

Copper Polyhydrides

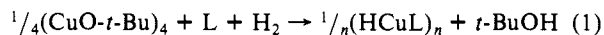
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We continue¹ here our exploration of soluble phosphine complexes of Cu(I) hydrides directed toward improved understanding of the conversion of CO/H₂ mixtures to methanol catalyzed by oxides of copper and zinc.² We established previously the unusual (positive δ value) ¹H chemical shift and fluxionality of the hydride ligands in [HCuP(*p*-tolyl)₃]₆,¹ but two X-ray diffraction studies³ have failed to establish the structural preference of the hydride ligands in such polyhydrides. We report here the resolution of this question, as well as the surprising variability of aggregate size in these clusters.

Hydrogenolysis of Cu-O-*t*-Bu bonds (eq 1, in THF) is a quite



versatile synthetic method for copper phosphine polyhydrides. Thus, for L = P(NMe₂)₃ we isolate red crystals of H₆Cu₆[P(NMe₂)₃]₆. The analogous deuteride (from D₂ in eq 1) shows an infrared spectrum identical (400–4000 cm⁻¹) with that of the hydride, precluding location of metal hydride vibrations. If NMR spectra are recorded at -70 °C, a ³¹P{¹H} singlet (112 ppm) and ¹H{³¹P} NMe singlet (2.81 ppm) are detected.⁴ The ²H NMR spectrum of D₆Cu₆[P(NMe₂)₃]₆ exhibits a D-Cu resonance at δ 2.57 (-70 °C, full width at half-height = 7 Hz) devoid of detectable D/P coupling. A single-crystal X-ray diffraction structure determination (Figure 1A)⁵ reveals a trigonal-antiprismatic array of six coppers, each with a terminal phosphorus ligand.⁶ The Cu₆ unit lacks rigorous octahedral symmetry in that the Cu/Cu distances are of two types: six longer ones (2.804 Å) form two parallel equilateral triangles on opposite faces of the trigonal antiprism. The apices of these triangles are interconnected by six shorter Cu/Cu distances (2.508 Å). This trigonal-antiprismatic Cu₆ form is also seen in (HCuPAR₃)₆, Ar = C₆H₅ and *p*-tolyl.³ Unlike these earlier structure determinations, the hydride ligands have been located and refined by using X-ray data collected at -162 °C. These hydride ligands triply bridge the six symmetry-equivalent lateral isosceles triangles which flank the S₆ axis of the hexamer. This polyhedral form is also present in Pd₆[Fe(CO)₄]₆,⁴⁻ Fe₆S₆Cl₆,^{7a} NaO-*t*-Bu,^{7c} and (LiC₆H₁₁)₆.^{7d} The hydride projects 0.8 Å out of the triangle bounded by the two 2.508-Å edges and one 2.804-Å edge. These metal-metal distances differ by as much as 0.14 Å from those in their PAR₃ analogues. Since the identity of the ligand does not typically influence metal-metal bond lengths to this extent,⁸ we conclude that such malleable distances indicate at most weak Cu-Cu interactions.

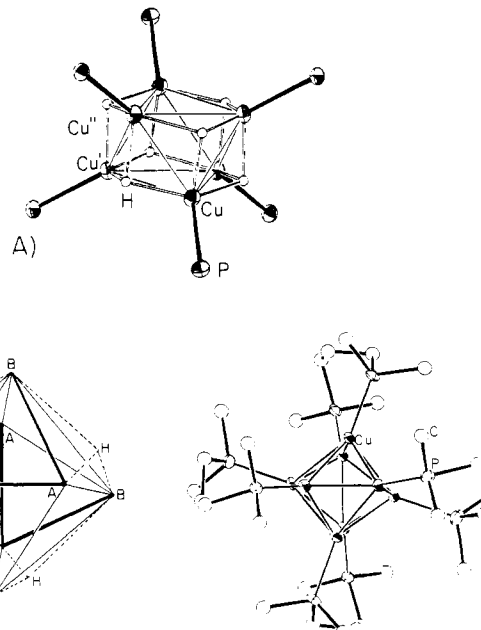


Figure 1. (A) ORTEP drawing of the (HCuP)₆ portion of [HCuP(NMe₂)₃]₆. The crystallographic S₆ axis lies vertically in this view. Bond lengths (Å): Cu-Cu' 2.804 (3), Cu-Cu'' 2.508 (2), Cu-H 1.66 (8), Cu'-H, 1.75 (8), Cu''-H 1.71 (8), Cu-P 2.234 (3). (B) (Right) ORTEP drawing of H₈Cu₈[Ph₂P(CH₂)₃PPh₂]₄, viewed down the idealized S₄ axis. Only ipso phenyl carbons are shown, and all hydrogens are omitted. (Left) Idealized view down the S₄ axis of the Cu₈ dodecahedron, showing the following reduction in symmetry to S₄: dark Cu-Cu lines 2.453 (3)–2.517 (3) Å, light Cu-Cu lines, 2.676 (3)–2.738 (3) Å. Dotted lines show proposed location of four of the eight hydride ligands. P-Cu(A site) = 2.227 (4) Å; P-Cu(B site) = 2.263 (4) Å.

