–P bonds, similar to those observed in



(2)

7: L = PPh_3; **8**: L = PMe_3;

9: L = P-t-$BuPh_2$; **10**: L = PCy_3;

11: L = P-i-Pr_3

solutions of planar complexes of t-butylphosphines [16]. Surprisingly, the published ^1H NMR data for the η^6-benzene complex $OsI_2((\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ suggest the presence of only one species in solution [6].

When complexes **2–6** were suspended in propan-2-ol and heated under reflux with an excess of anhydrous sodium carbonate for 3–4 h, the corresponding chloro(hydrido) complexes $OsHCl(\eta\text{-}C_6H_3Me_3)(L)$ (**7–11**) were formed in moderate yield (eq. 2). The yield of the trimethylphosphine derivative **8** was only 25%, but this could be increased to ca. 40% by use of triethylamine/ethanol instead of Na_2CO_3/propan-2-ol. The p-cymene complex $OsHCl(\eta\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)(PPh_3)$ has been made similarly [11] and the complexes $OsHI(\eta\text{-}C_6H_6)(L)$ (L = PMe_3, P-i-Pr_3, $P(O\text{-}i\text{-}Pr)_3$, $P(OMe)_3$) have been prepared from $OsI_2(\eta\text{-}C_6H_6)(L)$ by use of zinc dust and methanol [9].

Complexes **7–11** are yellow solids that are indefinitely stable to air, though their solutions in organic solvents darken on exposure to air after 5–6 h. Complexes **7**, **9**, **10** and **11** that contain fairly bulky tertiary phosphines show in their IR spectra a broad band due to ν(OsH) at 2080–2090 cm^{-1}, whereas in the trimethylphosphine derivative **8** the ν(OsH) band is at 2020 cm^{-1}. The ν(RuH) bands in the corresponding (hexamethylbenzene)ruthenium compounds appear in the range 1935–2010 cm^{-1} [7,17], suggesting that Os–H bonds are stronger than Ru–H bonds, in line with the usual trend. The ^1H NMR spectra of the complexes show a doublet resonance due to OsH in the region δ −8 to −9 ppm (J(PH) ca. 43–47 Hz) in addition to the usual signals due to mesitylene and to the tertiary phosphines. The hydride chemical shifts are similar to those in $RuHCl(\eta\text{-}C_6Me_6)(L)$, though the P–H coupling constants are 10–15 Hz smaller in the osmium compounds.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of the triisopropylphosphine derivative **11** (see Experimental) show that there are two species in solution in a ratio of about 6/1; these are presumed to be rotamers similar to those in **6**. Apparently neither $RuHCl(\eta\text{-}C_6Me_6)(P\text{-}i\text{-}Pr_3)$ [7] nor $OsHI(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ [9] behave similarly.

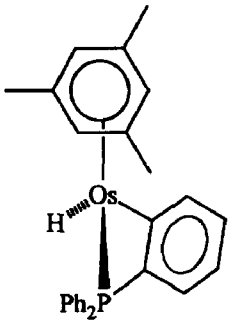
When $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**2**) was heated with propan-2-ol/Na_2CO_3 for more than 4 h, the initially formed chloro(hydrido) complex **6** slowly lost HCl to give the cyclometallated complex $OsH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6H_3Me_3)$ (**12**). This was

isolated as pale yellow, air-stable crystals in ca. 40% yield after a reaction time of ca. 15 days. Further heating did not increase the yield of **12** but favoured the formation of a by-product, which was identified by its NMR parameters as the dihydride $OsH_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (see below). The structure of **12** was readily deduced from the spectroscopic data. The mass spectrum contains a parent ion peak and the IR spectrum shows a broad band due to ν(OsH) at 2020 cm^{-1}, together with sharp bands at 1555, 1410 and 720 cm^{-1} that are characteristic of an *ortho*-metallated aryl group [18a–18c]. In the ^1H NMR spectrum there are resonances due to coordinated mesitylene, a series of multiplets between δ 8.20 and 6.50 ppm due to the aryl protons of triphenylphosphine, and a doublet hydride resonance at δ −7.67 ppm (J(PH) 31.6 Hz). The singlet $^{31}P\{^1H\}$ resonance at δ −50.8 ppm is shielded by ca. 60 ppm relative to that in **6**, consistent with the presence in **12** of a cyclometallated four-membered ring [18d]. A similar trend is evident in the corresponding ruthenium complexes $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$ and $RuH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6Me_6)$ [7], although the ^{31}P nuclei in **6** and **12** are 40–50 ppm more shielded than those in the corresponding ruthenium compounds.

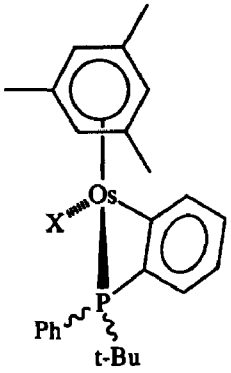
The P-t-$BuPh_2$ complex **4** undergoes cyclometallation even more readily than **2** in the presence of Na_2CO_3 and refluxing propan-2-ol. After 18 h a mixture of five complexes was obtained, viz. two diastereomers of the cyclometallated hydrido complex $OsH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6H_3Me_3)$ (**13a, 13b**), two diastereomers of the cyclometallated chloro-complex $OsCl(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6H_3Me_3)$ (**14a, 14b**), and the chloro(hydrido) complex **12** in proportions of ca 10/3/4/3/1, as estimated by ^{31}P NMR spectroscopy. The diastereomers of **14** were separated from the mixture by fractional crystallization, but attempts to separate the remaining compounds by crystallization or chromatography failed. The ^1H and $^{31}P\{^1H\}$ NMR data in Table 2 were obtained from careful examination of the spectra of the reaction mixture and of the mother liquor after removal of **14a** and **14b**. The structures assigned to **14a** and **14b** are based on satisfactory elemental analyses, the appearance of a parent ion cluster at m/z 588 in the mass spectra, and by the presence of characteristic *ortho*-metallation bands in the IR spectra. Also, reduction of **14a** with sodium borohydride gave a 3/1 mixture of the hydrido complexes **13a** and **13b**, the spectroscopic data for which agreed well with those for the corresponding compounds in the mixture formed by cyclometallation of **4**. We assume that the predominant isomer **13a** has the bulky t-butyl group pointing away from the coordinated mesitylene.

The ruthenium compounds $RuCl_2(\eta\text{-}C_6Me_6)(L)$ (L = PPh_3, P-t-$BuPh_2$) do not undergo cyclometallation on heating in propan-2-ol with Na_2CO_3; it is necessary to treat the chloro(hydrido) complexes with methyllithium to obtain the ruthenium analogues of **12** and **14** [7]. The kinetic product of reaction of $RuHCl(\eta\text{-}C_6Me_6)$(P-t-$BuPh_2$) with methyllithium at 0 °C is the t-butyl-metallated species $RuH(CH_2CMe_2PPh_2)(\eta\text{-}C_6Me_6)$, which spontaneously isomerizes to the thermodynamically more stable aryl-metallated complex $RuH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)(\eta\text{-}C_6Me_6)$ at 50 °C. The corresponding t-butyl metallated osmium complex $OsH(CH_2CMe_2PPh_2)(\eta\text{-}C_6H_3Me_3)$ has never been detected in the reaction of **4** with propan-2-ol/Na_2CO_3, but under the reaction conditions this is not surprising.

Reduction of the dichloro complexes **2–6** with $NaBH_4$ in refluxing propan-2-ol for 10–12 h gave the corresponding dihydrido complexes $OsH_2(\eta\text{-}C_6H_3Me_3)(L)$ (**15–19**). This procedure has been used successfully in the C_6Me_6Ru series but, with

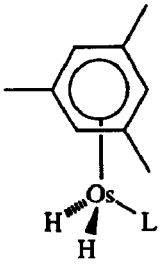


12



13a, 13b: X = H

14a, 14b: X = Cl



15: L = PPh_3; **16**: L = PMe_3;

17: L = P-t-$BuPh_2$; **18**: L = PCy_3;

19: L = P-i-Pr_3

the exception of the PCy_3 complex **18**, which was obtained in ca. 50% yield, the yields in the $C_6H_3Me_3Os$ series were only moderate (20–35%). In the case of L = PMe_3 (**16**), a reaction time of 4 days was required, and a second, red product containing coordinated mesitylene but no terminal hydride was also isolated. Although complexes **2–6** react with $Li(Et_3BH)$, $K[H(s\text{-}Bu)_3]$ and $LiAlH_4$, the products could not be identified; borohydride or aluminohydride complexes may have been present [19], but addition of triethylamine did not liberate the expected dihydrides. Treatment of **2–6** with RedAl $\{Na[AlH_2(OCH_2CH_2OMe)_2]\}$ gave traces of the dihydrido complexes, as shown by ^1H NMR spectra, but they could not be isolated. The dihydrido(η-benzene) complex $OsH_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ has been isolated from the reaction of $OsI_2(\eta\text{-}C_6H_6)(P\text{-}i\text{-}Pr_3)$ with RedAl in toluene, but the reported yield was only 28% [9].

The best reagent we have found in zinc borohydride, $Zn(BH_4)_2$, which is generated in situ by adding $ZnCl_2$ to $NaBH_4$ in ether. Although it has been used in

organic chemistry for the stereoselective reduction of ketones [20], zinc borohydride has found little application in organometallic chemistry [21*]. Treatment of complexes **7** and **8** separately with $Zn(BH_4)_2$ in ether at room temperature for 5 h gave $OsH_2(\eta\text{-}C_6H_3Me_3)(L)$ (L = PPh_3 (**15**), PMe_3 (**16**)) in ca. 80% isolated yield.

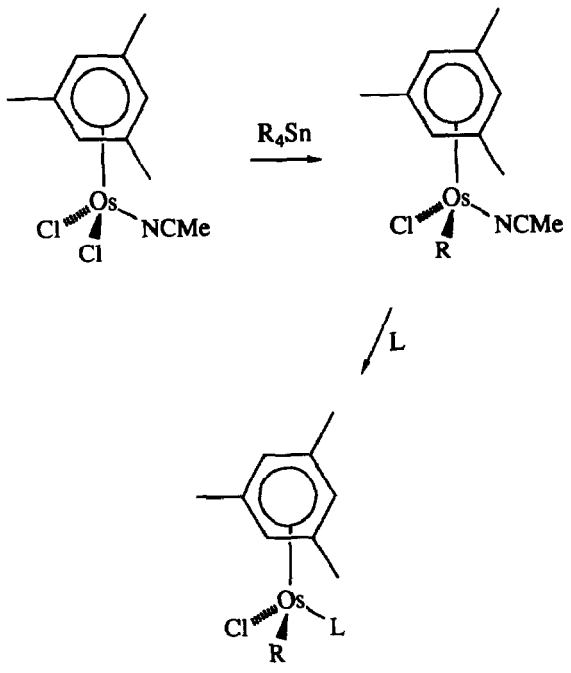
The dihydrido complexes are colourless or pale yellow, air-stable solids that are air-sensitive in solution. Their IR spectra show a broad band or two sharp bands due to ν(OsH) in the region 2010–2090 cm^{-1} and their ^1H NMR spectra show doublet hydride resonances in the range δ −10.90 to −12.20 ppm (J(PH) ca. 38 Hz), i.e. about 1 ppm more shielded than the corresponding resonance in the chloro(hydrido) complexes. The singlet resonances in the $^{31}P\{^1H\}$ NMR spectra become triplets when selective coupling to the hydride protons is allowed, thus confirming the presence of two hydride ligands.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of a crude sample of $OsH_2(\eta\text{-}C_6H_3Me_3)(P\text{-}i\text{-}Pr_3)$ (**19**) clearly showed the presence of two species in a 3/1 ratio. The close similarity of the hydride chemical shifts and P–H coupling constants (δ −12.08 ppm, J(PH) 37.2 Hz (major), δ −12.20 ppm, J(PH) 36.6 Hz (minor)) suggests that the minor component is not an impurity. Unexpectedly, the proportions of the two isomers of **19** changed on recrystallization: crystals obtained rapidly from hexane at −78°C contained mainly the major component and only a trace of the minor component. Also, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the mother liquor showed that only the major component was present, so that one species had changed into the other on recrystallization. Treatment of the crystals with $CDCl_3$ gave a solution containing both isomers of **6** in the same proportions as those observed for the compound prepared from **1** and P-i-Pr_3. The two isomers of **19** are presumably also rotamers; the possibility that one species is a dihydride and the other a η^2-dihydrogen complex [22] is apparently excluded by the similarity of their P-H coupling constants.

