The protonation of arene-bis(ethylene) complexes of ruthenium and osmium *

M.A. Bennett *, I.J. McMahon and S. Pelling

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, ACT 2601 (Australia)

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Abstract

Treatment of the bis(ethylene) complexes $M(\eta^6\text{-arene})(\eta^2\text{-}C_2H_4)_2$ (M = Ru, arene = C_6Me_6 (1); M = Os, arene = $1,3,5\text{-}C_6H_3Me_3$ (2)) with HPF_6 gives isolable monoprotonated salts 3 and 4. Variable temperature ^1H and ^{13}C NMR spectra show that the ruthenium compound 3 contains a β-agostic ethyl(ethylene) cation $[\overline{Ru(CH_2CH_2\text{-}\mu\text{-}H)}(C_2H_4)(\eta\text{-}C_6Me_6)]^+$ in which the bridging hydrogen atom migrates rapidly between the ethyl group and coordinated ethylene, even at $-100°C$. This process, combined with rotation of the ethylene ligand, causes all nine hydrogen atoms to become equivalent at high temperature. The osmium salt 4 contains a hydridobis(ethylene) cation $[OsH(C_2H_4)_2(\eta\text{-}C_6H_3Me_3)]^+$ in which the ethylene ligands rotate rapidly about the metal–olefin axis even at $-100°C$. Migration of the hydride ligand between the metal atom and the ethylene ligands in 4 is slow on the NMR time scale at room temperature; the presumed intermediate ethyl derivative can be trapped by addition of ligands (L) to give stable salts $[Os(C_2H_5)(C_2H_4)(L)(\eta\text{-}C_6H_3Me_3)]PF_6$ (L = Bu^tNC, $P(OMe)_3$).

Introduction

The discovery of β-agostic alkylmetal complexes, i.e. complexes in which one of the β-CH bonds of an alkyl group binds to an electronically unsaturated metal centre [1,2] has led to the recognition that some of the complexes formed by protonation of coordinated ethylene may also belong to this class. The factors that determine whether a particular compound adopts the β-agostic structure or the alternative hydrido(ethylene) structure are, however, not entirely clear, and the two forms probably do not differ much in energy. Thus, although the cation formed by

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* Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

protonation of $Co(\eta\text{-}C_5Me_4Et)(C_2H_4)_2$ was initially formulated as a hydrido(ethylene) complex $[CoH(\eta\text{-}C_5Me_4Et)(C_2H_4)_2]^+$ on the basis of its ^1H NMR spectrum [3], a recent re-examination of the NMR spectra of this species and of its $\eta\text{-}C_5Me_5$ analogue has shown that they should be considered as β-agostic ethyl complexes, $[\overline{Co(CH_2CH_2\text{-}\mu\text{-}H)}(\eta\text{-}C_5Me_4R)(C_2H_4)]^+$ (R = Me, Et) [4]. Low temperature NMR spectra of the cations formed by protonation of the tertiary phosphine derivatives $Co(\eta\text{-}C_5Me_5)(C_2H_4)(PR_3)$ suggest that they too have agostic structures [5–7], and this has been confirmed by an X-ray study of $[\overline{Co(CH_2CH_2\text{-}\mu\text{-}H)}(\eta\text{-}C_5Me_5)\{P(p\text{-}tolyl)_3\}]^+$ [5]. In contrast, treatment of the rhodium(I) complexes $Rh(\eta\text{-}C_5H_5)(C_2H_4)(L)$ (L = PMe_3, $P(OMe)_3$) with HBF_4 gives hydrido(ethylene) cations $[RhH(\eta\text{-}C_5H_5)(C_2H_4)(L)]^+$, as shown by IR and NMR spectra; the hydride ligand does, however, migrate reversibly on the NMR time scale between the metal atom and coordinated ethylene, possibly via a sixteen electron or agostic ethylrhodium intermediate [8,9]. An X-ray study of the hexamethylbenzeneruthenium(II) cation $[RuH(\eta\text{-}C_6Me_6)(C_2H_4)(PPh_3)]^+$ shows this to have a terminal hydrido(ethylene) structure, and hydride migration is slow on the NMR time scale between -80 and $+35\,^\circ C$ [10].

We report here on the protonation of the zerovalent metal arene bis(ethylene) complexes $Ru(\eta\text{-}C_6Me_6)(C_2H_4)_2$ (**1**) and $Os(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(C_2H_4)_2$ (**2**).

