distortion (ϕ) from a regular trigonal-prismatic coordination geometry, the metal–ligand bond distances (Ni–N in the present case), the bite distance of the chelate system (N(1)···N(2), etc., here), and the mean distance between metal-bonded atoms within the two triangular ends of the trigonal prism (*i.e.*, the mean of N(1)···N(1′) and N(2)···N(2′) distances in the present molecule). Based on the *distances* derived from the present structural analysis, the twist angle is calculated as 2° 12′ (found 1° 35′).

(ii) **Ligand Field Effects.**—Wentworth, *et al.*,[28] suggested that the tendency toward an octahedral (rather than trigonal-prismatic) geometry should decrease in the order: d^6 (low-spin) > d^8 > d^7 > d^{10} = d^5 (high-spin). That the present d^8 Ni(II) complex adopts a geometry very close to trigonal prismatic is indicative either of a very rigid cage or of the fulfillment of conditions outlined under (i).

(iii) **General Strain Effects.**—The simultaneous requirements for metal–ligand interactions coupled with retention of the total ligand geometry will almost certainly cause strain somewhere in the species. It is probably this net effect that causes the slight buckling of two of the three aldoximo moieties from their respective FB···(C_5H_3N)···P planes.

(iv) **Interionic Repulsion.**—We may note that there are some close contacts between the doubly primed aldoximopyridyl system and a BF_4^- anion. Thus H(5″)···F(3) = 2.348 Å, H(4″)···F(5) = 2.577 Å, and H(5″)···F(5) = 2.743 Å. [Accepted van der Waals radii for hydrogen and fluorine are ~1.2 and ~1.35 Å.[29]] Effects of this kind will not, of course, be maintained in solution.

The packing of ions within the unit cell is shown in Figure 4.

Further crystallographic studies on these systems, presently in progress, should help to clarify these findings. It should be noted that preliminary data on the d^6 iron(II) species [$\{FB(ONCHC_5H_3N)_3P\}(Fe^{II})^+$] show the mean twist angle, ϕ, to be 21° 32′.[16] Details of this structure, and of others in this series, will be published at a later date.

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Synthesis and Molecular Geometry of Hexameric Triphenylphosphinocopper(I) Hydride and the Crystal Structure of $H_6Cu_6(PPh_3)_6 \cdot HCONMe_2$

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The thermally stable phosphinocopper(I) hydride cluster $H_6Cu_6(PPh_3)_6$ has been prepared from the reaction of $(PPh_3CuCl)_4$ and sodium trimethoxyborohydride in dimethylformamide (DMF). It crystallizes from DMF as $H_6Cu_6(PPh_3)_6 \cdot DMF$ in the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}; No. 61) with $a = 40.10 \pm 0.04$, $b = 22.46 \pm 0.02$, $c = 21.86 \pm 0.02$ Å, and $Z = 8$. Observed and calculated densities are 1.367 ± 0.005 and 1.368 g cm^{-3}, respectively. A single-crystal X-ray diffraction study based on counter data ($\sin \theta_{max} = 0.65$, Cu Kα radiation) has led to the location of all 125 nonhydrogen atoms, the final discrepancy index being $R_F = 9.2\%$ for 3180 independent nonzero reflections. The crystal consists of discrete molecular units of $H_6Cu_6(PPh_3)_6$ and DMF, mutually separated by normal van der Waals distances. The $H_6Cu_6(PPh_3)_6$ molecule contains a (slightly distorted) octahedral cluster of copper atoms. Two mutually trans faces of this octahedron are enlarged with their copper–copper distances ranging from 2.632 (6) to 2.674 (5) and averaging 2.655 ± 0.017 Å, while the remaining six copper–copper bond lengths range from 2.494 (6) to 2.595 (5), averaging 2.542 ± 0.044 Å. Each copper atom is apically bonded to a triphenylphosphine ligand with copper–phosphorus distances varying from 2.217 (7) to 2.262 (7), averaging 2.240 ± 0.017 Å. Decomposition of the complex with $C_6H_5CO_2D$ yields H_2 and HD (but no D_2) in varying proportions. An assay of liberated [^{1}H]hydrogen indicates that the cluster is associated with *six* hydride ligands. Possible sites for these ligands (which were not located from the diffraction study) are discussed.

Introduction

Although Würtz prepared a "copper(I) hydride" rather more than a century ago,[3] no truly *stoichiometric* hydridocopper species has yet been isolated although indirect evidence has indicated that thermally unstable phosphine adducts of copper hydride [such as R_3P-$(CuH)_2$,[4] (diphos)$(CuH)_2$,[4] and (n-Bu_3P)CuH[5]] exist in solution.

We have now found that the reaction of tetrameric triphenylphosphinocopper chloride (also the corresponding bromide, iodide, cyanide, thiocyanate) with sodium trimethoxyborohydride in dimethylformamide (DMF) under an inert atmosphere yields hexameric

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triphenylphosphinocopper(I) hydride. The complex may be isolated as bright red crystals of composition $H_6Cu_6(PPh_3)_6 \cdot DMF$, which are soluble in benzene, slightly soluble in DMF, and insoluble in acetonitrile or water, and are apparently decomposed by alcohols, ethers, and chlorinated hydrocarbons. Solutions are air-sensitive, but the solid compound is thermally stable (mp 111° dec), may be handled in the air for several minutes without appreciable decomposition, and is stable indefinitely when stored at room temperature under argon or *in vacuo*. (In contrast to this, solid CuH is pyrophoric and decomposes above −20°.)

As described below, the partial identity of the copper cluster molecule was shown, by X-ray diffraction methods, to be $H_xCu_6(PPh_3)_6$. Determination of the number of hydride ligands (x) involved further chemical studies and was finally accomplished by analysis of the gaseous products (H_2, HD) resulting from the decomposition of the complex with monodeuteriobenzoic acid, $C_6H_5CO_2D$. No absorptions attributable to Cu–H vibrational modes were observed in the infrared spectrum, nor were any resonances attributable to hydride ligands seen in a ^1H nmr spectrum of the complex in C_6D_6 solution. [Similar negative observations are reported for solutions of $R_3P(CuH)_2$,[4] (diphos)$(CuH)_2$,[4] and (n-Bu_3P)CuH.[5]]

A preliminary account of this work has appeared previously.[6]

The X-Ray Diffraction Study

Unit Cell and Space Group.—The compound crystallizes as very thin hexagonal plates. Optical examination and the observed reciprocal lattice symmetry (D_{2h}; mmm) indicated that the crystals belonged to the orthorhombic system. Unit cell dimensions obtained from precession photographs taken with Cu Kα radiation (λ 1.5418 Å) at room temperature (23 ± 2°) and calibrated with lead nitrate ($a_{23°} = 7.8566$ Å[7]) were $a = 40.10 \pm 0.04$, $b = 22.46 \pm 0.02$, $c = 21.86 \pm 0.02$ A. The unit cell volume is 19,697 Å^3. Photographs of the levels $(0–1)kl$, $h(0–1)l$, and $hk(0–1)$ revealed the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$, characteristic only of space group $Pbca$ (D_{2h}^{15}; No. 61).[8] The calculated density for $H_6Cu_6(PPh_3)_6 \cdot DMF$ (mol wt = 2028) is 1.368 g cm^{-3} with $Z = 8$; the observed density was 1.367 ± 0.005 g cm^{-3}, determined by flotation in aqueous $CaBr_2$ solution.

Collection and Reduction of X-Ray Diffraction Data.—All crystals were extremely thin, fragile plates. Many gave a diffraction pattern with an unacceptably large mosaic spread and no crystal showed any data beyond $\sin\theta = 0.65$ on long-exposure (Cu Kα) Weissenberg photographs. The prospects for a successful X-ray structural analysis seemed remote. Happily, however, the limited amount of obtainable data proved sufficient to enable the structure to be solved.

Two crystals (each sealed, under argon, into a Lindemann glass capillary tube) were used during the collection of intensity data. Crystal B, mounted on its b axis, had approximate dimensions 0.016 × 0.42 × 0.30 mm (referred to **a**, **b**, **c**, respectively) while the c-mounted crystal C had dimensions of 0.024 × 0.30 × 0.30 mm.

In order to obtain reasonably strong diffraction data, and to minimize the possibility of overlap of adjacent reflections, intensity data were collected with Cu Kα radiation (λ 1.5418 Å) rather than with the less absorbed Mo Kα radiation. Data were collected on a Supper-Pace automated diffractometer using the "stationary-background, ω scan, stationary-background" technique which has been described previously.[9] Details specific to the present analysis include the following: (i) generator power was 49 kV/18 mA; (ii) $d\omega/dt = 2$ deg min^{-1}; (iii) $\omega = [1.7 + (0.8/L)]°$ for crystal B and $[1.4 + (0.7/L)]°$ for crystal C; (iv) check reflections were taken every 40 reflections; (v) initial and final backgrounds (B_1 and B_2 counts) were each taken for one-fourth the time of the ω-scan (C counts); (vi) the intensity, $I(hkl)$, of a reflection hkl was calculated by $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$. Weights were assigned to the data according to the scheme: $I(hkl) > 4900$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $I(hkl) \leqslant 4900$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$.

Reflections were omitted from the subsequent analysis on two bases: (a) reflection not significantly above background, *i.e.*, $I(hkl) \leqslant 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$, or (b) asymmetric background counts, indicating a possible overlap problem. The criterion used for rejection here was $B_1(hkl)/B_2(hkl)$ or $B_2(hkl)/B_1(hkl) \geqslant 3$.

