

Appendix

Davydov States for β - and γ -Tetrakis(μ -pivalato)dimolybdenum(II). The monoclinic, $I2/c$, structure possesses two crystallographically equivalent molecules in a primitive cell. $\Phi_1'(k)$ and $\Phi_2'(k)$ designate Frenkel exciton bands for the two symmetry-equivalent molecular transitions for the excitation of a site 1 and a site 2 molecule, respectively, where k is the wave vector. The two Davydov bands may be represented by

$$\Phi_1'(k) = [\Phi_1'(k) + \Phi_2'(k)]/\sqrt{2} \quad (2)$$

$$\Phi_{II}'(k) = [\Phi_1'(k) - \Phi_2'(k)]/\sqrt{2} \quad (3)$$

Transitions are allowed only to the two Davydov states, $\Phi_1'(0)$ and $\Phi_{II}'(0)$. If the transition moment operators for the two symmetry-related molecules are μ_1 and μ_2 , the transition moment vectors are given by $\mu_1 = \langle \Phi_1' | \mu_1 | \Phi_1^0 \rangle$ and $\mu_2 = \langle \Phi_2' | \mu_2 | \Phi_2^0 \rangle$ where Φ^0 and Φ' are ground- and excited-state molecular wave functions. The transition moments from the ground state, Φ^0 , to the Davydov states, $\Phi_1'(0)$ and $\Phi_{II}'(0)$, are given by

$$\mu_1 = \langle \Phi_1'(0) | \mu_1 + \mu_2 | \Phi^0 \rangle = \sqrt{N/2}(\mu_1 + \mu_2) \quad (4)$$

$$\mu_{II} = \langle \Phi_{II}'(0) | \mu_1 - \mu_2 | \Phi^0 \rangle = \sqrt{N/2}(\mu_1 - \mu_2) \quad (5)$$

where N is the number of unit cells in the crystal and the N factor results from the normalization of the exciton wave function. Since μ_1 is a vector, it can be expressed as

$$\mu_1 = xa + yb + zc \quad (6)$$

The c -glide plane reflection that converts molecule 1 into molecule 2 converts μ_1 into μ_2 , so

$$\mu_2 = xa - yb + zc \quad (7)$$

Therefore

$$\mu_1 + \mu_2 = 2xa + 2zc \quad (8)$$

$$\mu_1 - \mu_2 = 2yb \quad (9)$$

One of the transition moments will lie along the b axis, and the

other will be normal to the b axis.

The orthorhombic $Pbcn$ crystal has four symmetry-equivalent molecules in a primitive lattice cell. There are then transitions possible to four Davydov states with the wave vector, k , of 0.

$$\Phi_1'(0) = [\Phi_1'(0) + \Phi_2'(0) + \Phi_3'(0) + \Phi_4'(0)]/2 \quad (10)$$

$$\Phi_{II}'(0) = [\Phi_1'(0) + \Phi_2'(0) - \Phi_3'(0) - \Phi_4'(0)]/2 \quad (11)$$

$$\Phi_{III}'(0) = [\Phi_1'(0) - \Phi_2'(0) + \Phi_3'(0) - \Phi_4'(0)]/2 \quad (12)$$

$$\Phi_{IV}'(0) = [\Phi_1'(0) - \Phi_2'(0) - \Phi_3'(0) + \Phi_4'(0)]/2 \quad (13)$$

For $Pbcn$ the four symmetry-related molecular transition moment vectors have the form

$$\mu_1 = xa + yb + zc \quad (14)$$

$$\mu_2 = -xa - yb + zc \quad (15)$$

$$\mu_3 = xa - yb - zc \quad (16)$$

$$\mu_4 = -xa + yb - zc \quad (17)$$

$$\mu_1 = \langle \Phi_1'(0) | \mu_1 + \mu_2 + \mu_3 + \mu_4 | \Phi^0 \rangle = (N/2)(\mu_1 + \mu_2 + \mu_3 + \mu_4) = 0 \quad (18)$$

$$\mu_{II} = \langle \Phi_{II}'(0) | \mu_1 + \mu_2 + \mu_3 + \mu_4 | \Phi^0 \rangle = (N/2)(\mu_1 + \mu_2 - \mu_3 - \mu_4) = 2Nzc \quad (19)$$

$$\mu_{III} = \langle \Phi_{III}'(0) | \mu_1 + \mu_2 + \mu_3 + \mu_4 | \Phi^0 \rangle = (N/2)(\mu_1 - \mu_2 + \mu_3 - \mu_4) = 2Nxa \quad (20)$$

$$\mu_{IV} = \langle \Phi_{IV}'(0) | \mu_1 + \mu_2 + \mu_3 + \mu_4 | \Phi^0 \rangle = (N/2)(\mu_1 - \mu_2 - \mu_3 + \mu_4) = 2Nyb \quad (21)$$

Hence, a transition to state $\Phi_1'(0)$ is forbidden and three separate transitions will be aligned with the orthogonal a , b , and c axes, respectively.

Supplementary Material Available: Tables of anisotropic and isotropic thermal parameters (2 pages); tables of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Alcohol Elimination Chemistry of $(\text{CuO}^t\text{Bu})_4$

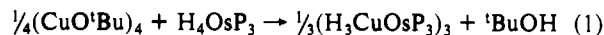
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The Bronsted basicity of $(\text{CuO}^t\text{Bu})_4$ was tested against a range of weak acids. With $(\text{Ph}_2\text{P})_2\text{CH}_2$, $^t\text{BuOH}$ is eliminated, with production of the cage molecule $\text{Cu}_3(\text{Ph}_2\text{PCHPPH}_2)_3$, which was characterized by ^1H and ^{31}P NMR spectra. With Ph_2PH , $^t\text{BuOH}$ is eliminated to precipitate $(\text{CuPPh}_2)_x$, which can be dissolved with $\text{L} = \text{Ph}_2\text{PH}$ or PPh_3 to give $[(\text{Ph}_2\text{PH})\text{CuPPh}_2]_x$ and monomeric $\text{Ph}_3\text{PCuPPh}_2$. With $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, deprotonation of a CH_2 group is followed by P-C bond cleavage to give LCuPPh_2 , where L may be either $\text{Ph}_2\text{PCH}=\text{CH}_2$ or excess phosphine chelate. The vinyl group in this phosphine (either generated from $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ or as added $\text{Ph}_2\text{PCH}=\text{CH}_2$) is catalytically hydrogenated in this reaction system (100 atm H_2 , 25 °C). $(\text{CuO}^t\text{Bu})_4$ reacts with PPh_3 to yield the dimer $(\text{Ph}_3\text{PCuO}^t\text{Bu})_2$, shown by X-ray diffraction to be a gull-winged dimer. This molecule does not dissolve intact in toluene, but shows partial phosphine ligand redistribution to $(\text{CuO}^t\text{Bu})_4$ and a more phosphine-rich species. Crystallographic data (-165 °C): $a = 10.327$ (4) Å, $c = 36.669$ (20) Å with $Z = 4$ in space group $P4_12_1$.

