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### Preliminary communication

## Synthesis of $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]$ ( $\text{R} = \text{Me}$ or $\text{Pr}^i$ ): butterfly clusters of ruthenium containing a triply bridging carbonyl ligand with an unusual mode of coordination. Crystal structure of $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]$

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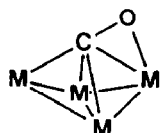
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### Abstract

Reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with a two molar proportion of  $(\text{RO})_2\text{PN(Et)P(OR)}_2$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ) in benzene under reflux affords a number of products including  $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]$ ,  $[\text{Ru}_3(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2\{\eta^1\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}]$  and, as the major species, the tetranuclear derivative  $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]$ . An X-ray diffraction study of  $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]$  has revealed that the skeletal framework adopts a butterfly structure and that one of the carbonyl groups functions as a triply bridging four-electron donor ligand capping the two wing-tip and one of the hinge ruthenium atoms.

A number of examples of metal carbonyl clusters in which a bridging carbonyl group coordinates to the metal atom framework via its oxygen as well as its carbon atom, thereby functioning as a four-electron donor, are now known [1–3]. The majority of these are tetranuclear species with butterfly skeletons with the carbon of the bridging carbonyl capping all four metal atoms and the oxygen being bonded to one of the wing tip atoms as illustrated. The disposition of the carbon is such that



while it is symmetrically situated with respect to the hinge atoms it is asymmetrically positioned with respect to the wing tip atoms. The synthesis of a tetranuclear

butterfly cluster containing a four-electron carbonyl which asymmetrically caps an open face of the butterfly is now reported.

Reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with the diphosphazane ligands  $(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^1$ ) has been found to afford products resulting from fragmentation and/or condensation as well as from carbonyl substitution, the nature and yields of the products from any particular reaction being dependent on the ligand and the reaction conditions employed. Products isolated and characterized include  $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ ,  $[\text{Ru}_3(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2\{\eta^1\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_1]$ ,  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ ,  $[\text{Ru}_3(\text{CO})_6\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_3]$ ,  $[\text{Ru}(\text{CO})_3\{(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_1]$ ,  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$  and  $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ .

Fragmentation was observed to occur even under the mildest conditions. Thus reaction of  $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$  with a twice-molar amount of trimethylamine oxide in acetone containing a small quantity of acetonitrile at  $-78^\circ\text{C}$  followed by the addition of an equimolar amount of the appropriate diphosphazane ligand, with the solution then allowed to warm slowly to room temperature, all in the absence of light, gave as major products  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$  and  $[\text{Ru}(\text{CO})_3\{(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_1]$ , with  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$  being produced only in low yield.

The complexes  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$  are expected to have a structure analogous to that of  $[\text{Ru}_3(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$  [4], with four equatorial carbonyl groups of the parent  $[\text{Ru}_3(\text{CO})_{12}]$  having been replaced by the two bridging ligands. However, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]$  at room temperature, was found to exhibit a singlet, which is inconsistent with this expectation, although the low temperature ( $-75^\circ\text{C}$ ) spectrum afforded the expected AA'BB' pattern of peaks. An X-ray diffraction study was thus carried out on this compound, and the stereochemistries of the two molecules in the asymmetric unit are illustrated in Fig. 1\*. The structures are in fact analogous to that of  $[\text{Ru}_3(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$  with the two diphosphazane ligands in each molecule bridging two of the edges of the triruthenium triangle in the equatorial plane. The pattern of the C–O stretching peaks in the solution infrared spectrum of this compound is very similar to that in the corresponding solid state spectrum, indicating that the solid state structure is retained in solution. As a consequence, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral data for  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]$  can be accounted for only in terms of some fluxional process. It is proposed that the diphosphazane ligands migrate around the triruthenium triangle in the equatorial plane arising from their interconversion between the bidentate and monodentate coordination modes.

\* Crystal data:  $\text{C}_{20}\text{H}_{34}\text{O}_{16}\text{N}_2\text{P}_4\text{Ru}_3$ ,  $M = 985.6$ , triclinic,  $P\bar{1}$ ,  $a$  12.815(6),  $b$  16.166(8),  $c$  20.284(10) Å,  $\alpha$  64.27(5),  $\beta$  68.91(6),  $\gamma$  82.19(5)°,  $U$  3531.3 Å<sup>3</sup>,  $D_c$  1.85 g cm<sup>-3</sup>,  $Z = 4$ , Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$  15.9 cm<sup>-1</sup>. 11767 unique reflection intensities were measured on a Nonius CAD-4 diffractometer (N.C.R.L., Pretoria) in the range  $2 \leq \theta \leq 23^\circ$ , 10622 of which were classed as observed ( $I > 4\sigma(I)$ ). These data were corrected for absorption using the empirical ( $\chi$  scan) method and used in the solution and refinement [5] of the structure. Final  $R = 0.044$ ,  $R_w = 0.050$  for 306 parameters, maximum shift over e.s.d. in the last full-matrix least-squares cycle = 0.68, featureless final difference Fourier with maximum peak height = 1.2 eÅ<sup>-3</sup>. Atomic coordinates, interatomic distances and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