Reactions of $OsCl_2(\eta\text{-}C_6H_3Me_3)(L)$ with alkylating agents

Treatment of the dichloro complexes **2** and **3** with an excess of methyllithium at room temperature gave the corresponding dimethyl complexes $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(L)$ (L = PPh_3 (**20**), PMe_3 (**21**)) in isolated yields of 50 and 26%, respectively. Complex **20** is a yellow crystalline solid, **21** is a yellow oil; both are stable to air when pure but are air-sensitive in solution. They show parent ion peaks in their mass spectra and a doublet (J(PH) ca. 7–8 Hz) close to δ 0 ppm due to Os-CH_3 in their ^1H NMR spectra. Similar complexes containing benzene and *p*-cymene in place of mesitylene have been prepared similarly [9,11,23]. Like other dimethyl(η^6-arene) complexes of ruthenium and osmium [23], **20** reacts with $[Ph_3C][PF_6]$ to give a hydrido(η^2-ethylene) complex $[OsH(C_2H_4)(\eta\text{-}C_6H_3Me_3)(PPh_3)]PF_6$ (**22**). Attempts to detect the presumed osmium-methylene intermediate $[Os(CH_2)(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)]PF_6$ by carrying the reaction out at low temperature were unsuccessful.

The chloro(methyl) complexes $OsCl(CH_3)(\eta\text{-}C_6H_3Me_3)(L)$ (L = PPh_3 (**23**), PMe_3 (**24**)) could not be made by reaction of the dichloro complexes with one equivalent of methyllithium; small amounts of the dimethyl compounds and unchanged starting materials were recovered. Use of CH_3MgCl in THF instead of CH_3Li was also unsuccessful. Maitlis and Cabeza [11] treated $OsCl_2(\eta\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)(Me_2SO)$ with a stoichiometric amount of $Al_2(CH_3)_6$ to give



23: R = CH_3, L = PPh_3

24: R = CH_3, L = PMe_3

25: R = C_6H_5, L = PPh_3

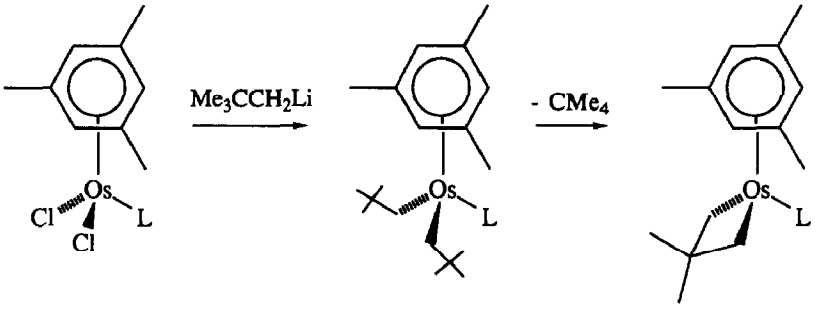
26: R = C_6H_5, L = PMe_3

Scheme 2

$OsCl(CH_3)(\eta\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)(Me_2SO)$ and then replaced the labile dimethylsulphoxide with the appropriate tertiary phosphine. We adopted the method used by Zelonka and Baird [24] to prepare the corresponding benzene-ruthenium compounds. A solution of **1** in acetonitrile reacted slowly with tetramethyltin at room temperature to give $OsCl(CH_3)(\eta\text{-}C_6H_3Me_3)(NCMe)$, which was stable only in the presence of an excess of acetonitrile and could not be isolated. After 4 days, addition of PPh_3 or PMe_3 gave **23** and **24** in yields of 45 and 30%, respectively. Longer reaction times, or heating, gave insoluble black residues. The phenyl compounds $OsCl(C_6H_5)(\eta\text{-}C_6H_3Me_3)(L)$ (L = PPh_3 (**25**), PMe_3 (**26**)) were obtained similarly, except that the reaction between **1** and tetraphenyltin in acetonitrile required heating under reflux for 7 days (Scheme 2).

Compounds **23–26** are yellow, air-stable solids that show parent ion peaks in their mass spectra. The ^1H NMR spectra of **23** and **24** show doublet Os-CH_3 resonances (J(PH) ca. 9 Hz) that are ca. 1 ppm less shielded than those in the dimethyl complexes.

Reaction of $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**2**) with an excess of neopentyllithium and subsequent methanolysis gave a mixture of two products. The ^1H and ^{31}P NMR



2 **27**: L = PPh_3

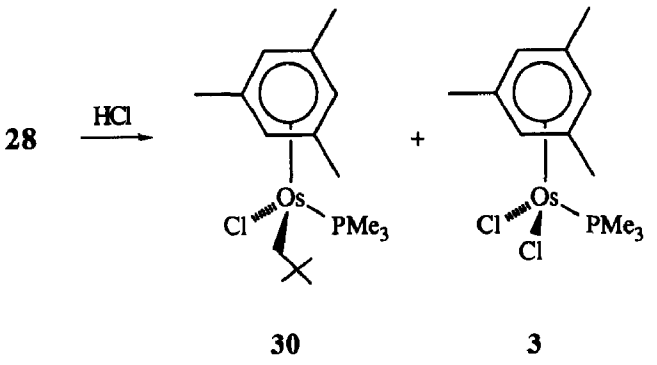
3 **29**: L = PMe_3 **28**: L = PMe_3

Scheme 3

spectroscopic data clearly identified the minor product as the cyclometallated complex **12**. The major component, isolated in 25% yield after fractional crystallization, is formulated on the basis of its spectroscopic properties as the 3,3-dimethylosmacyclobutane complex **27** (Scheme 3). The ^1H NMR spectrum contains a pair of singlets at δ 1.04 and 0.31 ppm due to inequivalent methyl groups, a multiplet at δ 0.50 ppm arising from the two CH_2 groups of the metallacyclobutane, and peaks due to coordinated mesitylene and PPh_3. The mass spectrum shows peaks due to $[M]^+$ and $[M - CMe_4]^+$.

Treatment of $OsCl_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**3**) with neopentyllithium, methanolysis, and vacuum sublimation of the crude product on to a probe at $-20\,^\circ C$ yielded a yellow crystalline solid that melted to an oil at just below room temperature. Its NMR (^1H, ^{31}P) and mass spectra show this to be a mixture of which the main component (ca. 90%) is also a 3,3-dimethylosmacyclobutane complex **28**. In addition to the usual resonances due to mesitylene and PMe_3 there are singlets in the ^1H NMR spectrum at δ 1.15 and 0.95 ppm due to the inequivalent methyl groups and a multiplet at δ 1.05 ppm due to the CH_2 groups of the metallacycle. The mass spectrum has peaks due to **28** at m/z 458 $[M^+]$ and 388 $[M - CMe_4]^+$, but there is also a peak at m/z 528 which probably arises from a small amount of the bis(neopentyl) complex $Os(CH_2CMe_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**29**). The ^1H NMR spectrum of the oil contains a singlet due to CMe_3 at δ 1.29 ppm and an additional set of mesitylene and PMe_3 signals assignable to **29**; the CH_2CMe_3 resonances are probably masked by other peaks.

These reactions provide further examples of the formation of metallacyclobutanes by δ-hydrogen abstraction from bis(alkyls) of the transition metals. They are assumed to proceed by internal oxidative addition of the δ-CH bond of one of the neopentyl groups to the osmium atom and subsequent reductive elimination of neopentane (Scheme 3) [25,26]. A closely related example is the formation of $Rh(\eta\text{-}C_5Me_5)(CH_2CMe_2CH_2)(PPh_3)$ from the reaction of $RhCl_2(\eta\text{-}C_5Me_5)(PPh_3)$ with neopentyllithium in ether or pentane, though in this case the presumed intermediate bis(neopentyl) complex could not be detected [27]. In the mesitylene-osmium series, the fact that the bis(neopentyl) can be seen when L = PMe_3 but not



30 3

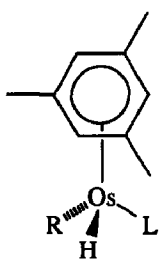
Scheme 4

when L = PPh_3 suggests that the oxidative addition step is preceded by dissociation of L, which will occur more readily for the bulkier ligand PPh_3.

Treatment of **28** with one equivalent of HCl, conveniently in the form of its 1/1 adduct with dimethylacetamide, gave the yellow, crystalline, air-stable chloro(neopentyl) complex $OsCl(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**30**) in ca. 60% yield (Scheme 4). This was separated by column chromatography from the by-product, $OsCl_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**3**), which was formed in ca. 20–30% yield. The ^1H NMR spectrum of **30** shows a pair of double doublets at δ 2.71 and 1.69 ppm due to the inequivalent methylene protons of the neopentyl group and a sharp singlet at δ 1.42 ppm due to the t-butyl protons. Although the overall yield of **30** based on **3** was only 25%, alternative approaches to **30** failed. Thus, treatment of **1** in acetonitrile with bis(neopentyl)mercury at room temperature for periods of up to 9 days gave no reaction; subsequent addition of PMe_3 gave only **3**. When the mixture was heated, it decomposed. Complex **3** did not react with neopentylmagnesium chloride.

Synthesis of hydrido(alkyl) and hydrido(phenyl) complexes $OsH(R)(\eta\text{-}C_6H_3Me_3)(L)$

The chloro(methyl) and chloro(phenyl) complexes **23–26** and the chloro(neopentyl) complex **30** were readily reduced by $NaBH_4$ in propan-2-ol or $LiAlH_4$ in THF to give the corresponding hydrido(alkyl) and hydrido(phenyl) complexes **31–35** in 60–80% yield. They are pale yellow or colourless solids or oils that are remarkably stable to air and heat; even in solution they survive several hours' exposure to air. Their mass spectra show strong peaks arising from elimination of RH and, in the



31: R = CH_3, L = PPh_3

32: R = CH_3, L = PMe_3

33: R = C_6H_5, L = PPh_3

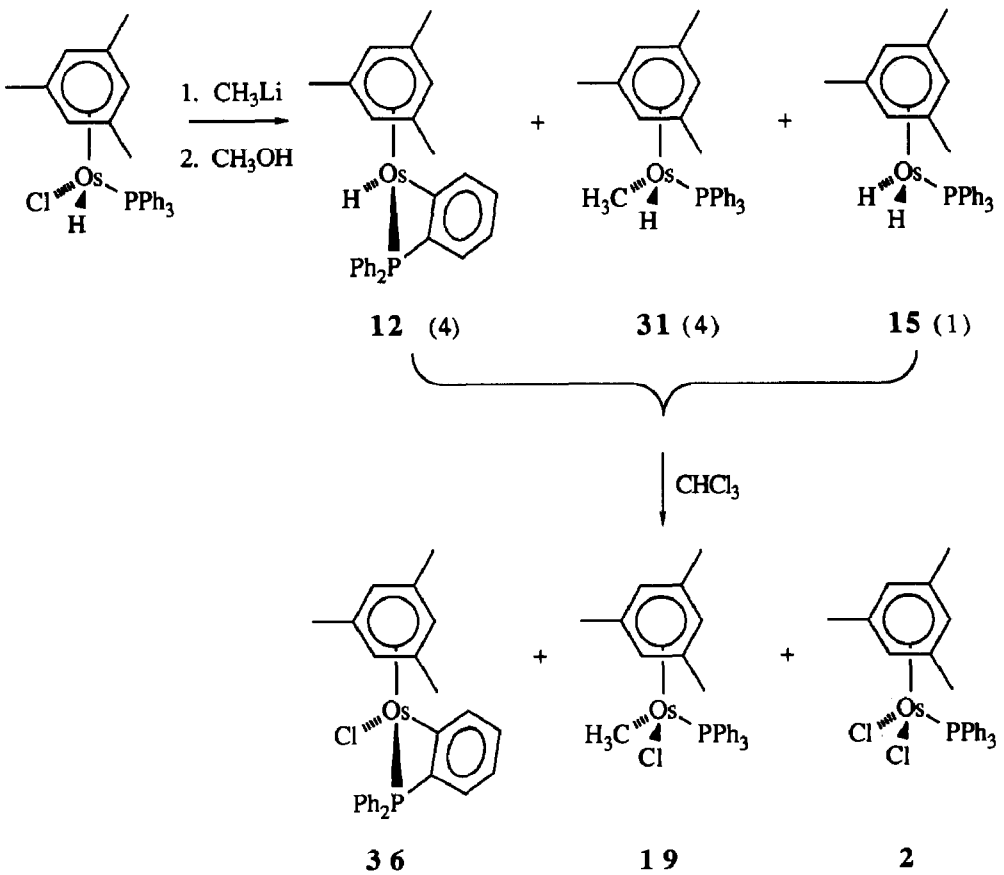
34: R = C_6H_5, L = PMe_3

35: R = CH_2CMe_3, L = PMe_3

case of **32** and **35**, weak parent ion peaks can also be observed. Their IR spectra contain broad bands in the region of 2010–2060 cm^{-1} due to ν(OsH) and in their ^1H NMR spectra the OsH resonances appear as doublets in the range δ −10 to −11.5 (J(PH) 42–45 Hz). The Os-CH_3 signals in the ^1H NMR spectra of **31** and **32** are doublets of doublets at ca. δ 0.7 ppm (J(PH) ca. 7 Hz, J(HH) ca. 1.8 Hz).

