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Preliminary Communication

Reactions of Ru_3 clusters with functional phosphines: formation of μ_3-acyl and μ_3-imidoyl complexes

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Abstract

Reactions of Ru_3 clusters with tertiary phosphines containing functional groups have given complexes containing μ_3-acyl and μ_3-imidoyl ligands, which have been characterised by single crystal X-ray studies in the cases of $Ru_3(\mu\text{-H})(\mu_3\text{-O=CC}_6H_4PPh_2)(\mu\text{-dppm})(CO)_6$ and $Ru_3(\mu\text{-H})(\mu_3\text{-CPh=NC}_6H_4PPh_2)(CO)_6$, respectively.

The chemistry of tertiary phosphines containing functional groups is currently of great interest, since their complexes are perceived as being potential catalyst precursors, particularly if the functional group can provide a weakly bonded donor atom which can protect a vacant site on the metal atom. These studies have been extended to ruthenium and osmium cluster complexes, an early demonstration of their potential being the facile dehydrogenation reactions undergone by derivatives of diphenyl(2-styryl)phosphine, $PPh_2(C_6H_4CH{=}CH_2\text{-}2)$ [1]. More recently, we have reported reactions of the ketophosphine $PPh_2(CH_2COPh)$ [2] and have begun a study of transformations of related *N*- and *O*-functional groups [3]. Common to all these systems is the ready deprotonation of the functional group to give a ligand which either bridges a M–M bond or caps the M_3 cluster [4].

In examining the reactions of the phosphino-aldehyde $PPh_2(C_6H_4CHO\text{-}2)$ and the phosphino-imide $PPh_2(C_6H_4N{=}CHPh\text{-}2)$, we have found further facile transformations of the initially-formed hydrido clusters into complexes containing examples of μ_3-acyl and μ_3-imidoyl ligands capping Ru_3 clusters.

The reaction between $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**; Scheme 1) and $PPh_2(C_6H_4CHO\text{-}2)$ afforded a mixture of dark red $Ru_3(\mu\text{-dppm})(CO)_9\{PPh_2(C_6H_4CHO\text{-}2)\}$ (**2**) and the hydrido cluster $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2C_6H_4\text{-CO})(\mu\text{-dppm})(CO)_7$ (**3**), which was readily characterised from its spectroscopic properties [5*] and by a single-crystal X-ray structure determination, which will be reported elsewhere [6]. After further heating of its solution in refluxing toluene for 10 min, changes in the IR $\nu(CO)$ spectrum indicated that **3** had been converted into a third complex (**4**) by loss of one CO ligand, as confirmed by its FAB mass spectrum [5*]. The structural identity of **4** was not clear from the spectroscopic properties (the possibility of the formation of a $\mu_3\text{-}C_6H_4$ complex by decarbonylation was canvassed), so a single-crystal X-ray structure determination was undertaken [7*].

A molecule of **4** is depicted in Fig. 1(a) and important bond parameters are noted in the caption. A triangular Ru_3 core has one edge bridged by the dppm ligand, the third P atom being attached to the third Ru atom; all P atoms occupy equatorial sites. The deprotonated phosphine ligand is attached by P(3) to Ru(3), while a benzoyl group caps the cluster, being bonded via the C(3) and O(3) atoms. The geometry of the μ_3-C–O unit is of interest, it being bonded in a $2\sigma,\eta^2\text{-}\|$ fashion, reminiscent of μ_3-alkynes. The Ru(1,3)–C(3) and Ru(1,2)–O(3) separations are 2.21(3), 2.04(2) and 2.16(2), 2.09(2) Å, respectively; with a C–O distance of 1.40(3) Å, the similarity between the μ_3-OCR group and the isoelectronic $\mu_3\text{-}C_2R_2$ ligand is further enhanced.

While there are many examples of cluster complexes containing edge-bridging μ-OCR ligands, the μ_3-OCR group has been found only rarely. An early example was $Os_3W(\mu_3\text{-OCCH}_2C_6H_4Me\text{-}4)(CO)_{11}(\eta\text{-}C_5H_5)$, which was obtained from $Os_3(\mu\text{-H})_2(CO)_{10}$ and $W({\equiv}C\text{-}C_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)$ [8]; the iron cluster $Fe_3(\mu_3\text{-OCR})(CO)_9$ is also known [9]. In both, the acyl C–O bond is easily broken, by heat and by electrophilic attack, respectively [9,10].

