Dinuclear *p*-Cymeneosmium Hydride Complexes; the Measurement of ^{187}Os Chemical Shifts using ^{1}H-{^{187}Os} Two-dimensional N.M.R. Spectroscopy

Javier A. Cabeza,[a] Brian E. Mann,[a] Christian Brevard,*[b] and Peter M. Maitlis*[a]

[a] *Department of Chemistry, The University, Sheffield S3 7HF, U.K.*
[b] *Bruker Spectrospin, 34 Rue de l'Industrie, 67160 Wissembourg, France*

The reaction of [(pc)$_2$Os$_2$Cl$_4$] (pc = η^6-*p*-cymene, 4-isopropyltoluene) with propan-2-ol gives [(pc)OsCl(μ-H)-(μ-Cl)ClOs(pc)], but only in the presence of a salt (KPF$_6$); *J*(^{187}Os–H) between 60.8 and 83.3 Hz have been measured for this complex and for [(pc)Os(μ-H)(μ-X)(μ-Y)Os(pc)]$^+$ (X = Y = H; X = H, Y = OAc; and X = OAc, Y = Cl) with the ^{187}Os chemical shift of [(pc)$_2$Os$_2$(μ-H)$_3$]$^+$, {quartet, [*J*(Os–H) 84 Hz]} at δ −2526 p.p.m. (referenced to OsO$_4$), as measured by ^{1}H-{^{187}Os} two-dimensional n.m.r. spectroscopy, confirming the structures.

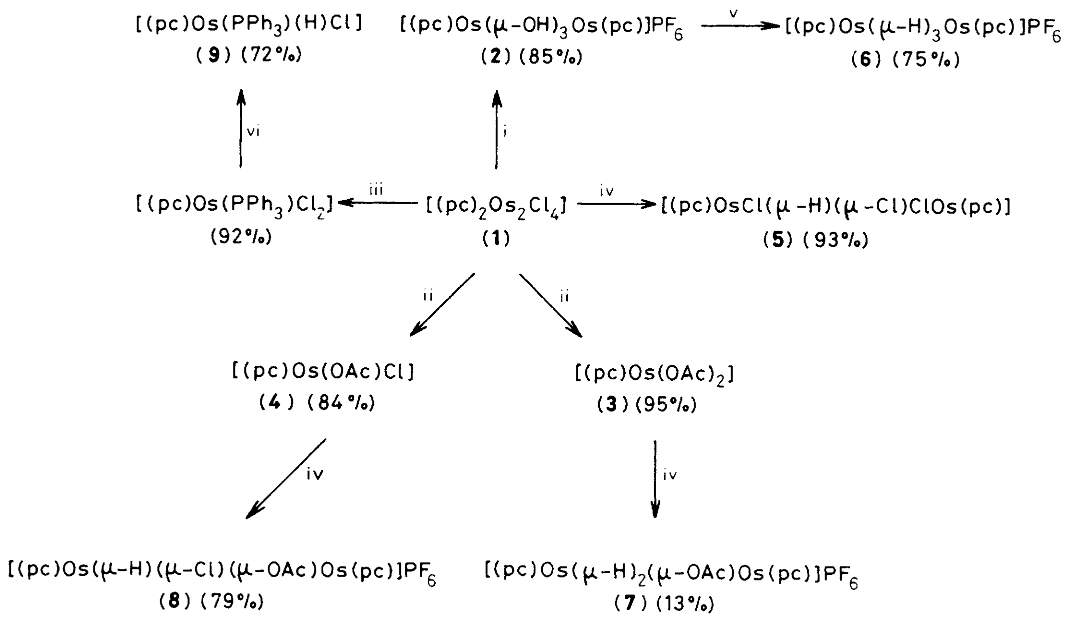
Although Bennett and his coworkers[1] and others[2] have described both mono- and di-nuclear areneruthenium hydride complexes, only a couple of mononuclear and no dinuclear η^6-arene osmium hydrides[3] have been described. We have recently found that the readily accessible *p*-cymeneosmium chloride complex, [(pc)$_2$Os$_2$Cl$_4$], (**1**) (pc = *p*-cymene, 4-isopropyltoluene)[4,5] has an η^6-arene–osmium bond which is reasonably inert. The *p*-cymene acts as a protecting group through a wide variety of substitutions at the metal without itself being attacked or displaced.[5] One such series of transformations (Scheme 1) involves the reactions of (**1**), the tri-μ-hydroxy complex (**2**),[6] the diacetato complex (**3**), or the chloro-acetato complex (**4**),† all derived from (**1**), with propan-2-ol to give a series of mono-, di-, and tri-μ-hydrido complexes.