Generation and reactivity of Os(η-$C_6H_3Me_3$)(L)

Our work on the formation of Ru(η-C_6Me_6)(L) [7] led us to study first the reaction of OsHCl(η-$C_6H_3Me_3$)(L) (L = PPh_3 (**7**), PMe_3 (**8**)), with organolithium reagents. Treatment of **7** with methyllithium gave, after methanolysis, a mixture of OsH(*o*-$C_6H_4PPh_2$)(η-$C_6H_3Me_3$) (**12**), OsH(CH_3)(η-$C_6H_3Me_3$)(PPh_3) (**31**) and OsH_2(η-$C_6H_3Me_3$)(PPh_3) (**15**) in a ratio of about 4/4/1 as estimated by ^{31}P NMR spectroscopy (Scheme 5). These compounds could not be separated by fractional crystallization and they did not survive attempted chromatography on acidic, basic or neutral alumina. Nevertheless, the components were easily identified by comparing their ^1H and $^{31}P\{^1H\}$ NMR parameters with those of the authentic materials. The formation of OsH(CH_3)(η-C_6H_6)(P-i-Pr_3), among other compounds, from the action of methyllithium on OsHI(η-C_6H_6)(P-i-Pr_3) has been reported independently [8,9]. The mixture of **12**, **31** and **15** reacted with chloroform to give the chloro-com-



Scheme 5

plexes **36**, **19** and **2**, respectively (Scheme 5). The cyclometallated chloro complex **36** was isolated as air-stable yellow crystals after column chromatography and was identified by elemental analysis, IR spectrum, and NMR (^1H, ^{31}P) spectroscopy.

Treatment of **8** with methyllithium and then with methanol gave a mixture of $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**32**), $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**20**) and $OsH_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**16**), in a ratio of about 5/2/1.

Similar reactions occurred with phenyllithium. Thus, **7** gave a 3/1 mixture of **12** and the hydrido(phenyl) complex $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**33**) which reacted with chloroform to give **32** and $OsCl(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**25**); **8** gave mainly hydrido(phenyl) complex $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**34**), but there was a small amount of a second species that may have been $Os(C_6H_5)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$.

As in the case of the corresponding RuC_6Me_6 chemistry, complex **12** presumably arises by cyclometallation of an intermediate fragment $Os(\eta\text{-}C_6H_3Me_3)(PPh_3)$. Because neither the hydrido(methyl) complex **31** nor the hydrido(phenyl) complex **33** undergo reductive elimination of RH (R = Me, Ph) under the reaction conditions, **12** must be formed by direct elimination of HCl from **7** induced by the strongly basic organolithium reagents i.e. the latter act both as bases (giving **12**) and as alkylating or arylating agents (giving **31** or **33**). Surprisingly, however, attempts to generate **12** from **7** by the action of strong, non-nucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene or sodium bis(trimethylsilylamide) were unsuccessful.

It is not clear how the complexes $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(L)$ and $OsH_2(\eta\text{-}C_6H_3Me_3)(L)$ are formed in the reactions of **7** and **8** with methyllithium, because the main products, $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(L)$, are stable to disproportionation. Presumably the dimethyl complexes result from direct displacement of coordinated H by CH_3. The dihydrides might be formed by β-elimination from intermediate methoxides $OsH(OCH_3)(\eta\text{-}C_6H_3Me_3)(L)$ produced from methoxide present as an impurity in the methyllithium. Alternatively, and perhaps more likely, they could arise by electron transfer from methyllithium to $OsHCl(\eta\text{-}C_6H_3Me_3)(L)$ leading to intermediates such as $OsH(\eta\text{-}C_6H_3Me_3)(L)]^-$ and $[OsH(\eta\text{-}C_6H_3Me_3)(L)$ (eqs. 3 and 4); these would be expected to rapidly abstract, respectively, a hydrogen atom and a proton from the solvent.

$$OsHCl(\eta\text{-}C_6H_3Me_3)(L) + CH_3Li \rightarrow OsH(\eta\text{-}C_6H_3Me_3)(L) + LiCl + CH_3^{\cdot} \quad (3)$$

$$OsHCl(\eta\text{-}C_6H_3Me_3)(L) + 2CH_3Li \rightarrow Li[OsH(\eta\text{-}C_6H_3Me_3)(L)] + LiCl + 2CH_3^{\cdot} \quad (4)$$

Alkyllithium reagents can act as one-electron transfer agents (e.g. in their reaction with $TiCl_4$), and the alkyl radicals generated in this way have been detected by ESR spectroscopy [28]. A similar mechanism has been suggested to account for the observation that $WH_2(\eta\text{-}C_5H_5)_2$ is the main product of the reaction of $WHI(\eta\text{-}C_5H_5)_2$ with methyllithium [29]. In the present context, it is of interest that the anion $[IrH(\eta\text{-}C_5Me_5)(PMe_3)]^-$, formed by deprotonation of $IrH_2(\eta\text{-}C_5Me_5)(PMe_3)$ with t-butyllithium, reacts with methyl triflate to give $IrH(CH_3)(\eta\text{-}C_5Me_5)(PMe_3)$ contaminated with $Ir(CH_3)_2(\eta\text{-}C_5Me_5)(PMe_3)$ and $IrH_2(\eta\text{-}C_5Me_5)(PMe_3)$ [30].

Unlike their $Ir(\eta\text{-}C_5Me_5)$ and $Rh(\eta\text{-}C_5Me_5)$ analogues, the hydrido(alkyl)- and hydrido(aryl)-osmium complexes containing η-mesitylene do not undergo reversible elimination of alkane or arene on heating. Thus, neither the hydrido(phenyl)

complex **33** nor the cyclometallated complex **12** were formed when a solution of $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**31**) in benzene was kept at room temperature for 48 h or heated to 120 °C; **31** was also unaffected by refluxing toluene. The analogous trimethylphosphine complexes $OsH(R)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ ($R = CH_3$ (**32**), CH_2CMe_3 (**35**)) did not react with benzene, toluene or cyclohexane, either at room temperature or on prolonged heating under reflux. The hydrido(phenyl) complexes **33** and **34** did not exchange with C_6D_6, even on heating, and in the case of **33**, the cyclometallated complex **12** was not formed.

Some of these reactions could be induced by u.v. irradiation, but there was extensive decomposition resulting in the liberation of mesitylene. For example, irradiation of **31** in C_6D_6 gave a mixture of **12** and $OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**33**-d_6) in about 5/1 ratio; in cyclohexane the only organometallic product was **12**. Similarly, irradiation of complexes **32** or **35** in benzene-d_6 gave some $OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**34**-d_6), but there was no evidence for the formation of a hydrido(cyclohexyl) complex on irradiation in cyclohexane.

The exchange reactions do, however, proceed efficiently at room temperature in the presence of a trace of alumina (acidic, basic or neutral), or silica. Small amounts of oxidizing agents such as H_2O_2, and Lewis acids such as HPF_6, $ZnCl_2$ and $BF_3 \cdot OEt_2$, only caused decomposition in the mesitylene-osmium system, whereas they catalyse alkane elimination from $IrH(R)(\eta\text{-}C_5Me_5)(PMe_3)$ complexes in the presence of benzene [1a,b]. Attempts to catalyse the exchange reactions with traces of acids were unsuccessful and led only to decomposition. The alumina-catalysed reactions can be carried out in NMR tubes and the products identified by their characteristic ^1H and ^{31}P NMR parameters. The results are summarized in Table 1. Thus, treatment of either **31** or **33** with benzene or toluene in the presence of alumina gave quantitatively a mixture of the cyclometallated complex **12** (ca. 80%) and **33** or its tolyl analogue $OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**37**) (ca. 20%). The relative amounts of the two products did not vary with time and were the same, within experimental error, as those found in the photochemical experiment. The reaction of **27** with C_6D_6 to give a mixture of **12** and **29**-d_6, monitored by ^1H NMR spectroscopy, showed no evidence of any detectable intermediate. Reliable kinetic data could not be obtained because the rates depended on the amount of alumina present and on the rate of stirring of the heterogeneous reaction mixture. Treatment of **31** or **33** with cyclohexane in the presence of alumina gave only **12**, there being no evidence for any $OsH(C_6H_{11})(\eta\text{-}C_6H_3Me_3)(PPh_3)$.

The trimethylphosphine complexes **32** and **35** also reacted with benzene, benzene-d_6, toluene or naphthalene (in THF) in the presence of alumina to give quantitatively the corresponding hydrido(aryl) complexes **34**, **34**-d_6, $OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**38**), and $OsH(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**39**), respectively. Complex **38** was isolated in ca. 70% yield as a sticky white solid. It shows a band at 2010 cm^{-1} due to ν(OsH) in its IR spectrum and a doublet hydride resonance at δ −10.43 ppm (J(PH) 43.4 Hz) in its ^1H NMR spectrum, in addition to singlets at δ (ppm) 4.48 ($C_6H_3Me_3$), 1.99 ($C_6H_3Me_3$), and 2.06 (C_6H_4Me) and a doublet at δ 1.18 (J(PH) 9.1 Hz, PMe_3). The $^{31}P\{^1H\}$ NMR spectrum contains just a singlet at δ −43.2 ppm. Jones and Feher [2a,2c] have reported that the tolyl aromatic resonances for the mixture of positional isomers $RhH(m\text{-}C_6H_4Me)(\eta\text{-}C_5Me_5)(PMe_3)$ and $Rh(p\text{-}C_6H_4Me)(\eta\text{-}C_5Me_5)(PMe_3)$ are fully resolved, whereas the other ^1H resonances have similar chemical shifts; unfortunately, no ^{31}P NMR data were

Table 1

Alumina-catalysed reactions of hydrocarbons with $OsH(R)(\eta\text{-}C_6H_3Me_3)(L)$

Starting complex	Solvent	Time (h)	Products
$OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (31)	benzene	1	$OsH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6H_3Me_3)$ (12) (80%)-$OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (33) (20%)
31	benzene-d_6	1	12 (80%) + $OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (33-d_6) (20%)
31	toluene	2	12 (80%) + $OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (37) (20%)
31	cyclohexane	16	12
$OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (33)	benzene-d_6	1	12 (80%) + 33-d_6 (20%)
33	toluene	2	12 (80%) + 37 (20%)
33	cyclohexane	16	12
$OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (32)	benzene	2	$OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (34)
32	benzene-d_6	2	$OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (34-d_6)
32	toluene	2	$OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (38)
32	naphthalene/THF	2	$OsH(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (40)
$OsH(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (35)	benzene	2	34
35	benzene-d_6	2	34-d_6
35	toluene	2	38
35	naphthalene/THF	2	40

given. The tolyl aromatic resonances of **38** consist of overlapping multiplets and we have not been able to determine from them whether both *para*- and *meta*-isomers are present. The NMR spectroscopic data for the hydrido(naphthyl) complex **40** are discussed below.

Treatment of solutions of **32** or **35** in cyclohexane or hexane with alumina caused darkening due to decomposition over a 4 h period, there being no reaction with the C–H bonds of these solvents. The complexes also did not react with norbornene, with ethylene (1 atm) in THF, or with CO (1 atm) in THF in the presence of alumina.

Werner and coworkers [6,8] have reported that the fragments $Os(\eta\text{-}C_6H_6)(L)$ ($L = PMe_3$, P-i-Pr_3), generated by reduction of $OsI_2(\eta\text{-}C_6H_6)(L)$ with sodium naphthalene, react with benzene or benzene-d_6 to give the corresponding hydrido(phenyl) or deuterido(perdeuteriophenyl) complexes, $OsH(C_6H_5)(\eta\text{-}C_6H_6)(L)$ and $OsD(C_6D_5)(\eta\text{-}C_6H_6)(L)$. With cyclohexane under the same conditions an air-sensitive mixture of products thought to contain the hydrido(cyclohexyl) complex $OsH(C_6H_{11})(\eta\text{-}C_6H_6)(PMe_3)$ was obtained [8]. We found that reduction of $OsCl_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**3**) with $NaC_{10}H_8$ (2.5 equiv.) in the presence of benzene gave, after treatment with methanol, a mixture consisting mainly of $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**34**) and $OsH_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**16**), identified by their ^1H and ^{31}P NMR spectra. Free mesitylene arising from decomposition was also detected. Complex **34** was isolated in 20% yield after column chromatography in benzene. Similarly, reduction of **3** with $NaC_{10}H_8$ in the presence of C_6D_6 gave

$OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**34**-d_6), identified by ^1H, ^2H and $^{31}P\{^1H\}$ NMR spectroscopy.