Of 5695 independent reflections collected from levels $h(0–14)l$ ($\sin\theta_{max} = 0.65$) of crystal B, 2651 were rejected. Of 2256 independent reflections from levels $hk(0–5)$ of crystal C, 989 were rejected. (Almost all rejected reflections were not statistically above background level.) All data were corrected for Lorentz and polarization effects and absorption corrections were applied.[10] With $\mu = 30.67$ cm^{-1}, transmission coefficients ranged from 0.607 to 0.952 for crystal B (volume 1.15×10^{-6} cm^3) and from 0.516 to 0.929 for crystal C (volume 1.86×10^{-6} cm^3). All data were merged to a common scale by a least-squares procedure[11] and the resulting 3180 independent nonzero reflections were used to calculate a Wilson plot[12] from which the (approximate) absolute scale of the data and an overall thermal parameter ($\bar{B} = 1.45$ Å^2) were obtained.

Solution and Refinement of the Structure.—All crystallographic calculations were (unless otherwise specified) carried out using the CRYRM[13a] or CRYM[13b] systems on the Harvard University IBM 7094 and IBM 360/65 computers. Scattering factors for neutral phosphorus, nitrogen, carbon, oxygen, and hydrogen were taken from the compilation of Ibers.[14a] The phosphorus values and the Thomas–Fermi–Dirac values for neutral copper[14b] were corrected both for the real and for the imaginary component of dispersion [$\Delta f'(Cu) = -2.1$ e, $\Delta f''(Cu) = +0.7$ e, $\Delta f'(P) = +0.2$ e, $\Delta f''(P) = +0.5$ e].[14c]

Discrepancy indices used in this text are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|$,[4] where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\} = \sigma\{I(hkl)\}[F^2(hkl)]/[I(hkl)]$.

Attempts to locate "heavy atom" positions from a three-dimensional Patterson map proved fruitless; the phase problem was then solved by Sayre's method,[15] using a locally modified version of the IBM 7094 program REL.[16] Normalized structure factors, $E(hkl)$, were calculated from the expression

$$|E(hkl)| = |F(hkl)|\left[\epsilon^2 \sum_{j=1}^{j=N} f^2[j,\theta(hkl)]\right]^{-1/2}$$

Here, $|F(hkl)|$ is the structure factor amplitude for the reflection hkl, the sum $j = 1 \rightarrow N$ is over all atoms in the unit cell, $f[j,\theta(hkl)]$ is the scattering factor for the jth atom at the Bragg angle θ, ϵ adjusts for the degeneracy in $F(hkl)$ for reflections at symmetry locations in reciprocal space (in space group $Pbca$, $\epsilon = 2$ for $0kl$, $h0l$, $hk0$ reflections and $\epsilon = 1$ for all other reflections), and $\langle|E^2(hkl)|\rangle$ is normalized by application of a scale factor.

The origin of the unit cell was defined by assigning positive signs to three reflections of appropriate parity and high E value [*i.e.*, $E(2,1,11) = +3.54$, $E(134) = +3.37$, $E(2,11,4) = +2.24$]. Possible signs for the 234 reflections with $E \geqslant 1.5$ were obtained from phase pyramids based on the 16 possible sign combinations for the reflections 14,7,1 ($|E| = 3.43$), 631 ($|E| = 3.19$), 275 ($|E| = 3.11$), and 14,1,7 ($|E| = 2.99$). The 16 possible solu-

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TABLE I: FINAL PARAMETERS FOR $H_6Cu_6(PPh_3)_6\cdot HCONMe_2$

(A) Positional and Isotropic Thermal Parameters[a]

(i) Atoms of the Copper Cluster

Atom	x	y	z	B, Å²
Cu(1)	0.11902 (10)	−0.00671 (15)	0.16339 (18)	
Cu(2)	0.08279 (9)	0.06100 (15)	0.23288 (19)	
Cu(3)	0.14693 (9)	0.07533 (15)	0.23521 (19)	
Cu(4)	0.15440 (9)	−0.03938 (16)	0.25931 (19)	
Cu(5)	0.09278 (9)	−0.05474 (15)	0.25434 (19)	
Cu(6)	0.11915 (10)	0.02807 (15)	0.32702 (18)	
P(1)	0.10843 (18)	−0.03405 (29)	0.06687 (36)	
P(2)	0.04434 (18)	0.13139 (29)	0.21459 (34)	
P(3)	0.18219 (17)	0.15368 (29)	0.23741 (36)	
P(4)	0.19672 (18)	−0.10298 (31)	0.26511 (38)	
P(5)	0.05894 (17)	−0.13196 (29)	0.26991 (37)	
P(6)	0.10829 (20)	0.04524 (30)	0.42625 (35)	
C(1)	0.0664 (6)	−0.0612 (11)	0.0537 (13)	3.7 (0.7)
C(2)	0.0408 (10)	−0.0273 (14)	0.0777 (17)	8.1 (1.0)
C(3)	0.0080 (9)	−0.0486 (15)	0.0689 (18)	9.2 (1.0)
C(4)	−0.0003 (7)	−0.0962 (13)	0.0340 (15)	6.5 (0.8)
C(5)	0.0256 (8)	−0.1280 (12)	0.0145 (14)	5.8 (0.8)
C(6)	0.0578 (7)	−0.1112 (12)	0.0210 (13)	4.6 (0.7)
C(7)	0.1337 (6)	−0.0955 (12)	0.0363 (14)	3.2 (0.7)
C(8)	0.1421 (8)	−0.0982 (13)	−0.0267 (16)	5.9 (0.9)
C(9)	0.1619 (8)	−0.1461 (15)	−0.0457 (15)	6.6 (0.9)
C(10)	0.1689 (7)	−0.1911 (13)	−0.0099 (16)	5.9 (0.8)
C(11)	0.1599 (7)	−0.1928 (13)	0.0523 (16)	6.7 (0.8)
C(12)	0.1423 (7)	−0.1444 (14)	0.0723 (14)	5.8 (0.8)
C(13)	0.1136 (7)	0.0236 (9)	0.0073 (12)	3.4 (0.6)
C(14)	0.1412 (7)	0.0609 (12)	0.0146 (14)	5.4 (0.8)
C(15)	0.1481 (8)	0.1078 (13)	−0.0307 (16)	7.0 (0.9)
C(16)	0.1252 (8)	0.1078 (12)	−0.0789 (14)	5.6 (0.8)
C(17)	0.0988 (8)	0.0755 (14)	−0.0842 (16)	7.0 (0.9)
C(18)	0.0909 (7)	0.0320 (12)	−0.0396 (15)	4.9 (0.7)
C(19)	0.0472 (6)	0.1904 (11)	0.2737 (13)	3.9 (0.7)
C(20)	0.0460 (7)	0.1732 (12)	0.3337 (16)	5.5 (0.8)
C(21)	0.0512 (7)	0.2151 (13)	0.3809 (14)	5.0 (0.8)
C(22)	0.0565 (7)	0.2753 (12)	0.3649 (14)	4.3 (0.7)
C(23)	0.0595 (6)	0.2941 (11)	0.3039 (14)	4.0 (0.7)
C(24)	0.0542 (6)	0.2522 (11)	0.2610 (13)	3.5 (0.7)
C(25)	0.0000 (6)	0.1166 (11)	0.2121 (14)	4.2 (0.7)
C(26)	−0.0229 (7)	0.1299 (11)	0.2584 (14)	5.5 (0.8)
C(27)	−0.0559 (7)	0.1157 (11)	0.2521 (14)	4.7 (0.8)
C(28)	−0.0676 (7)	0.0904 (12)	0.2004 (16)	5.0 (0.8)
C(29)	−0.0474 (8)	0.0762 (12)	0.1541 (15)	6.1 (0.9)
C(30)	−0.0139 (7)	0.0909 (11)	0.1581 (14)	4.6 (0.7)
C(31)	0.0505 (6)	0.1710 (10)	0.1440 (11)	3.1 (0.6)
C(32)	0.0788 (7)	0.1577 (10)	0.1076 (14)	4.5 (0.7)
C(33)	0.0851 (8)	0.1917 (14)	0.0559 (16)	7.2 (0.9)
C(34)	0.0634 (9)	0.2332 (14)	0.0351 (16)	7.4 (1.0)
C(35)	0.0344 (7)	0.2424 (12)	0.0627 (15)	5.6 (0.8)
C(36)	0.0277 (7)	0.2125 (11)	0.1196 (13)	4.1 (0.7)
C(37)	0.1643 (7)	0.2285 (11)	0.2403 (14)	4.4 (0.7)
C(38)	0.1403 (7)	0.2433 (13)	0.1945 (15)	6.2 (0.8)
C(39)	0.1260 (8)	0.2988 (16)	0.1940 (17)	7.8 (1.0)
C(40)	0.1373 (7)	0.3421 (13)	0.2345 (16)	6.2 (0.9)
C(41)	0.1600 (7)	0.3297 (13)	0.2759 (15)	5.9 (0.8)
C(42)	0.1747 (6)	0.2741 (12)	0.2826 (13)	4.1 (0.7)
C(43)	0.2107 (7)	0.1542 (11)	0.3065 (14)	4.6 (0.7)
C(44)	0.1995 (7)	0.1265 (11)	0.3561 (15)	4.4 (0.7)
C(45)	0.2179 (8)	0.1279 (12)	0.4092 (14)	5.2 (0.8)
C(46)	0.2482 (9)	0.1561 (13)	0.4095 (16)	6.9 (0.9)
C(47)	0.2614 (7)	0.1809 (12)	0.3563 (16)	5.9 (0.9)
C(48)	0.2412 (8)	0.1822 (12)	0.3040 (15)	6.4 (0.8)
C(49)	0.2106 (7)	0.1604 (13)	0.1734 (14)	4.8 (0.7)
C(50)	0.2233 (8)	0.1071 (14)	0.1488 (16)	7.1 (0.9)
C(51)	0.2452 (9)	0.1109 (15)	0.0995 (17)	7.8 (0.9)
C(52)	0.2556 (7)	0.1638 (15)	0.0776 (15)	6.0 (0.8)
C(53)	0.2429 (9)	0.2158 (15)	0.0993 (17)	8.1 (1.0)
C(54)	0.2206 (8)	0.2142 (13)	0.1471 (15)	5.9 (0.8)
C(55)	0.2264 (7)	−0.0962 (11)	0.2008 (14)	4.0 (0.7)
C(56)	0.2132 (8)	−0.0740 (13)	0.1449 (18)	7.0 (0.9)
C(57)	0.2338 (11)	−0.0678 (16)	0.0939 (20)	10.4 (1.2)
C(58)	0.2656 (11)	−0.0863 (16)	0.0973 (21)	10.4 (1.2)
C(59)	0.2799 (9)	−0.1051 (14)	0.1512 (20)	8.4 (1.0)
C(60)	0.2593 (9)	−0.1138 (13)	0.2010 (17)	7.4 (0.9)
C(61)	0.1847 (7)	−0.1818 (12)	0.2650 (15)	6.0 (0.8)
C(62)	0.1616 (8)	−0.1984 (14)	0.3130 (15)	6.4 (0.9)
C(63)	0.1506 (7)	−0.2552 (15)	0.3098 (15)	6.2 (0.8)
C(64)	0.1604 (8)	−0.2985 (13)	0.2659 (17)	6.9 (0.9)
C(65)	0.1816 (8)	−0.2816 (14)	0.2225 (16)	8.2 (0.9)
C(66)	0.1943 (7)	−0.2210 (13)	0.2185 (14)	5.5 (0.8)
C(67)	0.2236 (7)	−0.0974 (13)	0.3326 (13)	4.8 (0.7)
C(68)	0.2262 (7)	−0.0411 (12)	0.3571 (14)	4.7 (0.8)
C(69)	0.2487 (9)	−0.0343 (15)	0.4077 (17)	8.6 (1.0)
C(70)	0.2645 (8)	−0.0822 (17)	0.4328 (16)	7.4 (1.0)
C(71)	0.2629 (8)	−0.1332 (17)	0.4112 (17)	8.3 (1.0)
C(72)	0.2416 (8)	−0.1475 (13)	0.3569 (15)	6.7 (0.9)
C(73)	0.0586 (7)	−0.1861 (10)	0.2087 (12)	3.3 (0.7)
C(74)	0.0315 (7)	−0.2031 (12)	0.1739 (15)	6.5 (0.7)
C(75)	0.0359 (8)	−0.2451 (14)	0.1271 (16)	7.1 (0.9)
C(76)	0.0655 (9)	−0.2711 (12)	0.1182 (14)	6.0 (0.8)
C(77)	0.0928 (7)	−0.2560 (12)	0.1475 (14)	4.6 (0.8)
C(78)	0.0884 (7)	−0.2114 (11)	0.1923 (13)	4.7 (0.7)
C(79)	0.0154 (6)	−0.1113 (12)	0.2800 (14)	4.4 (0.7)
C(80)	−0.0049 (7)	−0.1371 (11)	0.3248 (14)	4.9 (0.7)
C(81)	−0.0368 (7)	−0.1166 (13)	0.3340 (14)	5.0 (0.8)
C(82)	−0.0498 (7)	−0.0739 (13)	0.2979 (16)	5.6 (0.8)
C(83)	−0.0303 (8)	−0.0483 (13)	0.2540 (16)	7.0 (0.9)
C(84)	0.0033 (7)	−0.0679 (13)	0.2436 (15)	6.1 (0.8)
C(85)	0.0666 (5)	−0.1751 (10)	0.3399 (11)	1.7 (0.8)
C(86)	0.0783 (7)	−0.1464 (10)	0.3894 (14)	4.3 (0.7)
C(87)	0.0878 (8)	−0.1776 (15)	0.4435 (17)	7.8 (1.0)
C(88)	0.0804 (7)	−0.2376 (13)	0.4448 (15)	6.2 (0.8)
C(89)	0.0688 (7)	−0.2684 (11)	0.3951 (15)	5.2 (0.8)
C(90)	0.0624 (6)	−0.2368 (12)	0.3414 (13)	3.7 (0.7)
C(91)	0.1259 (6)	0.1134 (11)	0.4594 (13)	3.7 (0.7)
C(92)	0.1408 (7)	0.1145 (13)	0.5209 (15)	5.7 (0.8)
C(93)	0.1542 (7)	0.1677 (14)	0.5380 (15)	6.4 (0.8)
C(94)	0.1566 (8)	0.2166 (14)	0.5016 (17)	6.8 (0.9)
C(95)	0.1413 (7)	0.2158 (12)	0.4433 (15)	5.5 (0.8)
C(96)	0.1274 (6)	0.1611 (12)	0.4225 (13)	4.4 (0.7)
C(97)	0.1207 (7)	−0.0134 (10)	0.4807 (13)	3.3 (0.7)
C(98)	0.1048 (7)	−0.0274 (12)	0.5364 (15)	5.3 (0.8)
C(99)	0.1204 (8)	−0.0714 (13)	0.5732 (15)	5.7 (0.8)
C(100)	0.1459 (9)	−0.1001 (14)	0.5554 (18)	7.7 (1.0)
C(101)	0.1632 (9)	−0.0900 (16)	0.5067 (19)	8.5 (1.1)
C(102)	0.1505 (8)	−0.0417 (14)	0.4671 (15)	7.2 (0.9)
C(103)	0.0649 (6)	0.0529 (10)	0.4395 (13)	3.6 (0.7)
C(104)	0.0501 (7)	0.0875 (11)	0.4866 (14)	4.9 (0.8)
C(105)	0.0163 (7)	0.0941 (11)	0.4948 (14)	5.2 (0.7)
C(106)	−0.0044 (7)	0.0639 (13)	0.4541 (16)	6.7 (0.8)
C(107)	0.0076 (8)	0.0307 (13)	0.4089 (15)	6.6 (0.9)
C(108)	0.0420 (7)	0.0239 (11)	0.4000 (12)	4.1 (0.7)