Introduction

We recently reported several cases^{1,2} in which $(\text{CuO}^t\text{Bu})_4$ reacts with transition-metal hydride complexes to couple the two metals with simultaneous elimination of alcohol (eqs 1 and 2; $\text{P} =$



PMe_2Ph). Such a bimolecular reductive elimination is particularly interesting since it gives the appearance of proton transfer to basic alkoxide oxygen, yet an X-ray crystallographic study³ of the copper reagent 1 has shown it to contain three-coordinate oxygen. Such a μ_2 -alkoxide oxygen would appear to be, at best, a weak base.

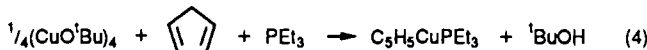
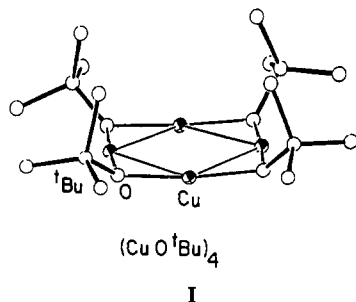
Part of the reason for suggesting a proton-transfer mechanism for eqs 1 and 2 rests on the work of Saegusa et al.,⁴ who reported that $(\text{CuO}^t\text{Bu})_4$ reacts with carbon acids to form $^t\text{BuOH}$ and a Cu-C bond (eqs 3 and 4). Additional evidence for basicity at

(1) Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Intl. Ed. Engl.* **1986**, *25*, 262.

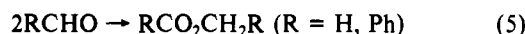
(2) Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Intl. Ed. Engl.* **1987**, *26*, 135.

(3) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

(4) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.



the oxygens of (CuO^tBu)₄ comes from reports⁵ that this compound will catalyze the Tishchenko reaction (eq 5), a transformation normally promoted by strong bases.



We report here observations on the reactions of (CuO^tBu)₄ with a variety of phosphines, some of which are weak carbon and phosphorus acids. This has led to an example of P–C bond cleavage under exceptionally mild conditions.

Experimental Section

General Procedures. All operations were carried out under nitrogen purified with R3-11 (BASF) and 4-Å molecular sieves/Dri-Rite by employing standard Schlenk techniques or in a Vacuum Atmospheres glovebox with prepurified nitrogen. Vinylidiphenylphosphine, (Ph₂P)₂CH₂ (dppm), triphenylphosphine, and diphenylphosphine were purchased from Aldrich Chemical Co. and were used as received. Toluene, tetrahydrofuran (THF), and benzene were distilled from sodium benzophenone ketyl. Hexane was distilled from Na/K alloy containing benzophenone. *tert*-butyl alcohol was dried over BaO. Deuterated solvents were vacuum transferred from Na/K alloy. Proton NMR spectra were recorded on a Nicolet NT-360 spectrometer while ³¹P{¹H} NMR spectra were recorded on Varian XL-100 and Nicolet NT-360 spectrometers. All chemical shifts are reported on the δ scale, with downfield shifts being positive.

(CuO^tBu)₄. This procedure is a modification of a previously reported synthesis.⁴ Four grams of CuCl (40 mmol) and 2.9 g of LiO^tBu (36 mmol) were combined in 30 mL of THF, and the resulting mixture was vigorously stirred for 5 h. The pale yellow mixture was then evaporated to dryness under reduced pressure. The product was vacuum sublimed from the crude yellow powder with infrared heating.⁶ After 4 h, 4.35 g (87% yield) of the bright yellow crystalline product was collected. The complex is extremely oxygen- and moisture-sensitive. ¹H NMR (C₆D₆): δ 1.30 (s).

[^tBuOCuPPh₃]₂. Triphenylphosphine (0.30 g) and (CuO^tBu)₄ (0.20 g, 1 equiv of PPh₃/Cu) were combined in 10 mL of hexane, and the mixture was vigorously stirred. The product began to precipitate immediately as a pale yellow powder. After 1 h, the mixture was filtered and the precipitate was washed with two 5-mL portions of hexane and dried to give 0.49 g (85%) of the complex. Recrystallization was performed from toluene/hexane. ¹H NMR (C₆D₆): δ 1.43 (br s, 4.5 H), 1.57 (br s, 4.5 H), 7.05 (m, 9 H), 7.68 (m, 6 H); ³¹P NMR (toluene, –30 °C): δ +1.5 (br s). At –65 °C, two resonances are resolved, at +0.4 and –3.8 ppm.

Crystallographic Study of [Cu(OCMe₃)PPh₃]₂. The crystals were grown from a toluene solution of (CuO^tBu)₄ and PPh₃ (Cu:P = 1:1) by addition of hexanes to the cloud point; subsequent cooling to –20 °C gave pale yellow crystals. The sample consisted of elongated prisms showing 4-fold morphology. The crystal chosen was cleaved from the end of a larger specimen. A systematic search of reciprocal space yielded a tetragonal cell with systematic absences of *l* even for 00*l* and *h* even for *h*00. Data were collected (6° ≤ 2θ ≤ 45°) by using a relatively short scan width of 1.5°, due to the large *c* axis. Cell constants and parameters of the data collection are presented in Table I. No absorption correction was applied to the data.⁷ The structure was solved by direct methods

