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Copper(I) Alkyls. Synthesis and Characterization of Tertiary Phosphine Adducts and the Crystal Structure of the Dimethylcuprate Complex $[Cu(PMe_3)_4][CuMe_2]$

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Alkylation of copper(II) acetate with dialkylmagnesium reagents in the presence of tertiary phosphines gives the colorless copper(I) alkyl species $[Cu(PMe_3)_4][CuMe_2]$, $CuMe(PMePh_2)_3$, $[Cu(PMe_3)_4][Cu(CH_2SiMe_3)_2]$, $[Cu(PMe_2Ph)_4][Cu(CH_2SiMe_3)_2]$, $Cu(CH_2SiMe_3)(PMePh_2)_3$, and $Cu(CH_2CMe_3)(PMePh_2)_3$. With sterically small phosphines, the complexes are ionic and possess $[Cu(PR_3)_4]$ cations and $[CuR_2]$ anions; larger phosphines give electrically neutral $CuR(PR_3)_3$ coordination complexes. Solution NMR data indicate that reversible phosphine dissociation is a facile process for all of the complexes and that extensive ion pairing occurs in nonpolar solvents. The X-ray crystal structure of the dimethylcuprate complex $[Cu(PMe_3)_4][CuMe_2]$ has been determined, and the anion found to be rigorously linear with Cu–C = 1.94 (1) Å. The cation is nearly a perfect tetrahedron with Cu–P distances of 2.269 (3) and 2.253 (3) Å. Crystal data: cubic, space group $P2_13$, $a = 13.666$ (2) Å, $V = 2552$ (1) Å^3, $Z = 4$, $R_F = 4.3\%$, $R_{wF} = 4.2\%$ for 442 reflections and 62 variables.

Introduction

Lithium dialkylcuprates, $LiCuR_2$, are used extensively in organic synthesis as excellent reagents for the specific replacement of halogen in organic halides, the conversion of epoxides to alcohols, and the addition of alkyl and alkenyl groups across carbon–carbon multiple bonds and cyclopropane rings.[1-3] Organocopper(I) reagents, CuR, and their tertiary phosphine adducts have also been used for these purposes, although they are somewhat less stable and usually less reactive than their $LiCuR_2$ analogues. In general, organocopper reagents are preferred in many cases over organolithium or organomagnesium compounds due to their higher selectivity.

Despite the widespread use of organocuprates in organic synthesis, their structures remain in general poorly understood.[4-6] Organocopper reagents are usually prepared by treatment of copper salts with alkyllithium, -magnesium, -zinc, or -lead reagents, but most compounds are prepared as solutions and used in situ.[5-11] Attempts to isolate them, free from the alkylating agents and reaction byproducts, have in general been unsuccessful due to their instability and insolubility in common organic solvents. X-ray diffraction studies of electrically neutral organocopper complexes have typically revealed a polyhedral cage structure, often held together by bridging alkyl or aryl groups. In this category are the tetramers $[Cu(CH_2SiMe_3)]_4$,[12] $[Cu(C_7H_6CH_2NMe_2)]_4$,[13] $[Cu(CCPh)(PMe_3)]_4$,[14] and $Cu_4(C_6H_2Me_3)_4(SC_4H_8)_2$,[15] the planar pentamer $[Cu(C_6H_2Me_3)]_5$,[15] the octahedral hexamers $Cu_6(CCPh)_2(C_6H_4CH_2NMe_2)_4$[16] and $Cu_6Br_2(C_6H_4NMe_2)_4$,[17] and the square-antiprismatic octamer $[Cu(C_6H_4OMe)]_8$.[18] The dimeric ylide complex $Cu_2[(CH_2)_2PMe_2]_2$ is also known.[19]

Structural investigations of organocopper species more closely related chemically to diorganocuprates are few. The copper phenyl species $[Li(THF)_4][Cu_5Ph_6]$,[20] $[Li(Et_2O)_4][LiCu_4Ph_6]$,[21] $[Li_2Cu_3Ph_6]$,[22] and others[23] have been shown to possess cluster geometries with bridging phenyl groups that are similar to the neutral cluster complexes described above. Only recently have discrete dialkylcuprate monomers been crystallographically characterized. Mononuclear diorganocuprate species have been obtained by use of very bulky substituents,[24,25] as in the complexes $[Cu(dppe)_2][Cu\{C_6H_2Me_3\}_2]$ and $[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$. More significantly, pure diorganocuprates with smaller alkyl groups have been synthesized by addition of 12-crown-4 (1,4,7,10-tetraoxacyclododecane) to solutions of organocuprates to give isolable salts of stoichiometry $[Li(12\text{-crown-}4)_2][CuR_2]$, where R is Me or Ph.[26] These

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salts have been shown to possess linear two-coordinate $[CuR_2]$ anions as well.

Other Lewis base adducts of copper alkyls have been reported in the literature that are less well-characterized. Several tertiary phosphine adducts, $CuR(PR_3)_x$, have been described;[27-38] however, the reported stoichiometries vary considerably ($x = 1$, 2, or 3), little spectroscopic data are available, and apart from $[Cu(C{\equiv}CPh)(PMe_3)]_4$[14] no structural work has been done. Since phosphine adducts of copper alkyls are often used as reagents in organic synthesis, we now report an investigation of the nature of such species, including the X-ray crystal structure of the dimethylcuprate salt $[Cu(PMe_3)_4][CuMe_2]$. Our results suggest that Lewis base adducts of organocopper reagents may adopt ionic structures in more cases than previously recognized.