Results

The η^6-mesityleneosmium(0) complex $Os(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(C_2H_4)_2$ (**2**) is prepared similarly to $Ru(\eta\text{-}C_6Me_6)(C_2H_4)_2$ (**1**) by reaction of ethylene with $[OsCl_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$, anhydrous Na_2CO_3 and 2-propanol at $80\,^\circ C$. It is an almost colourless, moderately air-sensitive solid. The ^1H NMR spectrum of **2** at $30\,^\circ C$, like that of **1**, shows a mirror-image pair of four-proton multiplets at δ 2.07 and 0.93 ppm due to coordinated ethylene, and there is just one resonance at δ 21.8 ppm due to equivalent ethylenic carbon atoms. This evidence suggests that **2** is structurally similar to the rhodium(I) complexes $Rh(\eta\text{-}C_5H_5)(C_2H_4)(C_2F_4)$ [11] and $Rh(\eta\text{-}C_5Ph_4Cl)(C_2H_4)_2$ [12], in which the C=C bonds are parallel to each other and to the cyclopentadienyl or arene ring. In this structure the ethylene protons are inequivalent in pairs (inner and outer, H^a and H^b, respectively). On warming a chlorobenzene solution of **2** to $110\,^\circ C$, the ethylene proton resonances broaden reversibly but do not coalesce; considerable decomposition is evident at this temperature. Thus the barrier to rotation of coordinated ethylene in **2** is greater than those in $Rh(\eta\text{-}C_5R_5)(C_2H_4)_2$ (R = H, Me) [13,14], and is probably of the same order as those in **1** and in $Ir(\eta\text{-}C_5Me_5)(C_2H_4)_2$ [15].

2   **4**
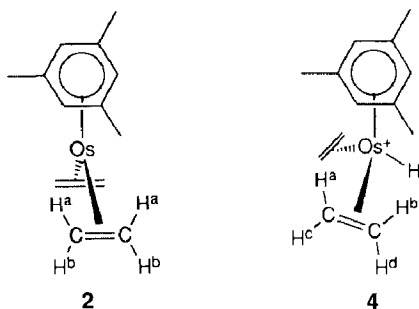
Addition of 60% aqueous HPF_6 to solutions of **1** and **2** in ether causes immediate precipitation of the monoprotonated salts, orange $[RuH(\eta-C_6Me_6)(C_2H_4)_2]PF_6$ (**3**) and white $[OsH(\eta-C_6H_3Me_3)(C_2H_4)_2]PF_6$ (**4**). These compounds revert to their precursors on treatment with aqueous Na_2CO_3. Although the solids are only slightly air-sensitive, the solutions are much more so, and the osmium compound decomposes at room temperature even in degassed dichloromethane. The IR spectrum of **4** shows a sharp band at 2140 cm^{-1} assignable to $\nu(Os-H)$, but no band assignable to $\nu(Ru-H)$ could be found in the spectrum of **3**. The ^1H NMR spectrum of **3** in CD_2Cl_2 at $-90°C$ (Fig. 1) shows four two-proton multiplets due to the ethylene protons, consisting of two approximate quartets at δ 0.59 and 1.25 ppm with spacings of 9.7 Hz and a triplet at δ 1.53 ppm with a spacing of 9.9 Hz; the fourth resonance is partly obscured by the C_6Me_6 singlet at δ 2.07 ppm. The hydride resonance at $-90°C$ appears as a multiplet, with just discernible quintet structure, at δ -11.25 ppm. On warming, the ethylene and hydride resonances initially broaden and then collapse into the baseline at room temperature. At 80°C a new resonance corresponding to nine protons appears at δ 0.08 ppm.

In addition to the resonances arising from C_6Me_6, the ^{13}C NMR spectrum of **3** at $-100°C$ in CD_2Cl_2 (Fig. 2) shows a triplet at δ 41.1 ppm ($J(CH)$ 158 Hz) and a doublet of triplets at δ 23.0 ppm ($J(CH)$ 155, 28.4 Hz) due to inequivalent carbon atoms of coordinated ethylene (Fig. 2). These resonances coalesce into one signal at δ 34.3 ppm at room temperature.