(ii) Atoms of the Dimethylformamide Molecule

Atom	x	y	z	B, Å²
C(109)	0.3341 (16)	0.0221 (22)	0.2212 (28)	14.1 (2.0)
O(1)	0.3663 (8)	0.0030 (12)	0.2242 (16)	14.5 (1.1)
N(1)	0.3169 (10)	0.0291 (15)	0.2661 (22)	12.6 (1.2)
Me(1)	0.2846 (12)	0.0446 (18)	0.2425 (22)	11.9 (1.5)
Me(2)	0.3352 (14)	0.0117 (20)	0.3251 (27)	15.8 (1.9)

(B) Anisotropic Thermal Parameters ($\times 10^5$) for Copper and Phosphorus Atoms[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	48 (4)	124 (10)	126 (13)	13 (11)	−19 (11)	−10 (19)
Cu(2)	58 (3)	119 (10)	145 (13)	45 (10)	−57 (12)	2 (20)
Cu(3)	46 (3)	114 (10)	185 (14)	−38 (10)	−29 (12)	−20 (20)
Cu(4)	47 (3)	152 (11)	197 (14)	43 (10)	−49 (12)	−17 (21)
Cu(5)	59 (3)	95 (10)	161 (14)	−40 (10)	3 (12)	33 (19)
Cu(6)	70 (4)	122 (10)	120 (13)	−4 (11)	−6 (12)	−27 (19)
P(1)	62 (7)	124 (19)	185 (26)	22 (10)	−38 (23)	−42 (39)
P(2)	64 (7)	128 (20)	145 (25)	26 (19)	−29 (22)	76 (37)
P(3)	56 (6)	151 (20)	207 (27)	−33 (19)	8 (24)	−17 (38)
P(4)	57 (6)	227 (22)	225 (28)	70 (20)	−31 (24)	40 (42)
P(5)	61 (7)	154 (20)	218 (27)	−43 (19)	0 (24)	51 (40)
P(6)	80 (8)	159 (21)	132 (24)	−19 (22)	−34 (23)	−84 (38)

(C) Axes of Thermal Vibration Ellipsoids (Å²)[c]

Atom	B_{major}	B_{median}	B_{minor}
Cu(1)	3.31	2.48	2.21
Cu(2)	4.55	2.57	1.60
Cu(3)	3.88	3.22	1.70
Cu(4)	4.55	3.04	2.07
Cu(5)	4.02	3.08	1.57
Cu(6)	4.63	2.58	2.04
P(1)	4.69	2.83	2.49
P(2)	4.73	3.44	1.70
P(3)	4.15	3.48	2.60
P(4)	5.33	4.55	2.65
P(5)	4.69	4.06	2.35
P(6)	5.68	3.82	1.66

[a] Estimated standard deviations are shown in parentheses; they are right adjusted to the least significant digit of the preceding number. [b] The anisotropic thermal parameter is defined as $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. [c] The major, median, and minor axes of the atomic thermal vibration ellipsoids are defined in terms of the isotropic thermal parameter B, since this is a unit familiar to most crystallographers. The transformation to root-mean-square displacement, $(\overline{U^2})^{1/2}$, is $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$.

tions were then ordered in terms of their consistency indices, C (defined below), which ranged from 0.827 to 0.434.

$$C = \left\langle \left| E_h \sum_{h=h_1+h_2} E_{h_1}E_{h_2} \right| \right\rangle \Big/ \left\langle \left| E_h \right| \sum_{h=h_1+h_2} \left(\left| E_{h_1} \right| \right) \left(\left| E_{h_2} \right| \right) \right\rangle$$

(Sums are over all pairs of reflections h_1 and h_2 for which $h = h_1 + h_2$, and $\langle\,\rangle$ designates the average over all values of h.)