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

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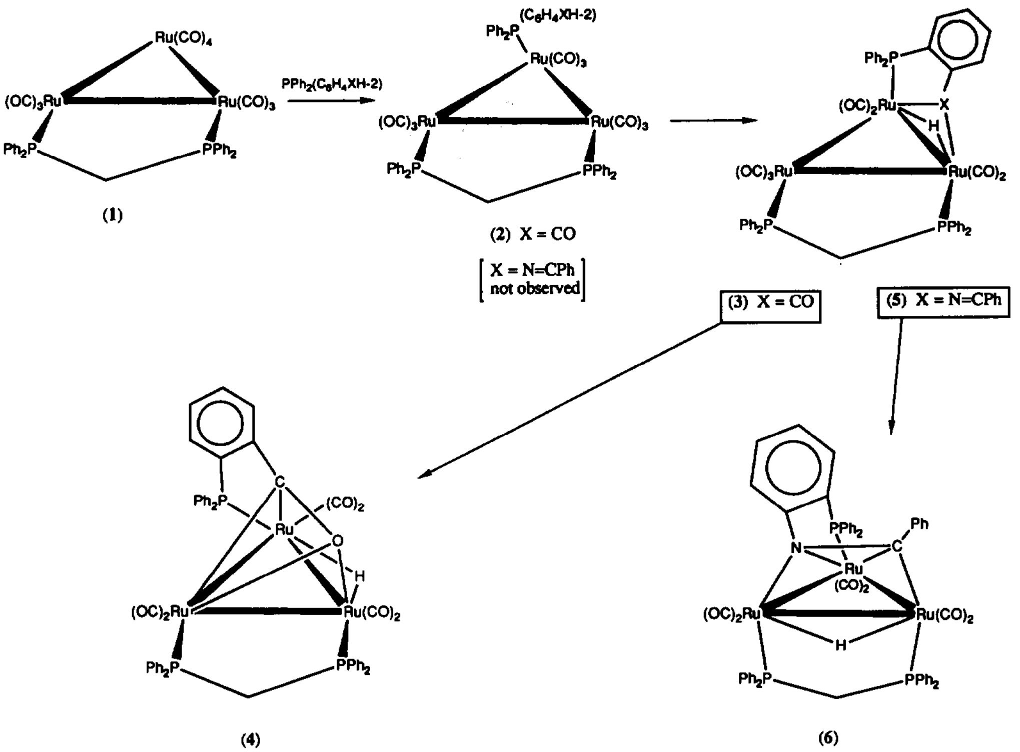

Scheme 1

Similar reactions between **1** and $PPh_2(C_6H_4N{=}CHPh)$ proceeded via **5**, the analogue of **2**; this complex will be fully described elsewhere [6]. However, further heating of **5** in refluxing cyclohexane (1 h) resulted in direct conversion to **6**, which was characterised from its spectroscopic data [5*] and an X-ray structural determination [7*] as a direct analogue of **4**, namely $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh{=}NC_6H_4PPh_2)(\mu\text{-}dppm)(CO)_6$.

A molecule of **6** is shown in Fig. 1(b); significant bond parameters are given in the caption. The triangular Ru_3 core is capped by the μ_3-imidoyl ligand, again in the $2\sigma,\eta^2$-‖ mode, with Ru(2,3)–C(3) and Ru(1,3)–N(3) distances of 2.06(1), 2.19(1) and 2.03(1), 2.11(1) Å, respectively. The μ-dppm ligand unusually occupies axial coordination sites on Ru(1) and Ru(2), while P(3) from the substituted tertiary phosphine is attached to Ru(3) in an equatorial site.

In this case, there are several analogous complexes containing μ_3-RN=CR′ ligands, most being obtained by hydrogenation of cluster-bound nitrile [11] or isonitrile ligands [12], or from the reactions of cyclic tertiary amines with Ru_3 and Os_3 clusters [13,14].

Comparison of the two structures reveals some interesting differences. In **4**, the dppm occupies equatorial sites on the Ru–Ru vector which is also bridged by O(3). As a result, this vector is shortened to 2.673(4) Å (*cf.* 2.834(1) Å in $Ru_3(\mu\text{-}dppm)(CO)_{10}$ [15]). In **6**, the dppm is coordinated in axial sites, bridging the longest Ru–Ru vector [2.870(6) Å] which is also bridged by the C(3)–N(3) group and probably also by the hydride atom. Atom P(3) is coordinated to Ru(3) in **4**, which is σ-bonded to C(3); in **6**, the corresponding Ru atom is η^2-bonded to the C(3)–N(3) moiety. The cluster-bonded H atoms were not located directly: in **4**, the likely position is bridging Ru(2)–Ru(3) [2.918(3) Å] (which vector is also bridged by the C–O moiety); in **6**, it is likely that the H atom bridges Ru(1)–Ru(2). These locations are supported by the characteristic splaying of the CO groups about the H-bridged Ru–Ru vectors: in **4**, Ru(2)–Ru(3)–C(32) 112.2(9), Ru(3)–Ru(2)–C(22) 110(1)°; in **6**, Ru(1)–Ru(2)–C(21) 108.9(5), Ru(2)–Ru(1)–C(11) 118.7(5)°.

