Organometallics 1989, 8, 2724-2728

Characterization and Structure of Some Four-Coordinate Methylcopper(I) Compounds

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Received April 18, 1989

The structure and the solution behavior of the compounds MeCuL$_n$ (L$_n$ = (PPh$_3$)$_3$, (PMePh$_2$)$_3$, and (Ph$_2$PCH$_2$)$_3$CMe) have been characterized by variable-temperature ^{1}H and ^{31}P NMR studies and (for PPh$_3$) X-ray diffraction. All three compounds exist as monomeric, four-coordinate, 18-electron species at low temperatures in noncoordinating solvents, but ligand dissociation is already evident for PPh$_3$ and PMePh$_2$ at -80 °C. The PPh$_3$ complex, which crystallizes from THF/pentane as MeCu(PPh$_3$)$_3$·THF (THF is in the crystal lattice and does not coordinate to copper), is shown by X-ray diffraction to have a nearly tetrahedral structure with Cu–C = 2.043 (12) and Cu–P = 2.313 (3) Å. The crowded intramolecular packing of phenyl groups is evident from the X-ray study, which then rationalizes the tendency of this complex to dissociate PPh$_3$. The thermal decomposition of MeCu(PPh$_3$)$_3$ in solution is indicated to proceed via unsaturated MeCu(PPh$_3$)$_2$. Crystallographic data for MeCu(PPh$_3$)$_3$·THF (at -154 °C): space group $P2_1$ with a = 13.153 (5) Å, b = 10.125 (3) Å, c = 18.083 (7) Å, β = 93.19 (2)°, and Z = 2.

Introduction

Among copper(I) alkyls, the focus of recent solid-state structural characterization has been directed toward anionic species ("alkyl cuprates") because of their utility in organic synthesis.[1] While this quest has led to the definitive characterization of CuR$_2^-$ species,[2-5] it has also revealed that a coordination number of 2 in these anions is so low that interaction with the electrophiles Li$^+$ and Mg^{2+} (commonly present in recipes employed to produce "alkyl cuprates") must be assumed. Examples characterized to data include Cu$_5$Ph$_6^-$, LiCu$_4$Ph$_6^-$, Li$_2$Cu$_3$Ph$_6^-$, and MgCu$_4$Ph$_6$.[6-8] The chemistry of arylcopper aggregates has been reviewed.[9]

Our own interest in the catalytic hydrogen transfer chemistry of uncharged Cu(I) species,[10,11] together with a desire to compare the isolobal ligands H and CH$_3$ in a comparable Cu(I)L$_n$ environment, attracted us to a fuller characterization of MeCuL$_n$ complexes, some of which have been reported earlier. Of particular interest, given our report[12] of bridging hydrides in "HCu[(Ph$_2$PCH$_2$)$_3$CMe]", was whether these copper *alkyl* compounds might be oligomeric with bridging methyl groups.[12] The work of Miyashita and Yamamoto[13] identified *solid-state* compositions of variable phosphine ligand content as well as materials which might be interpreted as involving coordinated ether (e.g., MeCu(PPh$_3$)$_2$(Et$_2$O)$_{0.5}$). This earlier work[13] reports certain chemical shift data that we were unable to confirm in our initial studies; other workers have reported[5] similar disparities. We report here results which bear on the structure of *solution* equilibria of a number of molecular MeCuL$_n$ species which are essential to a detailed interpretation of the reactivity of uncharged copper alkyls.

Table I. Crystallographic Data for CuCH$_3$(PPh$_3$)$_3$•THF

chem formula	C$_{59}$H$_{56}$OP$_3$Cu	space group	$P2_1$
a, Å	13.153 (5)	T, °C	-141
b, Å	10.125 (3)	λ, Å	0.71069
c, Å	18.083 (7)	ρ_{calcd}, g cm^{-3}	1.295
β, deg	93.19 (2)	μ(Mo Kα), cm^{-1}	5.92
V, Å^3	2404.49	R	0.0650
Z	2	R_w	0.0568
fw	937.56		

Experimental Section

All manipulations were carried out by using standard Schlenk and glovebox procedures under prepurified nitrogen or vacuum. All solvents used were dried and deoxygenated with Na/K benzophenone. Cu(acac)$_2$ was purchased from Harshaw Chemical and dried under vacuum before use. The phosphines PPh$_3$ (EM Science) and PMePh$_2$ (Strem Chemical) were used as received. MeC(CH$_2$PPh$_2$)$_3$ was synthesized as previously described.[14a] AlMe$_2$(O^{i}Pr) was prepared by slow addition of ^{i}PrOH (Mallinckrodt, deoxygenated by bubbling prepurified nitrogen for 0.5 h) to a hexane solution of Al$_2$Me$_6$ (Ethyl Corp., used as received) at -78 °C and purified by vacuum distillation (34-36 °C (0.05 mm)).[14b]

