

## Effect of the Phosphine Ligand Cone Angle on the Metal Frameworks of Heteronuclear Cluster Compounds Containing $\text{Cu}(\text{PR}_3)$ ( $\text{R} = \text{alkyl or aryl}$ ) Groups: X-Ray Structure Analyses of $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PR}_3)_2]$ ( $\text{R} = \text{cyclo-C}_6\text{H}_{11}$ or $\text{CHMe}_2$ )

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The cone angle of the phosphine ligands in the heteronuclear cluster compounds  $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PR}_3)_2]$  ( $\text{R} = \text{alkyl or aryl}$ ) has a marked effect on the metal framework structure adopted; when  $\text{R} = \text{CHMe}_2$ , two skeletal isomers, which interconvert at ambient temperature, are present in solution and when  $\text{R} = \text{cyclo-C}_6\text{H}_{11}$ , the cluster exhibits a previously unobserved type of  $\text{Cu}_2\text{Ru}_4$  metal core structure.

Comparison of the structures of a series of analogous heteronuclear cluster compounds  $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PR}_3)_2]$ , which formally differ only in the nature of  $\text{R}$  [ $\text{R} = \text{cyclo-C}_6\text{H}_{11}(\text{Cy})$ ,  $\text{CHMe}_2$ , or  $\text{Ph}$ ], demonstrates that the metal framework is significantly altered by variations in the cone angles<sup>1</sup> of the monodentate phosphine ligands attached to the Cu atoms.

Treatment of a  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{N}(\text{PPh}_3)_2]_2[\text{Ru}_4(\mu\text{-H})_2(\text{CO})_{12}]^2$  with 2 equiv. of the complex  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$  at  $-30^\circ\text{C}$ , followed by the addition of 2 equiv. of  $\text{PR}_3$ , affords the dark red cluster compounds  $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PR}_3)_2]$  [ $\text{R} = \text{Cy}$  (**1**) or  $\text{CHMe}_2$  (**2**)] in ca. 60% yield. Although the i.r. and n.m.r. spectroscopic data<sup>†</sup> for (**1**) and

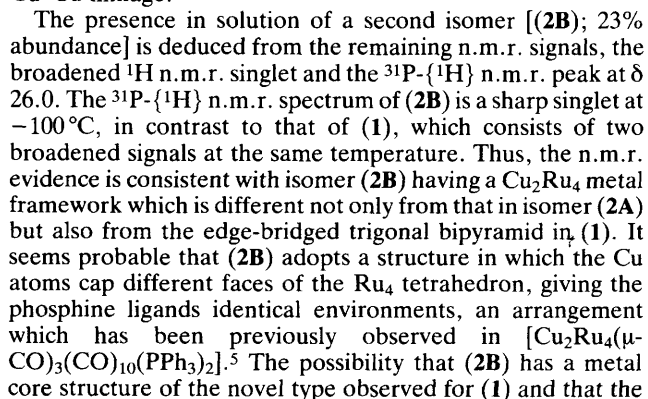
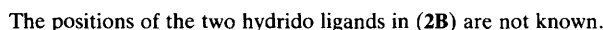
(**2**) are consistent with the proposed formulations, the spectra of (**1**) are significantly different from those reported for the analogous  $\text{PPh}_3$ -containing species  $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PPh}_3)_2]$  (**3**), implying that (**1**) adopts a different metal core structure from the capped trigonal bipyramidal skeletal geometry previously established for (**3**).<sup>3</sup> An X-ray diffraction study<sup>‡</sup> of (**1**) reveals a novel metal framework structure consisting of a  $\text{Ru}_4$  tetrahedron with one edge bridged by a  $\text{Cu}(\text{PCy}_3)$  unit and a non-adjacent face capped by the second  $\text{Cu}(\text{PCy}_3)$  group (Figure 1). At ambient temperature, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of (**1**) is a singlet, broadened by quadrupolar effects,<sup>3</sup> so the two  $\text{Cu}(\text{PCy}_3)$  units must be interchanging between edge-bridging and face-capping bond-

