

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 CHMe_2)

Trushar Adatia,^a Paul J. McCarthy,^b Mary McPartlin,^{*a} Mine Rizza,^a and Ian D. Salter^{*b}

^a School of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.

^b Department of Chemistry, University of Exeter, Exeter EX4 4QD, U.K.

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 Cu_2Ru_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 R [$\text{R} = \text{cyclo-C}_6\text{H}_{11}(\text{Cy})$, CHMe_2 , or Ph], demonstrates that the metal framework is significantly altered by variations in the cone angles¹ of the monodentate phosphine ligands attached to the Cu atoms.

Treatment of a CH_2Cl_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°C , followed by the addition of 2 equiv. of 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 CHMe_2 (**2**)] in ca. 60% yield. Although the i.r. and n.m.r. spectroscopic data[†] for (**1**) and

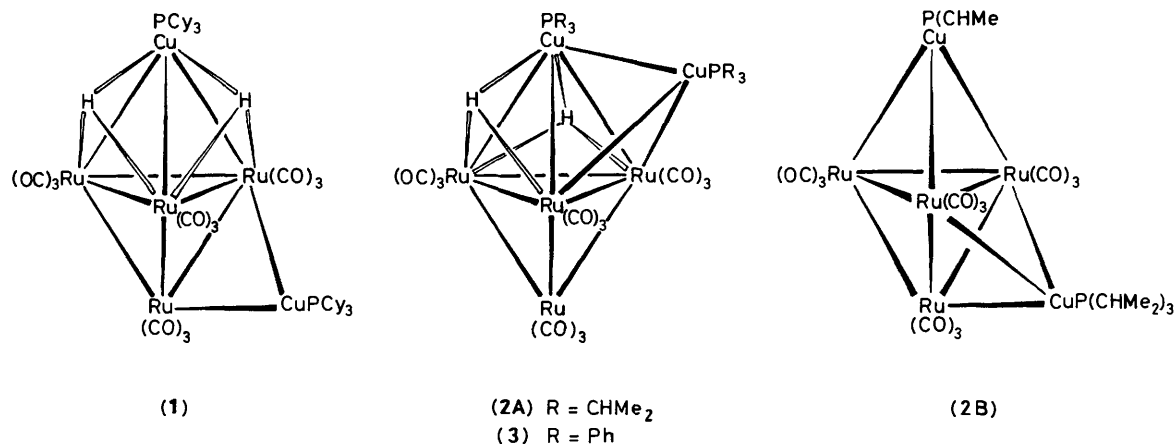
(**2**) are consistent with the proposed formulations, the spectra of (**1**) are significantly different from those reported for the analogous PPh_3 -containing species $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PPh}_3)_2]$ (**3**), implying that (**1**) adopts a different metal core structure from the capped trigonal bipyramidal skeletal geometry previously established for (**3**).³ An X-ray diffraction study[‡] of (**1**) reveals a novel metal framework structure consisting of a 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,³ so the two $\text{Cu}(\text{PCy}_3)$ units must be interchanging between edge-bridging and face-capping bond-

[†] Selected spectroscopic data (i.r. in CH_2Cl_2 ; n.m.r. in CD_2Cl_2 ; coupling constants in Hz). Compound (**1**): i.r. ν_{CO} 2063m, 2030s, 2000vs, br., 1975sh, 1943m, br., 1928sh, and 1915sh cm^{-1} ; ^1H n.m.r. δ -16.44 [t, 2 H, $\mu_3\text{-H}$, $J(\text{PH})$ 5] and 1.25–2.15 (m, 66 H, cyclo- C_6H_{11}); $\mu_3\text{-H}$ at -100°C δ -17.12 (br. s, 1 H) and -16.18 (br. s, 1 H); $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. δ 19.4 (br. s); at -100°C δ 17.6 (br. s) and 17.2 (br. s). Compound (**2**): i.r. ν_{CO} 2063m, 2027s, 2000vs, br., 1980sh, and 1940m, v. br. cm^{-1} ; ^1H n.m.r. δ -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, CHMe_2 , $J(\text{PH})$ and $J(\text{HH})$ 7]; $\mu_3\text{-H}$ at -100°C δ -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. δ 28.3 (br. s); at -90°C δ 32.0 (s, isomer A, 1 P), 26.0 (s, isomer B, 0.6 P), and 18.7 (s, isomer A, 1 P).