A Fourier synthesis based on the 234 phased reflections from the solution of highest consistency index ($C = 0.827$ for $-++-$)[17] revealed no chemically feasible structure, but an F map[18] based on the phased set of second highest consistency index ($C = 0.809$ for $++++$)[17] revealed the central Cu_6P_6 core of the molecule. Following two cycles of refinement of positional parameters for copper and phosphorus atoms (with isotropic thermal parameters held constant at 1.8 Å^2 for Cu and 2.0 Å^2 for P), a series of difference Fourier syntheses yielded the positions of the 108 carbon atoms in the six triphenylphosphine ligands. Nine cycles of positional parameter refinement (with $B(C) = 5.0$ Å^2) led to a reduction in the discrepancy index from $R_F = 30.8\%$ to $R_F = 17.0\%$. A further three cycles of refinement of all positional parameters, isotropic thermal parameters for carbon atoms, and anisotropic thermal parameters for copper and phosphorus atoms led to $R_F = 12.9\%$. At this stage a three-dimensional difference-Fourier synthesis revealed the presence of a dimethylformamide (DMF) molecule of crystallization. Hydrogen atoms of the phenyl groups were placed in calculated positions and a further nine cycles of refinement led to convergence at $R_F = 9.2\%$ and $R_{wF^2} = 4.4\%$. (The corresponding discrepancy indices with hydrogen atoms omitted are $R_F = 10.1\%$ and $R_{wF^2} = 6.0\%$.) Application of Hamilton's R-factor ratio test[19] shows that both anisotropic parameter refinement and inclusion of hydrogen atoms provide significant improvements. A final difference Fourier synthesis showed no residual electron density in excess of 0.5 e Å^{-3}, thus providing independent verification as to the correctness of the crystal structure.

It should be noted that, due to storage limitations of the IBM 7094 computer, parameters were partitioned into several submatrices. Matrix 1 held positional and anisotropic thermal parameters for copper and phosphorus atoms and included the overall scale factor; matrices 2–7 each contained parameters for all 18 carbon atoms of a given triphenylphosphine ligand; and matrix 8 held parameters for the nonhydrogen atoms of the dimethylformamide molecule. Hydrogen atom positions were recalculated after each cycle of refinement but were not refined. Their isotropic thermal parameters were held constant at a value of 6.0 Å^2.

Final values for observed and calculated structure factor amplitudes are listed elsewhere.[20] Atomic positional and thermal parameters are collected in Table I.

The Crystallographically Determined Structure

The crystallographic analysis revealed uniquely the positions of all 125 nonhydrogen atoms in the structure and proved that the crystalline sample had the partial composition $H_xCu_6(PPh_3)_6 \cdot DMF$, where x is unknown (since hydrogen atoms were not located directly from the diffraction study).

The metal cluster and dimethylformamide molecules are mutually separated by normal van der Waals distances and there are no abnormally short intermolecular contacts. It should be emphasized that the dimethylformamide molecule is not incorporated into any copper atom coordination sphere.

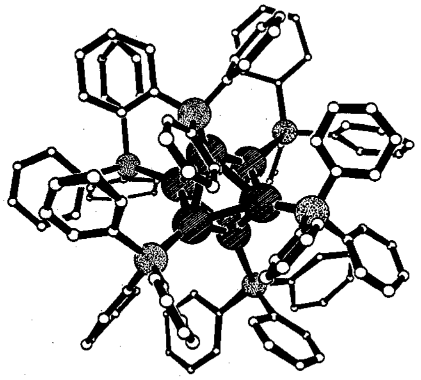

Figure 1.—Overall stereochemistry of the $H_6Cu_6(PPh_3)_6$ molecule, with hydrogen atoms omitted.

The stereochemistry of the $H_xCu_6(PPh_3)_6$ molecule is shown in Figure 1. Intramolecular distances and their estimated standard deviations (esd's) are shown in Table II. Bond angles, with their esd's, are collected in Table III. Least-squares planes are given in Table IV.

The numbering scheme and thermal ellipsoids for the Cu_6P_6 core of the molecule are shown in Figure 2. Carbon atoms of the phenyl groups are numbered cyclically and sequentially, with the lowest number in each ring designating the carbon atom that is bound directly to phosphorus. Thus the phosphorus atom P(n) is linked directly to C($18n - 17$), C($18n - 11$) and C($18n - 5$), where n = 1–6. The dimethylformamide molecule of crystallization is defined by C(109), O(1), N(1), Me(1), and Me(2),

As shown clearly in the figures, the $H_xCu_6(PPh_3)_6$ molecule contains an octahedral cluster of six copper atoms. This Cu_6 cluster is distorted significantly from precise O_h symmetry, with individual copper–copper bond distances ranging from 2.494 (5) to 2.674 (5), averaging 2.599 ± 0.067 Å.[21,22] The overall pattern of metal–metal bond lengths (see Figure 2) is such that distances within two mutually trans faces [*viz.*, Cu(1)–Cu(3)–Cu(4) and Cu(2)–Cu(5)–Cu(6)] range from 2.632 (6) to 2.674 (5) Å (averaging 2.655 ± 0.017 Å),[22] while the remaining six copper–copper bond lengths vary from 2.494 (6) to 2.595 (5) Å (mean 2.542 ± 0.044 Å). Thus, as shown in Figure 2, the octahedron defining the Cu_6 system has two large transoid "equilateral" triangular faces and six smaller (approximately) isosceles triangular faces.

The significance of the variations in copper–copper distance is heightened by a survey of the intrinsically less accurately determined copper–phosphorus distances, which range only from 2.217 (7) to 2.262 (8) Å, with a mean value of 2.240 ± 0.017 Å.[22]

Each copper atom is bonded to a single triphenylphosphine ligand, with ($P\text{–}Cu\cdots Cu_{trans}$) angles varying from 168.3 (3) to 177.3 (3)°; the triphenylphosphine ligands are, on the average, distorted by 8.0 ± 3.4°[22] from truly apical positions. Careful studies with a molecular model suggest that these distortions

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[17] Signs refer, in turn, to phases for the reflections 14,7,1; 631; 275; 14,1,7.

[18] We have found on more than one occasion that an E map is not readily interpretable whereas the corresponding F map reveals the solution immediately. We now always use F maps. See M. R. Churchill, J. Cooke, J. P. Fennessey, and J. Wormald, *Inorg. Chem.*, **10**, 1031 (1971).

[19] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[20] A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number INORG-72-1818. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[21] The large value of the deviation from the mean simply reflects the nonequivalence of all 12 copper–copper bonds.

[22] Throughout the text estimated standard deviations on individual bond length will be given in parentheses while the "scatter" from a mean value (as defined in footnote *a* of Table II) will be given as ±*x.xx* Å.