Results and Discussion

Synthesis and Structure of $[Cu(PMe_3)_4][CuMe_2]$. The reaction of anhydrous cupric acetate with dimethylmagnesium and trimethylphosphine results in loss of the blue-green color of copper(II) to give colorless solutions from which a copper methyl complex of stoichiometry $CuMe(PMe_3)_2$ may be crystallized. This air-sensitive compound is a 1:1 electrolyte in tetrahydrofuran,[39,40] and the molar conductivity of 2.2 Ω^{-1} mol^{-1} cm^2 at −78 °C corresponds to the formula $[Cu(PMe_3)_4][CuMe_2]$ (**1**). The

$$Cu_2(O_2CMe)_4 + 2MgMe_2 + \text{excess } PMe_3 \rightarrow \underset{\mathbf{1}}{[Cu(PMe_3)_4][CuMe_2]}$$

infrared spectrum of **1** contains bands at 2760, 600, and 530 cm^{-1} that can be assigned to ν_{CH}, ν_{CuC}, and δ_{CuC} modes of the $[CuMe_2]$ anion. Low-frequency ν_{CH} bands in copper alkyls have been noted previously.[31]

The ^1H NMR spectrum of **1** at room temperature in toluene showed a broad phosphine peak at δ 0.93. The spectra were temperature-dependent presumably due to ion pairing and reversible phosphine dissociation (see below); spectra below −30 °C could not be obtained due to the insolubility of the complex at low temperature. The Cu–Me peak appears as a sharp singlet at δ 0.15, and this may be compared with the ^1H NMR chemical shift of "$LiCuMe_2$" solutions of δ −1.0 to δ −1.4,[6,10] while "$CuMe(PR_3)_x$" species have reported shifts of δ +0.3 to δ −0.9.[30-35] Upfield chemical shifts appear to be correlated with the presence of electropositive metals such as lithium; this suggests that there are strong interactions between the alkyl groups and the lithium cation in lithium cuprates.

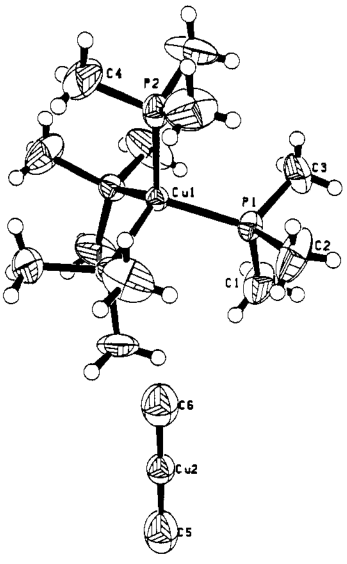

Figure 1. ORTEP diagram of $[Cu(PMe_3)_4][CuMe_2]$ (**1**). Thermal ellipsoids are drawn at the 35% probability level.

In view of the limited structural information obtainable from the NMR spectra, a single-crystal X-ray diffraction study has been performed. The structural analysis shows that crystals of **1** are composed of discrete $[Cu(PMe_3)_4]$ cations and $[CuMe_2]$ anions; perspective views of the ions are shown in Figure 1. Both ions lie on a crystallographic threefold axis, which imposes a rigorously linear C–Cu–C backbone in the anion. The Cu–C distance of 1.94 (1) Å is very similar to the 1.935 (8) Å distance in the crown ether salt $Li(12\text{-crown-}4)_2][CuMe_2]$ and other monomeric dialkylcuprate complexes.[26] The $[Cu(PMe_3)_4]$ cation exhibits Cu–P distances of 2.269 (3) and 2.253 (3) Å, and these values compare favorably with those in phosphine complexes of copper(I) halides.[41,42] The P–Cu–P angles in the cation of 109.2 (1)° and 109.8 (1)° are very close to the idealized tetrahedral angle of 109.47°.

The anions are disposed so that one Cu–Me group points directly at the center of a face of the tetrahedral cation. The Cu···Cu distance along this axis is 7.65 Å, and there are no significant van der Waals contacts between the cations and anions.

It has generally been assumed that phosphine adducts of copper alkyls are electrically neutral coordination complexes. It is somewhat surprising, therefore, that $[Cu(PMe_3)_4][CuMe_2]$ adopts an ionic structure instead, particularly since nonionic phosphine adducts, $CuR(PR_3)_x$, do in fact exist (see below). The structure is also unexpected in that the four-coordinate copper centers are ligated by relatively large PMe_3 groups, whereas the two-coordinate centers are ligated by relatively small methyl groups. The coordinative unsaturation of the 14-electron $[CuMe_2]$ anion is most noticeably manifested in the high air sensitivity of the complex. Clearly, the $[Cu(L)_{2x}][CuR_2]$ constitution must be considered as a structural possibility for all $CuR(L)_x$ coordination complexes where $x \le 2$. We particularly wish to point out that molecular weight determinations would not discriminate between the two pos-

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sibilities, and we suspect that many of the $CuR(L)_x$ coordination complexes reported in the literature[27-38] may in fact be ionic dialkylcuprate salts.

Synthesis of Other Methyl Complexes. The reaction of copper(II) acetate with dimethylmagnesium in the presence of the phosphine ligand $PMePh_2$ gives a yellow crystalline copper alkyl of stoichiometry $CuMe(PMePh_2)_3$ (**2**). This complex is significantly more soluble in pentane

$$^1/_2Cu_2(O_2CMe)_4 + MgMe_2 + \text{excess } PMePh_2 \rightarrow \underset{\mathbf{2}}{CuMe(PMePh_2)_3}$$

than alkane-insoluble $[Cu(PMe_3)_4][CuMe_2]$, and its molar conductivity at −78 °C in tetrahydrofuran of 0.05 Ω^{-1} mol^{-1} cm^2 indicates that $CuMe(PMePh_2)_3$ is a nonionic coordination complex.[43] The IR spectrum again shows a low ν_{CH} band at 2760 cm^{-1}, while the ^1H NMR spectrum contains a peak at δ 0.29 due to the Cu–Me group; no splitting of this resonance due to coupling with ^{31}P, ^{63}Cu, or ^{65}Cu is observed doubtlessly as a result of fast chemical exchange. The $^{31}P\{^1H\}$ coordination chemical shift ($\delta_{coord} - \delta_{free}$) of $CuMe(PMePh_2)_3$ is rather small at +10 ppm.