<sup>†</sup> Selected spectroscopic data (i.r. in  $\text{CH}_2\text{Cl}_2$ ; n.m.r. in  $\text{CD}_2\text{Cl}_2$ ; coupling constants in Hz). Compound (**1**): i.r.  $\nu_{\text{CO}}$  2063m, 2030s, 2000vs, br., 1975sh, 1943m, br., 1928sh, and 1915sh  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r.  $\delta$  -16.44 [t, 2 H,  $\mu_3\text{-H}$ ,  $J(\text{PH})$  5] and 1.25–2.15 (m, 66 H, cyclo- $\text{C}_6\text{H}_{11}$ );  $\mu_3\text{-H}$  at  $-100^\circ\text{C}$   $\delta$  -17.12 (br. s, 1 H) and -16.18 (br. s, 1 H);  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r.  $\delta$  19.4 (br. s); at  $-100^\circ\text{C}$   $\delta$  17.6 (br. s) and 17.2 (br. s). Compound (**2**): i.r.  $\nu_{\text{CO}}$  2063m, 2027s, 2000vs, br., 1980sh, and 1940m, v. br.  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r.  $\delta$  -16.64 [t, 2 H,  $\mu_3\text{-H}$ ,  $J(\text{PH})$  5], 1.25 [d of d, 36 H, Me,  $J(\text{PH})$  14 and  $J(\text{HH})$  7], and 2.26 [overlapping d of sept, 6 H,  $\text{CHMe}_2$ ,  $J(\text{PH})$  and  $J(\text{HH})$  7];  $\mu_3\text{-H}$  at  $-100^\circ\text{C}$   $\delta$  -17.09 [d, isomer A,  $J(\text{PH})$  10] and -16.15 (s, v. br., isomer B);  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r.  $\delta$  28.3 (br. s); at  $-90^\circ\text{C}$   $\delta$  32.0 (s, isomer A, 1 P), 26.0 (s, isomer B, 0.6 P), and 18.7 (s, isomer A, 1 P).

<sup>‡</sup> Crystal data for (**1**):  $\text{C}_{48}\text{H}_{68}\text{O}_{12}\text{Cu}_2\text{P}_2\text{Ru}_4$ ,  $M = 1429.37$ , monoclinic, space group  $P2_1/n$ ,  $a = 23.450(3)$ ,  $b = 22.475(3)$ ,  $c = 10.816(2)$  Å,  $\beta = 101.45(2)^\circ$ ,  $U = 5587.00$  Å<sup>3</sup>,  $F(000) = 2744$ ,  $\mu(\text{Mo-K}\alpha) = 20.24$   $\text{cm}^{-1}$ ,  $Z = 4$ ,  $D_c = 1.70$   $\text{g cm}^{-3}$ ;  $R = 0.0735$  for 2544 unique absorption-corrected data with  $I/\sigma(I) > 3.0$ .

Crystal data for (**2A**):  $\text{C}_{30}\text{H}_{44}\text{O}_{12}\text{Cu}_2\text{P}_2\text{Ru}_4$ ,  $M = 1189.37$ , monoclinic, space group  $P2_1$ ,  $a = 12.666(2)$ ,  $b = 15.115(3)$ ,  $c = 12.317(2)$  Å,  $\beta = 104.01(2)^\circ$ ,  $U = 2287.90$  Å<sup>3</sup>,  $F(000) = 1168$ ,  $\mu(\text{Mo-K}\alpha) = 21.60$   $\text{cm}^{-1}$ ,  $Z = 2$ ,  $D_c = 1.71$   $\text{g cm}^{-3}$ ;  $R = 0.0795$  for 2031 unique absorption-corrected data with  $I/\sigma(I) > 3.0$ .