These observations are very similar to those reported for the species formed by protonation of the bis(ethylene)cobalt(I) complexes $Co(\eta-C_5Me_4R)(C_2H_4)_2$ (R = Me, Et) [4]. In particular, the doublet of triplets pattern can be assigned to a methyl carbon atom that is strongly coupled to two protons and weakly coupled to an agostic hydrogen atom. The spectra indicate that at low temperature complex **3** exists as a pair of β-agostic ethyl isomers **3a** and **3b** that are in rapid equilibrium on the NMR time scale, possibly via the terminal hydridobis(ethylene) species **3c**. The ^{13}C resonance at δ 41.1 ppm is assigned to the time average of C^2 and $C^{2'}$, and the resonance at δ 23.0 ppm is due to the time average of C^1 and $C^{1'}$. The smaller coupling (28.4 Hz) represents an average of 56.8 and 0 Hz, these being the values of $J(C^{1'}-H^c)$ in **3a** and **3b**, or of $J(C^1-H^c)$ in **3b** and **3a**; the value of 56.8 Hz is in the

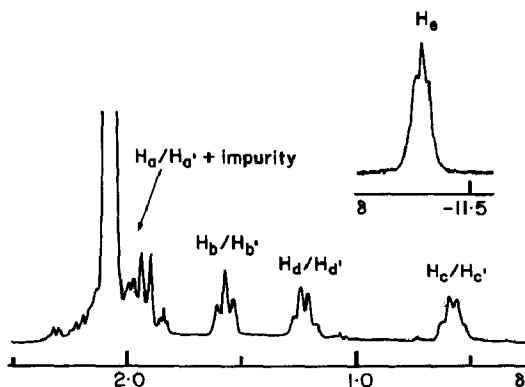Fig. 1. ^1H NMR spectrum at 270 MHz of $[\overline{Ru(CH_2CH_2\text{-}\mu\text{-}H)}(C_2H_4)(\eta-C_6Me_6)]PF_6$ (**3**) in CD_2Cl_2 at $-90°C$.

178
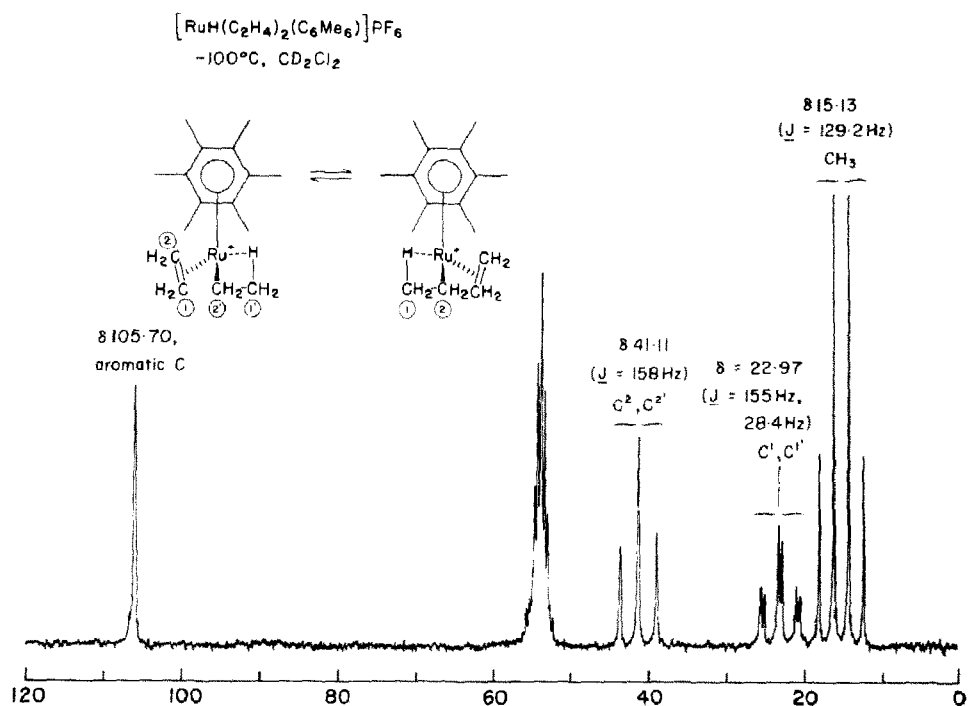
Fig. 2. ^{13}C NMR spectrum at 67.89 MHz of $[\overline{Ru(CH_2CH_2\text{-}\mu\text{-}H)}(C_2H_4)(\eta\text{-}C_6Me_6)]PF_6$ (3) in CD_2Cl_2 at $-100\,^{\circ}C$.
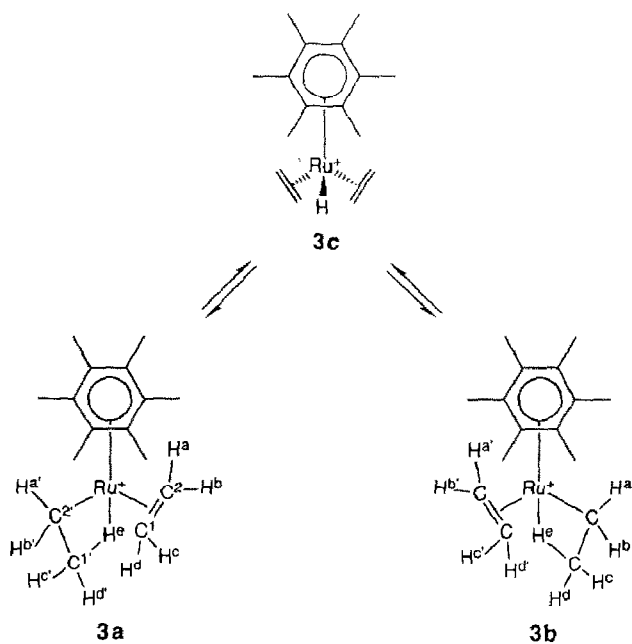
range of 50–80 Hz characteristic of C–H (agostic) coupling constants [1,2]. Similarly, the larger coupling (155 Hz) represents the average of the coupling of $C^{1'}$ to the two equivalent protons, $H^{c'}$ and $H^{d'}$ in 3a and 3b (or of C^1 to H^c and H^d in 3b and 3a); both values probably lie in the range 150–170 Hz.