Attempts to improve the yield of **34** by varying the amount of reducing agent were unsuccessful. When less than 2.5 equiv. of $NaC_{10}H_8$ was used, reduction was incomplete, whereas larger amounts of $NaC_{10}H_8$ caused extensive decomposition and over-reduction. This could not be avoided even when the reducing agent was added via a syringe pump (0.2 ml/min). Other reducing agents were investigated, without success. Treatment of **3** with 1% sodium amalgam in benzene/THF gave only $OsHCl(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**8**), 40% sodium amalgam or sodium-potassium alloy gave mainly **16** and a trace of **34**, with much decomposition.

The dihydride **16** is probably formed by over-reduction of the presumed fragment $Os(\eta\text{-}C_6H_3Me_3)(PMe_3)$ to a monoanion or dianion, and subsequent protonation, cf. the formation of **16** from **7** and methyllithium. We were unable, however, to identify the source of the protons. The dihydride, not the dideuteride, was formed when the reaction was carried out in benzene-d_6, when the $NaC_{10}H_8$ was prepared in THF-d_8, or when the reaction mixture was worked up with methanol-d_4. It seems unlikely that traces of water adsorbed on the glass surface of the reaction vessel are responsible, because flame-dried glassware was used. The only other possibilities appear to be coordinated mesitylene, free naphthalene, or coordinated trimethylphosphine; intramolecular or intermolecular hydrogen abstractions from each of these molecules in complexes of ruthenium or osmium are known [31–33].

Reduction of **3** with $NaC_{10}H_8$ in the presence of an excess of cyclohexane gave mainly the dihydride **16** and unidentified decomposition products. We found no evidence for any hydrido(cyclohexyl) complex. A doublet hydride resonance at δ −10.35 ppm (J(PH) 43.3 Hz) in the NMR spectrum of the crude reaction mixture was assigned to the hydrido(naphthyl) complex $OsH(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**40**), presumably formed by reaction of the fragment $Os(\eta\text{-}C_6H_3Me_3)(PMe_3)$ with a small amount of free naphthalene that is present in solutions of $NaC_{10}H_8$. Complex **40** was isolated as a yellow oil in 20% yield by reducing **3** with $NaC_{10}H_8$ in the presence of an excess of naphthalene, methanolysis, and chromatography on alumina with use of THF/cyclohexane (1/99) as eluant. Elution with benzene or toluene gave the hydrido(phenyl) or hydrido(tolyl) complexes **34** and **38** owing to Al_2O_3-catalysed exchange. The mass spectrum of **40** shows a parent ion peak at m/z 516 and the IR spectrum shows a band due to ν(OsH) at 2020 cm^{-1}. The ^1H NMR spectrum contains a multiplet at δ 7.90–6.90 ppm due to $C_{10}H_7$ in addition to the usual coordinated mesitylene and trimethylphosphine resonances. On treatment with chloroform **40** was converted into the yellow, crystalline chloro-complex $OsCl(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**41**). We assume that **40** and **41** contain 2-naphthyl groups by analogy with the structurally characterized compounds $MH(2\text{-}C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$ (M = Ru, Os) [32,34], which are prepared by a similar method.

There was no evidence for activation of the C–H bonds in ethylene, norbornene, tetrahydrofuran or tetramethylsilane when **3** was treated with $NaC_{10}H_8$ in the presence of a large excess of these compounds. The only identifiable products were the dihydride **16**, traces of **35**, and occasionally unchanged **3**.

Reduction of $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**2**) with $NaC_{10}H_8$ (2.5 equiv.) in benzene gave, after the usual work-up, a mixture consisting mainly of the cyclometallated complex **12** and the dihydride **16** in variable proportions, together with small

amounts of the hydrido(phenyl) complex **33**. There was also much free mesitylene owing to decomposition. Similar reactions with naphthalene or cyclohexane in place of benzene gave only **12** and **16**.

Discussion

The chemistry of (η-mesitylene)osmium complexes is generally similar to that of the corresponding (η-C_6Me_6)Ru, (η-C_5Me_5)Rh and (η-C_5Me_5)Ir systems [35]. Arenes such as benzene [36], *p*-cymene [11] or mesitylene are not easily displaced from osmium(II), except by photolysis. The hydrido(alkyls) of osmium, OsH(R)(η-$C_6H_3Me_3$)(L) (L = PMe_3, PPh_3) are thermally more stable than their (η-C_5Me_5)Rh or (η-C_5Me_5)Ir counterparts and do not exchange with arenes or alkanes even on prolonged heating. Thus the fragment Os(η-$C_6H_3Me_3$)(L) is less accessible by reductive elimination than Rh(η-C_5Me_5)(L) or Ir(η-C_5Me_5)(L), a trend that is in line with the generally greater tendency of osmium(0) and ruthenium(0) relative to iridium(I) and rhodium(I) to undergo oxidative additions [37]. Intermolecular oxidative addition of C–H bonds to Os(η-$C_6H_3Me_3$)(L) should, therefore, be thermodynamically very favourable. We believe that these fragments are generated transiently in the reactions of $OsCl_2$(η-$C_6H_3Me_3$)(L) with $NaC_{10}H_8$ and of OsHCl(η-$C_6H_3Me_3$)(L) with methyllithium; disappointingly, however, there is no evidence that they undergo oxidative addition with aliphatic C–H bonds, implying that there is a substantial kinetic barrier to the process. Although it has been asserted [38] that the kinetic barrier to C–H oxidative addition is low, such a barrier has been invoked previously [39] to account for the fact that UV irradiation of Re(η-C_5H_5)$(CO)_3$ in alkane and arene solvents fails to give C–H oxidative addition products, even though independently synthesized hydrido(alkyl) rhenium complexes ReH(R)(η-C_5H_5)$(CO)_2$ are stable towards reductive elimination of alkane in solution.

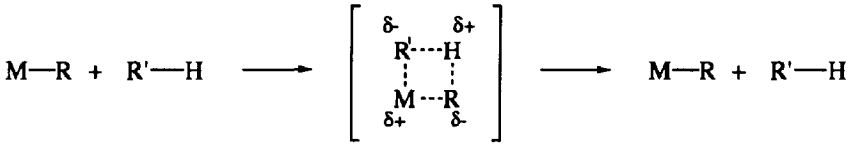
The fragment Os(η-$C_6H_3Me_3$)(PPh_3) clearly undergoes *ortho*-metallation more readily than does its isoelectronic counterpart Ir(η-C_5Me_5)(PPh_3). Thus, when Os(η-$C_6H_3Me_3$)(PPh_3) is generated in benzene by any of the methods described above, an approximately 5/1 mixture of intramolecular and intermolecular C–H addition products (**12**) and (**33**) results. In contrast, when IrH_2(η-C_5Me_5)(PPh_3) is irradiated in benzene, approximately equal amounts of the cyclometallated complex IrH(*o*-$C_6H_4PPh_2$)(η-C_5Me_5) and the hydrido(phenyl) complex IrH(C_6H_5)(η-C_5Me_5)(PPh_3) are formed [1a]. Even when IrH_2(η-C_5Me_5)(PPh_3) is irradiated in cyclohexane, some of the intermolecular addition product IrH(C_6H_{11})(η-C_5Me_5)(PPh_3) is formed in addition to the cyclometallated species [1a]. There is no evidence for cyclometallation of PMe_3 in either Os(η-$C_6H_3Me_3$)(PMe_3) or Ir(η-C_5Me_5)(PMe_3). In contrast, the fragment Re(η-C_5H_5)$(PMe_3)_2$, generated by UV irradiation of Re(η-C_5H_5)$(PMe_3)_3$ in cyclohexane gives a mixture of ReH(η^2-CH_2PMe_2)(η-C_5H_5)(PMe_3) and ReH(η^1-CH_2PMe_2)(η-C_5H_5)$(PMe_3)_2$ [39].

The inertness of Os(η-$C_6H_3Me_3$)(PR_3) towards alkanes is particularly surprising because Os(η-$C_6H_3Me_3$)(CO), generated by UV photolysis of the dicarbonyl or other precursors in a methane matrix, forms OsH(CH_3)(CO)(η-$C_6H_3Me_3$) [12b]. Irradiation of OsH_2(CO)(η-C_6Me_6) in cyclohexane or neopentane gives hydrido(alkyls) OsH(R)(CO)(η-C_6Me_6) together with free hexamethylbenzene. The fragment Os(η-C_6Me_6)(CO) shows only a slight kinetic preference for activation of C–H bonds in benzene over those in cyclohexane, in complete contrast to Os(η-$C_6H_3Me_3$)(PR_3) [40].

Two points emerge from these comparisons. First, in theoretical calculations, the effect of increasing the oxidation state in neutral, isoelectronic fragments such as (η-C_5H_5)Ni and (η-C_6H_6)Co has been treated as negligible [41], but clearly changes of this sort strongly influence chemistry at the metal atom. Second, increasing the electron-richness of a metal fragment, either by replacing CO by PMe_3 or by lowering the formal oxidation state ($Ir^I \rightarrow Os^0$), does not necessarily increase the reactivity towards C–H bonds, and may decrease it.

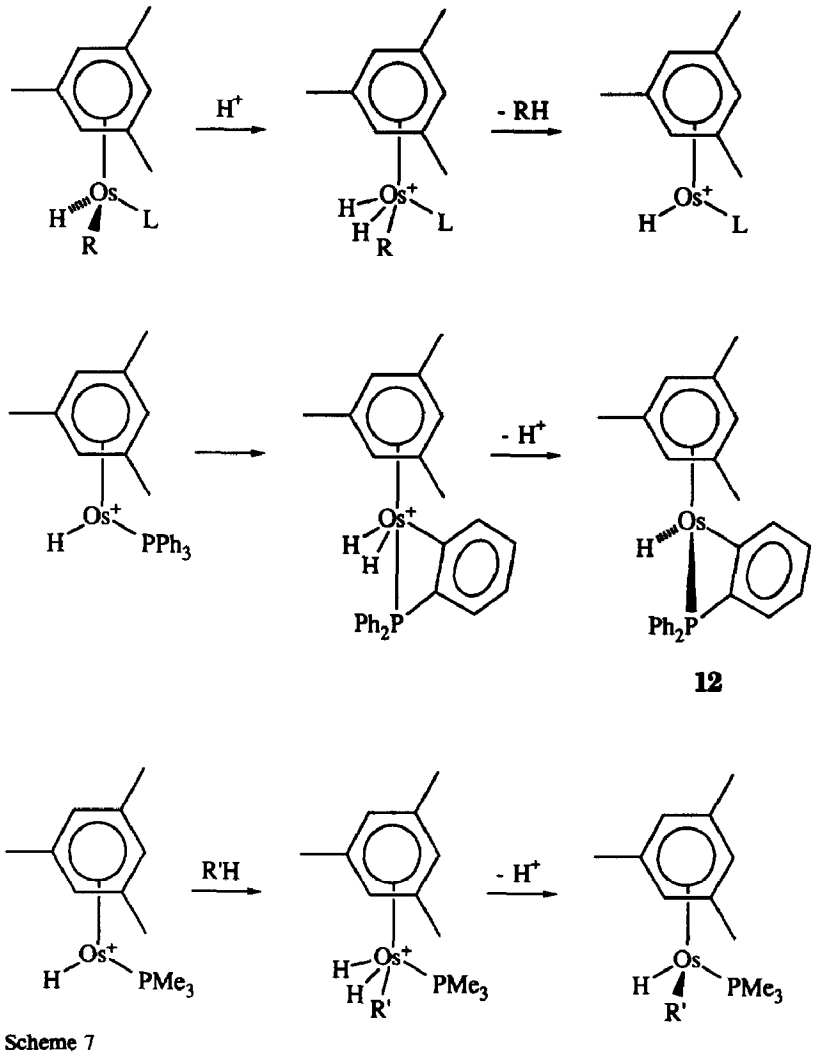
It might be argued that the kinetic barrier to C–H activation by Os(η-$C_6H_3Me_3$)(PR_3) is steric i.e. that the six-membered ring shields the metal atom more effectively from reagents than does the five-membered ring in Ir(η-C_5Me_5)(PR_3). Estimated cone angles based on X-ray data for various fragments, including the Van der Waals radii for all the hydrogen atoms, are: (η-C_5Me_5)Rh^{III} (188°), (η-C_5Me_5)Rh^I ((182°), (η-C_5H_5)Rh^{III} (148°), (η-C_5H_5)Rh^I (150°), (η-C_6Me_6)Ru^0 (192°), (η-C_6H_6)Ru^{II} (162°) [35]. Since metal–ligand bond lengths in comparable complexes of 4*d* and 5*d* elements are generally almost equal, the value for osmium should not differ greatly from that for ruthenium, and the value for rhodium should hold for iridium. Regardless of oxidation state, the introduction of each methyl group causes an average increase in cone angle of 5–6°. On this admittedly crude basis, the calculated cone angle for (η-$C_6H_3Me_3$)Os^0 (177°) is actually slightly less than that of (η-C_5Me_5)Ir^I. The difference is certainly small enough to suggest that steric effects cannot be primarily responsible for the difference in behaviour of Ir(η-C_5Me_5)(PR_3) and Os(η-$C_6H_3Me_3$)(PR_3).