Table I. Crystallographic Data for [Cu(OCMe₃)PPh₃]₂

chem formula	Cu ₂ P ₂ O ₂ C ₄₄ H ₄₈	space group	P4 ₁ 2 ₁ 2
<i>a</i> , Å	10.327 (4)	<i>T</i> , °C	–165 °C
<i>b</i> , Å	10.327 (4)	<i>λ</i> , Å	0.71069
<i>c</i> , Å	36.669 (20)	<i>ρ</i> _{calcd} , g cm ^{–3}	1.355
<i>V</i> , Å ³	3910.90	<i>μ</i> (MoKα), cm ^{–1}	12.05
<i>Z</i>	4	<i>R</i>	0.0412
<i>fw</i>	797.9	<i>R</i> _w	0.0390

Table II. Fractional Coordinates^a and Isotropic Thermal Parameters^b for [Cu(OCMe₃)PPh₃]₂

	<i>x</i>	<i>y</i>	<i>z</i>	10 <i>B</i> _{iso} , Å ²
Cu(1)	1168 (1)	806 (1)	7526.1 (2)	17
P(2)	2999 (2)	1674 (2)	7654.7 (5)	16
C(3)	2897 (6)	3353 (7)	7809 (2)	16
C(4)	1693 (7)	3872 (7)	7886 (2)	18
C(5)	1551 (7)	5151 (7)	8004 (2)	20
C(6)	2627 (8)	5892 (8)	8041 (2)	29
C(7)	3818 (8)	5392 (8)	7968 (3)	41
C(8)	3965 (7)	4144 (8)	7851 (2)	31
C(9)	4280 (7)	1841 (6)	7312 (2)	18
C(10)	5593 (7)	1620 (7)	7383 (2)	20
C(11)	6520 (7)	1880 (7)	7124 (2)	19
C(12)	6176 (8)	2308 (7)	6793 (2)	25
C(13)	4890 (8)	2542 (8)	6707 (2)	25
C(14)	3956 (7)	2295 (7)	6969 (2)	20
C(15)	3854 (6)	830 (7)	8026 (2)	16
C(16)	4035 (8)	–499 (7)	7989 (2)	27
C(17)	4673 (8)	–1194 (8)	8251 (2)	27
C(18)	5153 (7)	–590 (8)	8554 (2)	24
C(19)	4978 (8)	717 (8)	8595 (2)	26
C(20)	4316 (8)	1417 (7)	8334 (2)	22
O(21)	–47 (4)	197 (4)	7153 (1)	19
C(22)	111 (7)	277 (6)	6770 (2)	17
C(23)	154 (8)	1722 (8)	6667 (2)	25
C(24)	1353 (8)	–372 (8)	6656 (2)	27
C(25)	–1044 (7)	–338 (7)	6581 (2)	20

^a Fractional coordinates are ×10⁴. ^b Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Bond Distances (Å) for [Cu(OCMe₃)PPh₃]₂

Cu–Cu'	2.890 (2)	C(3)–C(4)	1.384 (9)
Cu–P	2.144 (2)	C(3)–C(8)	1.381 (10)
Cu–O	1.960 (4)	C(4)–C(5)	1.397 (10)
Cu–O'	1.996 (4)	C(5)–C(6)	1.356 (11)
		C(6)–C(7)	1.361 (12)
P–C(3)	1.827 (7)	C(7)–C(8)	1.367 (11)
P–C(9)	1.834 (7)		
P–C(15)	1.841 (7)	C(9)–C(10)	1.400 (10)
O–C(22)	1.418 (7)	C(9)–C(14)	1.383 (10)
		C(10)–C(11)	1.376 (10)
C(22)–C(23)	1.539 (10)	C(11)–C(12)	1.340 (10)
C(22)–C(24)	1.507 (10)	C(12)–C(13)	1.386 (11)
C(22)–C(25)	1.519 (9)	C(13)–C(14)	1.383 (10)
		C(15)–C(16)	1.391 (10)
		C(15)–C(20)	1.369 (10)
		C(16)–C(17)	1.368 (11)
		C(17)–C(18)	1.367 (11)
		C(18)–C(19)	1.371 (11)
		C(19)–C(20)	1.381 (11)

(MULTAN78) and Fourier techniques and refined by full-matrix least-square methods. All hydrogen atoms were located and refined. The residuals were not significantly improved by switching the model to the enantiomorphic coordinates, so the absolute configuration remains undetermined. A final difference Fourier synthesis was featureless, with the largest peak being 0.45 e/Å³. Non-hydrogen fractional coordinates are collected in Table II, with bond lengths and angles in Tables III and IV. Anisotropic thermal parameters, hydrogen atom parameters and *F*_o and *F*_c values are available as supplementary material. The molecular structure is shown in Figures 1–3. Phenyl rings are planar, and the dimensions within the phenyl and *tert*-butoxy groups are unexceptional.

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

(6) Pool, G. C.; Teuben, J. H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darnsborg, M. Y., Eds.; ACS Symposium Series 357, American Chemical Society: Washington, DC, 1987.

(7) For general crystallographic procedures and programs, see: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

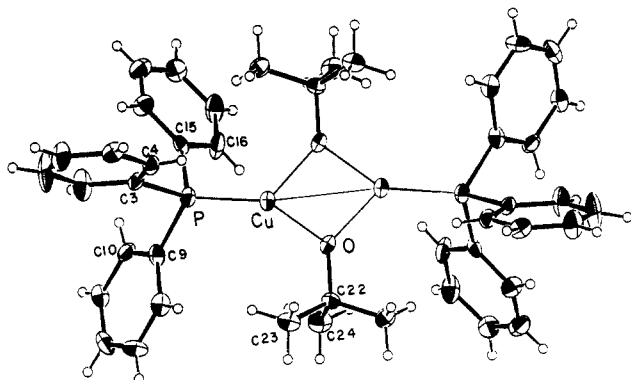


Figure 1. ORTEP portrayal of the structure of $[\text{Cu}(\text{OCMe}_3)\text{PPh}_3]_2$, showing atom labeling in the unique half of the molecule. Atoms related to those shown by the crystallographic 2-fold axis of symmetry are designated with a prime. Unlabeled carbon atoms follow in sequence from those shown.

Phenyl carbon-to-hydrogen distances average 0.86 Å, ranging from 0.80 (5) to 0.94 (7) Å. Methyl C-H distances average 0.96 Å, ranging from 0.93 (6) to 1.01 (7) Å. Within the *tert*-butyl group, the methyl groups all adopt staggered conformations. The C-C-H angles average 112°, ranging from 109 (4) to 117 (5)°. The H-C-H angles average 107°, ranging from 99 (5) to 115 (5)°.

