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Dicationic Tetranuclear Tetrahydrides of Iridium, Ruthenium, and Osmium*

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In 1979 the Sheffield group reported the synthesis of the dicationic tetrarhodium tetrahydrido complex, $[(\eta^5\text{-}C_5Me_5Rh)_4(\mu_3\text{-}H)_4]^{2+}$ (**1**) by reaction of $[(\eta^5\text{-}C_5Me_5Rh)_2(\mu\text{-}OH)_3]^+$ (**2**) with hydrogen [1]. The X-ray structure determination of the tetrafluoroborate salt showed the dication to have a distorted (D_{2d}) tetrahedral arrangement of the rhodiums with two short and four long rhodium–rhodium bonds. A later low temperature neutron diffraction study established that the four hydrides bridged the four faces of the distorted tetrahedron (μ_3-H); a detailed analysis of the ^1H and ^{13}C NMR spectra showed that this geometry was also retained in solution [2].

We now report, (i) that **1** can be made more conveniently by prolonged (6 days/60 °C) reaction of **2** with propan-2-ol and (ii) the syntheses of the related tetrahydridotetra-iridium, -ruthenium, and -osmium dications, $[(\eta^5\text{-}C_5Me_5Ir)_4H_4](BF_4)_2$ (**3**), $[(\eta^6\text{-}p\text{-cymeneRu})_4H_4](PF_6)_2$ (**4**), and $[(\eta^6\text{-p-cymeneOs})_4H_4](BF_4)_2$ (**5**), (*p*-cymene = $4\text{-}Me_2CHC_6H_4Me$) by reaction of the appropriate dinuclear tri-μ-hydroxo salts with propan-2-ol, in the presence of KBF_4 or KPF_6. In each case, milder conditions resulted in the formation of hydrides of lower nuclearity, usually (for Ru, Ir, and Os) the tri-μ-hydrido dimetal monocationic complexes $[(LM)_2(\mu\text{-}H)_3]^+$. However, evidence for other hydride species was also obtained from reactions carried out under more severe conditions; some of these may be of higher nuclearity.

The iridium complex **3** (obtained in 20% yield as black crystals by reaction of $[(\eta^5\text{-}C_5Me_5Ir)_2(OH)_3]\cdot(OAc)\cdot 4H_2O$ [3] with propan-2-ol in the presence of KBF_4) was identified by microanalysis, ^1H NMR spectrum (δ2.03 and −12.84, 2 × s, ratio 15:1), and the FAB mass-spectrum which gave the correct isotope pattern (at *m/e* 1308, 1309, 1310, 1311, and 1312) for $[(C_5Me_5Ir)_4]^+$, *i.e.* by loss of $(4H)^+$ from the parent dication. (By contrast, the rhodium complex **1** showed a peak at *m/e* 956, corresponding to $[(C_5Me_5Rh)_4H_4]^+$.) The formulation of the iridium hydride as **3** is also confirmed by preliminary X-ray data [4] which show the molecule to be isostructural with the tetra-rhodium complex **1**.

Reaction of $[(\eta^6\text{-}p\text{-cymeneRu})_2(OH)_3](PF_6)$ [5] with propan-2-ol (4 days/80 °C) gave a black crystalline solid (43%) which dissolved to give a purple solution. This was formulated as 4 based on the microanalysis, the ^1H NMR spectrum [δ 6.59, 6.42 (2 × d, $J = 6$ Hz, aromatic 4H), 2.38, 1.37 (sp, 1H, and d, 6H, $J = 7$ Hz, isopropyl), 1.95 (s, 3H, methyl), and −18.53 (s, 1H)], and the FAB mass-spectrum which showed molecular ions between *m/e* 934 and 954 in excellent agreement with the isotope pattern expected for $[(p\text{-cymeneRu})_4H_4]^+$.