Both ^{1}H and ^{31}P NMR spectra were recorded on a Nicolet NT-360 spectrometer at 360 and 146 MHz, respectively. Sample tubes were flame-dried under vacuum and flame-sealed after filling. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as mineral oil mulls between NaCl plates. The thermal instability of several of the compounds described here prevents obtaining conventional elemental analysis data; this was also the case with earlier workers.[4,5]

CH$_3$Cu(PPh$_3$)$_3$·THF (I). Diethyl ether (20 mL) was added to a Schlenk flask containing Cu(acac)$_2$ (0.500 g, 1.91 mmol) and PPh$_3$ (1.75 g, 6.68 mmol). This dissolved the PPh$_3$ and formed a light blue suspension of Cu(acac)$_2$. The flask was cooled to -78

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(1) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980.

(2) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23.

(3) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337.

(4) A two-coordinate copper aryl structure has been reported: Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Comm.* **1983**, 240.

(5) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208.

(6) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072.

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

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

(9) Van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1980; Chapter 14.

(10) Goeden, G. V.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 2484 and references therein.

(11) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 291.

(12) For a review of bridging hydrocarbyl ligands, see: Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(13) Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1102.

(14) (a) Hewertson, H.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490. (b) Mole, T. *Aust. J. Chem.* **1966**, *19*, 373.

0276-7333/89/2308-2724$01.50/0

Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $CuCH_3(PPh_3)_3 \cdot THF$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2		10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Cu(1)	−8026 (1)	−2982*	−7091 (1)	12	C(33)	−6066 (10)	2422 (12)	−6743 (8)	31
C(2)	−8132 (9)	−4889 (12)	−6736 (7)	21	C(34)	−6235 (9)	1526 (11)	−7304 (7)	21
P(3)	−7569 (2)	−3066 (4)	−8306 (1)	14	C(35)	−6445 (8)	222 (12)	−7155 (7)	17
P(4)	−6818 (2)	−1960 (3)	−6308 (2)	13	C(36)	4453 (8)	7313 (11)	3740 (5)	23
P(5)	−9630 (2)	−2060 (3)	−7044 (2)	12	C(37)	4535 (9)	5945 (13)	3728 (6)	18
C(6)	2691 (8)	8463 (12)	1173 (6)	17	C(38)	−4505 (10)	−4639 (13)	−6228 (7)	22
C(7)	−6539 (9)	−1419 (13)	−9329 (7)	21	C(39)	−3634 (10)	−3901 (14)	−6204 (8)	25
C(8)	−6381 (9)	−225 (15)	−9672 (6)	25	C(40)	6304 (10)	7449 (14)	3785 (8)	31
C(9)	−6999 (10)	841 (13)	−9546 (7)	26	C(41)	5328 (9)	8078 (14)	3772 (8)	27
C(10)	−7787 (10)	739 (13)	−9078 (7)	25	C(42)	141 (8)	9673 (11)	2698 (6)	16
C(11)	−7936 (9)	−455 (12)	−8724 (6)	18	C(43)	−10752 (8)	168 (11)	−7654 (6)	12
C(12)	−8457 (8)	−3929 (12)	−8958 (6)	14	C(44)	−10877 (9)	1492 (12)	−7796 (6)	21
C(13)	−8919 (8)	−5084 (12)	−8687 (6)	14	C(45)	−10105 (9)	2381 (11)	−7569 (6)	17
C(14)	−9532 (8)	−5865 (12)	−9157 (6)	15	C(46)	−9218 (8)	1912 (14)	−7204 (6)	21
C(15)	−9735 (9)	−5484 (13)	−9895 (7)	20	C(47)	−9098 (8)	589 (12)	−7071 (7)	17
C(16)	−9309 (8)	−4367 (13)	−10147 (7)	23	C(48)	−10555 (7)	−2948 (15)	−7634 (5)	14
C(17)	−8652 (8)	−3586 (11)	−9683 (6)	14	C(49)	−10624 (7)	−2719 (12)	−8406 (6)	16
C(18)	−6401 (8)	−3997 (12)	−8392 (6)	12	C(50)	8739 (8)	6577 (11)	1122 (6)	13
C(19)	−5480 (9)	−3503 (13)	−8097 (6)	21	C(51)	8140 (9)	5594 (13)	1390 (6)	20
C(20)	5415 (9)	5823 (14)	1870 (7)	21	C(52)	−11827 (9)	−4695 (13)	−7854 (7)	21
C(21)	−4563 (10)	−5446 (15)	−8437 (7)	26	C(53)	−11177 (9)	−3978 (13)	−7373 (6)	17
C(22)	−5468 (9)	−5991 (13)	−8712 (7)	24	C(54)	9787 (9)	7845 (12)	3847 (6)	18
C(23)	−6383 (9)	−5255 (12)	−8698 (7)	21	C(55)	9097 (9)	8810 (12)	4077 (6)	18
C(24)	2857 (8)	7936 (13)	4663 (6)	18	C(56)	−11366 (9)	−1334 (14)	−5256 (7)	25
C(25)	−6628 (9)	−2894 (17)	−4832 (6)	28	C(57)	8867 (10)	7630 (13)	5217 (7)	25
C(26)	3023 (11)	6992 (20)	5896 (6)	38	C(58)	−10426 (9)	−3329 (11)	−5009 (6)	27
C(27)	−7797 (10)	−2334 (13)	−3910 (7)	26	C(59)	29 (8)	6806 (13)	4333 (6)	17
C(28)	1682 (11)	8465 (14)	5602 (8)	33	O(60)	3290 (8)	6556 (11)	8610 (6)	52
C(29)	2000 (9)	8636 (14)	4887 (7)	25	C(61)	3555 (13)	5774 (20)	9194 (10)	56
C(30)	−6529 (9)	−200 (12)	−6438 (6)	17	C(62)	3516 (15)	4383 (20)	8896 (12)	69
C(31)	−6363 (9)	696 (12)	−5851 (6)	20	C(63)	3927 (19)	4621 (28)	8131 (12)	92
C(32)	−6142 (9)	2034 (17)	−6016 (6)	29	C(64)	3567 (13)	5973 (22)	7966 (11)	60