Reaction of $(\text{CuO}^t\text{Bu})_4$ with dppm. Solid $(\text{CuO}^t\text{Bu})_4$ (250 mg, 0.46 mmol) was added to a Schlenk flask containing a stir bar. Benzene was added to the flask to dissolve the compound. Solid dppm (690 mg, 1.80 mmol) was added slowly from a solids addition tube. A yellow solid slowly precipitated, and the yellow slurry was filtered on a medium frit. ^1H NMR (C_6D_6 , 20 °C, 360 MHz) δ 8.3 (m), 7.55 (m), 7.25 (m), 7.05 (m), 6.85 (br s), 6.7 (br s), 6.5 (m), 6.3 (m), 2.5 (m), 2.1 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene -70 °C, 150 MHz) 1.8 (m), -17.8 (m).

Reaction of $(\text{CuO}^t\text{Bu})_4$ with PPh_2H . Solid $(\text{CuO}^t\text{Bu})_4$ (300 mg, 0.55 mmol) was weighed into a 100-mL Schlenk flask and dissolved in benzene. PPh_2H (410 mg, 2.20 mmol, 0.38 mL) was added slowly (syringe) to the vigorously stirred benzene solution. The yellow color of the $(\text{CuO}^t\text{Bu})_4$ was rapidly replaced by a red solid and light orange supernate. This slurry was filtered with a medium frit. The solid was insoluble in toluene, benzene, or THF. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{CuP}$: C, 57.95; H, 4.05. Found: C, 58.13; H, 4.00.

Reaction of $(\text{CuO}^t\text{Bu})_4$ + $2\text{PPh}_2\text{H}/\text{Cu}$. Solid $(\text{CuO}^t\text{Bu})_4$ (250 mg, 0.46 mmol) was weighed into a 100-mL Schlenk flask and dissolved in

Table IV. Bond Angles (deg) for $[\text{Cu}(\text{OCMe}_3)\text{PPh}_3]_2$

Cu-Cu'-P'	158.6 (1)	P-C(3)-C(4)	118.9 (5)
P-Cu-O	148.4 (1)	P-C(3)-C(8)	123.4 (6)
O-Cu-O'	80.4 (2)	C(4)-C(3)-C(8)	117.8 (7)
Cu-P-C(3)	114.5 (2)	C(3)-C(4)-C(5)	121.6 (7)
Cu-P-C(9)	121.6 (2)	C(4)-C(5)-C(6)	118.6 (7)
Cu-P-C(15)	112.8 (2)	C(5)-C(6)-C(7)	120.5 (8)
C(3)-P-C(9)	99.5 (3)	C(6)-C(7)-C(8)	121.3 (8)
C(3)-P-C(15)	104.3 (3)	C(3)-C(8)-C(7)	120.3 (8)
C(9)-P-C(15)	101.9 (3)		
Cu-O-Cu'	93.9 (2)	P-C(9)-C(10)	123.7 (5)
Cu-O-C(22)	126.9 (4)	P-C(9)-C(14)	118.8 (5)
Cu'-O-C(22)	132.1 (4)	C(10)-C(9)-C(14)	117.4 (7)
O(21)-C(22)-C(23)	107.6 (5)	C(9)-C(10)-C(11)	120.8 (7)
O(21)-C(22)-C(24)	110.3 (6)	C(10)-C(11)-C(12)	120.4 (7)
O(21)-C(22)-C(25)	109.7 (6)	C(11)-C(12)-C(13)	121.1 (7)
C(23)-C(22)-C(24)	109.8 (7)	C(12)-C(13)-C(14)	118.6 (7)
C(23)-C(22)-C(25)	108.5 (6)	C(9)-C(14)-C(13)	121.6 (7)
C(24)-C(22)-C(25)	110.9 (6)		
P-Cu-O'	131.1 (1)	P-C(15)-C(16)	117.4 (6)
		P-C(15)-C(20)	124.6 (6)
		C(16)-C(15)-C(20)	118.0 (7)
		C(15)-C(16)-C(17)	121.0 (8)
		C(16)-C(17)-C(18)	120.4 (8)
		C(17)-C(18)-C(19)	119.5 (8)
		C(18)-C(19)-C(20)	120.2 (8)
		C(15)-C(20)-C(19)	121.0 (8)

benzene. PPh_2H (2 equiv/Cu, 680 mg, 3.6 mmol, 0.64 mL) was measured out in a syringe. The neat liquid was added dropwise and intermediate production of a red solid was noted. When the addition was complete, a homogeneous yellow solution was obtained. A yellow solid may be obtained by removing the solvent in vacuo. The solid has a melting point of 90 °C; the color changes to red at 93 °C, and a clear liquid condensate is noted upon cooling. ^1H NMR (C_6D_6 , 20 °C, 360 MHz): δ 7.5 (m), 7.2 (m), 6.8 (m), 6.7 (m), 5.57 (d, $J_{\text{P-H}} = 300$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 30 °C, 40.5 MHz): δ -32.8 (br s). When this reaction was repeated in C_6D_6 , the above ^1H NMR signals were accompanied by those of $^t\text{BuOH}$.

Reaction of $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$ with PPh_2H . Solid $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$ (200 mg, 0.10 mmol)⁵ was weighed into a 100-mL flask and dissolved in benzene. Neat liquid PPh_2H (114 mg, 0.60 mmol, 0.11 mL) was added via a syringe while the solution was stirred. The red color of the solution was immediately replaced by a yellow color with concomitant gas evolution. This solution was filtered through a medium frit, and the benzene was removed in vacuo. ^1H NMR (C_6D_6 , 21 °C, 360 MHz): δ 7.4 (m), 7.3

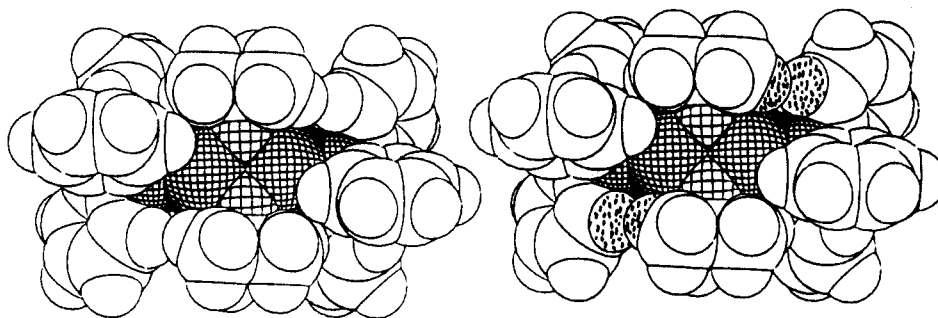


Figure 2. Stereo space-filling drawing of the molecule oriented as in Figure 1. For this figure, hydrogens have been placed with a C-H distance of 1.08 Å.

