

to be close to unity, a maximum isotope effect on the chemical shift will be observed when the equilibrium constant itself is close to unity. Noteworthy in this respect is *trans*-1,3-cyclohexanediol (**16**), for which  $K = P_{1ax,3eq}/P_{1eq,3ax} \approx 1$ . The chemical shift difference at C4 between the *cis*-isomer **15**, where the hydroxyls are equatorial, and the *trans*-isomer **16**, where the hydroxyls are half of the time axial and the other half equatorial, is 0.9 ppm. Thus, the value of  $\delta_b - \delta_a$  can be estimated at 1.8 ppm. The observed long-range isotope effect is 0.011 ppm. Solving eq 2 for  $k$  and using these values, one obtains  $k = 1.025$ , i.e., the deuterated hydroxyl prefers the equatorial orientation over the axial one by a factor of 1.025. Isotope effects of similar magnitude have been observed in dimethylcyclohexane derivatives.<sup>11</sup> Preference for the axial orientation of trideuteriomethyl groups has been demonstrated.<sup>11,12</sup> The equatorial preference of the deuteriohydroxyl is probably related to solvation effects.

In 2,2,4-trimethyl-1,3-pentanediol (**8**) only the carbon resonance of the CH<sub>2</sub>OH group exhibits the long-range isotope effect. The most likely origin of this effect is isotopic perturbation of an equilibrium involving the CHOH...*(OH)CH*<sub>2</sub> intramolecular hydrogen bond and a conformation lacking such a bond. Indeed, such equilibria for  $\beta$ -diols are well-known in the literature.<sup>13,14</sup> The absence of long-range isotope effects in other molecules investigated in this work suggests that in these molecules the equilibrium strongly favors only one of the structures.

The situation in 2,2,6,6-tetramethylcyclohexanol (**20**) is much more complex. Here C1 experiences long-range isotope effects from all four primary hydroxyls, whereas only the resonance of the *cis*-CH<sub>2</sub>OH groups exhibits a long-range effect. The ring hydroxyl, which must be equatorial, is probably involved in intramolecular hydrogen bonding with the hydroxymethyl groups both as a hydrogen donor and as an acceptor. This is probably also true for the *cis*-hydroxymethyls, which are axial.

### Conclusions

The isotopic multiplets in the <sup>13</sup>C NMR spectra of polyols with partially deuterated hydroxyls are analogous to spin-spin multiplets. Their pattern is predictable on statistical grounds. The variation of the  $\gamma$ -effect with the degree of substitution of the carbon atom suggests that the main mechanism for these effects is isotopic perturbation of the thermal distribution of molecules over excited vibrational states. Isotope effects extending over four and five bonds are due to isotopic perturbations of chemical equilibria involving intramolecular hydrogen bonding in  $\beta$ -diols or, in *trans*-1,3-cyclohexanediol, a preference for the equatorial orientation of deuterated hydroxyl groups.

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## Communications to the Editor

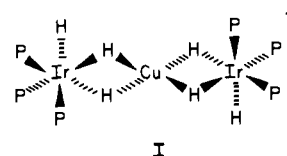
### Multiple Mixed-Metal Condensation Leading to the Pentagonal Bipyramidal Hexahydride $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$

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We have reported earlier that  $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ , an operational source of naked "Cu<sup>+</sup>", finds adequate electron density in the hydride ligands of several transition-metal polyhydride complexes to condense to hydride-rich mixed-metal clusters.<sup>1,2</sup> In the cases of  $\text{CuRe}_2\text{H}_{10}(\text{PMePh}_2)_6^{+1}$  and the structurally distinct *fac* and *mer* isomers of  $\text{CuIr}_2\text{H}_6(\text{PMe}_2\text{Ph})_6^{+2}$  the resulting trimetal backbone is linear. In the case of  $\text{Cu}_2\text{Re}_4\text{H}_{16}(\text{PMe}_2\text{Ph})_8^{2+}$ ,<sup>1</sup> a planar (rhomboidal) raft of six metals is formed in which two coppers are separated by 2.493 Å. Acetonitrile is absent from all of these products.