Two different mechanisms for cleavage of C–H bonds in alkanes and arenes by metal complexes have been recognized: (1) oxidative addition to a highly reactive, coordinatively unsaturated, electron-rich metal atom and (2) heterolytic cleavage by a coordinatively unsaturated, highly electrophilic metal atom [42]. The second process has been invoked especially for processes mediated by hydrides and alkyls of the early transition elements, lanthanides and actinides, and is thought to occur by a four-centre mechanism in which the metal atom abstracts a carbanion and the departing hydride or carbanion abstracts a proton [43] (Scheme 6). These limiting mechanisms also apply to the closely related processes of dihydrogen bond cleavage and cyclometallation. The distinction between the two mechanisms is not completely sharp, however, because electrophilic, cationic d^8 complexes such as $[Ir(cod)(PR_3)_2]^+$ can also add dihydrogen to give $[IrH_2(cod)(PR_3)_2]^+$ [44], and the dehydrogenation of alkanes to alkenes by $[IrH_2(solv)_2(PPh_3)_2]^+$ is thought to proceed by initial oxidative addition of the alkane to an electrophilic iridium centre [45]. The role of alumina or silica in promoting displacement of alkane or arene at room temperature from OsH(R)(η-$C_6H_3Me_3$)(L) may be to render the osmium



R, R' = H, alkyl, alkenyl, aryl

Scheme 6



Scheme 7

atom more electrophilic by proton transfer from the acidic hydroxyl groups on the surface. The resulting hydrido cation can then lose RH to give a coordinatively unsaturated cation $[OsH(\eta\text{-}C_6H_3Me_3)(L)]^+$. When $L = PPh_3$, this can undergo cyclometallation and deprotonation to give **12**, and when $L = PMe_3$ the cation can oxidatively add arenes (RH) to give, after loss of the proton, hydrido(aryl) complexes (Scheme 7).

The preference for the formation of osmium(II)–aryl bonds by both intermolecular and intramolecular C–H bond cleavage is consistent with the fact that $M\text{–}C_6H_5$ bonds are stronger than M–alkyl bonds; this has been confirmed by recent studies on the $M(\eta\text{-}C_5Me_5)(PMe_3)$ (M = Rh, Ir) systems [46,47]. In general, activation of stronger C–H bonds is thermodynamically favoured. The oxidative addition probably proceeds via a *dihapto*-complex in the case of arenes [2,47], similar to that established in the $Rh(\eta\text{-}C_5Me_5)(PMe_3)$ system, but it remains surprising that neither π-complex formation nor C–H bond cleavage are observed with alkenes. The oxidative additions of alkanes to $M(\eta\text{-}C_5Me_5)(PMe_3)$ (M = Rh, Ir) are thought to

Table 2

NMR data for (η^6-mesitylene)osmium tertiary phosphine complexes [a]

Complex	$\delta(^1H)$		$\delta(^{31}P)$
	Mesitylene [b]	Others	
$OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (2) [c]	4.92(C_6H_3), 2.08(Me)	7.75–7.60(m), 7.45–7.3(m)(Ph)	−6.3
$OsCl_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (3) [c]	5.18(C_6H_3), 2.26(Me)	1.58(d, *J*(PH) 10.5 Hz, P*Me*)	−42.0
$OsCl_2(\eta\text{-}C_6H_3Me_3)$(P-t-Bu$Ph_2$) (4) [c]	4.89(C_6H_3), 1.79(Me)	8.15–8.02(m, Ph), 1.25(d, *J*(PH) 13.9 Hz, t-Bu)	−16.2
$OsCl_2(\eta\text{-}C_6H_3Me_3)(PCy_3)$ (5) [c]	5.40(C_6H_3), 2.26(Me)	2.20–1.10(m, Cy)	−16.2
$OsCl_2(\eta\text{-}C_6H_3Me_3)$(P-i-$Pr_3$) (6) [d]	4.89, 4.85(C_6H_3), 1.93, 1.92(Me)	2.90–2.40(m, PCH), 1.40–1.10(m, PCHMe_2)	−5.54, −9.27
$OsHCl(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (7)	4.42(C_6H_3), 1.91(Me)	7.96–7.76(m), 7.26–6.92(m)(Ph), −8.12 (d, *J*(PH) 45.8 Hz, OsH)	8.7
$OsHCl(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (8)	4.45(C_6H_3), 2.05(Me)	1.37(d, *J*(PH) 9.8 Hz, P*Me*), −8.88 (d, *J*(PH) 46.9 Hz, OsH)	−42.5
$OsHCl(\eta\text{-}C_6H_3Me_3)$(P-t-$BuPh_2$) (9)	4.19(C_6H_3), 1.81(Me)	8.40–6.80(m,Ph), 1.38(d, *J*(PH) 13.4 Hz, t-Bu), −8.45(d, *J*(PH) 45.7 Hz, OsH)	20.9
$OsHCl(\eta\text{-}C_6H_3Me_3)(PCy_3)$ (10)	4.76(C_6H_3), 2.14(Me)	2.30–1.10(m, Cy), −8.70 (d, *J*(PH) 44.0 Hz, OsH)	13.0
$OsHCl(\eta\text{-}C_6H_3Me_3)$(P-i-$Pr_3$) (11)	4.69, 4.61 (C_6H_3), 2.07(Me)	2.50–2.10(m, PCH), 1.50–0.18 (m, PCHMe_2), −8.88(d, *J*(PH) 43.9 Hz, OsH), −8.99(d, *J*(PH) 43.9 Hz, OsH)	22.4, 13.3
$\overline{OsH(o\text{-}C_6H_4}PPh_2)(\eta\text{-}C_6H_3Me_3)$ (12)	4.70(C_6H_3), 2.04(Me)	8.20–6.50(m, Ph, C_6H_4), −7.67(d, *J*(PH) 31.2 Hz, OsH)	−50.8
$\overline{OsH(o\text{-}C_6H_4}PPh\text{-t-Bu})(\eta\text{-}C_6H_3Me_3)$ (13a)	4.66(C_6H_3), 2.07(Me)	7.90–6.50(m, Ph, C_6H_4), 1.22(d, *J*(PH) 14.7 Hz, t-Bu), −7.88(d, *J*(PH) 32.4 Hz, OsH)	−29.7
$\overline{OsH(o\text{-}C_6H_4}PPh\text{-t-Bu})(\eta\text{-}C_6H_3Me_3)$ (13b)	4.83(C_6H_3), 2.24(Me)	7.90–6.50(m, Ph, C_6H_4), 1.07(d, *J*(PH) 14.0 Hz, t-Bu), −8.19(d, *J*(PH) 34.8 Hz, OsH)	−31.9
$\overline{OsCl(o\text{-}C_6H_4}PPh\text{-t-Bu})(\eta\text{-}C_6H_3Me_3)$ (14a)	4.40(C_6H_3), 1.87(Me)	7.70–6.70(m, Ph, C_6H_4), 1.43(d, *J*(PH) 14.6 Hz, t-Bu)	−54.4
$OsCl(o\text{-}C_6H_4PPh\text{-t-Bu})(\eta\text{-}C_6H_3Me_3)$ (14b)	4.81(C_6H_3), 2.10(Me)	7.90–6.80(m, Ph, C_6H_4), 0.92(d, *J*(PH) 13.9 Hz, t-Bu)	−35.1
$OsH_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (15)	4.78(C_6H_3), 2.13(Me)	7.90–6.60(m, Ph), −10.93(d, *J*(PH) 37.8 Hz, OsH)	22.9
$OsH_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (16)	4.75(C_6H_3), 2.32(Me)	1.44(d, *J*(PH) 9.2 Hz, PMe), −11.1(d, *J*(PH) 38.5 Hz, OsH)	−46.5

$OsH_2(\eta\text{-}C_6H_3Me_3)$(P-t-$BuPh_2$) (17)	4.60(C_6H_3) 2.09(Me)	8.10–7.70(m), 7.20–6.70(m)(Ph), 1.27(d, *J*(PH) 13.4 Hz, t-Bu), −11.3(d, *J*(PH) 35.4 Hz, OsH)	44.3
$OsH_2(\eta\text{-}C_6H_3Me_3)(PCy_3)$ (18)	4.86(C_6H_3), 2.39(Me)	2.20–1.00(br m, Cy), −12.0(d, *J*(PH) 37.2 Hz, OsH)	32.0
$OsH_2(\eta\text{-}C_6H_3Me_3)$(P-i-$Pr_3$) (19)	4.83, 4.81(C_6H_3), 2.33(Me)	1.90–1.50(m, PCH), 1.20–0.80(m, PCHMe_2), −12.07(d, *J*(PH) 37.2 Hz, OsH), −12.19(d, *J*(PH) 36.6 Hz, OsH)	45.5, 30.2
$Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (20) [e]	4.35(C_6H_3), 1.81(Me)	7.50–7.20(m, Ph), 0.00(d, *J*(PH) 7.1 Hz, OsMe)	13.8
$Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (21)	4.16(C_6H_3), 1.90(Me)	1.10(d, *J*(PH) 8.8 Hz, PMe), 0.61 (d, *J*(PH) 8.3 Hz, OsMe)	−44.1
$[OsH(C_2H_4)(\eta\text{-}C_6H_3Me_3)(PPh_3)]PF_6$ (22) [f]	5.65(C_6H_3), 2.16(Me)	7.70–7.60(m, Ph), 1.84–1.25(br m, C_2H_4), −13.47(d, *J*(PH) 36.6 Hz, OsH)	n.m.
$OsCl(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (23)	4.23(C_6H_3), 1.80(Me)	8.00–6.90(m, Ph), 1.42(d, *J*(PH) 8.55 Hz, OsMe)	2.0
$OsCl(CH_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (24)	4.30(C_6H_3), 1.87(Me)	1.23(d, *J*(PH) 8.8 Hz, OsMe), 1.17(d, *J*(PH) 9.5 Hz, PMe)	−42.8
$OsCl(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (25)	4.48(C_6H_3), 1.64(Me)	7.60–6.80(m, Ph)	1.3
$OsCl(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (26)	4.33(C_6H_3), 1.72(Me)	7.80–6.90(m, Ph), 1.11(d, *J*(PH) 10.0 Hz, PMe)	−42.5
$\overline{Os(CH_2CMe_2CH_2)}(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (27)	4.41(C_6H_3), 1.82(Me)	7.90–7.70(m), 7.30–6.90(m)(Ph), 1.04(s, CMe), 0.50(m, $OsCH_2$), 0.31 (s, CMe)	16.3
$\overline{Os(CH_2CMe_2CH_2)}(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (28)	4.43(C_6H_3), 1.95(Me)	1.26(d, *J*(PH) 8.5 Hz, PMe), 1.15(s, CMe), 1.05(m, $OsCH_2$), 0.92(s, CMe)	−43.8
$Os(CH_2CMe_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (29)	4.48(C_6H_3), 2.06(Me)	1.28(d, *J*(PH) 9.8 Hz, PMe) 1.29(s, t-Bu)(CH_2CMe_3 masked by other peaks)	−46.9
$OsCl(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (30)	4.55(C_6H_3), 1.84(Me)	2.71(dd, *J*(HH) 12.7 Hz, *J*(PH) 2.7 Hz, C*H*H), 1.69(dd, *J*(HH) 14.2 Hz, *J*(PH) 12.2 Hz, CH*H*), 1.42(s, t-Bu), 1.21(d, *J*(PH) 9.5 Hz, PMe)	−44.7
$OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (31)	4.50(C_6H_3), 1.93(Me)	7.80–7.50(m), 7.20–6.80(m)(Ph), 0.67(dd, *J*(PH) 7.3 Hz, *J*(HH) 1.8 Hz, OsMe), −10.20(d, *J*(PH) 42.2 Hz, OsH)	21.9

Table 2 (continued)