Presumably, $CuMe(PMePh_2)_3$ adopts a nonionic structure because the $[Cu(PMePh_2)_4]$ cation would be prohibitively crowded. While we have been unable to test this hypothesis by isolating and characterizing the adduct of methylcopper with the intermediate-sized phosphine PMe_2Ph, this suggestion is supported by observations in the copper (trimethylsilyl)methyl system.

(Trimethylsilyl)methyl and Neopentyl Complexes. Copper(II) acetate and $Mg(CH_2SiMe_3)_2$ react in the presence of PMe_3 or PMe_2Ph to give colorless crystals of $[Cu(PMe_3)_4][Cu(CH_2SiMe_3)_2]$ (**3**) or $[Cu(PMe_2Ph)_4][Cu(CH_2SiMe_3)_2]$ (**4**). The behavior of **3** will be discussed

$$Cu_2(O_2CMe)_4 + 2Mg(CH_2SiMe_3)_2 + \text{excess } PR_3 \rightarrow [Cu(PR_3)_4][Cu(CH_2SiMe_3)_2]$$
$$\mathbf{3},\ PR_3 = PMe_3$$
$$\mathbf{4},\ PR_3 = PMe_2Ph$$

below in detail. Conductivity studies of **4** in tetrahydrofuran are consistent with the presence of a 1:1 electrolyte, where $\Lambda = 4.36\ \Omega^{-1}$ mol^{-1} cm^2. The ^1H and $^{13}C\{^1H\}$ NMR spectra in toluene at −90 °C show resonances at δ −0.59 and −0.2, respectively, that are assignable to the Cu–CH$_2$ group. The ^1H NMR chemical shift is significantly different from the value of δ −3.0 reported for "$LiCu(CH_2SiMe_3)_2$",[44] and the large upfield shift of the latter can again be ascribed to direct Li···R interactions. The ^{31}P coordination chemical shift of $[Cu(PMe_2Ph)_4][Cu(CH_2SiMe_3)_2]$ in toluene is +17 ppm.

Whereas the phosphine ligands PMe_3 and PMe_2Ph are small enough to form $[Cu(PR_3)_4]$ cations, alkylation in the presence of the larger phosphine $PMePh_2$ gives nonionic products. Thus, copper(II) acetate and $Mg(CH_2SiMe_3)_2$ or $Mg(CH_2CMe_3)_2$ react to give the (trimethylsilyl)methyl and neopentyl complexes $Cu(CH_2SiMe_3)(PMePh_2)_3$ (**5**) and $Cu(CH_2CMe_3)(PMePh_2)_3$ (**6**), respectively. Both species

$$^1/_2Cu_2(O_2CMe)_4 + MgR_2 + \text{excess } PMePh_2 \rightarrow CuR(PMePh_2)_3$$
$$\mathbf{5},\ R = CH_2SiMe_3$$
$$\mathbf{6},\ R = CH_2CMe_3$$

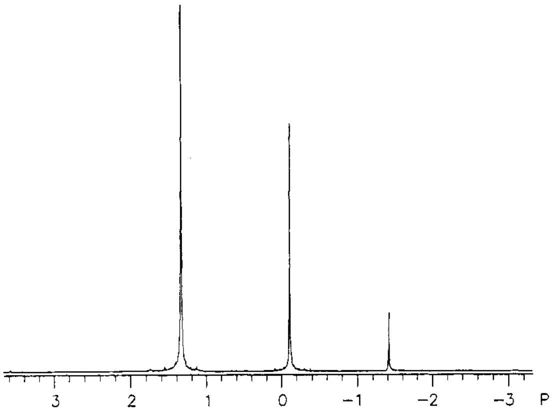

Figure 2. ^1H NMR spectrum of $[Cu(PMe_3)_4][Cu(CH_2SiMe_3)_2]$ (**3**) in THF-d_8 at 25 °C.

are nonelectrolytes in tetrahydrofuran with $\Lambda = 0.06\ \Omega^{-1}$ mol^{-1} cm^2. The spectroscopic parameters for these complexes are similar to the copper alkyls described above: IR features at 2790 and 2730 cm^{-1} arise from ν_{CH} stretches, and a ^1H NMR resonance in toluene for the Cu–CH$_2$ group in **5** appears at δ −0.18 (no Cu–CH$_2$ resonance was observable in the neopentyl complex). The Cu–CH$_2$ chemical shift in **5** is somewhat solvent- and temperature-dependent, and this is most likely due to reversible phosphine dissociation that is facile at room temperture but slow on the NMR time scale at −60 °C. The ^{31}P coordination chemical shifts in both toluene and THF are again fairly small at +4 and −5 ppm for **5** and **6**, respectively.

Ion Pairing and Phosphine Dissociation Equilibria. In view of the relative stability of $[Cu(PMe_3)_4][Cu(CH_2SiMe_3)_2]$ (**3**) compared with the other dialkyl cuprate salts, we have undertaken a more extensive investigation of this (trimethylsilyl)methyl complex in an effort to determine the details of its solution behavior. In particular, it is of interest to assess the extent of ion pairing and phosphine dissociation in various solvents.