The ^1H NMR spectrum of 3 at $-90\,^\circ C$ can also be interpreted in terms of the equilibrium between 3a and 3b. The multiplet at δ 2.0 ppm and the triplet at δ 1.53 ppm are assigned to $H^a/H^{a'}$ (averaged) and $H^b/H^{b'}$ (averaged), respectively; the quartets at δ 0.59 and 1.25 ppm are assigned to $H^c/H^{c'}$ (averaged) and $H^d/H^{d'}$ (averaged), respectively. The spacings observed represent average interproton couplings, e.g. for $H^b/H^{b'}$ (averaged) the spacing of 9.9 Hz corresponds to $\frac{1}{2}(J_{bc} + J_{b'c'})$ and $\frac{1}{2}(J_{bd} + J_{b'd'})$. The resonance at δ -11.25 ppm is due to the bridging hydride H^e, which is coupled approximately equally (J ca. 9 Hz) to $H^c/H^{c'}$ and $H^d/H^{d'}$, but not to $H^a/H^{a'}$ and $H^b/H^{b'}$.

The behaviour of the ^1H and ^{13}C NMR spectra at higher temperatures arises from averaging of all nine protons. This is conventionally interpreted as arising from cleavage of the Ru–H^e bond and formation of a sixteen-electron ethyl(ethylene) complex $[Ru(\eta-C_6Me_6)(C_2H_5)(C_2H_4)]^+$ accompanied by rotation of the ethylene ligand about the metal–olefin axis. Alternatively, the methyl protons of the agostic ethyl groups of 3a and 3b could undergo an 'in-place' rotation, averaging H^c, H^d, H^e, $H^{c'}$ and $H^{d'}$, as suggested recently for the complex $[MoH(C_2H_4)_2$-$(cis\text{-}Ph_2PCH=CHPPh_2)_2]CF_3CO_2$ [16]. This process, combined with ethylene rotation, would also lead to the observed averaging. Attempts to trap an unsaturated ethyl intermediate by addition of ligands such as $P(OMe)_3$ and Bu^tNC were unsuccessful.

The ^1H NMR spectrum of $[OsH(\eta-C_6H_3Me_3)(C_2H_4)_2]PF_6$ (4) at $-20\,^\circ C$ contains two mirror-image multiplets at δ 2.12 and 1.80 ppm, each containing four protons, due to coordinated ethylene and a singlet at δ -10.46 ppm due to Os–H; there are also singlets at δ 2.42 (9H) and 5.99 (3H) ppm due to the arene protons. This spectrum is consistent with a terminal hydride structure if it is assumed that the ethylene ligands are rotating rapidly on the NMR time scale about the metal–olefin axis at $-20\,^\circ C$. Such a rotation would separately average H^a and H^d, and H^b and H^c, giving two four-proton resonances, as observed, whereas a static structure would be expected to give four two-proton multiplets. On cooling below $-20\,^\circ C$, the multiplets due to the ethylene protons broaden and at $-100\,^\circ C$ collapse into the baseline, while the arene and hydride resonances remain sharp. The barrier to rotation of the ethylene ligands in the cationic osmium(II) complex 4 is clearly much lower than in its neutral osmium(0) precursor 2 or in the ruthenium(0) complex 1.