Complex (**1**) was recovered unchanged from reaction of (**1**) with propan-2-ol (4 h, 80 °C); however, the same reaction carried out in the presence of an excess of KPF$_6$ gave a 93% yield of the mono-μ-hydrido-trichloro complex (**5**). Since the product does not contain PF$_6$ the role of the salt must be to create momentary vacant sites on the metal at which the propan-2-ol can then attack. The salts KBF$_4$ and Na$_2$SO$_4$ also gave the same products but only in 52 and 23% yields respectively. Reflux of [(pc)Os(μ-Cl)$_3$Os(pc)]PF$_6$ in propan-2-ol gave complex (**5**) quantitatively, suggesting that such a cationic complex or an isomer thereof is intermediate in the salt-catalysed reactions of (**1**).

The tri-μ-hydroxy complex (**2**) reacted smoothly in propan-2-ol (4 h, 80 °C) to give the tri-μ-hydridodiosmium complex (**6**), analogous to the well-known [(C$_5$Me$_5$)Ir(μ-

---

† All new complexes gave satisfactory microanalytical data, and were characterised by their i.r. and n.m.r. spectra.



Scheme 1. *Reagents:* i, aqueous NaOH, KPF_6; ii, AgOAc; iii, PPh_3; iv, propan-2-ol, 80 °C, KPF_6; v, propan-2-ol, 80 °C; vi, ethanol, 80 °C, Et_3N.

$H)_3Ir(C_5Me_5)]^+$,[7] in 75% yield. This complex was identified by accurate integration of the hydrides against the ligand pc resonances in the ^1H n.m.r. spectrum. The other μ-hydrido-diosmium complexes (**7**) and (**8**) have also been made, as well as the mononuclear hydrido-triphenylphosphine complex (**9**). All these complexes exhibited coupling of the hydrides to ^{187}Os ($I = \frac{1}{2}$; 1.64% abundance), ranging from 60 to 83 Hz (Table 1). These values are substantially larger than previously reported $J(Os–H)$.[8]

Confirmation that (**6**) contains three hydride ligands bound to Os comes from the Os n.m.r. spectrum. Direct observation of the metal resonance, as was used to show that $[(C_5Me_5)RhH_2(SiEt_3)_2]$ contained two hydrides,[9] has not yet been possible. However, indirect observation, *via* the ^{187}Os satellites of the proton spectrum was successful. This involved finding the ^{187}Os frequency range by use of the echo type pulse sequence,[10]‡

$$90°_{(H)}–\tau–180°_{(H)},\ 180°_{(Os)}–\tau–AQT_{(H)},\ [\tau = \tfrac{1}{2}J_{H\text{-}Os}]$$

which, when the 180° (Os) pulse is applied nearby on resonance, gives an inversion of the osmium satellites in the proton spectrum leaving the rest of the spectrum unchanged. (AQT = acquisition time.)

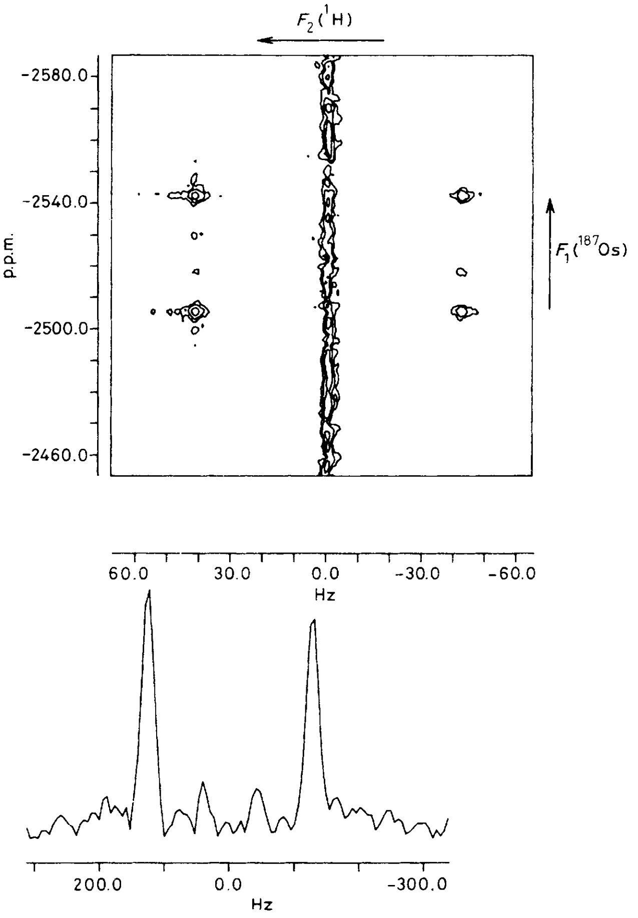


Figure 1. ^1H-{^{187}Os} delta–delta correlated 2D contour plot of $[(pc)_2Os_2(\mu\text{-}H)_3]^+$ and corresponding ^{187}Os spectrum obtained as an F_1 cross-section showing coupling to three hydrides [2D matrix: 1K FID (32 scans) × 256].