The influence of a chelating phosphine on eq 1 was probed using Ph₂P(CH₂)₃PPh₂ (dppp) at a dppp:Cu ratio of 0.5:1. Under 1000 psi of H₂ in THF, a yellow (cf. red [HCuP(NMe₂)₃]₆) solid was isolated. This compound is remarkable in displaying two ³¹P chemical shifts (1:1 intensity),⁹ each of whose broadening indicates coordination to quadrupolar copper; the spectrum is unchanged between +20 and -70 °C. The ²H NMR of the analogous deuteride revealed a resonance at δ 1.86 (8 Hz wide), but the absence of resolvable D/P coupling precludes probing stoichiometry and structure. Since two phosphorus environments are inconsistent with a trigonal-antiprismatic arrangement, the structure in Figure 1B was ascertained by using X-ray diffraction.¹⁰ H₈Cu₈(dppp)₄ is the first transition-metal homopolyatomic aggregate shown to adopt a dodecahedral form. The chelate ligand connects A to B copper sites within an A₂B₂ trapezoid,¹¹ consistent with the ³¹P NMR spectrum provided the dodecahedron is stereochemically rigid. H₈Cu₈(dppp)₄ is thus noteworthy for lacking facile deformability displayed by other dodecahedra.¹² Figure 1B reveals that the Cu/Cu distances effect a reduction in symmetry from rigorous dodecahedral (D_{2d}) to S₄. The S₄ form adopted has four each of three types of faces. While hydride ligands are not yet evident in the X-ray data, we suggest that four of these lie above the faces bounded by short/short/long Cu/Cu distances, with the remainder on short/long/long faces as sketched in Figure 1B. The long/long/long faces are unoccupied, as is the case for (HCuPR₃)₆.

The propensity for aggregation, by hydride bridging, of copper hydrides is also evident in numerous reports¹³⁻¹⁵ of phenyl/copper

(1) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(2) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.

(3) (a) Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818. (b) Ho, D. M.; Bau, R. *Inorg. Chim. Acta* **1984**, *84*, 213.

(4) Both the ³¹P and ¹H NMR spectra are time-dependent within 0.5 min of dissolving in toluene-d₈, revealing complex transformations currently under study, including liberation of free P(NMe₂)₃. Added P(NMe₂)₃ has been used to retard these reactions.

(5) Crystals of [HCuP(NMe₂)₃]₆·THF grown from THF adopt space group P $\bar{3}$ with (-162 °C) *a* = 13.401 (9) Å, *c* = 11.712 (0) Å, *Z* = 1. *R*(*F*) = 0.0490 and *R*_w(*F*) = 0.0423 for 1066 reflections (3 σ), refining all atoms, including hydrogens. The molecule possesses crystallographic $\bar{3}$ symmetry. Positional and thermal parameters are available as supplementary material.

(6) There is no evidence of N→Cu or N...HCu interactions.

(7) (a) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242. (b) Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R.; Coucouvanis, D. *J. Am. Chem. Soc.* **1985**, *107*, 953. (c) Greiser, T.; Weiss, E. *Chem. Ber.* **1977**, *110*, 3388. (d) Zerger, R.; Rhine, w.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048.

(8) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; p 156 ff.

(9) ³¹P chemical shifts: -9.5 and -14.6 ppm.

(10) Crystals grown from toluene/pentane assume space group P $\bar{1}$ with (-156 °C) *a* = 19.329 (9) Å, *b* = 19.405 (9) Å, *c* = 15.332 (7) Å, α = 104.62 (2)°, β = 84.38 (3)°, γ = 89.92 (3)°, and *Z* = 2. *R*(*F*) = 0.098 and *R*_w(*F*) = 0.092 for 12306 reflections. Positional parameters are available as supplementary material.

(11) Hoard, J. L.; Silvertown, I. V. *Inorg. Chem.* **1963**, *2*, 235.

(12) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.

(13) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1979**, *174*, 121.

(14) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149.

chemistry, where (1-electron donor) phenyl rings bridge between coppers. Finally, the results reported here call attention to the possibility that some of the numerous phosphino gold clusters,¹⁶⁻¹⁷ many of which are synthesized by using BH_4^- , contain undiscovered hydride ligands.