The ^1H NMR spectrum of **3** in toluene-d_8 at 25 °C shows a single resonance due to PMe_3 at δ 0.94 that is near the δ 0.99 value for free PMe_3; no coupling to ^{31}P is evident in this peak. The alkyl group shows singlets at δ 0.53 and −0.80 due to the SiMe$_3$ and Cu–CH$_2$ protons, respectively; in this case again, no coupling to ^{31}P or ^{63}Cu is apparent, although the Cu–CH$_2$ resonance is slightly broad: fwhm = 5 Hz. The $^{31}P\{^1H\}$ NMR spectrum at 25 °C shows a broad (fwhm = 450 Hz) resonance at δ −55.4. The $^{63}Cu\{^1H\}$ NMR spectrum of **3** at 25 °C in toluene consists of a binomial pentet at δ 213 (downfield of $[Cu\{P(OMe_3\}_4][NO_3]$) with $J_{Cu-P} = 795$ Hz; this indicates that the $[Cu(PMe_3)_4]$ cation is intact. Interestingly, no signal due to the $[Cu(CH_2SiMe_3)_2]$ anion is observed. Upon cooling to −60 °C, the complex precipitates from solution and the signals due to **3** disappear.

The effect of solvent polarity was determined by examining the ^1H NMR behavior of **3** in tetrahydrofuran-d_8. At room temperature, sharp singlets at δ 1.34, −0.11, and −1.42 occur due to the PMe$_3$, SiMe$_3$, and Cu–CH$_2$ groups, respectively (Figure 2) and the spectrum is essentially unchanged upon cooling to −60 °C. All of these chemical shifts are *significantly* different from those observed in toluene solution.

The $^{13}C\{^1H\}$ NMR spectrum in THF-d_8 at room temperature shows singlets at δ 17.9, 5.8, and −2.6 due to the PMe$_3$, SiMe$_3$, and Cu–CH$_2$ groups, respectively. At −60 °C, the PMe$_3$ resonance resolves into a pseudoquartet with an apparent P–C "coupling constant" of 42 Hz. The $^{31}P\{^1H\}$ NMR spectrum in THF-d_8 at 25 °C consists of a 1:1:1:1

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(43) The alkyl $CuMe(PMePh_2)_3$ has been reported previously, having been obtained by alkylation of $Cu(acac)_2$ with $AlMe_2(OEt)$ in the presence of the phosphine.[31] The product was reported to be insoluble in diethyl ether in contrast to our results; other physical properties differ significantly as well. It appears that different compounds can be obtained by using different synthetic procedures.

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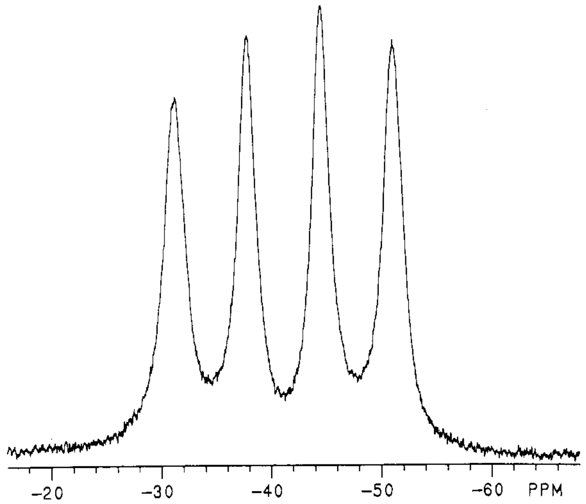


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Cu(PMe_3)_4][Cu(CH_2SiMe_3)_2]$ (**3**) in THF-d_8 at 25 °C.

quartet at δ −41.2 with J_{Cu-P} = 805 Hz, which exhibits the quadrupolar broadening expected upon cooling to −60 °C (Figure 3).[45] The $^{63}Cu\{^1H\}$ NMR spectrum at 25 °C again shows a pentet at δ 205, J_{Cu-P} = 805 Hz, due to the cation, but as above, no signal ascribable to the anion is seen.

The solvent-dependent ^1H and ^{31}P NMR chemical shifts and the presence of Cu–P coupling in THF but not in toluene strongly suggest that significant ion pairing occurs in nonpolar solvents. Thus, in THF the highly symmetric $[Cu(PMe_3)_4{}^+]$ cation exhibits coupling between the ^{31}P nuclei and the quadrupolar ^{63}Cu nucleus due to the zero electric field gradient at the tetrahedral center; the existence of well-separated ions in THF is confirmed by conductivity measurements, which are consistent with the presence of 1:1 electrolytes in this solvent. In toluene, ion pairing destroys the local tetrahedral symmetry of the cation and the coupling is lost due to rapid quadrupolar relaxation rates. Although a closely related alternative to the existence of $[Cu(PMe_3)_4][CuR_2]$ tight ion pairs in toluene is redistribution of the ligands to form electrically neutral $[CuR(PR_3)_2]_x$ species, we can rule out this possibility since only ionic centers are present in the solid-state structure of $[Cu(PMe_3)_4][CuMe_2]$ and the $^{63}Cu\{^1H\}$ NMR spectrum of **3** in toluene clearly shows the presence of a $[Cu(PMe_3)_4]$ cation.

The variable-temperature $^{13}C\{^1H\}$ NMR spectra in THF show changes in the PMe_3 line shape from a singlet at 25 °C to a pseudoquartet at −60 °C, and this is indicative of reversible phosphine dissociation that is rapid on the NMR time scale at room temperature but slow at −60 °C. This observation combined with the retention of Cu–P coupling in the $^{31}P\{^1H\}$ NMR spectrum at room temperature requires that ΔG^* for phosphine exchange must be ca. 13 kcal mol^{-1}.

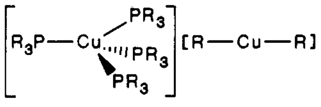
The $^{13}C\{^1H\}$ NMR spectra in the Cu–CH_2 region in THF solvent do not show coupling to the ^{63}Cu nucleus, contrary to what might be expected for an ion of local $D_{\infty h}$ symmetry. At least two mechanisms can account for this lack of Cu–C coupling. First, rapid exchange of alkyl groups between $[CuR_2]$ anions would destroy the correlation between the ^{13}C and ^{63}Cu spin states and therefore no coupling would be seen. Second, association of THF molecules to give $[CuR_2(THF)_x]$ solvated anions would lower the symmetry of the anion and quadrupolar relaxation effects would average out the coupling. At present we cannot distinguish these two possibilities, although the lack of coupling even at −60 °C, where alkyl exchange rates are apt to be slow, suggests that solvation of the anion is the more likely explanation. This explanation is also consistent with the absence of a ^{63}Cu signal for the anion.