TABLE II

BOND DISTANCES (Å) WITHIN THE $H_6Cu_6(PPh_3)_6$ MOLECULE

Atoms	Dist	Atoms	Dist
(A) Distances within Cu_6 octahedron			
(i) Those Defining the Two Large Mutually Trans Faces			
Cu(1)–Cu(3)	2.667 (5)	Cu(2)–Cu(5)	2.674 (5)
Cu(3)–Cu(4)	2.650 (5)	Cu(5)–Cu(6)	2.667 (5)
Cu(4)–Cu(1)	2.637 (6)	Cu(6)–Cu(2)	2.632 (6)
		Long Cu–Cu av	2.655 (17)[a]
(ii) "Short" Copper–Copper Distances			
Cu(1)–Cu(2)	2.592 (5)	Cu(6)–Cu(4)	2.545 (5)
Cu(2)–Cu(3)	2.595 (5)	Cu(4)–Cu(5)	2.498 (5)
Cu(3)–Cu(6)	2.530 (6)	Cu(5)–Cu(1)	2.494 (6)
		Short Cu–Cu av	2.542 (44)[a]
(B) Copper–Phosphorus Distances			
Cu(1)–P(1)	2.241 (9)	Cu(4)–P(4)	2.221 (8)
Cu(2)–P(2)	2.244 (8)	Cu(5)–P(5)	2.217 (7)
Cu(3)–P(3)	2.262 (8)	Cu(6)–P(6)	2.252 (9)
		Cu–P av	2.240 (17)[a]
(C) Phosphorus–Carbon Distances			
P(1)–C(1)	1.826 (26)	P(4)–C(55)	1.846 (31)
P(1)–C(7)	1.830 (27)	P(4)–C(61)	1.843 (28)
P(1)–C(13)	1.852 (26)	P(4)–C(67)	1.830 (29)
P(2)–C(19)	1.838 (29)	P(5)–C(73)	1.816 (26)
P(2)–C(25)	1.792 (26)	P(5)–C(79)	1.861 (26)
P(2)–C(31)	1.792 (26)	P(5)–C(85)	1.842 (25)
P(3)–C(37)	1.809 (25)	P(6)–C(91)	1.828 (26)
P(3)–C(43)	1.885 (31)	P(6)–C(97)	1.809 (27)
P(3)–C(49)	1.803 (30)	P(6)–C(103)	1.744 (25)
		P–C av	1.825 (31)[a]
(D) Carbon–Carbon Distances within Phenyl Groups			
C(1)–C(2)	1.402 (45)	C(55)–C(56)	1.410 (48)
C(2)–C(3)	1.426 (52)	C(56)–C(57)	1.390 (57)
C(3)–C(4)	1.372 (47)	C(57)–C(58)	1.319 (62)
C(4)–C(5)	1.329 (43)	C(58)–C(59)	1.375 (60)
C(5)–C(6)	1.371 (42)	C(59)–C(60)	1.367 (54)
C(6)–C(1)	1.376 (38)	C(60)–C(55)	1.341 (45)
C(7)–C(8)	1.427 (46)	C(61)–C(62)	1.449 (45)
C(8)–C(9)	1.379 (45)	C(62)–C(63)	1.325 (45)
C(9)–C(10)	1.296 (46)	C(63)–C(64)	1.404 (47)
C(10)–C(11)	1.417 (48)	C(64)–C(65)	1.314 (48)
C(11)–C(12)	1.383 (43)	C(65)–C(66)	1.446 (42)
C(12)–C(7)	1.404 (35)	C(66)–C(61)	1.421 (43)
C(13)–C(14)	1.409 (38)	C(67)–C(68)	1.369 (40)
C(14)–C(15)	1.477 (44)	C(68)–C(69)	1.422 (47)
C(15)–C(16)	1.372 (46)	C(69)–C(70)	1.336 (50)
C(16)–C(17)	1.295 (44)	C(70)–C(71)	1.267 (53)
C(17)–C(18)	1.400 (44)	C(71)–C(72)	1.477 (49)
C(18)–C(13)	1.391 (40)	C(72)–C(67)	1.425 (42)
C(19)–C(20)	1.360 (45)	C(73)–C(74)	1.397 (39)
C(20)–C(21)	1.410 (44)	C(74)–C(75)	1.395 (45)
C(21)–C(22)	1.418 (40)	C(75)–C(76)	1.329 (46)
C(22)–C(23)	1.414 (42)	C(76)–C(77)	1.326 (44)
C(23)–C(24)	1.368 (39)	C(77)–C(78)	1.384 (40)
C(24)–C(19)	1.463 (37)	C(78)–C(73)	1.369 (38)
C(25)–C(26)	1.382 (41)	C(79)–C(80)	1.406 (40)
C(26)–C(27)	1.397 (40)	C(80)–C(81)	1.373 (41)
C(27)–C(28)	1.360 (44)	C(81)–C(82)	1.349 (43)
C(28)–C(29)	1.350 (46)	C(82)–C(82)	1.388 (46)
C(29)–C(30)	1.415 (43)	C(83)–C(84)	1.436 (44)
C(30)–C(25)	1.408 (41)	C(84)–C(79)	1.344 (41)
C(31)–C(32)	1.397 (38)	C(85)–C(86)	1.351 (37)
C(32)–C(33)	1.363 (44)	C(86)–C(87)	1.431 (45)
C(33)–C(34)	1.348 (46)	C(87)–C(88)	1.383 (45)
C(34)–C(35)	1.332 (46)	C(88)–C(89)	1.358 (44)
C(35)–C(36)	1.442 (42)	C(89)–C(90)	1.403 (42)
C(36)–C(31)	1.410 (36)	C(90)–C(85)	1.409 (35)
C(37)–C(38)	1.444 (41)	C(91)–C(92)	1.464 (42)
C(38)–C(39)	1.379 (45)	C(92)–C(93)	1.378 (43)
C(39)–C(40)	1.393 (47)	C(93)–C(94)	1.371 (46)
C(40)–C(41)	1.294 (44)	C(94)–C(95)	1.407 (47)
C(41)–C(42)	1.391 (39)	C(95)–C(96)	1.403 (39)
C(42)–C(37)	1.449 (38)	C(96)–C(91)	1.337 (38)
C(43)–C(44)	1.353 (42)	C(97)–C(98)	1.409 (43)
C(44)–C(45)	1.384 (44)	C(98)–C(99)	1.431 (42)
C(45)–C(46)	1.397 (45)	C(99)–C(100)	1.329 (48)
C(46)–C(47)	1.387 (47)	C(100)–C(101)	1.268 (56)
C(47)–C(48)	1.392 (47)	C(101)–C(102)	1.453 (49)
C(48)–C(43)	1.369 (42)	C(102)–C(97)	1.408 (43)
C(49)–C(50)	1.433 (44)	C(103)–C(104)	1.419 (39)
C(50)–C(51)	1.408 (49)	C(104)–C(105)	1.404 (41)
C(51)–C(52)	1.321 (48)	C(105)–C(106)	1.379 (43)
C(52)–C(53)	1.371 (47)	C(106)–C(107)	1.315 (46)
C(53)–C(54)	1.368 (48)	C(107)–C(108)	1.407 (43)
C(54)–C(49)	1.371 (42)	C(108)–C(103)	1.422 (37)
		Phenyl C–C av	1.385 (43)[a]
(E) Distances within Dimethylformamide Molecule			
C(109)–O(1)	1.375 (70)	N(1)–Me(1)	1.449 (63)
C(109)–N(1)	1.206 (76)	N(2)–Me(2)	1.501 (74)

[a] Esd's on average bond lengths are calculated from the expression $\sigma = \{[\Sigma_{i=1}^{i=N} (X_i - \bar{X})^2]/(N - 1)\}^{1/2}$ where Xi is the ith bond length and $\bar{X}$ is the mean of N equivalent bond lengths.

most probably result from intramolecular phenyl··· phenyl repulsions. These same distortions also cause P–Cu–Cu(cis) angles to range from 123.5 to 145.4° (see Table III.D) and cause phosphorus atoms to deviate from the planes through "squares" of copper atoms (see Table IV).

Individual phosphorus–carbon distances range from 1.744 (25) to 1.885 (31) Å, the mean of the 18 independent values being 1.825 ± 0.031 Å—in good agreement with the distance of 1.823 (3) Å found in free triphenylphosphine.[23] Carbon–carbon bond lengths within the phenyl groups range from 1.267 (53) to 1.477 (49) Å, averaging 1.385 ± 0.043 Å[22]—comparable to the accepted C–C(aromatic) distances of 1.394 ± 0.005 Å.[24]

The overall molecular structure of this octahedral metal cluster derivative is such that the molecule presents an outer surface of phenyl groups, thus explaining the pronounced solubility of this high molecular weight (1955) species in benzene.

Determination of the Number of Hydride Ligands Associated with the Cu_6 Cluster.—The presence of hydride ligands could not be ascertained from crystallographic or spectroscopic studies, so a chemical solution to this problem was sought. Initial observations showed that the complex reacted with acetic or benzoic acid with evolution of hydrogen, but the volume of hydrogen liberated per mole of complex appeared to be variable. The complex was therefore decomposed by reaction with a benzene solution of monodeuteriobenzoic acid, $C_6H_5CO_2D$ (97% isotopic purity), and the gaseous hydrogen thus generated was collected and its volume measured. Mass spectral isotopic analysis of this gas revealed large quantities of H_2 and HD (in varying proportions, from one run to another), but no D_2 (*cf.* ref 25). Clearly, the decomposition of the hydridocopper phosphine species is not simply a proton–

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(23) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(24) "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959," *Chem. Soc. Spec. Publ.*, **No. 18**, S 16s (1965).

(25) J. A. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 5769 (1968); see, especially, Table II.