[a] Parameters marked by an asterisk (*) were not varied. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by; Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

°C, and $AlMe_2(O^iPr)$ (0.888 g, 7.64 mmol) was added. The flask was allowed to warm slowly to −25 °C at which point the color of the suspension began to lighten to yield a yellow solid and a yellow solution. The solution was cooled to −100 °C and filtered as cold as possible to yield a yellow solid. The yellow solid was dissolved in a minimum of THF, carefully layered with an equal volume of pentane, and held at −15 °C for several days, to yield yellow needles. The solid can be handled briefly at 25 °C without significant decomposition. ^{1}H NMR (25 °C); C_6D_6, δ 7.42 (br s, *o*-Ph), 7.01 (br s, m, *p*-Ph), 3.57 (m) and 1.39 (m); THF, δ 0.44 (br s, Cu-*Me*). ^{31}P NMR (25 °C, C_6D_6): δ 4.3 (br s). IR: 2770 cm^{-1} (CuMe C–H).

Crystallography of $CuCH_3(PPh_3)_3 \cdot THF$. A suitable crystal was located and transferred to a goniostat by using standard inert-atmosphere handling techniques and cooled to −154 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a monoclinic cell of space group $P2_1$ or $P2_1/m$. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric choice. Data were collected in the usual manner[15] by using a continuous θ–2θ scan (6° ≤ 2θ ≤ 45°) with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner.[15] Table I shows parameters of the crystal, data collection, and refinement.

The structure was solved by a combination and direct methods (MULTAN78) and Fourier techniques. In the course of the refinement, a THF molecule was evident in the lattice. This (uncoordinated) molecule is ordered, and the oxygen was identified by bond lengths as well as hydrogen peaks in difference maps. A difference Fourier phased on the non-hydrogen atoms was used to locate most of the hydrogen atoms, including two methyl hydrogens, but when allowed to vary, some of the hydrogen positions and thermal parameters failed to converge. For this reason, they were included in fixed, idealized positions (d(C–H) = 0.95 Å) for the final cycles of the refinement.

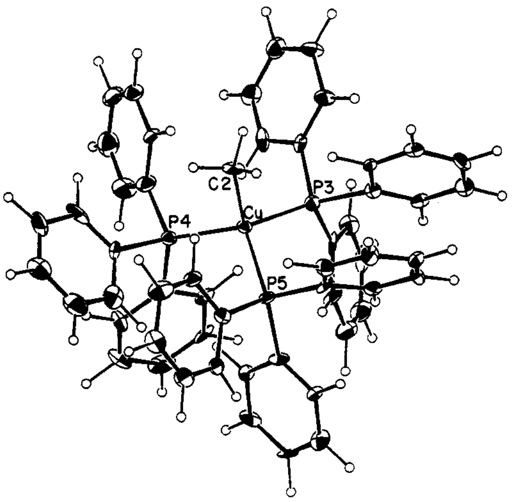

Figure 1. ORTEP drawing of $MeCu(PPh_3)_3$ showing selected atom labeling.