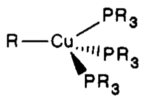
In contrast to the results above, the ^1H, ^{13}C, and ^{31}P NMR spectra of $Cu(CH_2SiMe_3)(PMePh_2)_3$ (**5**) in toluene and THF are relatively similar, no ^{63}Cu coupling in the $^{31}P\{^1H\}$ NMR spectrum is evident even at low temperature, and no ^{63}Cu NMR signal can be located. These observations clearly indicate that no $[Cu(PR_3)_4]$ centers are present and that the tris(phosphine) complexes are nonionic.

Reactions of Copper Alkyls with Hydrogen. The copper alkyls $[Cu(PMe_2Ph)_4][Cu(CH_2SiMe_3)_2]$ and $Cu(CH_2SiMe_3)(PMePh_2)_3$ were hydrogenated under 3 atm of H_2 in toluene. The color of the solutions changed quickly from yellow to orange, and copper metal precipitated. Examination of the solutions by ^1H NMR showed the presence of free phosphine and TMS; no evidence of copper hydrides[46–50] was noted.

Conclusions

Our investigations of phosphine adducts of copper(I) alkyls have established the existence of $CuR(PR_3)_2$ and $CuR(PR_3)_3$ stoichiometries depending on the steric bulk of the phosphine. For small phosphines, $CuR(PR_3)_2$ species are formed, which in actuality are ionic compounds of composition $[Cu(PR_3)_4][CuR_2]$ (A), as shown by conductivity studies and the X-ray crystal structure of $[Cu(PMe_3)_4][CuMe_2]$. These species exhibit extensive ion pairing in nonpolar solvents such as toluene but are 1:1 electrolytes in more polar solvents such as THF. The $CuR(PR_3)_3$ complexes, B, are by contrast molecular species of composition identical with their empirical formula. Our ^1H NMR data suggest that the large upfield chemical shifts often observed for lithium dialkylcuprates are due to direct Li···R interactions, since we see no such shifts in our lithium-free dialkylcuprate salts. The facile formation of dialkylcuprate species upon addition of phosphines to copper(I) alkyls may be a general phenomenon and is of considerable importance in understanding the nature of these useful synthetic reagents.


A


B

Experimental Section

All operations were carried out under vacuum or under argon. Although previous workers have suggested that $CuR(PR_3)_x$ complexes are photosensitive,[31,32] we have not observed such behavior and no protection from light was necessary. Solvents were distilled under nitrogen from sodium (toluene) or sodium–benzophenone (pentane, diethyl ether) immediately before use. Tetrakis(acetato)dicopper(II) was prepared from the dihydrate by refluxing for 10 h in acetic anhydride, followed by filtering the precipitate, washing with diethyl ether, and drying under vacuum. Dialkylmagnesium reagents were prepared from the corresponding alkyl chlorides and used as stock solutions in diethyl ether.[51] Trimethylphosphine,[52] dimethylphenylphosphine,[53] and me-

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thyldiphenylphosphine[53] were prepared by literature routes.

Microanalyses were performed by Mr. Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B as Nujol mulls. The ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 at 300 and 75.4 MHz, while the ^{31}P NMR spectra were obtained on a locally constructed instrument at 101.2 MHz. The ^{63}Cu NMR spectra were recorded on a General Electric GN-300NB and referenced to $[Cu\{P(OMe)_3\}_4][NO_3]$.[54] Chemical shifts are reported in δ units (positive chemical shifts to higher frequency). All peak integrals are consistent with the assignments and are therefore omitted. Electrical conductivity measurements were performed in tetrahydrofuran on a YSI Model 35 conductance meter. Melting points were determined on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

[Tetrakis(trimethylphosphine)copper(I)] Dimethylcuprate(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.93 g, 2.56 mmol) in diethyl ether (300 mL) at 0 °C was added dimethylmagnesium (11.3 mL of a 0.45 M solution in diethyl ether, 5.08 mmol) and trimethylphosphine (2.10 mL, 21.3 mmol). The slurry slowly turned colorless upon stirring for 4 h. After being warmed to room temperature, the solvent was removed under vacuum. The residue was washed with pentane (30 mL) and extracted with toluene (30 mL). The filtered extract was cooled to −20 °C, resulting in the formation of colorless prisms: yield 0.64 g (55%); mp 89 °C dec. Reproducible microanalyses were not obtainable due to the air sensitivity of the complex. IR (cm^{-1}): 2760 w, 1420 m, 1305 m, 1288 m, 940 s, 725 m, 660 m, 600 m, 530 m. ^{1}H NMR (25 °C, PhH-d_6): δ 0.93 (br, P*Me*$_3$), 0.15 (s, Cu*Me*).