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Supplementary Material Available: Atomic positional and thermal parameters for the two copper hydrides (4 pages). Ordering information is given on any current masthead page.

(15) Khan, S. I.; Edwards, P. G.; Yuan, H. S. H.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1682.

(16) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.

(17) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237.

Formation of Stable Tungsten Alkene Carbyne Complexes by Carbonyl Substitution Reactions

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Reactions of alkenes and alkynes with metal complexes containing unsaturated metal-carbon bonds have been the subject of continued interest because of their involvement in olefin¹ and acetylene² metathesis, as well as polymerization³ reactions. *trans*-Halotetracarbonyltungsten carbyne complexes have been shown to induce polymerization of both certain alkenes⁴ and alkynes.⁵ We have recently⁶ developed simple synthetic routes to substituted carbyne complexes $\text{X}(\text{CO})_2(\text{L})_2\text{M}\equiv\text{CR}$ (X = halide; L = nitrogen donor ligand; M = Cr, Mo, W) and have begun to investigate reactions of tungsten systems with unsaturated organic molecules. Here we wish to report ligand substitution reactions that provide easy access to a new class of tungsten carbyne complexes containing alkene ligands.⁷

Reaction of the bis(pyridine)-substituted carbyne complexes $\text{Cl}(\text{CO})_2(\text{py})_2\text{W}\equiv\text{CR}$, **1** and **2** (1, R = C_6H_5 ; 2, R = CH_3), with excess (10 equiv) tetraethylammonium chloride in dichloromethane affords the anionic carbyne complexes $\text{NEt}_4[\text{Cl}_2(\text{py})(\text{CO})_2\text{W}\equiv\text{C}$

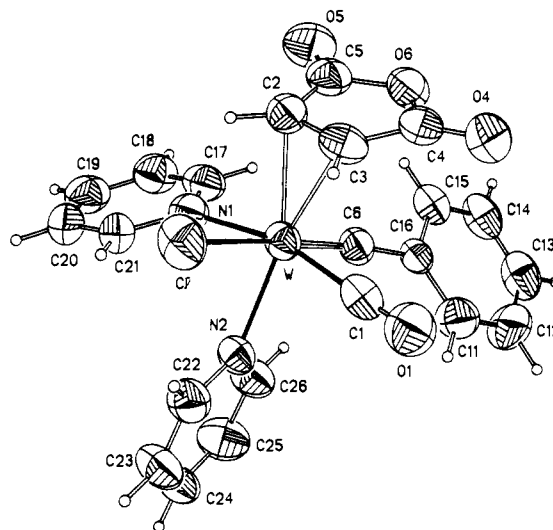
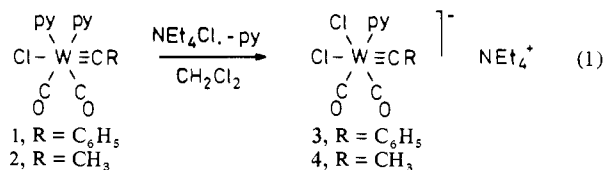
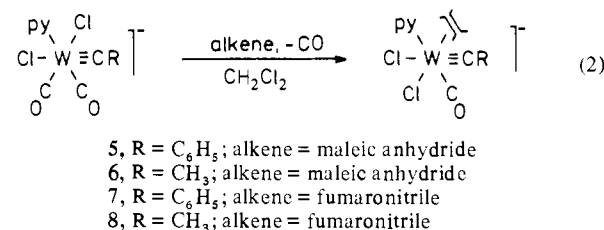


Figure 1. Molecular structure of $\text{Cl}(\text{CO})(\text{maleic anhydride})(\text{py})_2\text{W}\equiv\text{CPh}$ (**9**). 50% thermal ellipsoids. W-C(6), 1.801 (6); W-N(1), 2.233 (5); W-N(2), 2.253 (4); W-Cl, 2.538 (1); W-C(1), 2.033 (6); W-C(2), 2.215 (6); W-C(3), 2.272 (6); C(2)-C(3), 1.408 (8) Å. Cl-W-C(6), 171.2 (2)°; N(1)-W-C(1), 165.4 (2)°; [M = midpoint of C(2)-C(3)] M-W-N(2), 170.8 (2)°; M-W-C(6), 96.4 (2)°; M-W-C(1), 91.4 (2)°; M-W-N(1), 102.1 (2)°; M-W-Cl, 83.2 (1)°.