TABLE III

ANGLES (DEG) WITHIN THE $H_6Cu_6(PPh)_6$ MOLECULE

Atoms	Angle	Atoms	Angle
(A) Angles in Triangular Faces of Cu_6 Octahedron			
Cu(2)–Cu(1)–Cu(3)	59.1 (1)	Cu(1)–Cu(4)–Cu(3)	60.6 (1)
Cu(3)–Cu(1)–Cu(4)	60.0 (1)	Cu(3)–Cu(4)–Cu(6)	58.2 (1)
Cu(4)–Cu(1)–Cu(5)	58.2 (1)	Cu(6)–Cu(4)–Cu(5)	63.8 (1)
Cu(5)–Cu(1)–Cu(2)	63.4 (1)	Cu(5)–Cu(4)–Cu(1)	58.0 (1)
Cu(1)–Cu(2)–Cu(3)	61.9 (1)	Cu(1)–Cu(5)–Cu(2)	60.1 (1)
Cu(3)–Cu(2)–Cu(6)	57.9 (1)	Cu(1)–Cu(5)–Cu(6)	69.1 (1)
Cu(6)–Cu(2)–Cu(5)	60.3 (1)	Cu(6)–Cu(5)–Cu(4)	58.9 (1)
Cu(5)–Cu(2)–Cu(1)	56.5 (1)	Cu(4)–Cu(5)–Cu(1)	63.8 (2)
Cu(1)–Cu(3)–Cu(2)	59.0 (1)	Cu(2)–Cu(6)–Cu(3)	60.3 (1)
Cu(2)–Cu(3)–Cu(6)	61.8 (1)	Cu(3)–Cu(6)–Cu(4)	63.0 (1)
Cu(6)–Cu(3)–Cu(4)	58.8 (1)	Cu(4)–Cu(6)–Cu(5)	57.2 (1)
Cu(4)–Cu(3)–Cu(1)	59.5 (1)	Cu(5)–Cu(6)–Cu(2)	60.6 (1)
(B) Angles in Square Planes of Cu_6 Octahedron			
Cu(2)–Cu(1)–Cu(4)	90.1 (2)	Cu(3)–Cu(4)–Cu(5)	90.8 (2)
Cu(5)–Cu(1)–Cu(3)	90.5 (2)	Cu(1)–Cu(4)–Cu(6)	89.8 (2)
Cu(1)–Cu(2)–Cu(6)	88.9 (2)	Cu(1)–Cu(5)–Cu(6)	90.2 (2)
Cu(3)–Cu(2)–Cu(5)	88.2 (2)	Cu(2)–Cu(5)–Cu(4)	91.3 (2)
Cu(1)–Cu(3)–Cu(6)	89.5 (2)	Cu(2)–Cu(6)–Cu(4)	91.2 (2)
Cu(2)–Cu(3)–Cu(4)	89.7 (2)	Cu(3)–Cu(6)–Cu(5)	89.7 (2)
(C) Phosphorus–Copper···Copper(Trans) Angles			
P(1)–Cu(1)···Cu(6)	168.6 (3)	P(4)–Cu(4)···Cu(2)	173.9 (3)
P(2)–Cu(2)···Cu(4)	172.2 (3)	P(5)–Cu(5)···Cu(3)	177.3 (3)
P(3)–Cu(3)···Cu(5)	171.9 (3)	P(6)–Cu(6)···Cu(1)	168.3 (3)
(D) Phosphorus–Copper–Copper(Cis) Angles			
P(1)–Cu(1)–Cu(2)	127.5 (3)	P(4)–Cu(4)–Cu(1)	129.5 (3)
P(1)–Cu(1)–Cu(3)	145.4 (3)	P(4)–Cu(4)–Cu(3)	136.3 (3)
P(1)–Cu(1)–Cu(4)	140.6 (3)	P(4)–Cu(4)–Cu(5)	132.0 (3)
P(1)–Cu(1)–Cu(5)	123.5 (3)	P(4)–Cu(4)–Cu(6)	140.7 (3)
P(2)–Cu(2)–Cu(1)	134.1 (3)	P(5)–Cu(5)–Cu(1)	135.8 (3)
P(2)–Cu(2)–Cu(3)	126.4 (2)	P(5)–Cu(5)–Cu(2)	133.9 (2)
P(2)–Cu(2)–Cu(5)	145.3 (3)	P(5)–Cu(5)–Cu(4)	134.6 (3)
P(2)–Cu(2)–Cu(6)	135.8 (3)	P(5)–Cu(5)–Cu(6)	133.9 (3)
P(3)–Cu(3)–Cu(1)	144.6 (3)	P(6)–Cu(6)–Cu(2)	126.8 (3)
P(3)–Cu(3)–Cu(2)	135.9 (2)	P(6)–Cu(6)–Cu(3)	141.4 (3)
P(3)–Cu(3)–Cu(4)	133.2 (2)	P(6)–Cu(6)–Cu(4)	140.4 (3)
P(3)–Cu(3)–Cu(6)	125.9 (3)	P(6)–Cu(6)–Cu(5)	128.0 (3)
(E) Copper–Phosphorus–Carbon Angles			
Cu(1)–P(1)–C(1)	114.7 (9)	Cu(4)–P(4)–C(55)	112.8 (9)
Cu(1)–P(1)–C(7)	117.5 (10)	Cu(4)–P(4)–C(61)	114.1 (10)
Cu(1)–P(1)–C(13)	117.1 (8)	Cu(4)–P(4)–C(67)	117.1 (10)
Cu(2)–P(2)–C(19)	109.5 (9)	Cu(5)–P(5)–C(73)	114.2 (9)
Cu(2)–P(2)–C(25)	123.4 (8)	Cu(5)–P(5)–C(79)	113.3 (9)
Cu(2)–P(2)–C(31)	113.5 (9)	Cu(5)–P(5)–C(85)	115.7 (8)
Cu(3)–P(3)–C(37)	118.4 (9)	Cu(6)–P(6)–C(91)	115.7 (9)
Cu(3)–P(3)–C(43)	114.8 (9)	Cu(6)–P(6)–C(97)	116.4 (8)
Cu(3)–P(3)–C(49)	116.9 (10)	Cu(6)–P(6)–C(103)	111.7 (10)
(F) Phosphorus–Carbon–Carbon Angles			
P(1)–C(1)–C(2)	116.3 (2.2)	P(4)–C(55)–C(56)	117.1 (2.2)
P(1)–C(1)–C(6)	125.5 (2.0)	P(4)–C(55)–C(60)	123.6 (2.5)
P(1)–C(7)–C(8)	123.4 (2.1)	P(4)–C(61)–C(62)	116.3 (2.2)
P(1)–C(7)–C(12)	120.5 (2.3)	P(4)–C(61)–C(66)	121.9 (2.3)
P(1)–C(13)–C(14)	114.3 (2.0)	P(4)–C(67)–C(68)	115.3 (2.1)
P(1)–C(13)–C(18)	124.9 (2.0)	P(4)–C(67)–C(72)	123.3 (2.2)
P(2)–C(19)–C(20)	119.4 (2.0)	P(5)–C(73)–C(74)	125.8 (2.1)
P(2)–C(19)–C(24)	124.0 (2.1)	P(5)–C(73)–C(78)	115.4 (2.4)
P(2)–C(25)–C(26)	126.7 (2.2)	P(5)–C(79)–C(80)	120.7 (2.1)
P(2)–C(25)–C(30)	118.1 (2.1)	P(5)–C(79)–C(84)	116.9 (2.2)
P(2)–C(31)–C(32)	121.1 (1.9)	P(5)–C(85)–C(86)	117.0 (1.8)
P(2)–C(31)–C(36)	123.3 (2.0)	P(5)–C(85)–C(90)	120.7 (1.9)
P(3)–C(37)–C(38)	117.1 (2.0)	P(6)–C(91)–C(92)	121.0 (2.0)
P(3)–C(37)–C(42)	125.1 (2.0)	P(6)–C(91)–C(96)	119.3 (2.2)
P(3)–C(43)–C(44)	113.8 (2.1)	P(6)–C(97)–C(98)	126.8 (2.1)
P(3)–C(43)–C(48)	122.8 (2.3)	P(6)–C(97)–C(102)	116.7 (2.2)
P(3)–C(49)–C(50)	117.2 (2.3)	P(6)–C(103)–C(104)	125.6 (2.0)
P(3)–C(49)–C(54)	126.2 (2.3)	P(6)–C(103)–C(108)	119.6 (2.0)
(G) Carbon–Carbon–Carbon Angles within Phenyl Groups			
C(1)–C(2)–C(3)	117.4 (2.9)	C(55)–C(56)–C(57)	118.8 (3.1)
C(2)–C(3)–C(4)	124.2 (3.2)	C(56)–C(57)–C(58)	120.0 (3.9)
C(3)–C(4)–C(5)	113.4 (2.9)	C(57)–C(58)–C(59)	121.3 (4.1)
C(4)–C(5)–C(6)	127.0 (2.8)	C(58)–C(59)–C(60)	119.3 (3.4)
C(5)–C(6)–C(1)	119.2 (2.5)	C(59)–C(60)–C(55)	120.8 (3.2)
C(6)–C(1)–C(2)	118.1 (2.6)	C(60)–C(55)–C(56)	119.2 (3.0)
C(7)–C(8)–C(9)	118.0 (2.8)	C(61)–C(62)–C(63)	115.6 (2.9)
C(8)–C(9)–C(10)	123.3 (3.1)	C(62)–C(63)–C(64)	125.4 (3.0)
C(9)–C(10)–C(11)	122.9 (2.9)	C(63)–C(64)–C(65)	119.3 (2.9)
C(10)–C(11)–C(12)	114.1 (2.8)	C(64)–C(65)–C(66)	121.9 (3.0)
C(11)–C(12)–C(7)	125.0 (2.9)	C(65)–C(66)–C(61)	116.0 (2.7)
C(12)–C(7)–C(8)	116.0 (2.5)	C(66)–C(61)–C(62)	121.6 (2.6)
C(13)–C(14)–C(15)	120.1 (2.6)	C(67)–C(68)–C(69)	118.2 (2.7)
C(14)–C(15)–C(16)	111.4 (2.6)	C(68)–C(69)–C(70)	120.6 (3.1)
C(15)–C(16)–C(17)	130.2 (3.1)	C(69)–C(70)–C(71)	123.1 (3.5)
C(16)–C(17)–C(18)	118.9 (3.1)	C(70)–C(71)–C(72)	122.0 (3.3)
C(17)–C(18)–C(13)	118.3 (2.5)	C(71)–C(72)–C(67)	114.5 (2.7)
C(18)–C(13)–C(14)	120.7 (2.4)	C(72)–C(67)–C(68)	121.3 (2.7)
C(19)–C(20)–C(21)	112.7 (2.6)	C(73)–C(74)–C(75)	119.4 (2.6)
C(20)–C(21)–C(22)	117.8 (2.7)	C(74)–C(75)–C(76)	119.1 (3.0)
C(21)–C(22)–C(23)	123.0 (2.6)	C(75)–C(76)–C(77)	125.7 (2.9)
C(22)–C(23)–C(24)	115.1 (2.4)	C(76)–C(77)–C(78)	113.9 (2.6)
C(23)–C(24)–C(19)	125.0 (2.6)	C(77)–C(78)–C(73)	126.0 (2.6)
C(24)–C(19)–C(20)	116.2 (2.5)	C(78)–C(73)–C(74)	115.4 (2.4)
C(25)–C(26)–C(27)	122.9 (2.7)	C(79)–C(80)–C(81)	118.1 (2.5)
C(26)–C(27)–C(28)	119.9 (2.7)	C(80)–C(81)–C(82)	123.5 (2.8)
C(27)–C(28)–C(29)	120.6 (2.7)	C(81)–C(82)–C(83)	116.8 (2.8)
C(28)–C(29)–C(30)	119.5 (2.9)	C(82)–C(83)–C(84)	122.8 (2.8)
C(29)–C(30)–C(25)	122.0 (2.7)	C(83)–C(84)–C(79)	116.3 (2.8)
C(30)–C(25)–C(26)	115.1 (2.4)	C(84)–C(79)–C(80)	112.4 (2.5)
C(31)–C(32)–C(33)	121.7 (2.5)	C(85)–C(86)–C(87)	118.5 (2.4)
C(32)–C(33)–C(34)	122.3 (3.0)	C(86)–C(87) C(88)	118.0 (2.9)
C(33)–C(34)–C(35)	119.7 (3.1)	C(87)–C(88)–C(89)	123.1 (3.0)
C(34)–C(35)–C(36)	120.1 (2.7)	C(88)–C(89)–C(90)	118.5 (2.5)
C(35)–C(36)–C(31)	120.1 (2.4)	C(89)–C(90)–C(85)	118.8 (2.4)
C(36)–C(31)–C(32)	115.4 (2.3)	C(90)–C(85)–C(86)	122.2 (2.3)
C(37)–C(38)–C(39)	121.3 (2.8)	C(91)–C(92)–C(93)	116.4 (2.7)
C(38)–C(39)–C(40)	116.1 (3.0)	C(92)–C(93)–C(94)	122.9 (3.0)
C(39)–C(40)–C(41)	125.8 (2.9)	C(93)–C(94)–C(95)	120.5 (2.8)
C(40)–C(41)–C(42)	121.4 (2.8)	C(94)–C(95)–C(96)	116.7 (2.6)
C(41)–C(42)–C(37)	117.6 (2.5)	C(95)–C(96)–C(91)	123.5 (2.7)
C(42)–C(37)–C(38)	117.7 (2.3)	C(96)–C(91)–C(92)	114.8 (1.4)
C(43)–C(44)–C(45)	118.2 (2.6)	C(97)–C(98)–C(99)	117.8 (2.6)
C(44)–C(45)–C(46)	121.6 (2.0)	C(98)–C(99)–C(100)	120.5 (3.0)
C(45)–C(46)–C(47)	117.2 (3.0)	C(99)–C(100)–C(101)	126.9 (3.4)
C(46)–C(47)–C(48)	121.8 (2.8)	C(100)–C(101)–C(102)	115.1 (3.2)
C(47)–C(48)–C(43)	117.5 (2.9)	C(101)–C(102)–C(97)	123.2 (3.0)
C(48)–C(43)–C(44)	123.3 (2.9)	C(102)–C(97)–C(98)	116.1 (2.5)
C(49)–C(50)–C(51)	119.0 (2.9)	C(103)–C(104)–C(105)	124.8 (2.6)
C(50)–C(51)–C(52)	120.6 (3.1)	C(104)–C(105)–C(106)	114.5 (2.6)
C(51)–C(52)–C(53)	121.9 (3.1)	C(105)–C(106)–C(107)	125.4 (2.9)
C(52)–C(53)–C(54)	118.7 (3.0)	C(106)–C(107)–C(108)	120.0 (2.8)
C(53)–C(54)–C(49)	123.2 (2.8)	C(107)–C(108)–C(103)	120.5 (2.5)
C(54)–C(49)–C(50)	116.5 (2.7)	C(108)–C(103)–C(104)	114.8 (2.3)