Table III. Selected Bond Distances (Å) and Angles (deg) for $CuCH_3(PPh_3)_3 \cdot THF$

Bond Distances			
Cu(1)–P(3)	2.311 (3)	Cu(1)–P(5)	2.313 (3)
Cu(1)–P(4)	2.313 (3)	Cu(1)–C(2)	2.043 (12)
Bond Angles			
P(3)–Cu(1)–P(4)	113.10 (12)	P(4)–Cu(1)–P(5)	113.17 (12)
P(3)–Cu(1)–P(5)	109.64 (11)	P(4)–Cu(1)–C(2)	106.7 (4)
P(3)–Cu(1)–C(2)	106.9 (4)	P(5)–Cu(1)–C(2)	106.9 (4)

A final difference Fourier was featureless, the largest peak being 0.6 e/Å^3. An examination of the data indicated that there was no need to correct for absorption. The results of the structure determination are shown in Tables II and III and Figures 1–3.

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(15) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

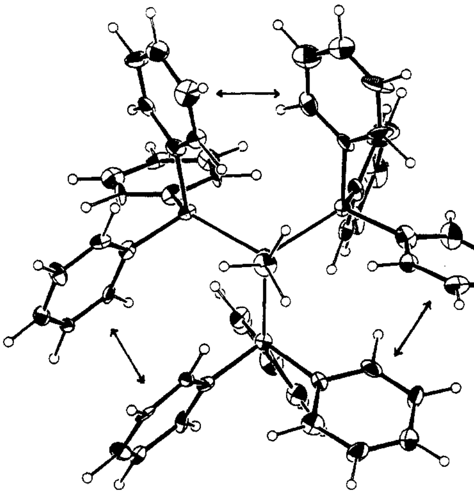

Figure 2. ORTEP drawing of $MeCu(PPh_3)_3$ viewed down the idealized C_3 axis (the H_3C–Cu bond). Graphitic stacking of six phenyl rings is indicated by double-headed arrows.

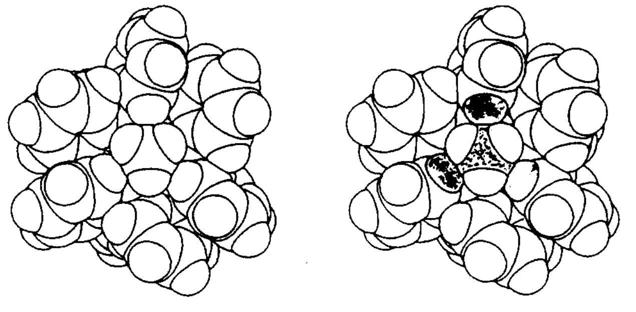

Figure 3. Stereo space-filling drawing of $MeCu(PPh_3)_3$ (oriented as in Figure 2), showing how three ortho hydrogens (shaded) dictate the methyl (stippled) rotational conformation. The graphitic stacking of three pairs of phenyl rings is also evident. All hydrogen atoms are represented with d(C–H) = 1.08 Å.

$MeCu(PMePh_2)_3$ (II). (a) In Et_2O. Diethyl ether (15 mL) was added to a Schlenk flask containing $Cu(acac)_2$ (0.25 g, 0.955 mmol), and methyldiphenylphosphine (0.71 mL, 3.82 mmol) was added via syringe. The flask was cooled to −110 °C and $AlMe_2(O^iPr)$ (0.444 g, 3.82 mmol) was added with stirring. The blue suspension was allowed to slowly warm to −5 °C. As the suspension warmed, the color lightened to yield a yellow solution and a small amount of yellow powder. The solution was cooled to −110 °C and filtered as cold as possible to yield a yellow powder. The powder was dissolved in THF (5 mL), layered with an equal volume of hexanes, and placed in the freezer overnight (−15 °C). The next day, a yellow solid was filtered, washed with hexanes (1 × 10 mL), and dried under vacuum. ^1H NMR (25 °C, C_6D_6): δ 7.39 (m, *o*-Ph), 7.01 (m, *m*- + *p*-Ph), 1.40 (s, P-*Me*), 0.31 (br s). ^{31}P NMR (25 °C, C_6D_6): δ −18.7. IR: 2780 cm^{-1} (CuMe C–H).

(b) In Pentane. Pentane (30 mL) was added to a Schlenk flask containing $Cu(acac)_2$ (0.5 g, 1.91 mmol). Methyldiphenylphosphine (1.24 mL, 6.68 mmol) was added via syringe. The blue suspension was cooled to −78 °C, and $AlMe_2(O^iPr)$ (0.888 g, 7.64 mmol) was added with stirring. The flask was allowed to warm to −10 °C and kept at this temperature for 5 h. As the suspension warmed, the blue color faded to yield a yellow solution and yellow precipitate. The solution was filtered to yield a yellow solid and a light yellow solution. The yellow solid was dissolved in a minimum of diethyl ether (4 mL) and layered with pentane (25 mL). This yellow solution was cooled to −20 °C overnight to yield yellow crystals.