This convenient synthesis of both μ- and μ_3-acyl and -imidoyl complexes from the appropriate functional phosphines (which are themselves readily available [16]) will allow further study of their chemistry which will be described in due course. So far, we have not been able to obtain complexes analogous to **4** and **6** from either $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$. As expected, the greater reactivity of the ruthenium carbonyl complexes has precluded the isolation of the simple CO-substitution products $Ru_3(CO)_{11}(PR_3)$ although their implication in the reaction sequence is shown by the successful preparation of the osmium analogues and their smooth conversion, albeit under harsher reaction conditions (refluxing xylene, 7 h), into $Os_3(\mu\text{-}H)(\mu\text{-}PPh_2C_6H_4\text{-}CX\text{-}2)(CO)_{10}$ (X = O or N=CPh).

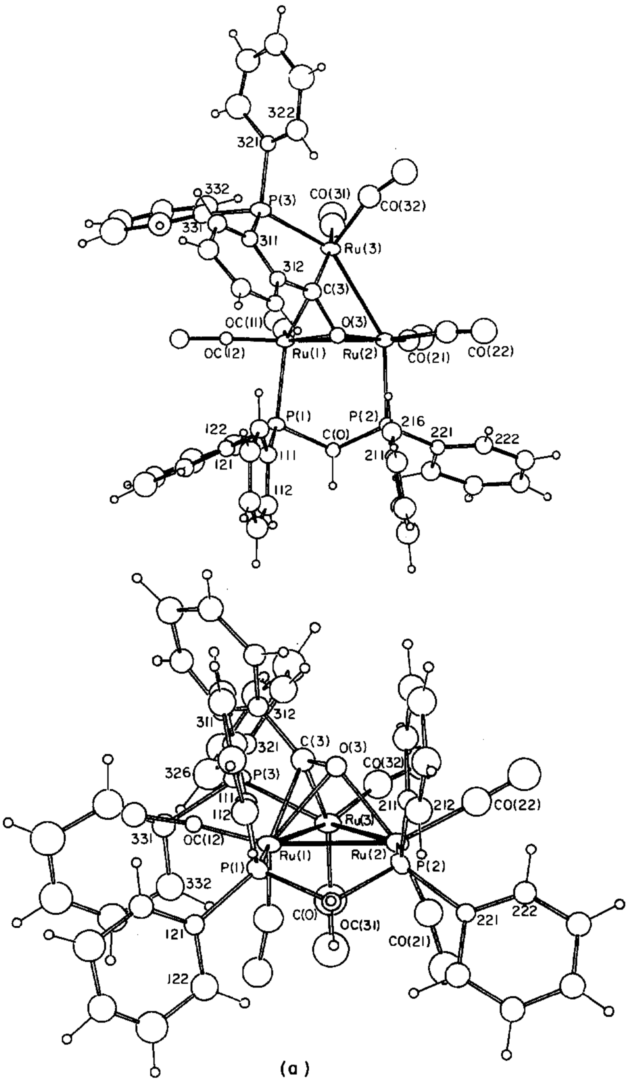

Fig. 1(a). A molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}O{=}CC_6H_4PPh_2)(\mu\text{-}dppm)(CO)_6$ (4) oblique and normal to the Ru_3 plane showing atom-numbering system. Significant bond parameters: Ru(1)–Ru(2) 2.673(4), Ru(1)–Ru(3) 2.806(4), Ru(2)–Ru(3) 2.918(3), Ru(1)–P(1) 2.309(8), Ru(2)–P(2) 2.341(8), Ru(3)–P(3) 2.306(9), Ru(1)–O(3) 2.16(2), Ru(2)–O(3) 2.09(2), Ru(1)–C(3) 2.21(3), Ru(3)–C(3) 2.04(2), C(3)–O(3) 1.40(3) Å; Ru(3)–P(3)–C(311) 103.7(8), C(312)–C(3)–O(3) 119(2)°.