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



cluster framework undergoes dynamic behaviour similar to that of (1), with a lower free energy of activation, cannot be completely discounted on the evidence available. Only one type of crystal has so far been obtained from solutions of (2); thus, the isomer (2B) has not yet been observed in the solid state. Very few examples of transition metal cluster compounds exhibiting skeletal isomerism have been reported previously.<sup>6-8</sup>

As the temperature is raised, the three <sup>31</sup>P-{<sup>1</sup>H} n.m.r. peaks attributed to the two isomers of [Cu<sub>2</sub>Ru<sub>4</sub>(μ<sub>3</sub>-H)<sub>2</sub>(CO)<sub>12</sub>{P(CHMe<sub>2</sub>)<sub>3</sub>}<sub>2</sub>], (2A) and (2B), all coalesce, as do the <sup>1</sup>H n.m.r. hydrido ligand signals. Eventually, at room temperature, a singlet, broadened by quadrupolar effects,<sup>3</sup> and a high-field triplet [*J*(PH) 5 Hz] are observed in the <sup>31</sup>P-{<sup>1</sup>H} and <sup>1</sup>H n.m.r. spectra, respectively. Clearly, the isomers (2A) and (2B) are interconverting in solution at ambient temperature and the isomer (2A) additionally undergoes the fluxional process involving coinage metal site-exchange that has been previously observed for (3).<sup>3</sup> Dynamic behaviour involving rapid intramolecular rearrangements of the metal skeletons of Group 1B metal heteronuclear clusters is well established,<sup>3,4</sup> but reports of an equilibrium between two skeletal isomers in solution are rare.<sup>7,8</sup>

The variation in the metal framework structures of the series of clusters (1)–(3) can be related to the steric requirements of the phosphine ligands present. The capped trigonal bipyramidal metal core, with the Cu atoms in close contact, appears to be the preferred geometry for relatively small phosphines.<sup>9</sup> Thus, it is the only structure observed for the PPh<sub>3</sub>-containing species (cone angle 145°)<sup>1</sup> (3).<sup>3</sup> However, with the slightly larger phosphine P(CHMe<sub>2</sub>)<sub>3</sub> (cone angle 160°),<sup>1</sup> a second isomer (2B), which probably has two face-capping Cu atoms with no bonding interaction between them, is also present in solution at low temperatures. The most bulky phosphine PCy<sub>3</sub> (cone angle 170°)<sup>1</sup> seems to be too large to allow two Cu(PCy<sub>3</sub>) units to be adjacent in the metal framework of (1) and, instead, a novel type of structure, in

which only one Cu atom adopts a face-capping position and the other occupies a sterically less demanding edge-bridging site, is observed.

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## References

- 1 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- 2 S. S. D. Brown and I. D. Salter, *Organomet. Synth.*, vol. 4, in the press.
- 3 M. J. Freeman, A. G. Orpen, and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, 1987, 379.
- 4 I. D. Salter, *Adv. Organomet. Chem.*, in the press.
- 5 S. S. D. Brown, I. D. Salter, T. Adatia, and M. McPartlin, *J. Organomet. Chem.*, 1987, **332**, C6.
- 6 B. R. Sutherland, D. M. Ho, J. C. Huffman, and K. G. Caulton, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 135; G. A. Moehring, P. E. Fanwick, and R. A. Walton, *Inorg. Chem.*, 1987, **26**, 1861; K. Henrick, B. F. G. Johnson, J. Lewis, J. Mace, M. McPartlin, and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1985, 1617; C. E. Briant, K. P. Hall, and D. M. P. Mingos, *ibid.*, 1984, 290; B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *Polyhedron*, 1982, **1**, 105.
- 7 S. R. Drake, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1988, **340**, C31; B. R. Sutherland, K. Folting, W. E. Streib, D. M. Ho, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1987, **109**, 3489; S. R. Bunkhall, H. D. Holden, B. F. G. Johnson, J. Lewis, G. N. Pain, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 25.
- 8 C. P. Horwitz, E. M. Holt, C. P. Brock, and D. F. Shriver, *J. Am. Chem. Soc.*, 1985, **107**, 8136; C. P. Horwitz and D. F. Shriver, *ibid.*, p. 8147.
- 9 P. J. McCarthy, I. D. Salter, and V. Šik, *J. Organomet. Chem.*, 1988, **344**, 411.