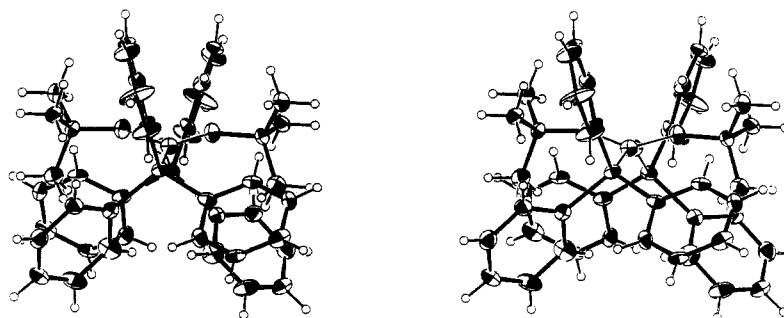


Figure 3. Stereo drawing of $[\text{Cu}(\text{OCMe}_3)\text{PPh}_3]_2$ viewed down the Cu-Cu line. Deviations of the Cu_2O_2 core from planarity are evident.

(m), 6.9 (m), 6.8 (m). ³¹P{¹H} NMR (C₆D₆, 30 °C, 40.5 MHz): δ -4.5 (d, J_{P-P} = 78 Hz), -32.2 (d, J_{P-P} = 80 Hz). When this reaction was repeated in C₆D₆, all of the above ¹H NMR peaks were evident, but also one at 4.5 ppm, due to H₂.

Reaction of (CuO^tBu)₄ with dppe. In a typical experiment, solid (CuO^tBu)₄ (10 mg, 0.018 mmol) was combined with Ph₂PC₂H₂PPh₂ (dppe) (29 mg, 0.073 mmol) and then dissolved in 0.5 mL C₆D₆. The solution was immediately yellow in color and cloudy, and more precipitate formed with the passage of time. Crystals formed after several weeks in a sealed tube. These crystals were of the same space group as (dppeCuPPh₂)₂. NMR spectroscopy revealed the presence of vinyl-diphenylphosphine in addition to (dppeCuPPh₂)₂, HO^tBu, and other products. ¹H NMR (C₆D₆, 20 °C, 360 MHz): δ 7.65 (m), 7.5 (m), 7.3 (m), 6.9 (m), 6.75 (m), 6.45 (d of d of d, J = 18, 14, 12 Hz, vinyl), 5.64 (d of d of d, J = 34, 12, 2 Hz, vinyl), 5.51 (t of m, J = 17 Hz, vinyl), 2.15 (br s), 1.95 (m), 1.85 (m). ³¹P{¹H} NMR (C₆D₆, 30 °C, 40.5 MHz): δ -1 (m), -5 (m), -10 (m), -12.9 (s).

Reaction of (CuO^tBu)₄ with dppe under H₂. Solid (CuO^tBu)₄ (400 mg, 0.73 mmol) and dppe (1.165 g, 2.93 mmol) were dissolved in 15 mL of THF. This orange mixture was then held under 1500 psi of H₂ for 2 h. Following venting of the pressure, the mixture of red and yellow solids was filtered on a medium frit. ¹H NMR (C₆D₆, 20 °C, 360 MHz): δ 7.62 (br s), 7.5 (m), 6.86 (m), 6.65 (m), 2.97 (br m), 2.28 (br m), 1.65 (q, J_{P-H} = 7.4 Hz), 0.80 (m). ³¹P{¹H} NMR (C₆D₆, 30 °C, 40.5 MHz): δ -14.6 (s).

Reaction of (CuO^tBu)₄ with dppe and PPh₂(vinyl) under H₂. Solid (CuO^tBu)₄ (100 mg, 0.183 mmol) and dppe (300 mg, 0.75 mmol) were charged into a pressure vessel and dissolved in THF. A ³¹P{¹H} NMR spectrum was obtained ("sample A"). This orange mixture was then hydrogenated under 1500 psi of H₂ for 1 h. Another ³¹P NMR spectrum ("sample B") was obtained (after venting H₂) and vinyl-diphenylphosphine (5 equiv/copper, 776 mg, 3.7 mmol, 0.725 mL) was then added to the pressure vessel. After 1 h more at 1500 psi of H₂, the pressure vessel was again depressurized and a last ³¹P NMR spectrum was obtained ("sample C") from the now red solution. ³¹P{¹H} NMR (C₆D₆, 30 °C, 40.5 MHz): sample A, δ -12.0 (s); sample B, δ -11.2 (s), -12.6 (s); sample C, δ -11.9 (s).

Results

Reaction with PPh₃. (a) **Isolation and Characterization.** Initially, we focused on the reactivity of the μ-O^tBu linkage in (CuO^tBu)₄, a topic which is inextricably linked to the degree of residual Lewis acidity of copper in this compound. Since a coordination number of 2 is relatively low for Cu(I), one might anticipate that alkoxide lone pairs would be utilized in π-donation to the metal, and the Cu-O distances (1.85 Å) are, in fact, short. However, as mentioned in the Introduction, the oxygen centers are distinctly pyramidal in (CuO^tBu)₄, and thus coordinative unsaturation pertains at copper. This characteristic, as well as the Bronsted basicity of alkoxide oxygen attached to a late transition metal,⁸ is essential to the heterolytic splitting of H₂, which supports catalytic hydrogenation.^{5,9-11}

A toluene/hexane solution containing (CuO^tBu)₄ and PPh₃ in a 1:1 Cu:PPh₃ ratio deposits colorless crystals on cooling. Such crystals have the empirical formula Cu(O^tBu)PPh₃. This 1:1 ratio of proton-containing ligands is confirmed by integrating the phenyl and methyl regions of the ¹H NMR in C₆D₆. However, the methyl region displays two resonances, of nearly equal intensity, at 1.43 and 1.57 ppm. These two resonances undergo little intensity alteration on recording the 360-MHz ¹H NMR spectrum in toluene-*d*₈ at -65 °C. The ³¹P{¹H} NMR spectrum at -30 °C in toluene shows one broad line. Given the complexity of PPh₃/CuX systems reported previously,¹² speculation about the origin of these spectral features seemed premature. An objective determination of the molecularly and structure of the crystalline solid was therefore made by X-ray diffraction.