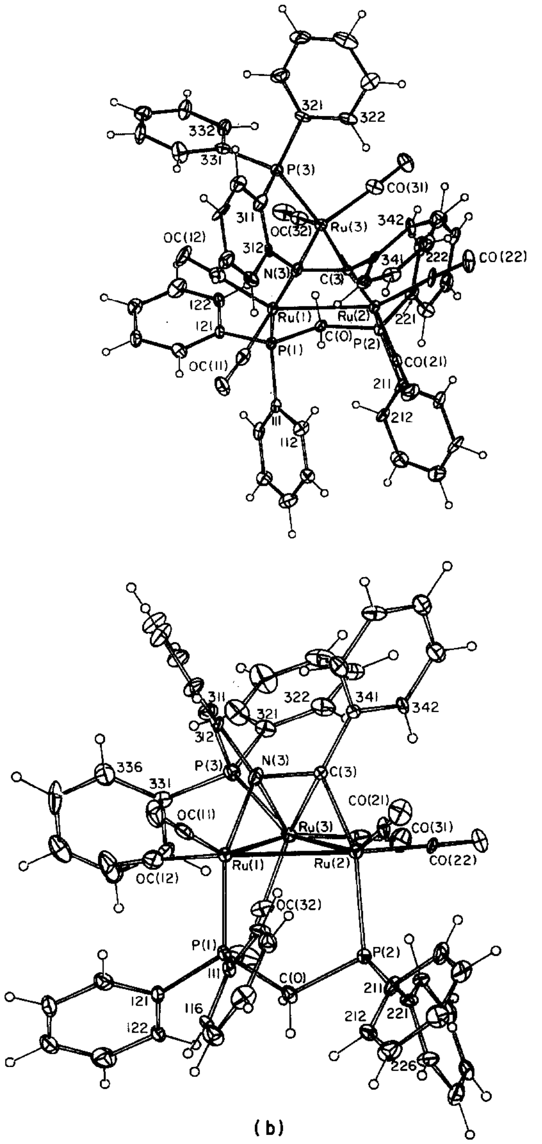

Fig. 1(b). A molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh{=}NC_6H_4PPh_2)(\mu\text{-}dppm)(CO)_6$ (6) oblique and normal to the Ru_3 plane showing atom-numbering system. Significant bond parameters: Ru(1)–Ru(2) 2.870(6), Ru(1)–Ru(3) 2.770(2), Ru(2)–Ru(3) 2.794(3), Ru(1)–P(1) 2.315(5), Ru(2)–P(2) 2.383(5), Ru(3)–P(3) 2.309(4), Ru(1)–N(3) 2.03(1), Ru(3)–N(3) 2.11(1), Ru(2)–C(3) 2.06(1), Ru(3)–C(3) 2.19(1), C(3)–N(3) 1.43(2) Å; Ru(3)–P(3)–C(311) 102.3(5), C(312)–N(3)–C(3) 121(3), C(341)–C(3)–N(3) 121(1)°.

Acknowledgements

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References and notes

1 M. I. Bruce, B. K. Nicholson and M. L. Williams, *J. Organomet. Chem., 243* (1983) 69.

2 P. Braunstein, S. Coco Cea, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, *423* (1992) C38; J. Chem. Soc., Dalton Trans., (1992) 2539.

3 M. I. Bruce and O. Kühl, unpublished results.

4 See, for example, G. Lavigne, in D. F. Shriver, H. D. Kaesz and R. D. Adams (eds.), *The Chemistry of Metal Cluster Complexes*, VCH, Weinheim 1990, Chap. 5, p. 201.

5 Selected spectroscopic data are as follows. For **2**: ν(CO) 2057 w, 2021 w, 2001 vs, 1982 vs, 1951 m cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 10.02 (s, C*H*O); FAB mass spectrum: M$^+$ at *m/z* 1230. For **3**: ν(CO) 2059 w, 2035 m, 1996 s, 1974 vs, 1953 m, 1927 w cm^{-1}; ^{1}H NMR δ(CDCl$_3$) −12.93 (dd, *J*(PH) 2.8, 5.3 Hz), −13.11 (dd, *J*(PH) 2.8, 5.4 Hz) (Ru-*H*); FAB mass spectrum: [M−CO]$^+$ at *m/z* 1147. For **4**: ν(CO) 2022 s, 2007 m, 1996 w, 1972 vs, 1957 m, 1919 w cm^{-1}; ^{1}H NMR δ(CDCl$_3$) −14.95 dd, *J*(PH) 3.2, 4.4 Hz, Ru-*H*); FAB mass spectrum: M$^+$ at *m/z* 1147. For **5**: ν(CO) 2055 m, 2035 w, 2020 m, 1997 vs, 1992 (sh), 1980 vs, 1963 m, 1943 w cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 8.10 (s, =C*H*); FAB mass spectrum: M$^+$ at *m/z* 1307. For **6**: ν(CO) 2016 w, 2003 s, 1992 w, 1959 vs, 1934 w, 1898 w cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 4.03 (m, CH), 6.57–7.47 (m, aromatic H), Ru-*H* not yet located; FAB mass spectrum: M$^+$ at *m/z* 1221.