---

‡ Measured on an AM 300 spectrometer with proton observation (5 mm tube) through the decoupling coil of a multinuclear 10 mm VSP probe. The ^{187}Os pulsing was achieved *via* the normal observing coil tuned on ^{187}Os frequency range. The ^{187}Os pulses were generated with a broad band BSV 3 decoupler and a frequency synthesizer with computer controlled phase shift capabilities[13] [90°(^1H) 27 μs, 90°(^{187}Os) 53 μs]. The original 2D sequence[11] is written as:

$$90°_{(H)}–\tau–180°_{(H)},\ 180°_{(X)}–\tau–90°_{(H)},\ 90°_{(X)}–t_1–180°_{(H)}–t_1–$$
$$90°_{(H)},\ 90°_{(X)}–\tau–180°_{(H)},\ 180°_{(X)}–\tau–[AQT_{(H)},\ \text{decouple (X)}]$$

and allows the detection of an X nucleus with the proton sensitivity. In our experiment, the $180°_{(H)}$ decoupling pulse in the middle of the evolution period (t_1) was removed to retain the $^1H–^{187}Os$ coupling information and osmium 187 decoupling was not performed during acquisition of the proton free induction decays (FID's).

Table 1. ^{1}H N.m.r. data for the hydride resonances.[a]

Compound	Solvent	δ/p.p.m.	$^1J(^{187}Os-^1H)$/Hz
(**5**)	$CDCl_3$	−12.73	60.8
(**6**)	CD_2Cl_2	−14.87	83.3
(**7**)	$CDCl_3$	−13.73	75.6
(**8**)	$CDCl_3$	−9.57	66.3
(**9**)	$(CD_3)_2CO$	−8.42	70.3

[a] Spectra run on a Bruker WH400 at 22 °C; Me_4Si as internal reference.

The precise ^{187}Os chemical shift (δ − 2526 ± 1 p.p.m. from molten OsO_4) and the multiplicity (quartet) were then elucidated by a ^{1}H-{^{187}Os} delta-delta correlated, retro-INEPT two-dimensional sequence,[11] in which the ^{187}Os chemical shift and multiplicity are obtained in the so-called F_1 dimension (Figure 1). This particular sequence is expected to modify the usual 1:3:3:1 quartet intensities of the osmium spectrum strongly because of the polarization transfers and pulse imperfections. Such an effect has already been shown in a similar ^{1}H-{^{15}N} experiment.[12] The measured J(Os–H) of 84 Hz, however, is in excellent agreement with that found by measurement of the satellites in the ^{1}H spectrum. Only one previous observation of an ^{187}Os n.m.r. spectrum, for OsO_4, has been reported.[14]

We thank the S.E.R.C. for support and the Spanish Ministry of Education for an award (to J. A. C.).

Received, 8th August 1984; Com. 1159

References

1 M. A. Bennett, T-N. Huang, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 312; M. A. Bennett, T-N. Huang, A. K. Smith, and T. W. Turney, *ibid.*, 1978, 582; however, see also, M. A. Bennett, J. P. Ennett, and K. I. Gell, *J. Organomet. Chem.*, 1982, **233**, C17.

2 R. Iwata and I. Ogata, *Tetrahedron*, 1973, **29**, 2752; I. Ogata, R. Iwata, and Y. Ikeda, *Tetrahedron Lett.*, 1970, 3011; H. Werner and R. Werner, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 683; *J. Organomet. Chem.*, 1979, **174**, C63 and C67.

3 H. Werner and R. Werner, *J. Organomet. Chem.*, 1980, **194**, C7; *Chem. Ber.*, 1982, **115**, 3781.

4 T. Arthur and T. A. Stephenson, *J. Organomet. Chem.*, 1981, **208**, 369.

5 J. A. Cabeza and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in the press.

6 See, for example, T. Arthur, D. R. Robertson, D. A. Tocher, and T. A. Stephenson, *J. Organomet. Chem.*, 1981, **208**, 389.

7 C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1973, 1901; see also P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

8 B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1970, 1041; E. C. Constable, B. F. G. Johnson, J. Lewis, G. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.

9 M.-J. Fernandez and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 310.

10 D. A. Vidusek, M. F. Roberts, and G. Bodenhausen, *J. Am. Chem. Soc.*, 1982, **104**, 5452.

11 G. Bodenhausen, *Chem. Phys. Lett.*, 1980, **69**, 185.

12 A. G. Redfield, *Chem. Phys. Lett.*, 1983, **96**, 537.

13 C. Brevard and R. Schimpf, *J. Magn. Reson.*, 1982, **47**, 528.

14 W. Sahm and A. Schwenk, *Z. Naturforsch., Teil A*, 1974, **29**, 1763.