hydride coupling reaction, since this could not explain the production of H_2. The number of active hydride ligands was calculated by assuming that all of the generated [^{1}H]hydrogen in the H_2–HD mixture was derived from the hydridocopper phosphine cluster (see Table V). Three experiments, performed on two independently prepared samples of the complex, yielded a mean H^-:Cu ratio of 1.05 ± 0.05:1 indicating a molecular stoichiometry of $H_6Cu_6(PPh_3)_6$. (The H^-:Cu ratio has been corrected for the 97% isotropic purity of the $C_6H_5CO_2D$. It was assumed that there was no isotope effect.)

Since deuterium exchange with the phenyl hydrogens of the benzoate anion or the triphenylphosphine moiety could lead to an erroneously large H^-:Cu ratio, triphenylphosphine was extracted from the reaction residue as $[PPh_3CuBr]_4$ and the benzoate anion as benzoic acid. Mass spectra of these two species were identical with those from authentic nondeuterated samples, thus indicating no deuteration of the phenyl rings in either case.

The reaction of the $H_6Cu_6(PPh_3)_6$ molecule with a proton source is thus quite complicated. Presumably the initial reaction involves hydride abstraction from the cluster, yielding HD. However, subsequent decomposition may go by alternative (competing) pathways involving spontaneous loss of H_2 (presumably *via* a Cu^I/Cu^0 electrochemical couple) or further

TABLE IV

LEAST-SQUARES PLANES[a,b] WITHIN Cu_6P_6 CORE OF THE MOLECULE

Atom	Dev, Å	Atom	Dev, Å
(A) $0.6291X + 0.7592Y - 0.1669Z = 2.284$			
Cu(1)	0.007	P(1)*	−0.374
Cu(2)	−0.007	P(2)*	0.298
Cu(4)	−0.007	P(4)*	−0.044
Cu(6)	+0.007	P(6)*	−0.345
(B) $0.8052X - 0.5797Y + 0.1246Z = 4.388$			
Cu(1)	−0.014	P(1)*	−0.255
Cu(3)	0.014	P(3)*	0.135
Cu(5)	0.014	P(5)*	−0.026
Cu(6)	−0.014	P(6)*	−0.320
(C) $-0.0556X + 0.1818Y + 0.9818Z = 5.044$			
Cu(2)	0.016	P(2)*	0.002
Cu(3)	−0.016	P(3)*	0.274
Cu(4)	0.017	P(4)*	−0.215
Cu(5)	−0.017	P(5)*	0.079

[a] Least-squares planes are defined in terms of the Cartesian coordinates, X, Y, Z. These are related to the fractional cell coordinates by the transformation $[X, Y, Z] = [xa, yb, zc]$. [b] Atoms marked with an asterisk were given zero weight in calculating the least-squares planes. All other atoms were given unit weight.

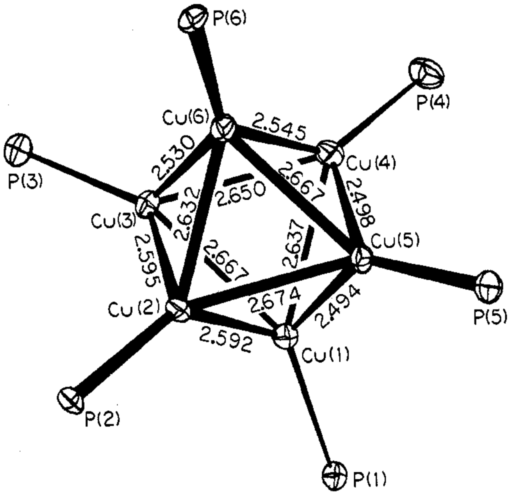

Figure 2.—Copper–copper distances within the $H_6Cu_6(PPh_3)_6$ molecule. This diagram also shows the thermal ellipsoids for copper and phosphorus atoms (diagram was constructed using OTLIPS, an IBM 1620 program, by Dr. P. H. Bird).

TABLE V

DETERMINATION OF H^- IN CLUSTER COMPOUND

Ratio D^+:Cu	% H_2 in H_2–HD mixture[a]	Mol of gas/ equiv of Cu	Active H^-/Cu
1.45:1	45.6	0.718	1.045
1.35:1	44.3	0.729	1.052
1.26:1	32.9	0.788	1.047

[a] These values have been corrected for the 97% isotopic purity of the deuteriobenzoic acid. Isotopic effects on the relative reaction rates of H^- with H^+ or D^+ were assumed to be negligible since the molar excess of acid over copper was kept to a minimum.

abstraction of hydride ion by D^+; either of these stages could be accompanied, or preceded, by dissociation of PPh_3 or a PPh_3Cu species from the cluster.

Possible Locations for the Six Hydride Ligands.—Although the hydride ligands were not located in the X-ray diffraction study, there are certain restraints on their positions.

(1) The six triphenylphosphine ligands are in apical positions. Thus, angles around Cu(5) are almost equivalent: P(5)–Cu(5)–Cu(1) = 135.8 (3), P(5)–Cu(5)–Cu(2) = 133.9 (2), P(5)–Cu(5)–Cu(6) = 133.9 (3), and P(5)–Cu(5)–Cu(4) = 134.6 (3)°. While other ($P–Cu–Cu_{cis}$) angles range from 123.5 to 145.4° and ($P–Cu\cdots Cu_{trans}$) angles vary from 168.3 to 177.3°, these distortions appear to result from intramolecular phenyl···phenyl repulsions. It therefore seems unlikely that *terminal* hydride ligands are present. (This is consistent with the absence of a characteristic metal–hydrogen stretching frequency in the infrared spectrum.[26–30])

(2) In the present molecule, assuming that all six hydride ligands are equivalent, the pattern of copper–copper distances (six "long"—2.632–2.674 Å; six "short"—2.494–2.595 Å)[31] is consistent with three arrangements of hydride ligands: (a) bridging hydride ligands on the six long copper–copper bonds; (b) bridging hydrides on the six short copper–copper bonds; (c) triply bridging hydrides on the six smaller "isosceles" triangular faces of the Cu_6 octahedron.