The ^{13}C NMR spectrum of 4 at $-20\,^\circ C$ shows, in addition to the usual arene resonances, a simple triplet at δ 35.3 ppm ($J(CH)$ 162 Hz) due to the ethylene carbon atoms (Fig. 3). The absence of a doublet of triplets pattern indicates that 4 does not have an agostic structure. The ethylene carbon atoms must be equivalent on the NMR time scale at $-20\,^\circ C$ owing to the rapid rotation of the ethylene ligands. At $-100\,^\circ C$ the signal at δ 35.3 ppm collapses into the baseline, but the rotation cannot be slowed sufficiently to observe the expected two resonances. Thus both the IR and NMR spectra suggest that 4, unlike 3, should be formulated as a terminal hydridobis(ethylene) complex.

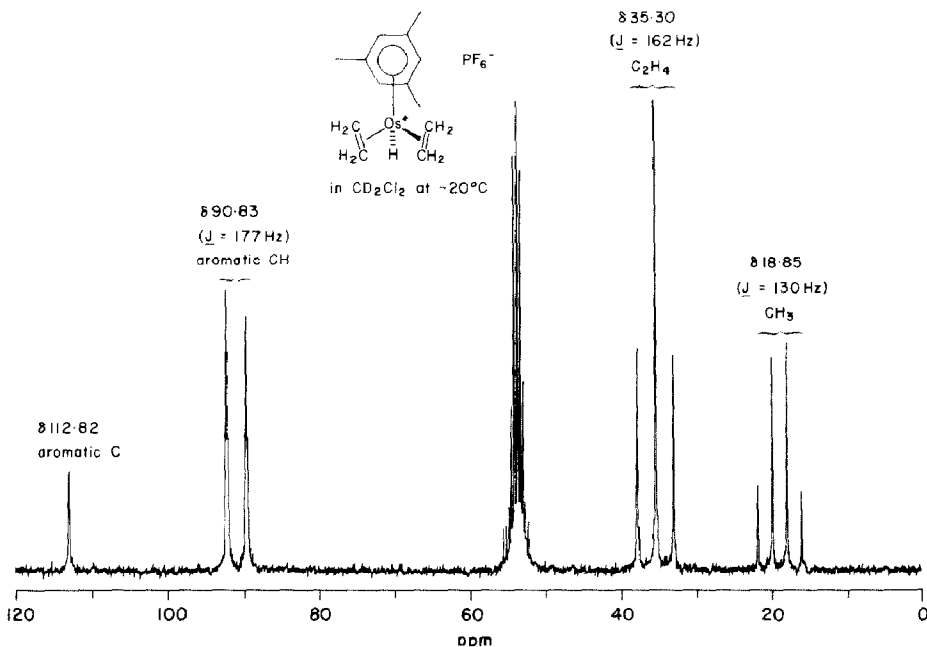When solutions of 4 are brought to room temperature, the arene proton reso-

Fig. 3. ^{13}C NMR spectrum at 67.89 MHz of $[OsH(C_2H_4)_2(\eta\text{-}C_6H_3Me_3)]PF_6$ (4) in CD_2Cl_2 at $-20\,^\circ C$.

nances remain sharp but the hydride and ethylene resonances broaden, probably owing to reversible hydride migration between the metal atom and ethylene. This process could occur via the sixteen electron ethyl(ethylene) intermediate $[Os(\eta\text{-}C_6H_3Me_3)(C_2H_5)(C_2H_4)]^+$ (5) and would finally cause all nine protons to become equivalent, as occurs in the ruthenium complex 3. Unfortunately, the thermal instability of 4 in solution prevented studies at temperatures above $20\,^\circ C$. Intermediate 5 can, however, be intercepted by reaction of 4 with two-electron donor ligands. Thus, treatment of 4 with an excess of trimethylphosphite or t-butyl isocyanide in dichloromethane gives thermally stable yellow solids $[Os(C_2H_5)(C_2\text{-}H_4)(L)(\eta\text{-}C_6H_3Me_3)]PF_6$ (L = $P(OMe)_3$ (6a), Bu^tNC (6b)). The ^1H NMR spectrum of 6a shows a four-proton multiplet due to ethylene at δ 2.41 ppm in addition to resonances characteristic of $P(OMe)_3$ and η^6-mesitylene. Because the osmium atom in 6a is a chiral centre, the methylene protons of the ethyl group are diastereotopic and appear as a pair of one proton multiplets at δ 1.54 and 1.77 ppm, and the methyl protons appear as a distorted triplet at δ 1.42 ppm. The NMR spectrum of 6b is similar to that of 6a except that the t-butyl singlet obscures one of the methylene proton resonances.