(b) **Structure Determination of [Cu(OCMe₃)PPh₃]₂.** The crystalline solid is comprised of dimeric molecules that experience no unusually short intermolecular contacts. The [Cu(OCMe₃)-

PPh₃]₂ dimer sits around a crystallographic 2-fold rotational axis in the solid state. The 2-fold axis is perpendicular to both the Cu...Cu and O...O lines, making half of the dimer, Cu(OCMe₃)PPh₃, the crystallographically unique unit. The CuPOO' unit is planar to within 0.027 Å. The trigonal planar coordination about copper has an acute OCuO' angle (80.4°) and large (but asymmetric) OCuP angles to the bulky phosphorus ligand (148.4 and 131.1°). It is also evident, from a top view of the molecule (Figure 1), that the projection of the P-Cu line is not colinear with the Cu-Cu line. This is clearly (Figure 2) related to a short contact (2.12 Å) between phenyl ortho and *tert*-butyl hydrogens (stippled in Figure 2). As a consequence, the two Cu-O distances differ by 0.036 Å or 6σ (difference). Also in response to this short contact, the angle Cu-P-C9 is over 7° larger than the other two Cu-P-C angles.

While the CuPOO' unit is planar, the Cu₂P₂O₂ unit is not planar; the dihedral angle about the O...O' line is 143.4°. The fold along the O...O' line is accompanied by a slight bending of the *tert*-butyl groups in the same direction (Figure 3) so that the bridging oxygen is slightly pyramidal. The sum of the angles about oxygen is 352.9°, while those about Cu sum to 359.9°. An end view of the molecule (Figure 3) shows the gull-wing effect. The rotational conformation about the CuP bond is such that two phenyl rings from each phosphine are on this same (concave) side of the Cu₂O₂ fold. The net result of all of these conformational choices is to leave an open and a closed side to the Cu₂O₂ unit. The open side is evident in Figure 2 and shows the metals to be unusually accessible to an external reagent. For example, it is evident from Figure 2 that H₂ readily fits into the open side of [Cu(OCMe₃)PPh₃]₂, a result relevant to the synthesis of (HCuPPh₃)₆.^{5,9-11}

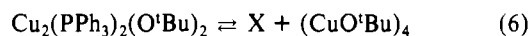
(c) **Solution Equilibration.** We return now to the anomalous observation of two O^tBu methyl resonances (of similar but not identical intensity) in the ¹H NMR of pure solid [Cu(PPh₃)O^tBu]₂ when dissolved in C₆D₆. The following additional observations were made in benzene:

(1) Addition of (CuO^tBu)₄ to [Cu(PPh₃)O^tBu]₂ (gram atom ratio of copper 0.5:1) causes the δ 1.43 resonance to disappear and the δ 1.57 resonance to grow.

This indicates that the two methyl resonances are due to distinct molecular species, not conformers or isomers. The absence of a resonance of (CuO^tBu)₄ (δ 1.30) also shows that the δ 1.43 peak has disappeared by virtue of a chemical reaction between this compound and (CuO^tBu)₄.

(2) Sequential additions of PPh₃ to a C₆D₆ solution of (CuO^tBu)₄ gives (for low P/Cu ratios) mainly the δ 1.57 resonance. As the P/Cu ratio increases above 1.0, the δ 1.43 resonance becomes the major one.

We suggest that all of these observations can be understood in terms of the following equilibrium (eq 6). Species X has a



P/Cu ratio greater than unity (e.g., Cu₂(PPh₃)₃(O^tBu)₂ or Cu(PPh₃)₂O^tBu, either of which would exhibit one *tert*-butyl resonance). Observation 1 above is a mass-action experiment, pushing the equilibrium to the left. Thus, the 1.43 ppm resonance is attributed to X, and that at 1.57 ppm is attributed to [Cu(PPh₃)O^tBu]₂. An attempt to extend these studies by using ³¹P NMR (including the more soluble *p*-tolyl₃ analogues) at -80 °C in toluene revealed two resonances. Further studies at varying overall P:Cu ratios yielded numerous resonances, but small chemical shift dispersion, phosphine ligand exchange, and the rather undiagnostic signals (singlets) frustrated detailed interpretation and led us to turn to chelating phosphines for possibly simpler solution behavior.

Reaction with (Ph₂P)₂CH₂. An attempt was made to form a well-defined CuO^tBu/phosphine derivative by using a chelate ligand. Addition of 1 mol of (Ph₂P)₂CH₂ (dppm) per Cu atom to a benzene solution of (CuO^tBu)₄ immediately results in deposition of a yellow precipitate, leaving a yellow supernate. The latter may be shown (¹H NMR) to contain ^tBuOH, as well as resonances for a metal complex that duplicates those of the yellow

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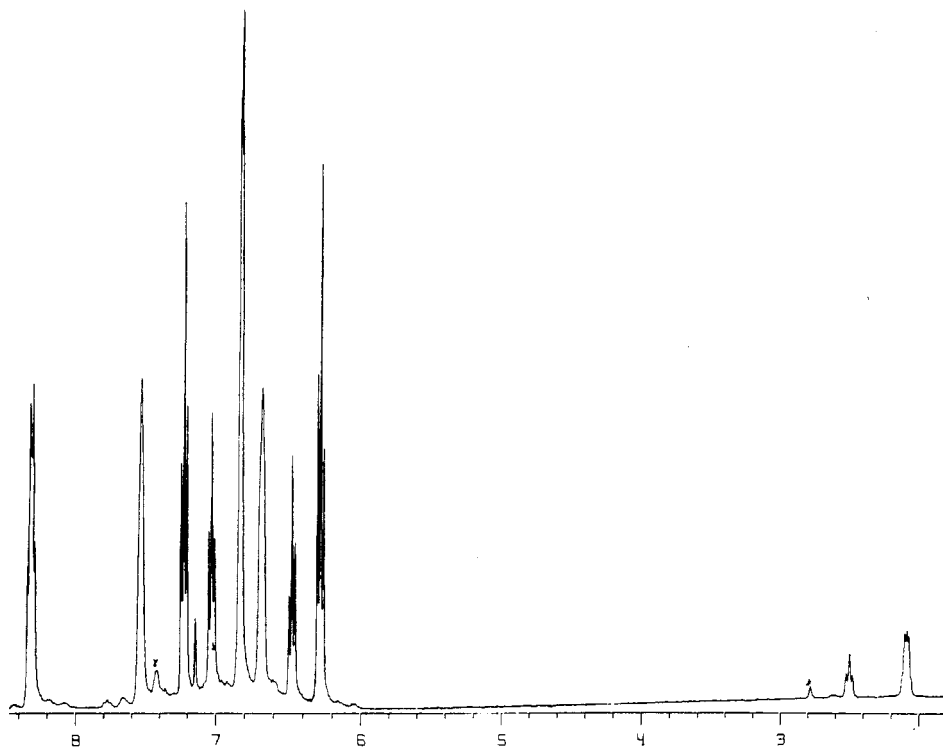