Although there is insufficient evidence to enable us to differentiate unambiguously between these three possibilities, we presently favor structural possibility a. The long and statistically equivalent bonds are then hydride bridged, while the six shorter bonds are "normal" copper–copper bonds that vary in length as a result of intramolecular overcrowding. We have previously demonstrated that the bridging hydride ligands in $[H_2Re_3(CO)_{12}^-]$ cause a lengthening of ~0.14 Å in the bridged rhenium–rhenium bonds[32,33] and that triply bridging hydride ligands in $H_2Ru_6(CO)_{18}$ cause an elongation of ~0.09 Å in the bridged ruthenium–ruthenium bonds.[34,35] In the $H_6Cu_6(PPh_3)_6$ molecule the mean "long" bond length is 2.655 ± 0.017 Å and the average "short" distance is 2.542 ± 0.044 Å. The difference of 0.113 Å lies midway between the two cases described above! [A reviewer has suggested that the metal cluster might be disordered, "particularly since the observed intensities drop off rapidly with sin θ." We make the following observations: (1) the data are *all* weak, due principally to the small size (volume 1.15–1.86 × 10^{-6} cm^3) and poor quality of the available crystals; (2) since the packing of the Cu_6 cluster is dictated by its peripheral phenyl groups (which

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(26) Even in species where the terminal hydride ligands appear to occupy no obvious stereochemical position, a metal–hydrogen stretching mode is observable in the infrared spectrum. Thus $HRh(PPh_3)_4$, which is pseudotetrahedral (ref 27), has ν(Rh–H) 2140 cm^{-1} (ref 28). $HRh(PPh_3)_3(AsPh_3)$, which also has a tetrahedral RhP_3As framework, presumably exists as two isomers since it shows two Rh–H stretches, at 2180 and 2125 cm^{-1} (ref 29). We may note that this argument also applies to $HCo(CO)_4$ and $H_2Fe(CO)_4$, both of which were shown to be quasi-tetrahedral by electron diffraction studies (ref 30).

(27) R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

(28) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).

(29) R. W. Baker, B. Ilmaier, P. J. Pauling, and R. S. Nyholm, *Chem. Commun*, 1077 (1970).

(30) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

(31) It is clear that the six "short" copper–copper bonds demonstrate a statistically significant variation in length. Strictly they can be divided into three subgroups: Cu(4)–Cu(5) = 2.498 (5) and Cu(5)–Cu(1) = 2.494 (6) Å, Cu(3)–Cu(6) = 2.530 (6) and Cu(6)–Cu(4) = 2.545 (5) Å, and Cu(1)–Cu(2) = 2.592 (5) and Cu(2)–Cu(3) = 2.595 (5) Å. We have no explanation of this; perhaps it arises as a consequence of interligand repulsions.

(32) M. R. Churchill, P. H. Bird, H. D. Kaesz, and B. Fontal, *J. Amer. Chem. Soc.*, **90**, 7135 (1968).

(33) See also H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, **91**, 1021 (1969).

(34) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).

(35) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 5670 (1971).

cannot thereby be disordered), any internal disorder would affect the copper atoms more than it would the phosphorus atoms. The thermal parameters of the copper atoms should then be larger than those of the phosphorus atoms. In fact, the *opposite* is observed. We therefore reject the possibility of disorder.]

Copper–Copper Distances.—Assuming that each triphenylphosphine and hydride ligand contributes two electrons to the octahedral cluster of d^{10} Cu(I) ions, a noble gas configuration is attained provided that each copper atom is linked to its four nearest neighbors by a bond of unit bond order. Even so, the cluster has only 84 outer electrons—two short of the closed system of 86 electrons which is characteristic of octahedral metal carbonyl clusters such as $Co_6(CO)_{16}$,[36] $[Co_6(CO)_{15}{}^{2-}]$,[37] $[Co_6(CO)_{14}{}^{4-}]$,[38] $[Ni_2Co_4(CO)_{14}{}^{2-}]$,[39] $Rh_6(CO)_{16}$,[40] $[Rh_6(CO)_{15}{}^{2-}]$,[41–43] $[Rh_6(CO)_{14}{}^{4-}]$,[42] $Ir_6(CO)_{16}$,[43] $[Ir_6(CO)_{15}{}^{2-}]$,[43] $[Rh_{12}(CO)_{30}{}^{2-}]$,[44] $Co_2Rh_4(CO)_{16}$,[45] $H_2Ru_6(CO)_{18}$,[34–35] $Ru_6(CO)_{17}C$,[46–47] $Ru_6(CO)_{14}$(arene),[46,48] and $[Fe_6(CO)_{16}C^{2-}]$.[49,50]

A problem that obviously requires further work is the correlation of copper–copper distance and bond order. There are some serious anomalies here. Thus, copper–copper interactions are believed to be absent in $[AsEt_3CuI]_4$ (Cu–Cu = 2.60 Å),[51] $[Cu(S_2CNEt_2)]_4$ (Cu–Cu = 2.69 Å),[52] and $[Cu(SOCNPr_2)]_6$ (Cu–Cu = 2.701–3.057 Å, av 2.88 Å),[53] but present in $[Cu_8\{S_2CC(CN)_2\}_6{}^{4-}]$ (Cu–Cu = 2.783–2.871, av 2.83 Å)[54] and the present $H_6Cu_6(PPh_3)_6$ (Cu–Cu = 2.494–2.674, av 2.60 Å).

Experimental Section

Tetrameric Triphenylphosphinocopper(I) Chloride.—CuCl (4.95 g, 0.05 mol) was added to a solution of PPh_3 (13.1 g, 0.05 mol) in $CHCl_3$ (400 ml); the mixture was refluxed for 1 hr and the unreacted CuCl removed by filtration. Concentration of the filtrate under reduced pressure and addition of absolute ethanol resulted in the precipitation of white crystals of $[PPh_3CuCl]_4$. This was washed with diethyl ether and recrystallized from $CHCl_3$–EtOH, mp 240°.

Hexameric Triphenylphosphinocopper(I) Hydride.—$[PPh_3CuCl]_4$ (0.40 g) was dissolved in dimethylformamide (30 ml) which had been deoxygenated by bubbling dry argon through it for 15 min. *Absolutely fresh* solid sodium trimethoxyborohydride from Alfa Inorganics (0.43 g) was added to the solution, with stirring and under argon, at room temperature. (Note well: even partially decomposed sodium trimethoxyborohydride will not produce the required product.) The solution turned red and was filtered to remove particulate matter. After cooling at 0° for 30 min, the mixture was filtered under argon, and the collected red crystals were washed in turn with cold dimethylformamide, water, and acetonitrile and were dried *in vacuo* (yield 0.071 g). The composition of the crystals was shown to be $H_6Cu_6(PPh_3)_6 \cdot HCONMe_2$. This material melts at 111° with decomposition. *Anal.* Calcd: P, 9.18; C, 65.7; H, 4.78. Found: P, 10.23; C, 63.9; H, 4.99.

Preparation and Isotopic Purity of $C_6H_5CO_2D$.—A mixture of benzoyl chloride (6.96 g, 0.05 mol) and D_2O (5 g, 0.276 mol) was refluxed for 2 hr under dry N_2. The resulting monodeuteriobenzoic acid was recrystallized from heptane and dried *in vacuo*.

The isotopic purity was estimated as 97% by comparison of the ^1H nmr spectra of our sample (peaks at 12.6, 8.2, 7.5; relative intensity 1:68:102) with authentic $C_6H_5CO_2H$ (peak ratios 1:2:3, respectively).

Quantitative Determination of Hydrogen Liberated by Decomposition of $H_6Cu_6(PPh_3)_6$.—Samples of $H_6Cu_6(PPh_3)_6$ were prepared as described above except that the washing involved D_2O, rather than H_2O. The benzene used in this experiment was dried over molecular sieves and degassed on a vacuum line by several cycles of the conventional "freeze–pump–thaw" technique.

A precisely weighed sample (∼0.2 g) of solid $H_6Cu_6(PPh_3)_6 \cdot HCONMe_2$ was placed in a 50-ml three-necked flask; one neck was connected to a previously evacuated gas-sampling bulb, shut off from the flask by a stopcock; the second neck was attached, by a rotating joint, to a bulb containing 5 ml of a benzene solution of $C_6H_5CO_2D$ (∼0.1 g, precisely weighed); the third neck was attached to an argon-filled vacuum line consisting of an Hg-filled gas buret and manometer, with appropriate leveling bulbs. After the benzoic acid solution had been frozen by immersion of the bulb in liquid N_2, the entire system was evacuated. The line was then sealed from the vacuum pump and the benzoic acid solution allowed to attain room temperature *slowly* (to prevent "bumping"). Argon was then led into the system (excluding the gas sampling bulb) until the internal pressure was equal to the external barometric pressure, with the Hg level of the gas buret close to the zero mark. The ambient pressure and temperature and initial Hg level on the gas buret were noted. The acid bulb was then rotated, spilling the benzoic acid solution onto the solid $H_6Cu_6(PPh_3)_6$ sample. The reaction mixture was stirred magnetically until all generation of hydrogen ceased (about 140 min). The volume of gas produced was measured in the gas buret after equalizing internal and external pressures with the leveling bulb. The number of moles of gas generated was calculated using the ideal gas equation. The previously evacuated gas sampling bulb was then opened to the system and a portion of the generated gas was withdrawn for mass spectral analysis.

Determination of Isotopic Composition of Generated Hydrogen.—The mass spectra of gas samples were measured on an AEI-MS9 mass spectrometer some 30 min to 24 hr after their collection. Relative peak heights for *m/e* 2, 3, and 4 yielded the H_2:HD:D_2 ratio. No significant concentration of D_2 was detected. The results are shown in Table V. A "blank" of pure argon was also examined to ensure that the carrier gas contained no significant amount of hydrogen.

Mass Spectral Analysis of Solid Reaction Residues.—Benzene was removed from the reaction mixture at room temperature and under reduced pressure. One portion of the solid residue was dissolved in acetone and treated with an acetone solution of LiBr. The resulting gray-white precipitate was recrystallized from $CHCl_3$–EtOH, yielding white $[PPh_3CuBr]_4$, mp 245°. The mass spectrum of this species was identical with that of authentic nondeuterated $[PPh_3CuBr]_4$, mp 245°.

A second portion of the solid residue was dissolved in acetone and treated with excess concentrated HCl solution. The mixture was filtered; concentration of the filtrate, followed by addition of H_2O, yielded a white solid which was recrystallized from acetone–H_2O (mp 121°). The mass spectrum of this substance was identical with that of authentic nondeuterated benzoic acid.

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