$MeCu(CH_3C(CH_2PPh_2)_3)$ (III). (a) From $AlMe_2(O^iPr)$. Toluene (20 mL) was added to a Schlenk flask containing $Cu(acac)_2$ (0.25 g, 0.95 mmol) and $CH_3C(CH_2PPh_2)_3$ (0.597 g, 0.955 mmol). This dissolved the $CH_3C(CH_2PPh_3)_3$ and formed a deep blue suspension of $Cu(acac)_2$. The flask was then cooled to −70 °C, and $AlMe_2(O^iPr)$ (0.444 g, 3.82 mmol) was added. The flask was allowed to warm to −20 °C over 45 min. At this point, the color of the suspension began to lighten as the $Cu(acac)_2$ was consumed. The flask was allowed to further warm and was held at −15 °C. After 1.5 h, a yellow solid had precipitated from the yellow solution. The solution was cooled to −90 °C and filtered cold. The yellow solid was dissolved in a minimum of THF, layered with an equal volume of pentane, and held at −15 °C overnight, to yield a pale yellow microcrystalline solid.

(b) From MeLi. CuCl (79 mg, 0.80 mmol) was suspended in 20 mL of THF. $CH_3C(CH_2PPh_2)_3$ (0.50 g, 0.80 mmol) was added with stirring. After 5 min, a large amount of white solid had precipitated. This suspension was stirred for 30 min and then cooled to −78 °C. MeLi (0.58 mL, 1.4 M) was added via syringe, causing an immediate color change to orange. The flask was allowed to slowly warm to room temperature. At −30 °C, the solution became yellow. After room temperature was reached, the solution was layered with an equal amount of pentane and cooled to −20 °C overnight. The resulting yellow solid was filtered away from the yellow solution and recrystallized from THF/pentane. ^1H NMR (25 °C, C_6D_6): δ 7.57 (br s, *o*-Ph), 6.78 (br s, *m*- + *p*-Ph), 2.23 (br s, *Me*–C), 1.23 (br s, CH_2), 0.84 (br s, Cu-*Me*). ^{31}P NMR (25 °C, C_6D_6): δ −27.2 (br s). IR: 2800 cm^{-1} (CuMe C–H). Anal. Calcd for $C_{42}H_{42}CuP_3$: C, 71.7; H, 6.02. Found: C, 71.24; H, 6.02.

Results

$MeCu(PPh_3)_3 \cdot THF$ (I). (a) Synthesis and Structure. Using a modification of a previously reported synthetic procedure, $Cu(acac)_2$ was reacted with $AlMe_2(O^iPr)$ in the presence of excess PPh_3 to yield a yellow crystalline material, I. This represents a modification of the literature synthesis since the $AlMe_2(OEt)$ used earlier results in formation of a gelatinous material during attempted product isolation of copper methyl complexes containing basic phosphines (i.e., PMe_2Ph). Mole has reported[14b] that, while $AlMe_2(OMe)$ disproportionates to $AlMe_3$ and gelatinous $AlMe(OMe)_2$ in pyridine solution, $AlMe_2(O^iPr)$ does not. Use of $AlMe_2(O^iPr)$ here alleviated the problem of product workup. Crystals of I under N_2 gas darken and decompose slowly within a few days at room temperature but remain unchanged for several weeks when sealed under vacuum in glass ampules and stored at −15 °C. Aromatic solutions of this material begin to darken quickly at 25 °C (∼15 min) and later deposit Cu metal, thus necessitating handling at low temperatures. Crystals of I are freely soluble in aromatics and THF, sparingly soluble in Et_2O, and very poorly soluble in pentane.

Preliminary NMR spectra of this material showed concentration-dependent methyl chemical shifts, broad ^{31}P NMR signals, sample-dependent integrations of CH_3 vs phenyl hydrogens, and the absence of observable coupling between coordinated phosphines and protons on the copper-bound methyl group. These results fail to resolve questions of aggregation or of the number of coordinated phosphines and are a consequence of problems inherent in the system. First, Cu(I) is a d^{10} center and kinetically labile, so phosphine dissociation/association is expected to be facile. Second, both major naturally occurring isotopes of copper are quadrupolar and therefore can broaden signals of nearby nuclei. In addition, sample decomposition at 25 °C in C_6D_6 eroded confidence in the numerical chemical shifts and integrations obtained. Finally, the change in chemical shift of a phosphine upon coordination to Cu(I) is generally small.

