

### Preliminary communication

## CHAIN LENGTH EFFECTS ON THE COORDINATION MODE OF BIDENTATE PHOSPHINES IN $\text{Ru}_5\text{C}(\text{CO})_{13}[\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2]$ : COORDINATION TO NON-ADJACENT METAL ATOMS

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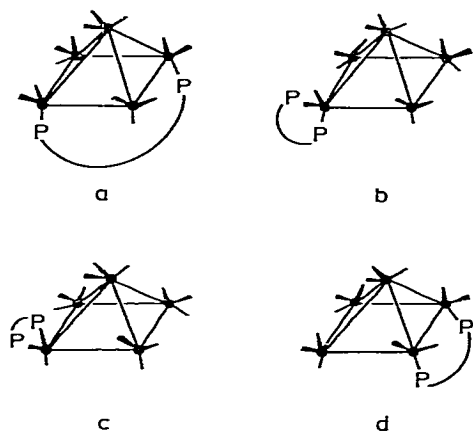
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### Summary

Three different phosphine coordination arrangements have been observed for  $\text{Ru}_5\text{C}(\text{CO})_{13}[\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2]$  ( $n = 1$  to 4); the phosphine in one isomer of  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppb})$  bridges the diagonal of the square face of the cluster.

The phosphine  $\text{PPh}_2\text{CH}_2\text{PPh}_2$  (dppm) has been widely found to have an appropriate bite to stabilise many dimeric complexes of the A-frame type by acting as a bridging ligand [1]. Stabilisation of larger arrays of metals is of current interest in catalyst design [2] and these offer different stereochemical situations. A chain length effect on the preferred coordination mode of bidentate phosphines was suggested for trinuclear complexes with  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  possessing a bridging ligand [3] and  $\text{Ru}_3(\text{CO})_{10}(\text{dppe})$  (dppe =  $\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2$ ) possibly a chelating one at a single metal centre [4], but the latter complex has recently been found also to possess an edge bridging diphosphine [5]. We have carried out a systematic study of the binding of four bidentate phosphines of general formula  $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$  with different chain lengths viz. dppm ( $n = 1$ ), dppe ( $n = 2$ ), dppp ( $n = 3$ ) and dppb ( $n = 4$ ) with ruthenium clusters of nuclearity three to six to determine if bite preferences exist in these clusters. In the course of this work a new coordination mode was found for the stable isomer of  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppb})$  (Ia) (Fig. 1) in which the phosphine bridges across a square face of ruthenium atoms.

Interaction of  $\text{Ru}_5\text{C}(\text{CO})_{15}$  [6] with dppb in  $\text{C}_6\text{H}_{12}$  for 2 h at 50°C affords complex Ia as the major product;  $[\text{Ru}_5\text{C}(\text{CO})_{14}]_2(\text{dppb})$  is also obtained. Complex Ia exhibits one  $\{^1\text{H}\}^{31}\text{P}$  resonance at  $\delta$  34.06 ppm (relative to 85%  $\text{H}_3\text{PO}_4$ ) and carbonyl IR absorptions at 2071m, 2046vs, 2020s, 2012s, 1994m, 1981w, 1966w and 1952w  $\text{cm}^{-1}$  in cyclohexane solution. The two phosphorus atoms are apparently equivalent and the molecular structure of Ia was determined by single crystal X-ray diffraction.



Complex	Ligand	Isomerism
(III)	dppm	$c \rightleftharpoons b$
(V)	dppe	$c(\text{solution}) \rightleftharpoons b(\text{solid})$
(II)	dppp	$a \rightarrow b \rightleftharpoons c$
(I)	dppb	$b \rightleftharpoons c \rightarrow a$

Fig. 1. Possible structures and isomerisation processes of the  $\text{Ru}_2\text{C}(\text{CO})_{13}[\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2]$  series.