A surprising feature of  $\text{Cu}(\eta^2\text{-fac-IrH}_3\text{P}_3)_2^{2,3}$  (**I**) is the presence of terminal hydride ligands, not involved in bonding to copper. We have now explored the  $\text{Cu}^+/\text{fac-IrH}_3(\text{PMe}_2\text{Ph})_3$  system, at Ir/Cu stoichiometries lower than 2:1, and find evidence for an



unexpected yet isolable aggregate. At a mole ratio of 2:3, *fac*- $\text{IrH}_3\text{P}_3$  and  $\text{Cu}(\text{NCMe})_4\text{PF}_6$  react in THF ( $-78^\circ\text{C}$ , subsequently warmed to  $25^\circ\text{C}$ ) to yield a colorless precipitate.<sup>4</sup> The <sup>1</sup>H NMR of the precipitated product shows single chemical shifts for MeCN,  $\text{Me}_2\text{PPh}$ , and hydride hydrogens in the *ligand* ratio 1.5:3:3. The  $\text{Me}_2\text{PPh}$  resonance is a doublet, consistent with *cis* disposition of the phosphines, and the hydride resonance is a broad doublet. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows only a singlet, but selective coupling to the hydride hydrogens reveals an AA'A'XX'X'' pattern. The infrared spectrum (Nujol) shows bands characteristic of coordinated MeCN (2302 and 2272 (s)  $\text{cm}^{-1}$ ) and of bridging hydrides (1759(s), 1789 (sh)  $\text{cm}^{-1}$ ).

The X-ray crystal structure<sup>5</sup> of this material, crystallized as hexagonal plates by cooling from  $\text{CH}_2\text{Cl}_2$ , shows it to have the

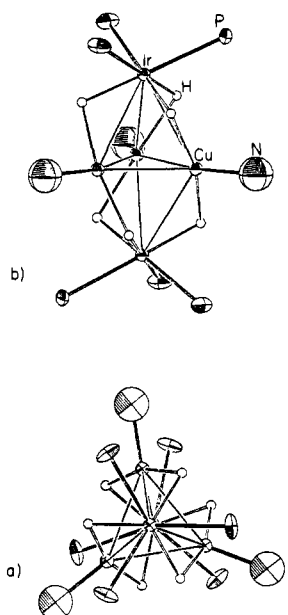
(4) The <sup>31</sup>P{<sup>1</sup>H} NMR of the filtrate showed the presence of some  $\text{Cu}(\eta^2\text{-fac-IrH}_3\text{P}_3)_2^{2+}$ .

(5) Crystallographic data ( $-158^\circ\text{C}$ ): space group  $R\bar{3}2$ ,  $a = b = 12.317$  (2) Å,  $c = 42.629$  (11) Å,  $Z = 3$ ;  $R_F = 7.1\%$ ,  $R_wF = 7.6\%$  for 1199 observed ( $I > 3\sigma$ ) reflections. The cation has a crystallographic  $C_3$  axis passing through the iridiums and three crystallographic  $C_2$  axes in the  $\text{Cu}_3$  plane. The cations suffer a disorder of the three copper atoms over a planar hexagonal shape (60:40 occupancy); the acetonitrile molecules bound to these coppers lie slightly off the crystallographic  $C_2$  axes and thus suffer additional disorder. The two crystallographically independent  $\text{PF}_6^-$  ions display high thermal motion.

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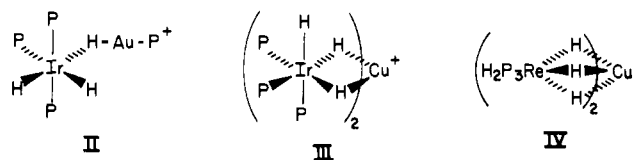


**Figure 1.** ORTEP views down (a) and nearly perpendicular to (b) the crystallographic  $C_3$  symmetry axis of  $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{NCMe})_3(\text{PMe}_2\text{Ph})_6^{3+}$ . Only the metals and the inner coordination sphere are shown (i.e., P, acetonitrile N, and hydride). The hydride positions have been added to the heavy atom structure determined by X-ray data by assuming colinearity with the Ir-P vectors and using an Ir-( $\mu$ -H) distance of 1.75.<sup>13</sup> This gives a Cu-( $\mu$ -H) distance of 1.91 Å. Selected structural parameters: Cu-Ir, 2.793 (9); Cu-Cu, 2.570 (22); Ir-P, 2.347 (6) Å;  $\angle$ P-Ir-P, 101.7 (2)°.