Discussion

The monoprotonated salt formed from $Ru(\eta\text{-}C_6Me_6)(C_2H_4)_2$ and HPF_6 is an agostic β-ethyl(ethylene) complex $[Ru(CH_2CH_2\text{-}\mu\text{-}H)(C_2H_4)(\eta\text{-}C_6Me_6)]PF_6$ (3), whereas the monoprotonated salt formed similarly from $Os(\eta\text{-}C_6H_3Me_3)(C_2H_4)_2$ is a terminal hydridobis(ethylene) complex $[OsH(C_2H_4)_2(\eta\text{-}C_6H_3Me_3)]PF_6$ (4). X-ray and NMR studies of the protonation of complexes of the type $M(\eta\text{-}arene)(1,3\text{-}diene)$ (M = Ru, Os) suggest similarly that the monoprotonated ruthenium complexes

have β-agostic η^3-enyl structures whereas the corresponding osmium compounds have terminal hydrido(1,3-diene) structures [17]. In the case of the ethylene complexes, the difference is unlikely to be due to the minor change in ancillary ligand from hexamethylbenzene to mesitylene, but probably reflects increasing M–H bond strengths in the order $5d > 4d > 3d$ [1,2]. Although there are few cases where exact comparisons can be made, i.e. where the auxiliary ligands are kept the same and only the metal atom is varied, there is a general tendency for $5d$-elements to form terminal hydrido(alkene) or hydrido(diene) complexes and for $3d$- and $4d$-elements to prefer agostic β-alkyl or β-enyl structures. For example, the cyclohexenyl manganese complex $Mn(C_6H_9)(CO)_3$ has an agostic structure $\overline{Mn(CH\dot{-}CH\dot{-}CH\dot{-}}$ $\overline{CH_2CH_2CH-\mu-H)(CO)_3}$, although its fluxional behaviour suggests that it is in equilibrium with the hydrido(1,3-cyclohexadiene) complex $MnH(CO)_3(1,3-C_6H_8)$ [18]. In contrast, the analogous compound (η^6-benzene)(cyclohexenyl)rhenium, $Re(\eta-C_6H_6)(C_6H_9)$, adopts a terminal hydrido(diene) structure, $ReH(\eta-C_6H_6)(\eta-1,3-C_6H_8)$ [19]. X-ray studies of the $5d$-element complexes $IrH(\eta^4-C_4H_6)(PPr^i_3)_2$ [20] and $ReH_3(\eta^4-1,3-C_6H_8)(PPh_3)_2$ [21] have shown them to be hydrido(diene) complexes, although 1,3-diene complexes of the latter type undergo reversible hydride transfer between the metal and the diene [22]. The monoprotonated complexes formed from $M(\eta-arene)(dicyclopentadiene)$ ($M = Ru$, arene = C_6Me_6; $M = Os$, arene = $C_6H_3Me_3$) and $M(\eta-C_5R_5)(dicyclopentadiene)$ ($M = Rh$, $R = H$, Me; $M = Ir$, $R = Me$) all have agostic structures, but the $J(CH)$ values suggest that the agostic interaction is weakest for the $5d$ elements iridium and osmium [23].

It is noteworthy that replacement of one ethylene ligand in **3** by the stronger σ-donor/weaker π-acceptor PPh_3 causes a change in structure from β-agostic to terminal hydrido(ethylene) [8,9]. This substitution presumably increases the electron density on the metal atom, thus reducing the interaction with the C–H bonding electrons. A similar trend is evident from the variation in the magnitude of $J(C-H-M)$ in the series of agostic complexes $Fe(\eta^3-enyl)(CO)_3$ (74 Hz) $< Fe(\eta^3-enyl)(CO)_2\{P(OMe)_3\}$ (84 Hz) $< Fe(\eta^3-enyl)\{P(OMe)_3\}_3$ (ca. 100 Hz): the smallest coupling constant, which implies the closest approach to a diene metal hydride, occurs with the strongest π acceptor [24].