Tris(methyldiphenylphosphine)methylcopper(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.47 g, 1.29 mmol) in pentane (30 mL) at 0 °C was added dimethylmagnesium (3.0 mL of a 0.45 M solution in diethyl ether, 1.35 mmol) and methyldiphenylphosphine (1.5 mL, 8.1 mmol). After being stirred for 2 h, the solution was warmed to room temperature and stirred an additional 3 h. The pale yellow solution was filtered from unreacted $Cu_2(O_2CMe)_4$ and the residue extracted with pentane (30 mL). The filtered extract was combined, concentrated to ca. 20 mL, and cooled to −20 °C to give yellow crystals: yield 0.76 g (43%); mp 40 °C dec. Anal. Calcd: C, 70.8; H, 6.19; Cu, 9.37. Found: C, 69.1; H, 6.18; Cu, 8.95. IR (cm^{-1}): 3045 w, 3030 w, 2760 w, 1575 m, 1465 m, 1425 m, 1300 m, 1275 m, 1172 w, 1150 w, 1090 m, 1060 w, 1018 m, 990 w, 880 sh, 872 s, 745 sh, 738 sh, 732 s, 712 s, 685 s, 502 s, 475 m, 437 m. ^{1}H NMR (20 °C, PhH-d_6): δ 7.36 (m, o-*H*), 7.02 (m, m-*H* and p-*H*), 1.39 (d, J_{PH} = 0.9 Hz, P*Me*Ph$_2$), 0.29 (br s, Cu-*Me*). ^{31}P{^{1}H} NMR (25 °C, PhMe-d_8): δ −20.2 (br). ^{31}P{^{1}H} NMR (−70 °C, PhMe-d_8): δ −18.4 (br).

[Tetrakis(trimethylphosphine)copper(I)] Bis[(trimethylsilyl)methyl]cuprate(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.78 g, 2.15 mmol) in diethyl ether (30 mL) at 0 °C was added bis[(trimethylsilyl)methyl]magnesium (11.00 mL of a 0.43 M solution in diethyl ether, 4.71 mmol) and trimethylphosphine (1.80 mL, 18.2 mmol). The solution was warmed to room temperature and the slurry slowly turned colorless over a 4-h period. The solvent was removed under vacuum, and the residue was extracted with pentane (5 × 30 mL). The filtered extracts were combined and concentrated to ca. 130 mL, and cooling to −20 °C resulted in the formation of colorless crystals: yield 0.53 g (41%); mp 128 °C dec. Anal. Calcd: C, 39.7; H, 9.59; Cu, 21.0. Found: C, 39.3; H, 9.04; Cu, 22.3. IR (cm^{-1}): 1305 m, 1289 m, 1225 m, 944 s, 864 s, 817 m, 727 s, 668 w. ^{1}H NMR (20 °C, PhMe-d_8): δ 0.94 (s, P*Me*$_3$), 0.53 (s, CH$_2$Si*Me*$_3$), −0.80 (s, *C*H$_2$SiMe$_3$). ^{1}H NMR (20 °C, THF-d_8): δ 1.34 (s, P*Me*$_3$), −0.11 (s, CH$_2$Si*Me*$_3$), −1.34 (s, *C*H$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (20 °C, PhMe-d_8): δ 16.8 (s, P*Me*$_3$), 14.3 (s, CH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (20 °C, THF-d_8): δ 17.9 (s, P*Me*$_3$), 5.8 (s, CH$_2$Si*Me*$_3$), −2.6 (s, CH$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (−60 °C, THF-d_8): δ 17.5 ("q", "J_{PC}" = 42 Hz, P*Me*$_3$), 5.9 (s, CH$_2$Si*Me*$_3$), −2.3 (s, *C*H$_2$SiMe$_3$). ^{31}P{^{1}H} NMR (25 °C, PhMe-d_8): δ −55.4 (br). ^{31}P{^{1}H} NMR (25 °C, THF-d_8): δ −41.2 (q, J_{CuP} = 805 Hz). ^{63}Cu{^{1}H} NMR (25 °C, PhH-d_6): δ 213 (pentet, J_{CuP} = 795 Hz). ^{63}Cu{^{1}H} NMR (25 °C, THF-d_8): δ 205 (pentet, J_{CuP} = 805 Hz).

Table I. Crystal Data for $[Cu(PMe_3)_4][CuMe_2]$ at 25 °C

space group: $P2_13$
a = 13.666 (2) Å
V = 2552 (1) Å^3
Z = 4
mol wt = 461.48
d_{calcd} = 1.201 g cm^{-3}
μ_{calcd} = 5.98 cm^{-1}
size = 0.2 × 0.3 × 0.4 mm

diffractometer: Enraf-Nonius CAD 4
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.71073 Å
monochromator: graphite crystal, 2θ = 12°
scan range, type: $2.0 < 2\theta < 46.0°$, ω/θ
scan speed, width: 3–16° min^{-1}, $\Delta w = 1.50(1.00 + 0.35 \tan \theta)°$
rflctns: 2162, 679 unique, 442 with $I > 2.58\sigma(I)$
internal consistency: R_i = 4.7%

R_F = 4.3%
R_{wF} = 4.2%
variables = 62
p factor = 0.020

Table II. Final Atomic Coordinates for $[Cu(PMe_3)_4][CuMe_2]$

	x/a	y/b	z/c
Cu1	0.03882 (9)	x	x
Cu2	0.3622 (1)	x	x
P1	−0.0323 (2)	0.0585 (2)	0.1875 (2)
P2	−0.0564 (2)	x	x
C1	0.018 (1)	0.1526 (9)	0.2662 (9)
C2	−0.029 (1)	−0.0469 (9)	0.2698 (9)
C3	−0.1604 (10)	0.094 (1)	0.1894 (10)
C4	−0.011 (1)	−0.076 (1)	−0.1774 (9)
C5	0.445 (1)	x	x
C6	0.2807 (9)	x	x