Complex	$\delta(^1H)$		$\delta(^{31}P)$
	Mesitylene [b]	Others	
$OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (32)	4.46(C_6H_3), 2.11(Me)	1.34(d, J(PH) 9.2 Hz, PMe), 0.76 (dd, J(PH) 8.2 Hz, J(HH) 1.8 Hz, OsMe), −10.58(d, J(PH) 44.0 Hz, OsH)	−44.5
$OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (33)	4.50 (C_6H_3), 1.84 (Me)	7.80–6.60(m, Ph), −10.14(d, J(PH) 44.6 Hz, OsH)	16.5
$OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (34)	4.47 (C_6H_3), 1.98 (Me)	7.40–6.90(m, Ph), 1.16(d, J(PH) 9.8 Hz, PMe), −10.44(d, J(PH) 43.3 Hz, OsH)	−43.0
$OsH(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (35)	4.48 (C_6H_3), 2.06 (Me)	1.28(d, J(PH) 8.55 Hz, PMe), 1.29 (s, t-Bu), 0.88(m, $OsCH_2$), −11.28 (d, J(PH) 43.3 Hz, OsH)	−46.0
$\overline{OsCl(o\text{-}C_6H_4PPh_2)}(\eta\text{-}C_6H_3Me_3)$ (36)	4.47 (C_6H_3), 1.93 (Me)	8.20–6.70(m, Ph, C_6H_4)	−61.1
$OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (37)	4.50 (C_6H_3), 1.86 (Me)	8.20–6.60(m, Ph, C_6H_4), 2.10(s, C_6H_4Me), −10.13(d, J(PH) 45.2 Hz, OsH)	16.5
$OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (38)	4.48 (C_6H_3), 1.99 (Me)	8.60–6.60(m, C_6H_4), 2.06(s, C_6H_4Me), 1.18(d, J(PH) 9.1 Hz, PMe), −10.43 (d, J(PH) 43.3 Hz, OsH)	−43.2
$OsCl(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (39)	4.33 (C_6H_3), 2.37 (Me)	7.70–6.70(m, C_6H_4), 2.37(s, C_6H_4Me), 1.11(d, J(PH) 9.8 Hz, PMe)	−42.5
$OsH(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (40)	4.48 (C_6H_3), 1.95 (Me)	7.90–6.90(m, $C_{10}H_7$), 1.12 (d, J(PH) 9.8 Hz, PMe), −10.35(d, J(PH) 43.3 Hz, OsH)	−43.0
$OsCl(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (41)	4.33 (C_6H_3), 1.68 (Me)	7.90–6.90(m, $C_{10}H_7$), 1.05(d, J(PH) 10.0 Hz, PMe)	−42.3

[a] Measured in C_6D_6, except where stated otherwise. [b] All resonances were singlets. [c] ^1H and $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$. [d] $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$. [e] ^1H and $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2. [f] ^1H NMR spectrum in CD_2Cl_2.

proceed via transient *dihapto*-alkane intermediates [1g], and the fragment Os(η-$C_6H_3Me_3$)(PMe_3), in contrast to Os(η-arene)(CO) [12b,40], may be insufficiently electrophilic to form such a species. In this context, it is relevant that agostic C–H–M interactions tend to occur more readily in cationic complexes than in corresponding isoelectronic neutral complexes, in complexes containing the more electropositive 3*d*-elements than in their 4*d*- or 5*d*-counterparts, and in complexes containing strong π-acceptor ligands such as CO than in those containing strong σ-donors such as tertiary phosphines [48]. It remains unclear on this basis, however, why alkanes or alkenes should not be activated like arenes by Os(η-$C_6H_3Me_3$)(L) in the presence of alumina.

Experimental

Air-sensitive complexes were handled by conventional Schlenk and syringe techniques under a positive pressure of purified nitrogen or argon. Solvents were freshly degassed by distillation under nitrogen. Benzene, toluene, ether, hexane and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl/tetraglyme. Propan-2-ol was dried by distillation from calcium hydride. Benzene-d_6 was degassed by several freeze-thaw cycles before being used as an NMR solvent. Chromatography was carried out under nitrogen on degassed neutral alumina (Brockman Activity 3), unless specified otherwise. Ultraviolet irradiations were performed with a medium pressure mercury lamp (Hanovia, Utilux H176, 150W). Samples in NMR tubes were placed near the lamp housing and were immersed in a water bath during irradiation.

NMR spectra were recorded on the following spectrometers: JEOL FX200 and Bruker CXP 200 (^{1}H, 200 MHz), Varian XL200 (^{1}H, 200 MHz; ^{2}H, 30.71 MHz; ^{31}P, 80.98 MHz) and JEOL FX 60 (^{31}P, 24.21 MHz). Chemical shifts are reported as δ-values relative to internal $(CH_3)_4Si$ (^{1}H, ^{13}C) or to external 85% H_3PO_4 (^{31}P). Infrared spectra were measured as KBr or CsI disks on Perkin Elmer 683 and FT1800 spectrometers. Mass spectra were recorded on a VG Micromass 7070 instrument at 70 eV. Elemental analyses were performed by staff of the Microanalytical Laboratory of the Research School of Chemistry.

Osmium tetraoxide (OsO_4) was obtained from Johnson–Matthey Co., U.K. Tertiary phosphines were either prepared by standard methods or were used as received from commercial suppliers. Methyllithium in ether (ca. 1–2 *M*, ca 0.3 *M* in alkoxide) was obtained from EGA-Chemie, phenyllithium [49] and neopentyllithium [50] were prepared by literature procedures. These organolithium reagents were standardized immediately before use [51]. Tetramethyltin and tetraphenyltin were obtained from Aldrich and Fluka, respectively. 1,3,5-Trimethyl-1,4-cyclohexadiene was made by reduction of mesitylene with lithium in liquid ammonia [52]. The crystalline 1/1 adduct of hydrogen chloride with dimethylacetamide (DMA · HCl) was prepared by bubbling HCl gas slowly into a 10% solution of dimethylacetamide in benzene. The resulting white precipitate was washed with benzene and ether, and was stored in a desiccator.

NMR spectroscopic data and elemental analyses are in Tables 2 and 3, respectively.

Table 3

Analytical data

Complex	Analysis (found (calcd.) (%))			
	C	H	Cl	P
$C_{18}H_{24}Cl_4Os_2$ (1)	28.68	3.25	18.72	
	(28.35)	(3.17)	(18.60)	
$C_{27}H_{27}Cl_2OsP$ (2)	49.96	4.15	11.24	4.83
	(50.39)	(4.23)	(11.02)	(4.81)
$C_{12}H_{21}Cl_2OsP$ (3)	31.15	4.54	15.65	6.89
	(31.51)	(4.63)	(15.50)	(6.77)
$C_{25}H_{31}Cl_2OsP$ (4)	48.11	4.92	11.19	4.74
	(48.15)	(5.01)	(11.37)	(4.97)
$C_{27}H_{45}Cl_2OsP$ (5)	49.39	7.12	10.81	4.39
	(49.01)	(6.85)	(10.72)	(4.68)
$C_{18}H_{33}Cl_2OsP$ (6)	40.14	6.27	12.89	5.65
	(39.92)	(6.14)	(13.09)	(5.72)
$C_{27}H_{28}ClOsP$ (7)	53.59	4.57	5.83	
	(53.24)	(4.63)	(5.82)	
$C_{12}H_{22}ClOsP$ (8)	33.93	5.45	8.07	7.00
	(34.08)	(5.24)	(8.38)	(7.32)
$C_{25}H_{32}ClOsP$ (9)	51.31	5.56	5.88	5.04
	(50.97)	(5.47)	(6.02)	(5.26)
$C_{27}H_{46}ClOsP$ (10)	51.90	7.59	5.99	4.68
	(51.70)	(7.39)	(5.65)	(4.94)
$C_{18}H_{34}ClOsP$ (11)	42.78	6.33		
	(42.63)	(6.76)		
$C_{27}H_{27}OsP$ (12)	56.63	4.85		5.28
	(56.63)	(4.75)		(5.41)
$C_{25}H_{30}ClOsP$ (14a)	51.61	5.17	6.43	5.05
	(51.13)	(5.11)	(6.04)	(5.28)
$C_{25}H_{30}ClOsP$ (14b)	51.42	5.24	7.69	5.77
	(51.13)	(5.11)	(6.04)	(5.28)
$C_{27}H_{29}OsP$ (15)	56.42	5.24		5.23
	(56.43)	(5.09)		(5.39)
$C_{25}H_{33}OsP$ (17)	54.09	6.28		5.57
	(54.13)	(6.00)		(5.58)
$C_{27}H_{47}OsP$ (18)	54.75	8.41		5.61
	(54.70)	(7.99)		(5.22)
$C_{18}H_{35}OsP$ (19)	45.59	7.69		6.76
	(45.74)	(7.46)		(6.55)
$C_{29}H_{33}OsP$ (20)	57.71	5.67		
	(57.79)	(5.52)		
$C_{29}H_{32}F_6OsP_2$ (22)	46.82	4.30		
	(46.65)	(4.32)		
$C_{28}H_{30}ClOsP$ (23)	54.02	4.73	5.92	4.88
	(53.96)	(4.85)	(5.95)	(4.97)
$C_{13}H_{24}ClOsP$ (24)	36.16	5.31	7.36	6.38
	(35.73)	(5.54)	(8.11)	(7.09)
$C_{33}H_{32}ClOsP$ (25)	58.08	4.61	5.45	4.39
	(57.84)	(4.71)	(5.17)	(4.52)
$C_{18}H_{26}ClOsP$ (26)	43.67	5.49	6.90	5.86
	(43.32)	(5.25)	(7.10)	(6.25)
$C_{27}H_{37}OsP$ (27)	59.34	6.06		4.49
	(59.79)	(5.80)		(4.82)
$C_{17}H_{32}ClOsP$ (30)	41.84	6.67		
	(41.41)	(6.54)		

Table 3 (continued)

Complex	Analysis (found (calcd.) (%))			
	C	H	Cl	P
$C_{28}H_{31}OsP$ (31)	56.77 (57.12)	5.48 (5.31)		5.06 (5.26)
$C_{33}H_{33}OsP$ (33)	61.25 (60.90)	5.46 (5.11)		4.52 (4.76)
$C_{27}H_{26}ClOsP$ (36)	53.63 (53.41)	4.51 (4.32)		
$C_{19}H_{28}ClOsP$ (39)	44.75 (44.48)	5.74 (5.50)	6.03 (6.91)	5.28 (6.04)
$C_{22}H_{28}ClOsP$ (41)	48.63 (48.12)	4.98 (5.14)		

Preparations

(1) Di-μ-chlorobis[chloro(η-mesitylene)osmium(II)], $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$ (1). The procedure is based on the modification by Cabeza and Maitlis [11] of the method reported by Arthur and Stephenson [53] for the corresponding η-benzene and η-*p*-cymene complexes.

Osmium tetraoxide (4 g, 5.7 mmol) was converted into $(NH_4)_2OsCl_6$ [54] and this was reduced to metallic osmium by heating in a tube furnace to 350 °C for 1 h in a stream of hydrogen [55]. The osmium powder was thoroughly mixed with an excess of sodium chloride and heated at 650 °C in a current of chlorine for 45 min. The resulting red-brown solid was extracted with two 50 ml portions of absolute ethanol, and the orange solution of Na_2OsCl_6 [56] was heated under reflux with 1,3,5-trimethyl-1,4-cyclohexadiene (10 ml) for 5 days; no attempt was made to isolate the Na_2OsCl_6. The yellow precipitate was filtered, washed successively with water, ethanol and ether, and dried in a vacuum to give **1** as a fine yellow powder (3.6 g, 60% based on OsO_4). ^1H NMR (DMSO-d_6): δ 5.75 (s, $C_6H_3Me_3$), 2.20(s, $C_6H_3Me_3$) ppm. IR (CsI): 309, 268 cm^{-1} (ν(OsCl)).

In an earlier report [57], OsO_4 was heated under reflux with conc. HCl and the unidentified oily material remaining after evaporation in a vacuum was heated with 1,3,5-trimethyl-1,4-cyclohexadiene to give a compound of empirical formula Os_4Cl_9(mesitylene)$_3$. Subsequently we have found both the yield and composition of this product to be very variable, whereas the procedure given above is reproducible.

(2) Dichloro(η-mesitylene)(triphenylphosphine)osmium(II), $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (2). A suspension of $[OsCl_2(\eta\text{-}C_6H_3Me_3)]_2$ (**1**) (0.26 g, 0.35 mmol) and triphenylphosphine (0.20 g, 0.75 mmol) in propan-2-ol (20 ml) was heated under reflux for 4 h. The resulting orange-yellow solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was recrystallized from $CHCl_3$/ether to give **2** as orange microcrystals (0.33 g, 75%).

(3) Dichloro(η-mesitylene)(trimethylphosphine)osmium(II), $OsCl_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (3). A suspension of **1** (0.25 g, 0.32 mmol) in benzene (20 ml) was treated with trimethylphosphine (0.1 ml, 0.95 mmol) and the mixture was heated under reflux for 4 h. The orange solution was cooled and the solvent was

removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/hexane to give **3** as orange microcrystals (0.21 g, 70%).