Figure 4. 360-MHz ^1H NMR spectrum (20 °C, in C_6D_6) of $\text{Cu}_3(\text{Ph}_2\text{PCHPPH}_2)_3$. "X" indicates impurities.

solid when the latter is redissolved in C_6D_6 . The ^1H NMR of the yellow solid is exceptionally complicated in the aryl region (Figure 4), showing eight distinct multiplets. The remaining (upfield) resonances, those of the phosphine chelate backbone, are a triplet and a non-first-order multiplet, these being in an intensity ratio of 1:2. The aryl:upfield resonances intensity ratio, together with the conversion of all *tert*-butoxide to $^t\text{BuOH}$ and an oxidation state of +1 for copper, indicates an empirical formula $\text{Cu}(\text{Ph}_2\text{PCHPPH}_2)$ for the yellow solid. That is, the ligand backbone has been deprotonated. It has been reported that CuR ($\text{R} = \text{Me}$ and Ph) reacts with dppm to give RH and $\text{Cu}(\text{Ph}_2\text{PCHPPH}_2)$, the latter being characterized only by an X-ray diffraction structure determination.¹³ The resulting structure of idealized C_{2v} symmetry (II), contains two P_3 ligated copper centers and one two-coordinate

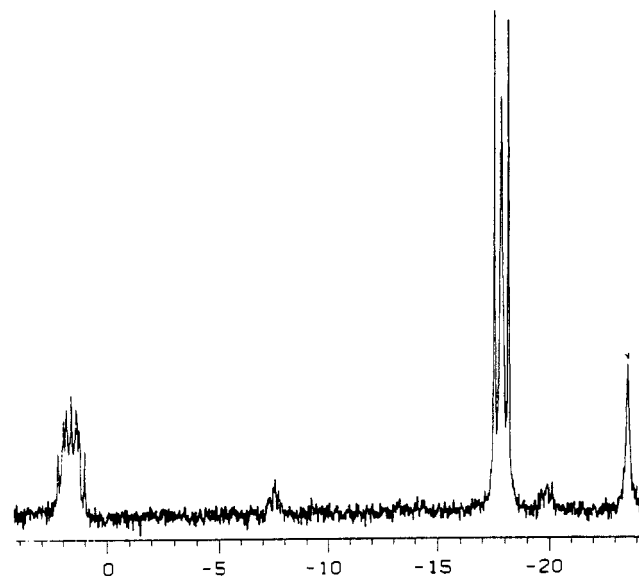
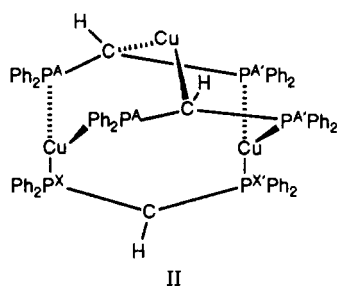
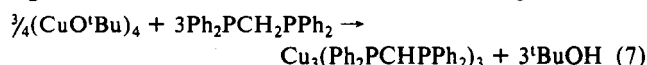


Figure 5. 145.8-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Cu}_3(\text{Ph}_2\text{PCHPPH}_2)_3$ at -70 °C in toluene. "X" indicates impurities.

copper bound only to the two carbanionic centers of deprotonated dppm . The remaining carbanionic center binds to no metal. Confirmation of the identity of the previous $\text{Cu}_3(\text{Ph}_2\text{PCHPPH}_2)_3$ with our yellow solid and proof that the structure dissolves unaltered in toluene come from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This spectrum (Figure 5), at -70 °C to eliminate broadening by quadrupolar copper, shows two chemical shifts of intensity 1:2, consistent with structure II. The actual $^{31}\text{P}\{^1\text{H}\}$ spin system is $\text{A}_2\text{A}'_2\text{XX}'$, and the fine structure in the spectrum (Figure 5) is consistent with this complexity. The four A sites present a virtual triplet pattern because $J_{\text{X-X}'} > J_{\text{A-X}}$. Retention of structure II in solution is in accord with the ^1H NMR data: the intensity 1 triplet is due to the unique bis(diphenylphosphino)methanide

hydrogen coupled only to its adjacent P_X nuclei. Since the phenyls on P_A are diastereotopic, nine aryl chemical shifts are expected; eight are resolved. The overall reaction is thus eq 7.



Reaction with Ph_2PH . Diphenyl phosphine is a weak acid, being deprotonated most frequently with BuLi . The slow addition of 1 mol of Ph_2PH per copper to a benzene solution of $(\text{CuO}^t\text{Bu})_4$ results in immediate deposition of a red precipitate. The supernate is faintly yellow and contains $^t\text{BuOH}$. The red solid is insoluble in aromatics, MeCN , and acetone and it neither dissolves in nor reacts with water. Elemental analysis yields a composition CuPPh_2 for the red solid.¹⁴ The reaction is thus eq 8, where x is used

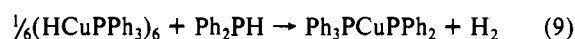
$$\frac{1}{4}(\text{CuO}^t\text{Bu})_4 + \text{Ph}_2\text{PH} \rightarrow (1/x)(\text{CuPPh}_2)_x + ^t\text{BuOH} \quad (8)$$

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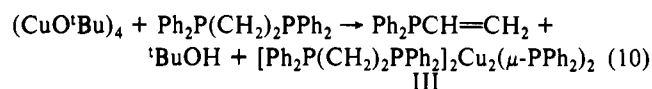
to suggest a polymer, based on solubility. All attempts to grow crystalline (CuPPh₂)_x by slow diffusion of a benzene solution of Ph₂PH into (CuO^tBu)₄ in benzene yielded only powders due to the rapidity of the reaction when the two reagent fronts meet.