Experimental

Nuclear magnetic resonance spectra (^1H, ^{13}C) were recorded on JEOL FX 200 (^{13}C at 50.10 MHz) and Bruker HFX270 (^{13}C at 67.89 MHz) instruments, with either Me_4Si or CD_2Cl_2 as the internal reference. Infrared spectra were measured on a Perkin–Elmer 683 spectrometer. Mass spectra were recorded on a VG Micromass 7070F instrument at 70 eV. Microanalyses were carried out in the Microanalytical Laboratory of this School. All reactions were carried out with use of standard Schlenk tube techniques or in a Vacuum Atmosphere Dri-Train HE-193-1 inert atmosphere box. Solvents were degassed before use by distillation under nitrogen or by several freeze-pump-thaw cycles.

The hexamethylbenzene ruthenium(II) complexes $[RuCl_2(\eta-C_6Me_6)]_2$ and $Ru(\eta-C_6Me_6)(C_2H_4)_2$ (**1**) were prepared as described in the literature [25]. The mesitylene osmium(II) complex $[OsCl_2(\eta-C_6H_3Me_3)]_2$ was made in ca. 30% yield by heating an ethanolic solution of Na_2OsCl_6 with 1,3,5-trimethyl-1,4-cyclohexadiene, the proce-

dure being essentially that described for the corresponding benzene and *p*-cymene complexes [26].

Preparations

Bis(η^2-ethylene)(η^6-mesitylene)osmium(0), Os(η-$C_6H_3Me_3$)(C_2H_4)$_2$ (2)

A steady stream of ethylene was bubbled through a stirred suspension of [OsCl$_2$(η-C$_6$H$_3$Me$_3$)]$_2$ (400 mg, 0.52 mmol) and anhydrous Na$_2$CO$_3$ (600 mg) in 2-propanol (20 ml) at 70°C for 3 h. The brown solution was evaporated to dryness under reduced pressure and the residue was extracted with hexane (3 × 20 ml). The orange extract was filtered, concentrated, and cooled in dry ice to precipitate **2** as a pale brown, microcrystalline solid. This was washed with cold hexane and dried in a vacuum to give 270 mg (70%) of **2**. A second recrystallization from hexane at −78°C gave analytically pure **2** as a cream-coloured, air-sensitive solid. MS (*m/e*) 368 (parent ion). ^{1}H NMR (C$_6$D$_6$): δ 4.60 (s, 3H, C$_6$H$_3$Me$_3$), 2.07 (m, 4H, C$_2$H$_4$), 1.74 (s, 9H, C$_6$H$_3$Me$_3$), 0.93 (m, 4H, C$_2$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 92.3 (CMe of C$_6$H$_3$Me$_3$), 83.4 (CH of C$_6$H$_3$Me$_3$), 21.8 (C$_2$H$_4$), 17.8 (Me). Anal. Found: C, 42.1; H, 5.4. C$_{13}$H$_{20}$Os calcd.: C, 42.6; H, 5.5%.

(η^2-Ethyl)(η^2-ethylene)(η^6-hexamethylbenzene)ruthenium(II), hexafluorophosphate, [Ru(CH$_2$CH$_2$-μ-H)(C$_2$H$_4$)(η-C$_6$Me$_6$)]PF$_6$ (3)

A solution of Ru(η-C$_6$Me$_6$)(C$_2$H$_4$)$_2$ (1) (100 mg, 0.31 mmol) in ether (ca. 10 ml) was treated dropwise with 60% aqueous HPF$_6$. The pale yellow precipitate of **3** that formed immediately was allowed to settle and the supernatant liquid was removed by syringe. The product was washed with ether and dried in a vacuum. The yield was ca. 100 mg (70%). Owing to its thermal instability, the complex could not be recrystallized, and elemental analyses were outside the normally accepted limits of error. ^{1}H NMR (CD$_2$Cl$_2$, −90°C): δ 2.07 (s, 18H, C$_6$Me$_6$), 1.53 (m, 2H), 1.25 (m, 2H), 0.59 (m, 2H) (CH$_2$CH$_2$; remaining CH$_2$ resonance at ca. 2.0 ppm, partly obscured by C$_6$Me$_6$ singlet); (CD$_2$Cl$_2$, 80°C): δ 1.90 (s, 18H, C$_6$Me$_6$), 0.08 (m, 9H, RuH, CH$_2$CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$, −100°C): δ 105.7 (C$_6$Me$_6$), 41.1 (t, *J* 158 Hz, CH$_2$), 23.0 (dt, *J* 155, 28.4 Hz, CH$_2$-μ-H), 15.1 (q, *J* 129 Hz, C$_6$Me$_6$); (CD$_2$Cl$_2$, 25°C): δ 34.3 (CH$_2$CH$_2$). Anal. Found: C, 39.6; H, 5.7; P, 7.1; Ru, 21.8. C$_{16}$H$_{27}$F$_6$PRu calcd.: C, 41.3; H, 5.85; P, 6.7; Ru, 21.7%.