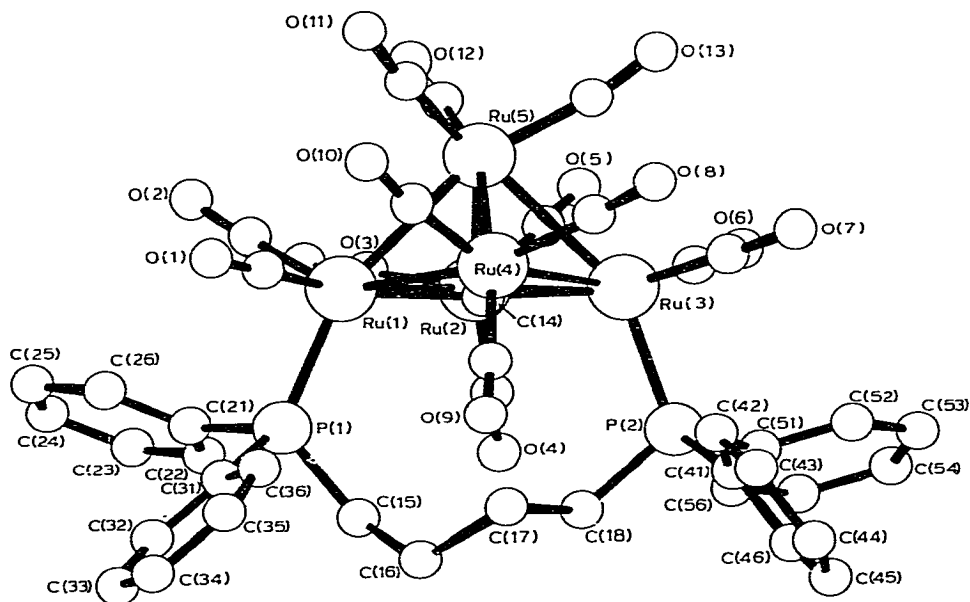
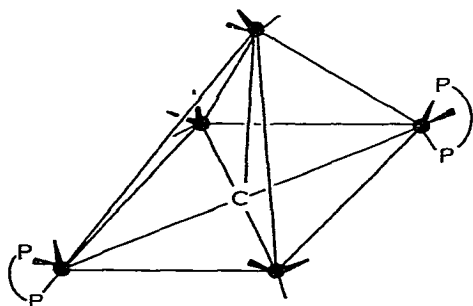


Fig. 2. Molecular structure of  $\text{Ru}_2\text{C}(\text{CO})_{13}(\text{dppb})$ . Bond lengths: Ru(1)—Ru(2) 2.873(1), Ru(1)—Ru(4) 2.891(1), Ru(1)—Ru(5) 2.847(1), Ru(2)—Ru(3) 2.837(1), Ru(2)—Ru(5) 2.778(1), Ru(3)—Ru(4) 2.894(1), Ru(3)—Ru(5) 2.881(1), Ru(4)—Ru(5) 2.760(1), Ru(1)—C(14) 2.024(9), Ru(2)—C(14) 2.073(9), Ru(3)—C(14) 2.002(9), Ru(4)—C(14) 2.064(9), Ru(5)—C(14) 2.163(9), Ru(1)—P(1) 2.367(3), and Ru(3)—P(2) 2.337(3) Å. Distance of C(14) below Ru(1), Ru(2), Ru(3) and Ru(4) plane 0.21 Å. Bond angles: P(1)—Ru(1)—Ru(5) 154.5(1), P(2)—Ru(3)—Ru(5) 152.6(1), C(4)—Ru(2)—Ru(5) 163.2(3) and C(9)—Ru(4)—Ru(5) 164.9(4)°.

Crystal data,  $C_{42}H_{28}O_{13}P_2Ru_5$ , monoclinic, space group  $P2_1/n$ ,  $a$  10.650(8),  $b$  17.440(3),  $c$  23.889(4) Å,  $\beta$  96.67(4)°,  $Z = 4$ ,  $U$  4406.7 Å<sup>3</sup>,  $\mu$ (Mo- $K\alpha$ ) 17.4 cm<sup>-1</sup>. The data were collected using an Enraf-Nonius CAD-4 diffractometer which gave 4077 unique reflections [ $F > 2.5\sigma(F)$ ]. The structure was solved by direct methods to locate the  $Ru_5$  cluster and subsequent structure factor and electron density calculations located the remaining non-hydrogen atoms. Least squares refinement (237 parameters) gave  $R = 0.049$ .

The molecular structure of Ia (Fig. 2) is derived from that of the parent  $Ru_5C(CO)_{15}$  [6] with the phosphorus atoms occupying axial positions on *trans* ruthenium atoms of the ruthenium square face. Although the phosphorus atoms are crystallographically distinct, they would be expected to be equivalent in solution, as observed by <sup>31</sup>P NMR. The binding of the phosphine to non-adjacent metal atoms is noteworthy and the bite of this particular ligand is appropriate to achieve this. The mean Ru(apical)—Ru(basal)—P angle (153.5°) is 10° less than the corresponding Ru(apical)—Ru(basal)—C(carbonyl) angle (164°). The strapping phosphine causes the  $ML_3$  units in the base of the square pyramid to tilt in this relatively small distortion.