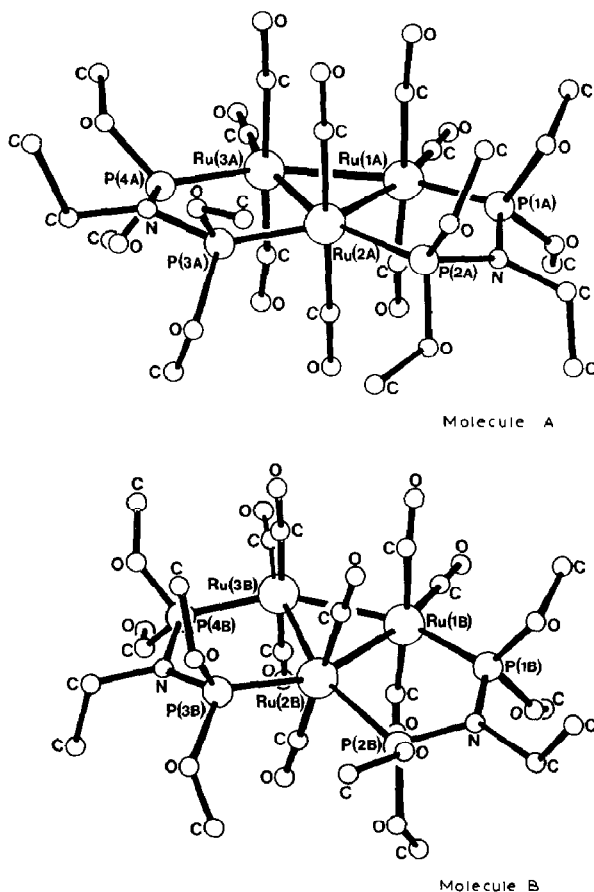


Fig. 1. The stereochemistry of the two molecules in the asymmetric unit of  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(MeO)}_2\text{PN(}i\text{Et)P(OMe)}_2\}_2]$ . Relevant interatomic distances: Ru(1A)–Ru(2A), 2.823(1); Ru(1A)–Ru(3A), 2.866(1); Ru(2A)–Ru(3A), 2.814(1); Ru(1A)–P(1A), 2.264(2); Ru(2A)–P(2A), 2.254(2); Ru(2A)–P(3A), 2.814(1); Ru(3A)–P(4A), 2.254(2); Ru(1B)–Ru(2B), 2.809(1); Ru(1B)–Ru(3B), 2.882(1); Ru(2B)–Ru(3B), 2.814(1); Ru(1B)–P(1B), 2.265(3); Ru(2B)–P(2B), 2.259(2); Ru(2B)–P(3B), 2.258(2); Ru(3B)–P(4B), 2.263(2) Å.

Significantly, the two molecules in the asymmetric unit of the unit cell of  $[\text{Ru}_3(\text{CO})_8\{\mu\text{-(MeO)}_2\text{PN(}i\text{Et)P(OMe)}_2\}_2]$  were found to adopt different conformations (Fig. 1). Thus while all of the axial carbonyls in the one molecule (**A**) are eclipsed with respect to each other, the axial carbonyls of the one ruthenium atom in the other molecule (**B**) are staggered with respect to those of the other two ruthenium atoms. Molecule **A** is thus analogous to the parent  $[\text{Ru}_3(\text{CO})_{12}]$  [6], which also adopts an eclipsed configuration, while molecule **B** is analogous to  $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-Ph}_2\text{PN(}i\text{Et)PPh}_2\}]$  [7],  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$  [8] and  $[\text{Ru}_3(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ , which also adopt a staggered conformation in the solid state.

The reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with the ditertiary phosphines  $\text{R}_2\text{PCH}_2\text{PR}_2$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) and  $\text{Ph}_2\text{PN(}i\text{Et)PPh}_2$  in benzene under reflux has been found to afford solely substitution products, and thus it was somewhat surprising to find that the major product of the reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with a two molar proportion of the diphosphazane ligands  $(\text{RO})_2\text{PN(}i\text{Et)P(OR)}_2$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ) under identical reac-

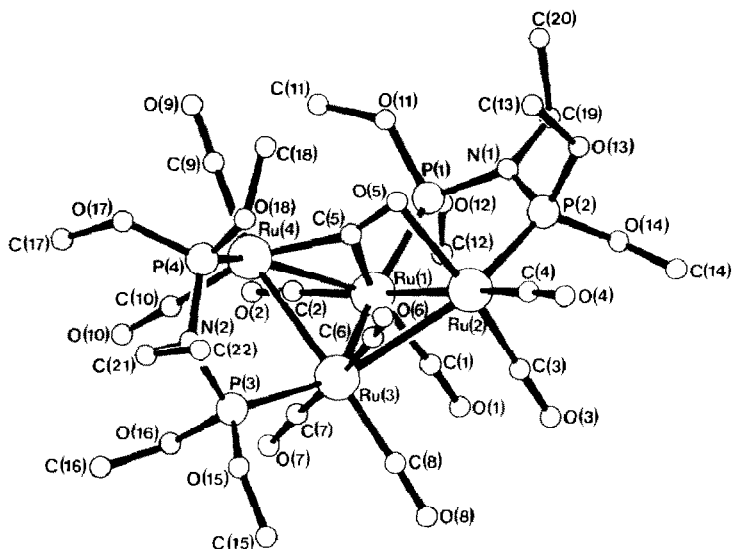


Fig. 2. The stereochemistry of  $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]$ . Relevant interatomic distances: Ru(1)–Ru(2), 2.723(1); Ru(1)–Ru(3) 2.858(1); Ru(1)–Ru(4), 2.806(1); Ru(2)–Ru(3), 2.929(1); Ru(3)–Ru(4), 2.865(1); Ru(1)–P(1), 2.243(3); Ru(2)–P(2), 2.241(2); Ru(3)–P(3), 2.271(2); Ru(4)–P(4), 2.228(2) Å.

tion conditions was the tetranuclear species  $[\text{Ru}_4(\mu_3\text{-}\eta^2\text{-CO})(\text{CO})_9\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]$ . The structure of the tetramethoxydiphosphazane derivative has been ascertained by means of a single crystal X-ray diffraction study and the molecular stereochemistry is illustrated in Fig. 2\*. The skeletal framework adopts a butterfly configuration with the dihedral angle between the two triruthenium planes being  $135^\circ$  and with two opposite edges being bridged by the two diphosphazane ligands.

The most salient feature of the structure of this species is the mode of coordination of one of the carbonyl groups. From the relevant ruthenium–carbon and ruthenium–oxygen distances {Ru(1)–C(5) 2.195(7); Ru(2)–C(5) 2.416(7); Ru(3)–C(5) 2.701(7); Ru(4)–C(5) 1.927(7) and Ru(2)–O(5) 2.159(4) Å} it is apparent that firstly this carbonyl functions as a four-electron donor ligand and that secondly it asymmetrically caps one of the open triruthenium triangles: the Ru(2)–C(5) bond length of 2.416(7) Å is essentially intermediate between a bonding and a non-bonding distance, while the Ru(3)–C(5) distance of 2.701(7) Å corresponds essentially with non-bonding. This mode of coordination for a carbonyl group is unique for a butterfly cluster, and provides a further example of the mode of coordination of an adsorbed carbon monoxide at the kink site of a metal surface.

\* Crystal data:  $\text{C}_{22}\text{H}_{34}\text{O}_{18}\text{N}_2\text{P}_4\text{Ru}_4$ ,  $M = 1142.7$ , monoclinic,  $P2_1/c$ ,  $a$  10.704(5),  $b$  12.216(6),  $c$  29.840(15) Å,  $\beta$  98.18(5)°,  $U$  3862.7 Å<sup>3</sup>,  $D_c$  1.96 g cm<sup>-3</sup>,  $Z = 4$ , Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$  16.0 cm<sup>-1</sup>. 5002 unique reflection intensities were measured on a Nonius CAD-4 diffractometer in the range  $2 \leq \theta \leq 23^\circ$ , 4285 of which were classed as observed ( $I > 3\sigma(I)$ ). These data were corrected for absorption using the empirical ( $\chi$  scan) method and used in the solution and refinement [5] of the structure. Final  $R = 0.040$ ,  $R_w = 0.053$  for 451 parameters, maximum shift over e.s.d. in the last full-matrix least-squares cycle = 0.09, featureless final difference Fourier with maximum peak height 0.90 eÅ<sup>-3</sup>. Atomic coordinates, interatomic distances and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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