6 C. J. Adams, M. I. Bruce, O. Kühl, B. W. Skelton, E. R. T. Tiekink and A. H. White, in preparation.

7 Single-crystal X-ray structure determinations were carried out using a CAD4 four-circle diffractometer (monochromatic Mo Kα radiation, λ 0.71073 Å). Data sets were obtained at *ca.* 295 K; structure solution and refinement used the XTAL2.6 suite of programs. Individual details follow.

For **4**: Ru$_3$(μ-H)(μ_3-O=CC$_6$H$_4$PPh$_2$)(μ-dppm)(CO)$_6$·CH$_2$Cl$_2$(?) ≡C$_{50}$H$_{37}$O$_7$P$_3$Ru$_3$·CH$_2$Cl$_2$, $M = 1230.8$. Triclinic, space group $P\bar{1}$, $a = 16.694(12)$, $b = 12.916(1)$, $c = 12.890(2)$ Å, $\alpha = 103.53(9)$, $\beta = 104.72(4)$, $\gamma = 94.54(4)°$, $= 2585(2)$ Å^3, $= 2$; $(000) = 1224$, $\rho_c = 1.58$ g cm^{-3}; $2\theta_{max} = 47.5°$, μ(Mo Kα) 10.9 cm^{-1}, A^*(min, max) = 1.08, 1.21 (Gaussian correction). 2874 'observed' data ($I \geq 3\sigma(I)$) from 7353 independent data were refined to $R = 0.088$, $R' = 0.084$.

For **6**: Ru$_3$(μ-H)(μ_3-CPh=NC$_6$H$_4$PPh$_2$)(μ-dppm)(CO)$_6$· 0.5CH$_2$Cl$_2$ ≡C$_{56}$H$_{42}$NO$_6$P$_3$Ru$_3$·0.5CH$_2$Cl$_2$, $M = 1263.6$. Monoclinic, space group $C2/c$, $a = 39.751(22)$, $b = 12.323(36)$, $c = 21.043(9)$ Å, $\beta = 95.87(4)°$, $V = 10254$ Å^3, $Z = 8$; $F(000) = 5048$, $\rho_c = 1.64$ g cm^{-3}; $2\theta_{max} = 45°$, μ(Mo Kα) = 10.3 cm^{-1}, A^*(min, max) = 1.04, 1.27 (Gaussian correction). 3660 'observed' data ($I \geq 3\sigma(I)$) from 6722 independent data were refined to $R = 0.056$, $R' = 0.056$.

Some experimental difficulties were encountered in both determinations in consequence of one or more of: sample size, crystal quality, solvent thermal motion/disorder problems. The limited data of **4** would support meaningful anisotropic thermal parameter refinement for Ru, P only; 'solvent' molecules were modelled as a pair of disordered, half-weighted CH$_2$Cl$_2$ molecules. For **6**, the CH$_2$Cl$_2$ molecule lies on a two-fold axis but with C disordered over two sites. C(3) and solvent C(1,1′) were refined with isotropic thermal parameters.

For both structures tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

8 J. T. Park, J. R. Shapley, M. R. Churchill and C. Bueno, *Inorg. Chem.*, *22* (1983) 1579.

9 W. K. Wong, K. W. Chiu, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 1557.

10 J. R. Shapley, J. T. Park, M. R. Churchill, J. W. Ziller and L. R. Beanan, *J. Am. Chem. Soc.*, *106* (1984) 1144.

11 M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, *101* (1979) 7255.

12 E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.*, *22* (1983) 269.

13 M. W. Day, S. Hajela, S. E. Kabir, M. Irving, T. McPhillips, E. Wolf, K. I. Hardcastle, E. Rosenberg, L. Milone, R. Gobetto and D. Osella, *Organometallics*, *10* (1991) 2743.

14 G. Süss-Fink, T. Jenke, H. Heitz, M. A. Pellinghelli and A. Tiripicchio, *J. Organomet. Chem.*, *379* (1989) 311.

15 A. W. Coleman, D. F. Jones, P. H. Dixneuf, C. Brisson, J.-J. Bonnet and G. Lavigne, *Inorg. Chem.*, *23* (1984) 952.

16 M. K. Cooper, J. M. Downes and P. A. Duckworth, *Inorg. Synth.*, *25* (1989) 129; D. Hedden and D. M. Roundhill, *Inorg. Synth.*, *27* (1990) 322.