The tetra-osmium complex **5** was obtained similarly (38%) as very dark brown crystals from $[(\eta^6\text{-}p\text{-cymeneOs})_2(OH)_3]PF_6$ [6]. Again the microanalysis and the ^1H NMR spectrum [δ 6.92, 5.96 (2 × d, $J = 6.2$ Hz, aromatic 4H), 2.96, 1.54 (sp, 1H, d, 6H, $J = 7$ Hz, isopropyl), 2.35 (s, 3H, methyl), and −11.15 (1H)] were in agreement with the suggested structure. The high field hydride signal showed satellites indicating coupling to ^{187}Os (1.6% abundant, $J = 36$ Hz). The ^{187}Os NMR spectrum [7] was also measured by use of the ^1H–^{187}Os retro-INEPT two-dimensional sequence, which showed a five line spectrum with the central line missing (Fig. 1) at −2171 ppm relative to OsO_4. The pulse sequence used in the experiment is expected to modify the quintet intensities usually expected. However, the separation of the lines of 36 Hz agrees with the $J(^{187}Os\text{–}^1H)$ found from the satellites of the hydride signal. This result shows that the hydrides are equally (at ambient temperature) coupled to four osmium atoms. Since each osmium has one *p*-cymene per hydride this indicates that the nuclearity of the complex is again four, and we formulate it by analogy to the others. One surprising result is that, in order for all the four hydrides to be equivalently coupled to the four osmiums, the molecule must be fluxional. The rhodium complex **1** by contrast, appears essentially rigid at ambient temperatures. Curiously enough, while both $[H_4Ru_4(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$ are fluxional in solution, the solid state NMR indicates that the osmium hydride is static up to 300 K in the solid while the ruthenium one is fluxional [8].

These results show the existence of a new series of tetranuclear tetrahydrides of the half-sandwich platinum group metals; this extends the known series which includes such complexes as, $[C_5H_5)_4Co_4H_4]$ [9], $[H_4Os_4(CO)_{12}]$ [10], $[H_4Re_4(CO)_{13}]^-$ [11],

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*With warmest greetings to Professor Rafael Uson on his 60th birthday.

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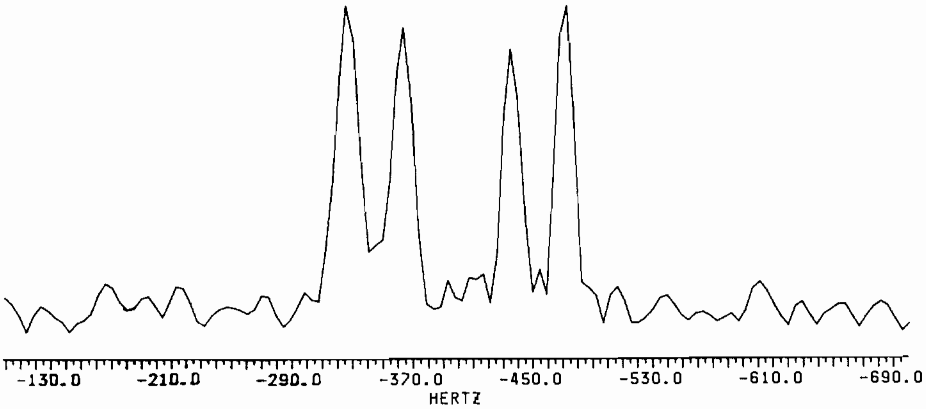

Fig. 1. ^{187}Os NMR spectrum obtained as an F_1 cross-section from a ^{1}H-{^{187}Os} delta–delta correlated 2D contour plot of [(*p*-cymeneOsH)$_4$](BF$_4$)$_2$ (5) (scale in Hz relative to arbitrary zero); the central line of the 'quintet' is missing and the intensities are modified by the pulse sequence used.

[H$_4$Re$_4$(CO)$_{15}$]$^-$ [12], [H$_4$Ru$_4$(CO)$_{12}$] [13], and [(C$_5$H$_5$)$_8$W$_4$Li$_4$H$_4$] [14].

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