The following $OsCl_2(\eta\text{-}C_6H_3Me_3)(L)$ complexes were prepared similarly to **2**, the recrystallization solvent and yield being in parenthesis: L = P-t-$BuPh_2$ (**4**) ($CHCl_3$/ether, 78%), L = PCy_3 (**5**) (propan-2-ol, 60%), L = P-i-Pr_3 (**6**) (propan-2-ol, 55%)

(4) Chloro(hydrido)(η-mesitylene)(triphenylphosphine), $OsHCl(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (7). A suspension of **2** (0.135 g, 0.20 mmol) and anhydrous Na_2CO_3 (0.15 g, 1.4 mmol) in propan-2-ol (20 ml) was heated under reflux for 4 h. The yellow-brown suspension was allowed to cool and the solvent was removed under reduced pressure. The residue was extracted with toluene (20 ml), the solution was filtered, and the filtrate was concentrated to ca one-third of its volume under reduced pressure. Addition of hexane gave **7** as yellow microcrystals (0.07 g, 55%). IR(KBr) 2080 cm^{-1} (ν(OsH)).

(5) Chloro(hydrido)(η-mesitylene)(trimethylphosphine), $OsHCl(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (8). (a) A mixture of **3** (0.11 g, 0.24 mmol) and anhydrous Na_2CO_3 (0.15 g, 1.4 mmol) in propan-2-ol (20 ml) was heated under reflux for 4 h. After cooling the yellow suspension, solvent was removed under reduced pressure and the residue was extracted with ether (10 ml). Yellow crystals of **8** (0.026 g, 25%) separated on cooling.

(b) A mixture of **3** (0.19 g, 0.41 mmol), ethanol (20 ml) and triethylamine (0.6 ml, 4.2 mmol) was heated under reflux for 5 h. The resulting yellow solution was cooled and concentrated, and the white precipitate of $[Et_3NH]Cl$ removed by filtration. The filtrate was concentrated and chromatographed on Florisil, the product being eluted with ether. Yield: 0.070 g (40%). IR (KBr): 2020 cm^{-1} (ν(OsH)).

The following $OsHCl(\eta\text{-}C_6H_3Me_3)(L)$ complexes were prepared similarly from $OsCl_2(\eta\text{-}C_6H_3Me_3)(L)$, propan-2-ol and Na_2CO_3: L = P-t-$BuPh_2$ (**9**) from **4**, heating for 1 h; yellow crystals from toluene/hexane (58%); IR (KBr): 2090 cm^{-1} (ν(OsH)). L = PCy_3 (**10**) from **5**, heating for 3 h; yellow crystals from ether (50%); IR (KBr): 2090 cm^{-1} (ν(OsH)). L = P-i-Pr_3 (**11**) from **6**, heating for 3 h, yellow crystals from ether at −78 °C (35%).

(6) [2-(Diphenylphosphino)phenyl-C^1,P](hydrido)(η-mesitylene)osmium(II), $\overline{OsH(o\text{-}C_6H_4PPh_2)}(\eta\text{-}C_6H_3Me_3)$ (12). A mixture of **2** (0.15 g, 0.23 mmol) and anhydrous Na_2CO_3 (0.16 g, 1.5 mmol) suspended in propan-2-ol (20 ml) was heated under reflux for 15 d. The pale yellow mixture was allowed to cool to room temperature and solvent was removed under reduced pressure. The residue was extracted with ether (ca. 20 ml), concentrated, and refrigerated overnight. The first crop of crystals, **7**, was discarded. The filtrate was further concentrated and on cooling to 0 °C gave pale yellow crystals of **12** (0.050 g, 40%). IR (KBr): 2020 (ν(OsH)), 1555, 1410, 720 cm^{-1} (characteristic of *ortho*-metallated ring). MS *m/z* 574 $[M]^+$.

(7) [2-{(t-Butyl)(phenyl)phosphino}phenyl-C^1,P](hydrido)(η-mesitylene)osmium(II), $\overline{OsH(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)}((\eta\text{-}C_6H_3Me_3)$ (13a / 13b) and [2-{(t-Butyl)(phenyl)phosphino}phenyl-C^1,P](chloro)(η-mesitylene)osmium(II), $\overline{OsCl(o\text{-}C_6H_4P\text{-}t\text{-}BuPh)}(\eta\text{-}C_6H_3Me_3)$ (14a / 14b). A mixture of **4** (0.20 g, 0.32 mmol) and anhydrous Na_2CO_3 (0.20 g, 1.8 mmol) suspended in propan-2-ol (20 ml) was heated under reflux for 18 h. Solvent was stripped, the residue was extracted with toluene (ca 20 ml), and the extract was evaporated to dryness to give a dark yellow oil. This was dissolved in ether (5 ml) and refrigerated overnight to give **14b** as yellow crystals. Yield: 0.015 g (8%). IR (CsI): 1560, 1435, 730 cm^{-1} (*ortho*-metallated ring). MS *m/z* 588 $[M]^+$.

On concentration and cooling, yellow crystals of the more soluble diastereomer **14a** deposited from the filtrate (0.02 g, 10%). IR (CsI): 1560, 1420, 730 cm^{-1} (*ortho*-metallated ring). MS *m/z* 588 $[M]^+$. The mother liquor contained **13a** and **13b**. These could not be isolated in a pure state or separated, but were identified by NMR (^1H, ^{31}P) spectroscopy.

(8) Dihydrido(η-mesitylene)(triphenylphosphine)osmium(II), $OsH_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (15). (a) A mixture of **2** (0.18g, 0.23 mmol) and sodium borohydride (0.09 g, 2.3 mmol) in propan-2-ol (20 ml) was heated under reflux for 4 d. The dark brown suspension was evaporated to dryness and the residue was extracted with toluene (10 ml). The concentrated extract was transferred to an alumina column and a dark orange fraction that eluted with toluene was stripped to give an orange oil. Crystallization from ether initially gave unidentified red crystals (0.10 g): ^1H NMR (δ, C_6D_6) 7.90–6.80 (m, Ph), 4.72 (s, C_6H_3), 2.14 (s, Me) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.0 ppm. MS *m/z* 945. Anal. Found C, 52.65; H, 4.66. Concentration of the filtrate gave pale yellow crystals of **15** (0.03 g, 20%). IR (KBr): 2070, 2010 cm^{-1} (ν(OsH)). MS *m/z* 574 $[M-2H]^+$.

(b) A mixture of $NaBH_4$ (0.10g, 2.6 mmol) and anhydrous $ZnCl_2$ (0.18 g, 1.3 mmol) suspended in ether (20 ml) was stirred at room temperature for 15 min and treated with **2** (0.17 g, 0.26 mmol). The mixture was stirred for a further 6 h and treated with water (0.5 ml). The ether layer was separated, dried ($MgSO_4$), filtered, and concentrated to give **15** as pale yellow crystals (0.12 g, 80%).

(9) Dihydrido(η-mesitylene)(trimethylphosphine)osmium(II), $OsH_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (16). (a) A suspension of **3** (0.16 g, 0.35 mmol) and $NaBH_4$ (0.13 g, 3.5 mmol) in propan-2-ol was heated under reflux overnight. The yellow-brown solution was evaporated to dryness, the residue was extracted with toluene (10 ml), and solvent again stripped to leave a yellow oil which was dried in vacuo. Sublimation at 40 °C/10^{-5} mmHg on to a probe at −20 °C gave pure **16** as a pale yellow oil (0.028 g, 25%). IR (KBr): 2010 cm^{-1} (ν(OsH)). MS *m/z* 388 $[M-2H]^+$.

(b) Treatment of **3** (0.15 g, 0.32 mmol) with $ZnCl_2/NaBH_4$ as described under 8(b) gave **16** (0.065 g, 50%) after vacuum sublimation.

The following $OsH_2(\eta\text{-}C_6H_3Me_3)(L)$ complexes were prepared as described in 8(a): L = P-t-$BuPh_2$ (**17**) from **4**, heating overnight; yellow crystals (30% yield) from ether at −78 °C after chromatography of the ether extract on alumina. IR (KBr): 2090, 2050, 2040 cm^{-1} (ν(OsH)). MS *m/z* 556 $[M-2H]^+$. L = PCy_3 (**18**) from **5**, heating for 2 h, colorless crystals (50%) from ether. IR (KBr): 2060 cm^{-1} (ν(OsH)). MS *m/z* 594. L = P-i-Pr_3 (**19**) from **6**, heating overnight, pale yellow crystals (35%) from hexane at −78 °C. IR (KBr): 2060, 2030 cm^{-1} (ν(OsH)). MS *m/z* 474 $[M]^+$.

(10) Dimethyl(η-mesitylene)(triphenylphosphine)osmium(II), $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (20) A suspension of **2** (0.27 g, 0.42 mmol) in ether (20 ml) was cooled to −78 °C and methyllithium (5 ml of 1.6 *M* solution, 8.0 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for a further 5 h. The yellow solution was again cooled to −78 °C and methanol (0.5 ml) was added dropwise. The solution was allowed to come to room temperature, solvents were stripped under reduced pressure, and the residue was extracted with toluene (10 ml). The extract was concentrated under reduced pressure and hexane was added to give yellow crystals of **20** (0.13g, 50%). MS *m/z* 604 $[M]^+$.

(11) Dimethyl(η-mesitylene)(trimethylphosphine)osmium(II), $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (21) A suspension of **3** (0.11 g, 0.23 mmol) in ether was treated

with methyllithium (8.0 mmol) and the mixture was worked up as described above. The oil resulting from extraction with toluene was sublimed at 50 °C/10^{-5} mmHg on to a −20 °C probe to give **21** as a yellow oil (0.025 g, 26%). MS *m/z* 418 $[M]^+$.

(12) (η-Ethylene)(hydrido)(η-mesitylene)(triphenylphosphine)osmium(II), hexafluorophosphate, [OsH(η-C_2H_4)(η-$C_6H_3Me_3$)(PPh_3)]PF_6 (22). A solution of **20** (0.13 g, 0.02 mmol) in dichloromethane (10 ml) was cooled to −78 °C and treated dropwise with a solution of $[Ph_3C][PF_6]$ (0.08 g, 0.20 mmol) in dichloromethane (5 ml). The mixture was allowed to warm to room temperature and ether (2 ml) was added. The precipitated product was filtered and recrystallized from CH_2Cl_2/ether to give white crystals of **22** (0.10 g, 70%). IR (KBr): 2130 cm^{-1} (ν(OsH)).

(13) Chloro(η-mesitylene)(methyl)(triphenylphosphine)osmium(II), OsCl(CH_3)(η-$C_6H_3Me_3$)(PPh_3) (23). A solution of $OsCl_2$(η-$C_6H_3Me_3$)(NCMe) was prepared by stirring **1** (0.11 g, 0.14 mmol) with acetonitrile (20 ml) overnight. Tetramethyltin (0.4 ml, 2.8 mmol) was then added and the solution was stirred at room temperature for 4 d. Triphenylphosphine (0.25 g, 0.95 mmol) was added, the mixture was stirred for 1 h, most of the acetonitrile was removed under reduced pressure, and the residue was transferred to an alumina column. Elution with acetonitrile gave first a yellow band containing **23** and then an orange band containing **2**. Solvent was removed from the yellow fraction and the residue was recrystallized from ether to give **23** as yellow microcrystals (0.08 g, 45%). MS *m/z* 624 $[M]^+$, 608 $[M - CH_4]^+$.

The complex OsCl(CH_3)(η-$C_6H_3Me_3$)(PMe_3) (**24**) was obtained similarly as yellow microcrystals in 30% yield by use of PMe_3 in place of PPh_3. MS *m/z* 438 $[M]^+$, 423 $[M - CH_3]^+$.

(14) Chloro(η-mesitylene)(triphenylphosphine)(phenyl)osmium(II), OsCl(C_6H_5) (η-$C_6H_3Me_3$)(PPh_3) (25). A mixture of **1** (0.10 g, 0.13 mmol) and tetraphenyltin (0.5 g, 1.2 mmol) in acetonitrile (20 ml) was heated under reflux for 7 d. Triphenylphosphine (0.075 g, 0.28 mmol) was added, the mixture was stirred at room temperature for 4 h, and the solvent was stripped. The residue was extracted with toluene and chromatographed on alumina. The yellow band eluted with toluene was collected, the solvent was evaporated, and the residue was recrystallized from ether to give yellow crystals of **23** (0.07 g, 40%). MS *m/z* 686 $[M]^+$.

The complex OsCl(C_6H_5)(η-$C_6H_3Me_3$)(PMe_3) (**26**) was prepared similarly as yellow crystals in 30% yield by use of PMe_3 in place of PPh_3. MS *m/z* 500 $[M]^+$.