formula  $[\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6](\text{PF}_6)_3$ . The metal atoms adopt a trigonal bipyramidal form (Figure 1), with iridium axial and a facial array of three phosphines on each iridium. Each copper is bonded to one acetonitrile. Unlike trigonal bipyramidal<sup>6,7</sup>  $\text{Cu}_5(\mu_2\text{-Ph})_6^-$  and  $\text{Cu}_5(\mu_2\text{-S-}i\text{-Bu})_6^-$ , both of which have nonbonded Cu...Cu distances of  $>3.1$  Å between the (equatorial) coppers, the copper-copper separation in  $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$  is bonding (2.57 (2) Å). Although hydride atoms were not located by using the diffraction data, they can be confidently placed in positions trans to the Ir-P vectors on the basis of the AA'A''XX'X'' patterns in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.<sup>8</sup> Curiously, this puts them neither precisely over the Cu-Ir lines nor symmetrically over the  $\text{Cu}_2\text{Ir}$  triangular faces (Figure 1a).

Each metal center in the observed structure achieves an 18 valence electron count if  $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$  is dissected into  $6\text{H}^+$  and  $\text{Ir}_2\text{Cu}_3(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3-}$  in order to eliminate the question of how to count  $\mu$ -hydrides. Every metal-metal edge must be considered as being a single bond in the 3-ion, and the actual ion is then reconstituted by protonating all six Ir-Cu bonds.<sup>9</sup> In this same formalism,  $\text{CuIr}_2\text{H}_6(\text{PMe}_2\text{Ph})_6^+$  has two Ir=Cu double bonds, each of which is doubly protonated (see I). Consistent with this, the Ir-Cu separation in  $\text{CuIr}_2\text{H}_6(\text{PMe}_2\text{Ph})_6^+$  (2.51 Å) is 0.28 Å shorter than that in the  $\text{Ir}_2\text{Cu}_3$  cation reported here (2.79 Å).

The structural chemistry developed thus far between group 11 cations and metal polyhydrides shows a persuasive analogy between the polyhydride unit and coordinated  $\text{BH}_4^-$ , II,<sup>10</sup> III, and IV corresponding to  $\eta^1$ -,  $\eta^2$ -, and  $\eta^3$ - $\text{BH}_4^-$ . In  $\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6^{3+}$  we have an analogue of  $\mu, \eta^3$ - $\text{BH}_4^-$  found in  $\text{Fe}_2\text{H}(\text{BH}_4)(\text{CO})_9$ .<sup>11</sup> This analogy works in both directions, suggesting



$\text{Cu}_3(\text{NCMe})_3(\mu, \eta^3\text{-BH}_4)_2^+$  as a plausible synthetic target. Finally, an accompanying paper shows how three  $\text{H}_3\text{RhP}_3$  units may bridge all edges of an  $\text{Ag}_3^{3+}$  triangle in a  $\mu_2, \eta^3$  fashion, analogous to the bridging borohydride in  $\{\text{CoBH}_4[\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2]\}_2$ .<sup>12</sup>

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**Registry No.** *fac*- $\text{IrH}_3\text{P}_3$ , 12099-83-1;  $\text{Cu}(\text{NCMe})_4\text{PF}_6$ , 64443-05-6;  $[\text{Ir}_2\text{Cu}_3\text{H}_6(\text{MeCN})_3(\text{PMe}_2\text{Ph})_6](\text{PF}_6)_3$ , 95018-01-2; Cu, 7440-50-8; Ir, 7439-88-5.

**Supplementary Material Available:** Listing of atom coordinates, bond lengths, and bond angles for  $[\text{Cu}_3(\text{NCMe})_3[\text{IrH}_3(\text{PMe}_2\text{Ph})_3]]_2(\text{PF}_6)_3$  (2 pages). Ordering information is given on any current masthead page.

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## Formation of a Planar Hexametallc Cluster Containing a Triangle of Silver Atoms within a Triangle of Rhodium Atoms

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One of the most recurrent features of transition-metal cluster chemistry is the presence of triangular metal units.<sup>1</sup> Such units have also been found in cluster compounds of the coinage metals and of gold in particular.<sup>2</sup> It has also been observed that these "building blocks" frequently contained one or more hydrogen atoms in bridging positions between two or more metal atoms.<sup>3</sup> Furthermore, tripodlike ligands facilitate both cluster<sup>4</sup> and hydrogen-bridge<sup>5</sup> formation. Thus, attempts to obtain mononuclear hydrido complexes of elements of the first transition series containing the ligand  $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$  (tripod) resulted in the formation of the binuclear compounds  $[(\text{tripod})\text{M}(\mu\text{-H})_3\text{M}(\text{tripod})]^+$  (M = Fe and Co).<sup>6</sup>

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