Recrystallization of the above material at −15 °C from THF/pentane yields material (I) shown by X-ray diffraction to contain four-coordinate $MeCu(PPh_3)_3$ molecules (Figure 1) together with THF molecules occupying lattice voids. The copper complex approaches closely tetrahedral geometry. In spite of the disparity in the size of CH_3 and PPh_3 groups, P–Cu–P angles (109.6–113.2°) are not dramatically larger than H_3C–Cu–P angles (106.7–106.9°). All three Cu–P distances are identical, although the molecule has no crystallographic symmetry elements. The remaining characteristic of the molecules that requires description is the intramolecular packing of the nine phenyl rings. This occurs in a systematic fashion such that the molecule has C_3, but not C_{3v}, symmetry. All Cu–P rotational conformations place one P–C vector anti to the Cu–CH_3 vector, such that the remaining six phenyls form a "nest" that cradles the $CuCH_3$ group. Each of these six phenyl rings adopt a P–C(ipso) rotational conformation such that there is a face-to-face ("graphitic") stacking with a phenyl on an adjacent phosphine (Figures 2 and 3). This has the effect of directing three ortho hydrogens toward the methyl group, with the consequence that the methyl conformation is fixed into that observed (see Figure 3). Similar conformational effects are seen in $XCu(PPh_3)_3$ (X = Cl, Br, I) and its acetone solvate as well as in $ClCu(PPh_3)_3\cdot 3THF$. While all of these contacts are permuted by rapid site exchange in solution, they nevertheless speak for a crowded molecule, the consequences of which we now describe.

(b) Solution Equilibria. With the solid-state stoichiometry established, we attempted to determine the composition of I in solution. ^1H NMR spectra of I at 25 °C in the presence of increasing equivalents of added PPh_3 show continuous alteration of the methyl chemical shift from 0.44 ppm, with no added phosphine, to 0.52 ppm with 20 equiv added. Lowering the temperature also produced a downfield movement of the methyl shift. Without added phosphine and at −90 °C in toluene, the chemical shift of I was 0.68 ppm, but unfortunately, the broadened resonance showed no fine structure (coupling to bound phosphines). These results suggest that an equilibrium (eq 1) phosphine dissociation takes place in solution. Either adding equivalents of phosphine or lowering the temperature should favor the tris(phosphine) species.

$$MeCu(PPh_3)_3 = MeCu(PPh_3)_2 + PPh_3 \qquad (1)$$

The ^{31}P NMR spectra also provide evidence for the tris(phosphine) species, but only at low temperature. At room temperature, the ^{31}P NMR of I shows only one resonance, which overlaps the chemical shift of free triphenylphosphine. However, at −90 °C, the ^{31}P spectrum shows two broad peaks, a small peak at the chemical shift (−7 ppm) of free phosphine and a large broad peak at +2.8 ppm, which we assign to intact $MeCu(PPh_3)_3$. Interestingly, the ^{31}P spectrum of I with 3 equiv of added triphenylphosphine at −90 °C shows only one very broad resonance at +2.2 ppm. This suggests that although $MeCu(PPh_3)_3$ is the major species (>90%) in solution at −90 °C, exchange with free phosphine is still occurring. In the course of handling samples of $MeCu(PPh_3)_3$ containing added PPh_3, we observed that free ligand retarded the decomposition which had complicated our room temperature manipulation in solution. This suggested the following experiments.

Synthesis of $MeCu(PMePh_2)_3$ (II). Two ways of increasing the strength of a bond between a phosphine and a metal center are to increase the basicity of the phosphine and to reduce the cone angle of the phosphine. Both are accomplished simultaneously with $PMePh_2$.

In a reaction similar to that used for complex I, a waxy yellow solid, II, is obtained. Unfortunately, *isolation* of complex II is much more difficult than is the isolation of complex I. Complex II is much more soluble in diethyl ether, and this severely limits the yield of complex II because only a small amount of product precipitates prior to coprecipitation of aluminum-containing products. Complex II is however more thermally stable than I. Solutions of complex II may be handled at room temperature for short periods without decomposition. Solid complex II will last several months when stored under nitrogen at −15 °C. However, preliminary NMR studies of complex II encountered the same problems as in NMR spectra of complex I. The ^1H NMR spectrum of complex II does not show any impurities, but integration of CuMe protons vs PMe protons indicate greater than three phosphines per copper. The ^{31}P NMR spectrum at −80 °C also indicates that excess phosphine is present: This spectrum shows two well-resolved sharp resonances, the smaller of which is identical with the chemical shift of free phosphine (−28 ppm). The other resonance, at −15 ppm, is assigned to $MeCu(PMePh_2)_3$.