The isomer Ia is thermodynamically favoured. However if  $Ru_5C(CO)_{15}$  is treated with dppb at 50°C for 10 minutes, then another material of the same stoichiometry can also be isolated by TLC. This material, considered to be a mixture of Ib and Ic as the major and minor isomers respectively, changes to Ia after 2 h in solution at room temperature. This stability order is reversed for  $Ru_5C(CO)_{13}(dppp)$  (II). Structure IIa is formed initially but the carbonyl IR absorptions rapidly change as new bands at 2073m, 2047m, 2039s, 2028vs, 2020m, 2009s, 2004m, 1996m, 1966w, and 1951w cm<sup>-1</sup> (in cyclohexane) appear due to a mixture of IIb and IIc in the isolated product. A similar IR spectrum is observed for  $Ru_5C(CO)_{13}(dppm)$  (III). At 17°C, the {<sup>1</sup>H} <sup>31</sup>P NMR spectrum of III contains a singlet at  $\delta$  14.97 ppm. This broadens at lower temperatures and at -90°C, three separate signals are observed. The two weaker signals at  $\delta$  27.78 and 14.04 ppm are of equal intensity. These are assigned to isomer IIIb as the most probable structure with inequivalent phosphorus atoms. The same chelating arrangement also appears to be observed for  $Ru_5C(CO)_{11}(dppm)_2$  (IV), from variable temperature <sup>13</sup>C and <sup>31</sup>P NMR studies\*. The chemical shift difference between the inequivalent <sup>31</sup>P nuclei in III and IV is ~13.8 ppm in each case; this is



(IV)

\* {<sup>1</sup>H} <sup>31</sup>P in CD<sub>2</sub>Cl<sub>2</sub> at -90°C:  $\delta$  3.52 and -10.26 ppm. {<sup>1</sup>H} <sup>13</sup>C in CD<sub>2</sub>Cl<sub>2</sub>/CHFCl<sub>2</sub> at -66°C:  $\delta$  206.35 (2 C), 205.93 (3C of rotating apical Ru(CO)<sub>3</sub>), 205.58 (2C), 203.43 (2C) and 198.01 (2C).

consistent with the phosphorus atoms occupying axial and equatorial sites on basal ruthenium atoms in both cases. The major  $^{31}\text{P}$  signal for III at  $-90^\circ\text{C}$  ( $\delta$  12.89 ppm), accounting for 90% of the total intensity, is due to another isomer which is considered to be IIIc (Fig. 1) because of the rapid interconversion between the two isomers. Interconversion between IIIb and IIIc only requires a twisting process while any other proposal would necessitate a facile dissociation of one arm of the phosphine and concomitant CO transfer. A limiting slow exchange  $^{13}\text{C}$  NMR spectrum of III, which could have confirmed this was not attained at  $-119^\circ\text{C}$ .

The fourth member of the series,  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppe})$  (V) exhibits a simpler IR spectrum than its dppm analogue ( $\nu(\text{CO})$  bands at 2073m, 2038s, 2027vs, 2010s and 2001m  $\text{cm}^{-1}$  in cyclohexane) corresponding to the more intense bands in the latter's spectrum. We therefore conclude that V has the same structure in solution as the major isomer of  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppm})$  (IIIc). Consistent with this isomer being Vc is the observation of a single  $\{^1\text{H}\}^{31}\text{P}$  resonance ( $\delta$  39.8 ppm) down to  $-90^\circ\text{C}$ .  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{dppe})$  is reported to have structure Vb in the crystal [7] and therefore appears to change structure with phase.

A summary of the isomerisation processes of these four  $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{L-L})$  derivatives is presented in Fig. 1. Three substitution patterns have been recognised on the  $\text{Ru}_5$  square pyramid and the identity of the kinetically or thermodynamically favoured form is a function of the phosphine chain length. There is no evidence for an edge bridging coordination mode *d* (Fig. 1). This contrasts with  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  [3],  $\text{Ru}_3(\text{CO})_{10}(\text{dppe})$  [5] and  $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppe})$  [8] for which edge bridging structures have been identified. We have carried out a similar study on  $\text{Ru}_6\text{C}(\text{CO})_{17}$  substitution by these four ligands and found only edge bridging forms, as confirmed by a single crystal X-ray study on  $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{dppm})$ . While all four nuclearities show some individual properties, the differences between the deltahedral clusters and the square faced  $\text{Ru}_5\text{C}(\text{CO})_{15}$  are most marked. Design of cluster stabilising ligands has therefore to be sensitive to facial character of the metal skeleton.

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