[‡] 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, $\beta = 101.45(2)^\circ$, $U = 5587.00$ Å³, $F(000) = 2744$, $\mu(\text{Mo-K}\alpha) = 20.24$ cm^{-1} , $Z = 4$, $D_c = 1.70$ 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, $\beta = 104.01(2)^\circ$, $U = 2287.90$ Å³, $F(000) = 1168$, $\mu(\text{Mo-K}\alpha) = 21.60$ cm^{-1} , $Z = 2$, $D_c = 1.71$ 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.



The positions of the two hydrido ligands in (2B) are not known.

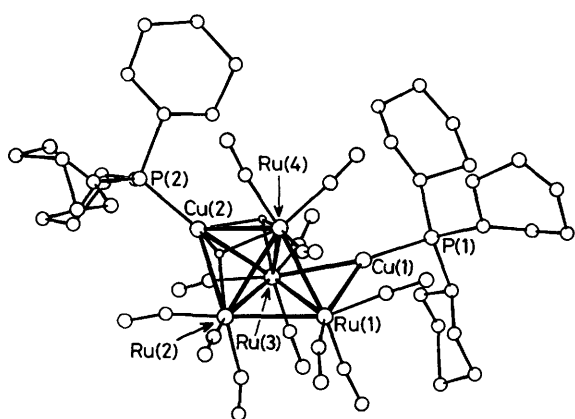


Figure 1. Molecular structure of $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}\{\text{P}(\text{cyclo-C}_6\text{H}_{11})_3\}_2]$ (1). Principal bond lengths: Ru(1)–Ru(2) 2.792(2), Ru(1)–Ru(3) 2.885(2), Ru(1)–Ru(4) 2.807(2), Ru(1)–Cu(1) 2.619(3), Ru(2)–Ru(3) 2.822(2), Ru(2)–Ru(4) 2.946(2), Ru(2)–Cu(2) 2.711(3), Ru(3)–Ru(4) 2.960(2), Ru(3)–Cu(1) 2.625(3), Ru(3)–Cu(2) 2.634(3), Ru(4)–Cu(2) 2.565(3), mean Cu–P 2.298(9), Ru–CO range 1.79–1.93(7) Å.

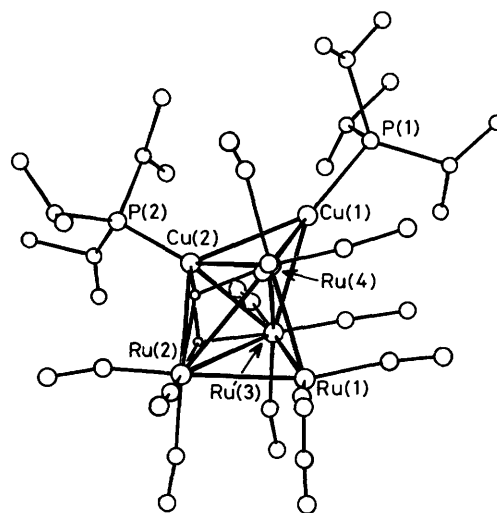


Figure 2. Molecular structure of $[\text{Cu}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}\{\text{P}(\text{CHMe}_2)_3\}_2]$ (2A). Principal bond lengths: Ru(1)–Ru(2) 2.835(4), Ru(1)–Ru(3) 2.699(7), Ru(1)–Ru(4) 2.743(8), Ru(2)–Ru(3) 3.253(4), Ru(2)–Ru(4) 3.204(4), Ru(2)–Cu(2) 3.049(5), Ru(3)–Ru(4) 2.906(5), Ru(3)–Cu(1) 2.780(8), Ru(3)–Cu(2) 2.616(10), Ru(4)–Cu(1) 2.911(9), Ru(4)–Cu(2) 2.585(10), Cu(1)–Cu(2) 3.010(6), mean Cu–P 2.318(11), Ru–CO range 1.78–2.06(4) Å.