Reaction of [Ru(CH$_2$CH$_2$-μ-H)(C$_2$H$_4$)(η-C$_6$Me$_6$)]PF$_6$ (3) with base. A sample of **3** (ca. 100 mg) was stirred with a solution of Na$_2$CO$_3$ (0.5 g) in water (5 ml) for 30 min and the mixture was then extracted with ether. The ether layer was separated, dried over Na$_2$SO$_4$, and evaporated to dryness in vacuum. The pale yellow solid residue was identified as **1** by its ^{1}H NMR spectrum. The yield was almost quantitative.

Hydridobis(η^2-ethylene)(η^6-mesitylene)osmium(II) hexafluorophosphate, [OsH(C$_2$-H$_4$)$_2$(η-C$_6$H$_3$Me$_3$)]PF$_6$ (4)

Dropwise addition of 60% aqueous HPF$_6$ to a solution of **2** (270 mg, 0.74 mmol) gave an immediate off-white precipitate of **4**, which was washed with ether and dried in a vacuum. The yield was 120 mg (30%). An analytically pure sample was obtained by rapid recrystallization from CH$_2$Cl$_2$/ether. IR (Nujol) 2140 cm^{-1} (ν(OsH)). ^{1}H NMR (CD$_2$Cl$_2$, −20°C): δ 5.99 (s, 3H, C$_6$H$_3$Me$_3$), 2.42 (s, 9H,

$C_6H_3Me_3$), 2.10 (m, 4H, C_2H_4), 1.80 (m, 4H, C_2H_4), -10.46 (s, 1H, OsH). ^{13}C NMR (CD_2Cl_2, $-20\,°C$): δ 112.8 (CMe), 90.8 (d, J 177 Hz, CH of $C_6H_3Me_3$), 35.3 (t, J 162 Hz, C_2H_4), 18.9 (q, J 130 Hz, $C_6H_3Me_3$). Anal. Found: C, 30.7; H, 4.2; P, 5.9. $C_{13}H_{21}F_6OsP$ calcd.: C, 30.5; H, 4.1; P, 6.0%.

Reaction of [OsH(C_2H_4)$_2$(η-$C_6H_3Me_3$)]PF$_6$ (4) with ligands L. (1) L = Bu^{t}NC. A solution of **4** (75 mg, 0.15 mmol) in dichloromethane (10 ml) was treated with a threefold excess of t-butyl isocyanide. The mixture was stirred for 1 h at room temperature, the colour changing from brown to straw. Evaporation to dryness under reduced pressure gave a yellow oil that crystallized on addition of hexane. The yield was 80 mg (quantitative). IR (Nujol) 2170 cm^{-1} (ν(CN)). ^{1}H NMR (CD_2Cl_2): δ 5.80 (s, 3H, $C_6H_3Me_3$), 2.65 (m, 2H, C_2H_4), 2.48 (m, 2H, C_2H_4), 2.22 (s, 9H, $C_6H_3Me_3$), 1.87 (m, 1H, CHH of C_2H_5), 1.47 (s, 9H, Bu^t), 1.40 (m, 4H, Me, CHH of C_2H_5). Anal. Found: C, 32.2; H, 5.0; N, 2.5. $C_{18}H_{30}F_6NOsP$ calcd.: C, 32.3; H, 5.1; N, 2.35%.

(2) L = P(OMe)$_3$. This was prepared similarly to the Bu^{t}NC derivative. ^{1}H NMR (CD_2Cl_2): δ 5.82 (s, 3H, $C_6H_3Me_3$), 3.68 (d, 9H, J(PH) 10.7 Hz, P(OMe)$_3$), 2.42–2.40 (m, 4H, C_2H_4), 1.77 (m, ^{1}H, CHH of C_2H_5), 1.54 (m, ^{1}H, CHH of C_2H_5), 1.42 (distorted t, 3H, J 7 Hz, CH$_3$ of C_2H_5).

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