[Tetrakis(dimethylphenylphosphine)copper(I)] Bis[(trimethylsilyl)methyl]cuprate(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.64 g, 1.76 mmol) in diethyl ether (30 mL) at 0 °C was added bis[(trimethylsilyl)methyl]magnesium (8.2 mL of a 0.43 M solution in diethyl ether, 3.53 mmol) and dimethylphenylphosphine (2.10 mL, 14.8 mmol). The solution slowly turned pale yellow upon stirring for 2 h. After the solution had warmed to room temperature, the ether was removed under vacuum. The residue was extracted with pentane (3 × 30 mL), and the filtered extracts were combined and concentrated to ca. 30 mL. Cooling to −20 °C resulted in the formation of colorless crystals: yield 0.65 g (43%); mp 75 °C dec. Anal. Calcd: C, 55.0; H, 7.96; Cu, 15.3. Found: C, 55.4; H, 8.00; Cu, 15.6. IR (cm^{-1}): 3040 w, 1435 m, 1325 w, 1310 w, 1300 m, 1285 m, 1235 m, 1220 s, 1150 w, 1095 w, 1070 w, 1020 w, 995 w, 930 s, 895 s, 870 sh, 855 s, 810 m, 740 s, 725 m, 690 s, 668 m, 655 m, 530 m, 490 s, 400 w. ^{1}H NMR (20 °C, PhH-d_6): δ 7.19 (m, o-H), 7.05 (m, m-H and p-H), 1.18 (s, P*Me*$_2$Ph), 0.49 (s, CH$_2$Si*Me*$_3$), −0.58 (s, *C*H$_2$SiMe$_3$). ^{1}H NMR (−90 °C, PhMe-d_8): δ 7.17 (m, o-H), 7.05 (m, m-H and p-H), 1.02 (s, P*Me*$_2$Ph), 0.63 (s, CH$_2$Si*Me*$_3$), −0.59 (s, *CH*$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (20 °C, PhH-d_6): δ 139.0 (br, ipso-C), 130.3 (d, J_{PC} = 10.3 Hz, o-*C*), 129.0 (s, p-*C*), 128.8 (s, m-*C*), 15.6 (s, P*Me*$_2$Ph), 5.9 (s, CH$_2$Si*Me*$_3$), −3.8 (s, *C*H$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (−90 °C, PhMe-d_8): δ 141.9 (br, ipso-*C*), 130.3 (d, J_{PC} = 10 Hz, o-*C*), 15.5 (s, P*Me*$_2$Ph), 6.5 (s, CH$_2$Si*Me*$_3$), −0.2 (s, *C*H$_2$SiMe$_3$). ^{31}P{^{1}H} NMR (20 °C, PhMe-d_8): δ −37.0 (br). ^{31}P{^{1}H} NMR (−75 °C, PhMe-d_8): δ −29.0 (br).

Tris(methyldiphenylphosphine)[(trimethylsilyl)methyl]copper(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.90 g, 2.47 mmol) in diethyl ether (30 mL) at 0 °C was added bis[(trimethylsilyl)methyl]magnesium (11.6 mL of a 0.45 M solution in diethyl ether, 5.22 mmol) and methyldiphenylphosphine (3.7 mL, 19.9 mmol). After being stirred for 5 h and warming to room temperature, the pale yellow solution was taken to dryness under vacuum and the residue extracted with pentane (3 × 30 mL). The filtered extracts were combined, concentrated to ca. 10 mL, and cooled to −20 °C to give yellow needles: yield 2.33 g (63%); mp 63 °C dec. Anal. Calcd: C, 68.8; H, 6.67; Cu, 8.5. Found: C, 67.8; H, 6.67; Cu, 8.4. IR (cm^{-1}): 3035 w, 3020 w, 2790 w, 1580 m, 1570 w, 1480 m, 1430 m, 1330 w, 1308 m, 1280 m, 1240 w, 1230 m, 1180 w, 1153 w, 1090 m, 1065 w, 1020 w, 995 w, 875 s, 848 s, 810 s, 736 s, 720 m, 710 m, 690 s, 670 m,

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Table III. Anisotropic Thermal Parameters for $[Cu(PMe_3)_4][CuMe_2]$

	$U(11)$, $U(iso)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Cu1	0.0447 (6)	$U(11)$	$U(11)$	−0.0019 (7)	$U(23)$	$U(23)$
Cu2	0.0780 (9)	$U(11)$	$U(11)$	−0.005 (1)	$U(23)$	$U(23)$
P1	0.069 (2)	0.054 (2)	0.054 (2)	−0.004 (2)	0.012 (2)	−0.002 (2)
P2	0.069 (2)	$U(11)$	$U(11)$	−0.014 (2)	$U(23)$	$U(23)$
C1	0.16 (1)	0.10 (1)	0.069 (9)	−0.041 (8)	0.03 (1)	−0.03 (1)
C2	0.26 (2)	0.086 (10)	0.075 (9)	0.006 (9)	0.05 (1)	−0.03 (2)
C3	0.07 (1)	0.21 (2)	0.12 (1)	−0.02 (1)	0.044 (10)	−0.01 (1)
C4	0.17 (2)	0.21 (2)	0.09 (1)	−0.08 (1)	0.02 (1)	−0.07 (1)
C5	0.126 (10)	$U(11)$	$U(11)$	−0.02 (1)	$U(23)$	$U(23)$
C6	0.108 (9)	$U(11)$	$U(11)$	−0.018 (10)	$U(23)$	$U(23)$
H	0.20 (2)					

Table IV. Bond Distances (Å) and Angles (deg) in $[Cu(PMe_3)_4][CuMe_2]$

Bond Distances			
Cu1–P1	2.269 (3)	P1–C1	1.81 (1)
Cu1–P2	2.253 (3)	P1–C2	1.83 (1)
Cu2–C5	1.95 (1)	P1–C3	1.82 (1)
Cu2–C6	1.93 (1)	P2–C4	1.79 (1)
Bond Angles			
P1–Cu1–P1′	109.2 (1)	C1–P1–C2	100.6 (6)
P1–Cu1–P2	109.8 (1)	C1–P1–C3	99.7 (7)
C5–Cu2–C6	180.0[a]	C2–P1–C3	103.1 (8)
Cu1–P1–C1	116.9 (5)	Cu1–P2–C4	115.1 (5)
Cu1–P1–C2	116.5 (5)	Cu1–P2–C4′	103.3 (7)
Cu1–P1–C3	117.2 (4)		

[a] Crystallographically imposed.