(15) (2,2-Dimethylpropane-1,3-diyl)(η-mesitylene)(triphenylphosphine)osmium(II), Os($CH_2CMe_2CH_2$)(η-$C_6H_3Me_3$)(PPh_3) (27). A suspension of **2** (0.13 g, 0.19 mmol) in ether (20 ml) was treated dropwise with neopentyllithium (5.0 ml of 0.7 *M* solution, 3.5 mmol) at −78 °C. The orange suspension dissolved on warming to give a yellow solution which was stirred at room temperature for 4 h. The solution was cooled to −78 °C, treated with methanol (0.5 ml), allowed to warm to room temperature, and evaporated to dryness under reduced pressure. The residue was extracted with ether (10 ml), and the filtered extract, on concentration and cooling, gave yellow crystals of **27** (0.03 g, 25%). MS *m/z* 645 $[M]^+$, 574 $[M - CMe_4]^+$.

(16) (2,2-Dimethylpropane-1,3-diyl)(η-mesitylene)(trimethylphosphine)osmium(II), Os($CH_2CMe_2CH_2$)(η-$C_6H_3Me_3$)(PMe_3) (28). Complex **3** (0.135 g, 0.29 mmol) was treated with neopentyllithium (7.0 ml of 0.7 *M* solution, 5.0 mmol) as described above. After methanolysis and evaporation to dryness the residual oil was sublimed at 40 °C/10^{-4} mmHg on to a −20 °C probe to give **28** (0.055 g, 40%) as a crystalline solid that melted below room temperature. MS *m/z* 458 $[M]^+$, 388

$[M - CMe_4]^+$. The oil contained ca. 10% of $Os(CH_2CMe_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**29**), tentatively identified from its NMR spectra (Table 2) and mass spectrum (m/z 528 $[M]^+$).

(17) Chloro(η-mesitylene)(neopentyl)(trimethylphosphine)osmium(II), $OsCl(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (30). A solution of DMA · HCl (0.012 g, 0.10 mmol) in dichloromethane (2 ml) was added dropwise to a solution of **28** (0.05 g, 0.10 mmol) in dichloromethane (15 ml) over a period of 5 min and the mixture was stirred for 1 h. The solvent was removed and the residue was chromatographed on alumina. A dark yellow fraction that eluted with THF/toluene (1/99) gave a yellow oil after removal of solvent. Recrystallization from ether gave yellow crystals of **30** (0.035 g, 60%). MS m/z 494 $[M]^+$, 423 $[M - CMe_4]^+$.

(18) Hydrido(η-mesitylene)(methyl)(triphenylphosphine)osmium(II), $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (31). A mixture of **23** (0.115 g, 0.18 mmol) and $NaBH_4$ (0.07 g, 1.8 mmol) in propan-2-ol (20 ml) was heated under reflux for 2 h. The resulting pale yellow suspension was allowed to cool and the solvent was removed under reduced pressure. The residue was extracted with ether (10 ml), and the filtered extract, after refrigeration overnight, deposited pale yellow crystals of **31** (0.085 g, 80%). IR (KBr): 2040 cm^{-1} (ν(OsH)). MS m/z 574 $[M - CH_4]^+$.

The following $OsH(R)(\eta\text{-}C_6H_3Me_3)(L)$ complexes were prepared similarly: R = CH_3, L = PMe_3 (**32**), yellow oil (60%), IR (KBr): 2010 cm^{-1} (ν(OsH)): MS m/z 388 $[M - CH_4]^+$. R = C_6H_5, L = PPh_3 (**33**), pale yellow crystals (80%). IR (KBr): 2060 cm^{-1} (ν(OsH)). MS m/z 572 $[M - C_6H_5]^+$. R = C_6H_5, L = PMe_3 (**34**), yellow oil (65%). IR (KBr): 2010 cm^{-1} (ν(OsH)). MS m/z 466 $[M]^+$, 388 $[M - C_6H_6]^+$

(19) Hydrido(η-mesitylene)(neopentyl)(trimethylphosphine)osmium(II), $OsH(CH_2CMe_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (35). To a suspension of **30** (0.025 g, 0.05 mmol) in THF (15 ml) was added $LiAlH_4$ (0.010 g, 0.26 mmol). The mixture was stirred for 3 h at room temperature and the excess of $LiAlH_4$ was then decomposed by addition of methanol (0.2 ml). The solvent was stripped and the residue was extracted with ether (10 ml). Evaporation of the filtered extract in a vacuum gave pure **35** as a sticky white solid (0.018 g, 75%), which was identified by its spectroscopic properties. IR (KBr): 2040 cm^{-1} (ν(OsH)). MS m/z 460 $[M]^+$, 388 $[M - CMe_4]^+$.

(20) Exchange reactions catalysed by alumina or silica. Two typical procedures are given in detail; the results of these experiments are summarized in Table 1.

(i) A solution of **31** (5 mg, 8 mmol) in benzene (5 ml) was treated with alumina (1 mg) and the mixture was stirred at room temperature for 1 h. The solution was filtered, evaporated to dryness, and dried in a vacuum to give a pale yellow solid, which was redissolved in benzene-d_6. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed that **31** had disappeared and that **12** and **33** were present in a ratio of about 4/1.

(ii) A solution of **32** (0.055 g, 0.14 mmol) in toluene (20 ml) was treated with alumina (5 mg) and the mixture was stirred at room temperature for 2 h. The solution was filtered and the filtrate was evaporated to dryness in a vacuum to give $OsH(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**38**) as a white semi-solid (0.045 g, 70%). IR (KBr): 2010 cm^{-1}. MS m/z 480 $[M]^+$.

Complex **38** was further characterized as follows. A solution of **38** (0.03 g, 0.06 mmol) in chloroform was heated under reflux for 1 h. Evaporation of solvent and recrystallization of the residue from ether gave $OsCl(C_6H_4Me)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**39**) as yellow crystals (0.025 g, 75%). MS m/z 514 $[M]^+$.

(21) Photochemical exchange reactions. Complexes **31**, **32**, **33** or **35** (ca. 5 mg)

were dissolved in benzene-d_6 or cyclohexane (2 ml) and the solutions were transferred under an inert atmosphere to NMR tubes. These were capped, sealed with Parafilm, and irradiated over a 5 h period. The ^1H, ^2H and $^{31}P\{^1H\}$ NMR spectra of the C_6D_6 solutions were recorded directly. The cyclohexane solutions were evaporated to dryness, and the residues were extracted with THF-d_8, and the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solutions were measured. The products were the same as those obtained by alumina or silica catalysis, but there was much accompanying decomposition.

(22) Reactions of chloro(hydrido) complexes with organolithium reagents. (i) A suspension of **7** (0.23 g, 0.37 mmol) in ether (20 ml) was cooled to −78°C and treated dropwise with methyllithium in ether (25 ml of 1.4 *M* solution, 3.7 mmol). The mixture was stirred and allowed to warm to room temperature. After 4 h the orange solution was again cooled to −78°C and methanol (0.5 ml) was added dropwise. The pale yellow solution was evaporated to dryness to give a yellow-brown solid, which was shown to contain an inseparable mixture of $\overline{OsH(o\text{-}C_6H_4PPh_2)}(\eta\text{-}C_6H_3Me_3)$ (**12**), $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**31**) and $OsH_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**15**) by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The solid (ca. 0.1 g) was treated with chloroform (10 ml) and the solution was heated under reflux for 1 h. Solvent was removed, the residue was dissolved in toluene, and the solution was chromatographed on alumina. The yellow band eluted with toluene was evaporated to dryness. The residue was recrystallized from ether to give $\overline{OsCl(o\text{-}C_6H_4PPh_2)}(\eta\text{-}C_6H_3Me_3)$ (**36**) (0.07 g, 30%). IR (KBr): 1560, 1420, 730 cm^{-1} (*ortho*-metallated ring). MS *m/z* 608 $[M]^+$.

(ii) A suspension of **8** (0.18 g, 0.42 mmol) in ether (20 ml) treated with 1.4 *M* methyllithium (1.8 ml, 2.5 mmol) as described above gave a yellow-brown mixture containing $OsH(CH_3)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**32**), $Os(CH_3)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**21**) and $OsH_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**13**), identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

(iii) A solution of **7** (0.32 g, 0.57 mmol) in benzene (20 ml) was treated with 0.73 *M* phenyllithium in ether (2.7 ml, 2.0 mmol) at −78°C. Work-up as described above gave a dark brown residue containing **12** and $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**33**). Treatment of this residue (ca. 0.1 g) with chloroform (10 ml) gave **36** in 45% yield.

(iv) A solution of **8** (0.18 g, 0.41 mmol) in benzene was treated with 0.73 *M* phenyllithium in ether (2.2 ml, 1.6 mmol) as described above. The brown residue obtained after the usual work-up contained $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**34**) and a species tentatively identified as $Os(C_6H_5)_2(\eta\text{-}C_6H_3Me_3)(PMe_3)$. ^1H NMR (δ, C_6D_6): 8.00–6.70(Ph), 4.31(s, C_6H_3), 1.60(s, $C_6H_3\mathit{Me}_3$), 1.05(d, *J*(PH) 9.2 Hz, PMe) ppm. Treatment of the mixture with chloroform gave yellow crystals of $OsCl(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**26**) (0.10 g, 50%).

(23) Reduction of dichloro(η-mesitylene)osmium(II) complexes with sodium naphthalene. (i) Preparation of $OsX(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (X = H (34), Cl (26)). A solution of **3** (0.12 g, 0.26 mmol) in benzene (20 ml) was cooled to −78°C and the frozen mixture was treated carefully with a dark green solution of $NaC_{10}H_8$ that had been prepared by reaction of naphthalene (0.08 g, 0.65 mmol) with an excess of sodium (0.05 g, 2.0 mmol) in THF (2 ml) at room temperature for 1 h. The mixture was allowed to warm slowly to room temperature with occasional shaking. After being stirred for a further 2 h, the dark brown mixture was again cooled to −78°C

and treated dropwise with methanol (0.5 ml). Solvents were removed under reduced pressure at room temperature and the excess of naphthalene was removed by sublimation (25 °C, 10^{-5} mmHg). The remaining dark brown solid was chromatographed on alumina. The yellow band that eluted with benzene was collected, the solvent was removed, and the residue was vacuum-dried to give **34** as a yellow oil (0.025 g, 20%). The spectroscopic properties were identical with those of a sample prepared independently (see (18)).

A solution of **34**, prepared as described above, in chloroform (10 ml) was heated under reflux for 1 h. Solvent was stripped and the residue was recrystallized from ether to give **26** as yellow crystals (0.018 g, 80%). The spectroscopic data and elemental analysis of this sample agreed with those of an independently prepared sample (see (14)).

(ii) Preparation of $OsD(C_6D_5)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (**34**-d_6). A solution of **3** (0.02 g, 0.04 mmol) in benzene-d_6 (10 ml) was treated with $NaC_{10}H_8$ (2.5 equiv.) as described above. The residue obtained after removal of the excess of naphthalene was extracted with benzene (10 ml). Evaporation of the extract to dryness gave **34**-d_6 as a yellow oil (ca. 5 mg, 20%) that was characterized by NMR spectroscopy. ^{2}H NMR (δ, C_6H_6): 7.90–6.60 (m, C_6D_5), −10.30(d, J(PD) 4.8 Hz, OsD) ppm. ^{1}H NMR (C_6D_6): δ 4.47(s, $C_6H_3Me_3$), 1.98(s, $C_6H_3Me_3$), 1.16 (d, J(PH)9.8 Hz, PMe) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −43.0 ppm.

(iii) Preparation of $OsX(C_{10}H_7)(\eta\text{-}C_6H_3Me_3)(PMe_3)$ (X = H (**40**), Cl (**41**)). A solution containing **3** (0.12 g, 0.26 mmol) and naphthalene (0.10 g, 0.78 mmol) in THF (20 ml) was treated with $NaC_{10}H_8$ (2.5 equiv.) at −78 °C and the mixture was worked up as described above. The residue obtained after removal of the excess of naphthalene was chromatographed on alumina. The pale yellow band that eluted with THF/cyclohexane (1/99) was collected, the solvents were stripped, and the residue was dried in a vacuum to give **40** as a yellow oil (0.027 g, 20%). Heating of **40** with chloroform gave yellow crystals of **41** in 80% yield.

(iv) Reaction of $OsCl_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**2**) with $NaC_{10}H_8$. Complex **2** (0.15 g, 0.23 mmol) was reduced with $NaC_{10}H_8$ (2.5 equiv.) as described above. The components of the crude mixture obtained after the usual work-up were $OsH(o\text{-}C_6H_4PPh_2)(\eta\text{-}C_6H_3Me_3)$ (**12**), $OsH(C_6H_5)(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**33**) and $OsH_2(\eta\text{-}C_6H_3Me_3)(PPh_3)$ (**15**).

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