The faint yellow color of the supernate following the synthesis in eq 8 is due to reaction of (CuPPh₂)_x with Ph₂PH. Addition of 2 mol of Ph₂PH in eq 8 or addition of 1 mol of Ph₂PH to isolated (CuPPh₂)_x results in a yellow solution with complete consumption of reagents. The ¹H NMR reveals two ortho and two meta + para aryl resonances characteristic of two types of phenyl groups. Also present is a doublet due to a proton directly bonded to phosphorus. The doublet splitting is 300 Hz when the Ph₂PH:CuPPh₂ ratio is 1:1, but it declines monotonically toward the value in free Ph₂PH as additional Ph₂PH is present. Rapid ligand (Ph₂PH) exchange is indicated in a species of formula [(Ph₂PH)CuPPh₂]_n. A PPh₃ analogue was obtained according to eq 9. The reaction in benzene is immediate, and is accompanied



by visible gas evolution. The growth of a resonance at 4.5 ppm identifies this as H₂. The ¹H NMR shows two distinct types of phenyl groups. The formulation of the product as monomeric rests on the ³¹P{¹H} NMR spectrum, which even at +20 °C is a well-resolved pair of doublets (AX pattern), with J_{AX} = 80 Hz. This value is large enough to be consistent with the trans stereochemistry expected for two-coordinate copper in Ph₃PCuPPh₂.

Reaction with Ph₂P(CH₂)₂PPh₂. Addition of this bidentate ligand, dppe, to (CuO^tBu)₄ in benzene or THF results in a yellow solution with subsequent precipitation of a yellow solid. The supernate contains (¹H NMR) ^tBuOH but also Ph₂PCH=CH₂ (eq 10), the latter most evident in its vinylic AMX ¹H NMR



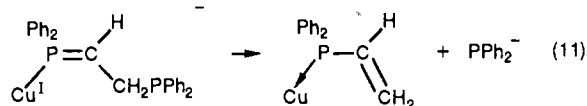
pattern, with additional coupling to phosphorus. This spin system was confirmed by spin-decoupling experiments. The identification as Ph₂PCHCH₂ was confirmed by comparison to the ¹H and ³¹P spectra of an authentic sample. The production of III has been confirmed by isolation of crystals from the reaction and comparison of measured unit cell parameters to those reported in the literature for this compound.¹⁵ Because of the lability of Cu(I) and the simultaneous presence of dppe and Ph₂PCHCH₂ as competitive ligands, the NMR of reaction solutions from eq 10 show complex patterns due to more than one metal complex. These spectral patterns depend upon the ratio of dppe:Cu employed in eq 10, and similar spectra were obtained from solutions of (CuPPh₂)_x and dppe.

Reaction with Ph₂P(CH₂)₂PPh₂ under H₂. When eq 10 was performed under 1500 psi of H₂, the ¹H NMR spectrum of the resulting mixture of red and yellow products contained a large number of resonances. A product firmly identified was PPh₂Et. This reaction system thus hydrogenates the vinyl group on the phosphine ligand. By repeating this experiment in the presence of a total of 7 equiv of PPh₂(CH=CH₂), we observed that all of the vinyl groups were hydrogenated to ethyl groups in 2 h at

1500 psi of H₂. The system is therefore capable of hydrogenating added vinyl groups, and the hydrogenation is thus catalytic.

Discussion

The proton-transfer chemistry reported here all involves weak acids that have (before deprotonation) some site for attachment to the copper metal center. In every case, coordination should enhance the acidity of the acid. Proton transfer, perhaps to O^tBu within the multimetal adduct, then follows. The resulting lone pair of the conjugate base then binds to copper to give the final products characterized here: μ-PPh₂ (from Ph₂PH) or the C-Cu linkage in II. The case of Ph₂P(CH₂)₂PPh₂ is more complex because P-C cleavage is involved. Yamamoto et al. have observed this same cleavage during the thermal decomposition (150 °C) of Me₂Cu₂(dppe)₃.^{16,17} We suggest that the P-C bond cleaved does not involve the deprotonated carbon (eq 11), in part because



that carbon develops ylidic P/C multiple bond character; this same factor enhances the acidity of the coordinated dppe. We also suggest that P-C cleavage, which resembles the base-catalyzed Hoffman elimination, is enhanced by coordination of Cu(I) to the developing PPh₂⁻ moiety. It must be mentioned that coordinated Ph₂PH has been added across the vinyl group in coordinated Ph₂PCH=CH₂ (catalyzed by KO^tBu) to form dppe.¹⁸

For Ph₂PCH₂PPh₂, this P-C bond scission is structurally precluded, so the reaction stops at the deprotonation stage. The group of Shaw has demonstrated¹⁹ the acidity of coordinated dppe, although their deprotonation was always with an external base (RLi) rather than by a coordinated ligand.

The catalytic hydrogenation observed in the dppe reaction systems does not extend to RHC=CH₂ where R = ^tBu or *n*-butyl. It thus appears to depend on the phosphine donor function for its success. In this way, there is a similarity to the hydrogenation of enones (containing a donor ketone) by (HCuPPh₂)₆.^{10,11} Moreover, although a phosphide complex is produced in eq 10, addition of hydrogen across the Cu-PPh₂ bond cannot be involved in the mechanism of catalytic hydrogenation, since this contradicts the thermodynamic position of such a reaction as indicated in eq 9.

Finally, it appears that formation constants for various Cu_n(O^tBu)₄(PPh₃)_m species are not sufficiently differentiated in magnitude to assure that stoichiometry (P:Cu ratio) yields a single predominant solution species.

Acknowledgment. This work was supported by the National Science Foundation. We also thank Scott Horn for skilled technical assistance.

Supplementary Material Available: Tables giving full details of the X-ray structure and anisotropic thermal parameters (2 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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