Girolami et al. recently reported a synthesis of $MeCu(PMePh_2)_3$ in which pentane was used for recrystallization.[5] In light of this observation, the synthesis of complex II was repeated with pentane as the reaction solvent. Recrystallization from pentane yields a yellow solid in much higher yield. The product from reaction in pentane appears, by ^1H NMR spectroscopy, to have less contamination by free phosphine. In a fashion similar to that of complex I, lowering the temperature causes a downfield shift of the CuMe resonance in the ^1H NMR spectra of complex II. This result indicates that a phosphine dissociation equilibrium also is operative for complex II in solution.

Interestingly, the product with greater phosphine contamination shows a poorly resolved quartet ($^3J_{P-H}$ = 5 Hz) for the CuMe resonance in the ^1H NMR spectrum in toluene-d_8 at −90 °C. However, the CuMe resonance for the more pure material shows only hints of fine structure at this temperature. The additional phosphine apparently shifts the phosphine dissociation equilibrium enough such that the phosphines maintain spin correlation to the protons on the Cu–CH_3 group.

The quartet fine structure of the CuMe resonance indicates that complex II has a solution structure at low temperature similar to that of complex I in the solid state (i.e., a μ-Me dimer is excluded) and that complex II is intact in solution at very low temperatures. Use of a more basic and less sterically demanding phosphine does indeed seem to improve the thermal stability and provide evidence for a four-coordinate structure of complex II in solution. This result prompted the following experiment.

Synthesis of $MeCu[(Ph_2PCH_2)_3CMe]$ (III). In an attempt to further enhance the stability of phosphine-stabilized copper alkyls, we employed the tridentate chelating ligand $MeC(CH_2PPh_2)_3$ (tripod) so that the chelate effect would keep the phosphines coordinated to the metal center. In a reaction analogous to those above (Cu:P:Al = 1:1:4), microcrystals of complex III are obtained. This material is much more thermally robust than complex II or especially complex I. Complex III may be stored at room temperature under nitrogen in the solid state. THF solutions of complex III are stable at room temperature for extended periods. In contrast to complexes I and II, complex III is poorly soluble in most common solvents except THF. Complexes of this ligand frequently show decreased solubility relative to the tris(phosphine) analogues. Complex III can also be synthesized by the following route:

$$\text{CuCl} + \text{tripod} \xrightarrow[\text{2. MeLi, −78 °C}]{\text{1. THF}} \text{MeCu(tripod)}$$

Both ^1H and ^{31}P NMR spectra in C_6D_6 reveal the C_3 symmetry of the tripod ligand, which is consistent with a monomeric formulation for complex III. Since the ^{31}P NMR spectrum of complex III at room temperature, in the presence of 1 equiv of added tripod, shows two well-separated resonances (free and coordinated phosphine), the phosphine ligand does not exchange rapidly on the NMR time scale. However, in the ^{1}H NMR spectrum of complex III at room temperature, the CuMe resonance shows no fine structure from coupling to bound phosphines. Switching solvents to THF-d_8 allows measurements below 5 °C; the ^{1}H NMR spectrum at −40 °C shows a well-defined quartet eith $^3J_{P-H} = 5$ Hz for the CuMe resonance. This confirms the symmetric binding of the tripod ligand (coupling to three equivalent phosphorus), and establishes complex III as a discrete monomer in solution. The variable-temperature ^{31}P NMR spectra in THF also support this claim. The single resonance observed at room temperature is maintained down to −80 °C. This is in contrast to $[(\mu_2\text{-H})\text{Cu}(\eta^2\text{-tripod})]_2$, where the room-temperature ^{31}P NMR spectrum shows one average environment while the low-temperature ^{31}P NMR spectrum resolves distinct phosphorus environments.[10] The increased thermal stability of complex III relative to previously isolated copper alkyls supports the idea that phosphine dissociation may be important in the decomposition of phosphine-stabilized copper alkyls.

Discussion

Reported here is the first structure determination of an uncharged terminal copper *alkyl*. The Cu–P distance in $\text{MeCu(PPh}_3)_3$ (average 2.313 Å) are very similar to (but systematically shorter than) those (2.34–2.37 Å) in other $\text{XCu(PPh}_3)_3$ compounds (X = Cl, Br, I.)[16–19] The Cu–P distances are most similar to those (2.310 (3)–2.325 (3) Å) in $\text{FCu(PPh}_3)_3\cdot2\text{EtOH}$,[16] whose Cu–F distance (2.062(6)) most closely approaches the Cu–CH_3 distance in our compound. The Cu–CH_3 distance (2.043 (12) Å) is very close to the Cu–C_6H_5 distance in[17] $[\text{CH}_3\text{C(CH}_2\text{PPh}_2)_3]\text{CuPh}$, 2.020 (4) Å; the single bond radius of an sp^2 carbon is 0.1 Å smaller than that of an sp^3 carbon. Copper–carbon distances in two-coordinate complexes are considerably shorter[2–5] (1.915 (9)–1.962 (15) Å) than in the four-coordinate compound reported here.