ing modes in solution at this temperature. However, at -100°C , two broadened singlets are observed in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum, which is consistent with the ground state structure. Compound (1) is an unusual example of a mixed-metal cluster containing both edge-bridging and face-capping $\text{M}(\text{PR}_3)$ ($\text{M} = \text{Cu}, \text{Ag},$ or Au) groups⁴ and its skeletal geometry is in marked contrast to that of (3), in which both $\text{Cu}(\text{PPh}_3)$ fragments are face-capping and the Cu atoms are in close contact [Cu–Cu 2.699(2) Å].³

In contrast to those of (1) and (3),³ the $^{31}\text{P}\{-^1\text{H}\}$ and ^1H n.m.r. spectra of (2)[†] are consistent with the presence of two distinct skeletal isomers in solution at low temperatures. Three singlets (relative intensities 1:0.6:1) are visible in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum at -90°C and the ^1H n.m.r. high-field hydrido ligand signal consists of a sharp doublet [$J(\text{PH})$ 10 Hz] and a broadened singlet at -100°C .

The two equal-intensity $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. singlets and the ^1H n.m.r. high-field doublet closely resemble the low temperature n.m.r. data reported for (3), so they can be assigned to an isomer [(2A); 77% abundance] with a metal core of the type observed for (3).³ An X-ray structure analysis[‡] of (2) (Figure 2) shows a metal framework of the type predicted for the

isomer (2A), which consists of a capped trigonal bipyramidal Cu_2Ru_4 unit, similar to that reported for (3),³ with a direct Cu–Cu linkage.

The presence in solution of a second isomer [(2B); 23% abundance] is deduced from the remaining n.m.r. signals, the broadened ^1H n.m.r. singlet and the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. peak at δ 26.0. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (2B) is a sharp singlet at -100°C , in contrast to that of (1), which consists of two broadened signals at the same temperature. Thus, the n.m.r. evidence is consistent with isomer (2B) having a Cu_2Ru_4 metal framework which is different not only from that in isomer (2A) but also from the edge-bridged trigonal bipyramid in (1). It seems probable that (2B) adopts a structure in which the Cu atoms cap different faces of the Ru_4 tetrahedron, giving the phosphine ligands identical environments, an arrangement which has been previously observed in $[\text{Cu}_2\text{Ru}_4(\mu\text{-CO})_3(\text{CO})_{10}(\text{PPh}_3)_2]$.⁵ The possibility that (2B) has a metal core structure of the novel type observed for (1) and that the

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.⁶⁻⁸

As the temperature is raised, the three ³¹P-{¹H} n.m.r. peaks attributed to the two isomers of [Cu₂Ru₄(μ₃-H)₂(CO)₁₂{P(CHMe₂)₃}₂], (2A) and (2B), all coalesce, as do the ¹H n.m.r. hydrido ligand signals. Eventually, at room temperature, a singlet, broadened by quadrupolar effects,³ and a high-field triplet [*J*(PH) 5 Hz] are observed in the ³¹P-{¹H} and ¹H 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).³ Dynamic behaviour involving rapid intramolecular rearrangements of the metal skeletons of Group 1B metal heteronuclear clusters is well established,^{3,4} but reports of an equilibrium between two skeletal isomers in solution are rare.^{7,8}

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.⁹ Thus, it is the only structure observed for the PPh₃-containing species (cone angle 145°)¹ (3).³ However, with the slightly larger phosphine P(CHMe₂)₃ (cone angle 160°),¹ 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 PCy₃ (cone angle 170°)¹ seems to be too large to allow two Cu(PCy₃) 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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