$\text{CR}]$, **3** and **4** (3, R = C_6H_5 ; 4, R = CH_3) (eq 1).⁸ These products are only stable in the presence of excess chloride.⁹



Complexes **3** and **4** react with maleic anhydride or fumaronitrile to give the stable anionic carbyne complexes $\text{NEt}_4[\text{Cl}_2(\text{py})(\text{CO})(\text{alkene})\text{W}\equiv\text{CR}]$, **5-8** (eq 2), which are isolated as non-



crystalline solids in 40-80% yield by extraction of the reaction residue with tetrahydrofuran (THF) and addition of ether to the reduced extracts.^{10,11} Only the isomers containing the two chloride

(1) (a) Grubbs, R. H. In "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 499-551.

(2) (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554-1562. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563-1573.

(3) (a) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331-2333. (b) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604-606.

(4) Fischer, E. O.; Wagner, W. R. *J. Organomet. Chem.* **1976**, *116*, C21-C22.

(5) Katz, T. J.; Ho, T. H.; Shih, N.-Y.; Ying, Y.-C.; Stuart, Van I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2659-2668.

(6) (a) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517-1518. (b) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608-610.

(7) The only previous example of this type of complex is $(\text{CF}_3\text{SO}_2)_3(\text{PMe}_2)_3(\text{C}_2\text{H}_4)\text{W}(\text{CH})$; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. *J. Organometallics* **1984**, *3*, 476-484.

(8) **3**: IR (cm^{-1} , CH_2Cl_2) ν_{CO} 1965 (s), 1867 (s); ^{13}C NMR (ppm, CDCl_3) 267.2 (CPh), 224.2 (CO), 221.8 (CO). **4**: IR (cm^{-1} , CH_2Cl_2) ν_{CO} 1961 (s), 1857 (s); ^{13}C NMR (ppm, CD_2Cl_2) 277.6 (CCH_3), 222.8 (CO), 219.9 (CO).

(9) Labile anionic dihalotetracarbonyltungsten carbyne complexes have previously been observed. Fischer, H.; Seitz, F. *J. Organomet. Chem.* **1984**, *268*, 247-258.

(10) **5**: IR (cm^{-1} , CH_2Cl_2) ν_{CO} 2041 (m), $\nu_{\text{C=O}}$ 1796 (m), 1728 (s); ^1H NMR (ppm, CDCl_3) 4.13 (d), 2.93 (d) ($J = 5.0$ Hz) ($\text{CH}=\text{CH}$); ^{13}C NMR (ppm, CDCl_3) 273.5 (CPh), 206.8 (CO), 175.3, 174.6 (C=O), 51.5 (d, $J_{\text{CH}} = 177$ Hz), 50.2 (d, $J_{\text{CH}} = 175$ Hz) (C=C). **6**: IR (cm^{-1} , CH_2Cl_2) ν_{CO} 2037 (s), $\nu_{\text{C=O}}$ 1793 (s), 1727 (s); ^1H NMR (ppm, CDCl_3) 3.99 (d), 2.79 (d) ($J = 4.9$ Hz) ($\text{CH}=\text{CH}$); ^{13}C NMR (ppm, CDCl_3) 285.6 (CMe), 207.2 (CO), 175.2, 174.7 (C=O), 49.8 (d, $J_{\text{CH}} = 177$ Hz), 47.9 (d, $J_{\text{CH}} = 176$ Hz) (C=C). **7**: Two diastereomers; IR (cm^{-1} , CH_2Cl_2) ν_{CN} 2210 (m), ν_{CO} 2046 (s); ^1H NMR (ppm, CDCl_3) 3.07 (d), 3.00 (d) ($J = 8.8$ Hz), 3.06 (d), 2.08 (d) ($J = 9.0$ Hz) ($\text{CH}=\text{CH}$); ^{13}C NMR (ppm, CDCl_3) 271.6, 270.4 (CPh), 208.8, 207.1 (CO), 30.9 (d, $J_{\text{CH}} = 164$ Hz), 30.6 (d, $J_{\text{CH}} = 184$ Hz), 28.8 (d, $J_{\text{CH}} = 166$ Hz), 27.9 (d, $J_{\text{CH}} = 185$ Hz). **8**: Two diastereomers; IR (cm^{-1} , CH_2Cl_2) ν_{CN} 2208 (m), ν_{CO} 2037 (s). ^1H NMR (ppm, CDCl_3) 2.92 (d), 2.82 (d) ($J = 8.3$ Hz), 2.80 (d), 1.97 (d) ($J = 8.5$ Hz) ($\text{CH}=\text{CH}$); ^{13}C NMR (ppm, CDCl_3) 285.1, 281.2 (CMe), 210.0, 207.7 (CO), 33.3, 29.9, 28.0, 26.6 (C=C).