Miyashita and Yamamoto report[13] that attempted synthesis of $\text{EtCu(PPh}_3)_3$ under conditions employed successfully for $\text{MeCu(PPh}_3)_3$ gave instead $\text{EtCu(PPh}_3)_2$. An examination of Figure 2 and especially Figure 3 reveals a probable steric origin for this result, since replacement of one methyl hydrogen by a CH_3 group would require total reorganization of all phenyl rings. In general, the crowding evident in the solid-state structure of $\text{MeCu(PPh}_3)_3$ (manifest also in its loss of phosphine in solution) makes understandable their isolation of $\text{CH}_3\text{Cu(PCy}_3)$.

Interpretation of the NMR spectra of both II and III indicates that these complexes exist as four-coordinate monomers in solution at low temperature. These complexes represent some of the first cases in which conclusive determination of solution composition of copper alkyls is possible. The low-temperature NMR spectrum of I is not as conclusive as those above but does give some indication that, in spite of the crowded nature of the coordination sphere about copper in this complex, I also exists as a discrete four-coordinate monomer at low temperature in solution. The above results are consistent with previously reported molecular weight studies.[13]

As mentioned above, the constitution of molecular copper alkyls is poorly understood. It has been established that an empirical formula as simple as $\text{MeCu(PMe}_3)_2$ exists both in the solid state and in solution as the strong electrolyte $[(\text{PMe}_3)_4\text{Cu}][\text{CuMe}_2]$. Complexes I and II presumably adopt four-coordinate uncharged structures instead of charged complexes (cf.[5] $(\text{PMe}_3)_4\text{Cu}^+\text{CuMe}_2^-$) because the L_4Cu^+ cations (L = PPh_3 and PMePh_2) would be too crowded. It must be noted that $(\text{PPh}_3)_4\text{Cu}^+$ cations are known in the solid state, but the Cu–P distances are quite long (2.60 (1) and 2.52 (1) Å) and these complexes lose phosphine upon dissolution.[20] Isolation and structural characterization of a copper alkyl with a phosphine that is intermediate in size between PMe_3 and PMePh_2 might help define the factors that determine whether a complex will adopt a charged or uncharged structure. However, we have been unable to isolate stable complexes with either PMe_2Ph or PEt_3. Previous workers were also unable to isolate a complex with PMe_2Ph.[5]

This steric argument for molecular constitution of $\text{MeCu(PPh}_3)_n$ is complicated by the recent report of a phosphine-stabilized copper silyl, complex $(\text{PMe}_3)_3\text{CuSiPh}_3$.[21] Although P_4Cu^+ cations are stable in Girolami's complex, in the triphenylsilyl case an uncharged structure seems to be stable. This result indicates that phosphine size alone does not determine whether a copper alkyl complex adopts a molecular or a salt formulation; in this case, excessive crowding might pertain in the unobserved anion $\text{Cu(SiPh}_3)_2^-$.

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

Registry No. I, 123074-76-0; II, 63330-51-8; III, 123074-77-1; $\text{CH}_3\text{Cu(PPh}_3)_3$, 38704-10-8; Cu(acac)_2, 13395-16-9; PPh_3, 603-35-0; $\text{AlMe}_2(\text{O}^i\text{Pr})$, 6063-89-4; PMePh_2, 1486-28-8; $\text{CH}_3(\text{CH}_2\text{PPh}_2)_3$, 22031-12-5; CuCl, 7758-89-6; MeLi, 917-54-4.

Supplementary Material Available: Tables of full crystallographic details (Table S1) and anisotropic thermal parameters (Table S2) (3 pages); a listing of observed and calculated structure factors (Table S3) (7 pages). Ordering information is given on any current masthead page.

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(16) Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chim. Acta* **1981**, *52*, 153.

(17) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444.

(18) Barron, P. F.; Dyason, J. C.; Healy, D. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1099.

(19) Folting, K.; Huffman, J. C.; Mahoney, W. S.; Stryker, J. M.; Caulton, K. G. *Acta Crystallogr.* **1987**, *C43*, 1490.

(20) Englehardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1987**, 125.

(21) Cowley, A. H.; Elkins, T. M.; Jones, R. A.; Nunn, C. M. *Angew. Chim., Int. Ed. Engl.* **1988**, *27*, 1349.