658 m, 505 s, 475 s, 430 s, 410 m. ^{1}H NMR (20 °C, PhH-d_6): δ 7.36 (m, o-H), 7.02 (m, m-H and p-H), 1.41 (s, PMePh$_2$), 0.48 (s, CH$_2$SiMe_3), 0.12 (s, CH_2SiMe$_3$). ^{1}H NMR (−60 °C, PhMe-d_8): δ 7.17 (m, o-H), 6.99 (m, m-H and p-H), 1.41 (s, PMePh$_2$), 0.56 (s, CH$_2$SiMe_3), −0.18 (s, CH_2SiMe$_3$). ^{1}H NMR (20 °C, THF-d_8): δ 7.41 (m, o-H), 7.30 (m, m-H and p-H), 1.61 (d, J_{PH} = 3.0 Hz, PMePh$_2$), 0.11 (s, CH$_2$SiMe_3), −0.68 (br, fwhm = 18 Hz, CH_2SiMe$_3$). ^{1}H NMR (−60 °C, THF-d_8): δ 7.29 (m, PMePh_2), 1.52 (s, PMePh$_2$), −0.14 (s, CH$_2$SiMe_3), −0.60 (s, CH_2SiMe$_3$). ^{13}C{^{1}H} NMR (20 °C, PhMe-d_8): δ 139.0 (d, J_{PC} = 4 Hz, ipso-C), 132.4 (d, J_{PC} = 17 Hz, o-C), 128.9 (s, p-C), 128.6 (d, J_{PC} = 7 Hz, m-C), 13.0 (s, PMePh$_2$), 5.3 (s, CH$_2$SiMe_3), 1.0 (CH_2SiMe$_3$). ^{13}C{^{1}H} NMR (20 °C, THF-d_8): δ 140.0 (d, J_{PC} = 4 Hz, ipso-C), 133.1 (d, J_{PC} = 17 Hz, o-C), 129.6 (s, p-C), 129.3 (d, J_{PC} = 7 Hz, m-C), 12.8 (d, J_{PC} = 4 Hz, PMe_3), 5.0 (s, CH$_2$SiMe_3). ^{13}C{^{1}H} NMR (−60 °C, THF-d_8): δ 140.3 (d, J_{PC} = 4 Hz, ipso-C), 133.0 (d, J_{PC} = 16 Hz, o-C), 129.3 (s, p-C), 129.0 (d, J_{PC} = 7 Hz, m-C), 13.4 (m, PMePh$_2$), 5.4 (s, CH$_2$SiMe_3). ^{31}P{^{1}H} NMR (20 °C, PhMe-d_8): δ −24.0 (s). ^{31}P{^{1}H} NMR (−70 °C, PhMe-d_8): δ −24.3 (s).

Tris(methyldiphenylphosphine)neopentylcopper(I). To a suspension of anhydrous tetrakis(acetato)dicopper(II) (0.65 g, 1.79 mmol) in diethyl ether (30 mL) at 0 °C was added dineopentylmagnesium (12.4 mL of a 0.30 M solution in diethyl ether, 3.72 mmol) and methyldiphenylphosphine (2.70 mL, 14.5 mmol). After being stirred for 7 h, the pale yellow solution was warmed to room temperature and the ether removed under vacuum. The residue was extracted with pentane (90 mL), and the filtered extract was concentrated to ca. 60 mL and cooled to −20 °C to give yellow crystals and a brown solid. Recrystallization from pentane gave the pure product as yellow needles: yield 1.83 g (68%); mp 60 °C dec. Anal. Calcd: C, 71.9; H, 6.81; Cu, 8.6. Found: C, 72.2; H, 6.90; Cu, 8.6. IR (cm^{-1}): 3060 w, 3040 w, 2735 w, 1585 m, 1565 w, 1430 m, 1345 w, 1305 w, 1280 w, 1220 w, 1180 w, 1250 w, 1085 m, 1065 m, 1020 w, 990 w, 915 w, 870 s, 732 s, 710 m, 690 s, 670 m, 615 m, 608 m, 540 w, 505 s, 475 s, 443 w, 420 m, 400 m, 380 w. ^{1}H NMR (20 °C, PhH-d_6): δ 7.41 (m, o-H), 7.05 (m, m-H and p-H), 1.68 (br, PMePh$_2$), 1.48 (s, CH$_2$CMe_3). ^{31}P{^{1}H} NMR (25 °C, PhMe-d_8): δ −37.3 (br). ^{31}P{^{1}H} NMR (−80 °C, PhMe-d_8): δ −33.0 (br).

Crystallographic Studies. Single crystals of $[Cu(PMe_3)_4][CuMe_2]$, grown from toluene, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures followed by least-squares refinement using 25 reflections yielded the cell dimensions given in Table I.

Data were collected in one octant of reciprocal space ($+h,-k,+l$) using measurement parameters listed in Table I. Systematic absences for $h00$, $h \neq 2n$, uniquely defined the cubic space group $P2_13$. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.598 and 0.514, respectively. Systematically absent reflections were eliminated, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by Patterson methods, from which correct positions for atoms Cu1 and P1 were deduced. A weighted difference Fourier synthesis gave positions for Cu2 and P2, and subsequent least-squares difference Fourier calculations revealed positions for the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.12/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients. Hydrogen atoms on C1, C2, C3, and C4 were located in the difference Fourier maps, fixed in "idealized" positions (staggered with respect to the attached sp^3 phosphorus atom) with C–H = 0.95 Å, and a group isotropic thermal parameter was varied. However, hydrogen positions for atoms C5 and C6 did not surface in the difference Fourier maps during the latter stages of the refinement process, and these hydrogen atoms were not included in the structure factor calculations. Successful convergence was indicated by the maximum shift/error of 0.003 for the last cycle. Refinement of the enantiomeric model significantly changed the weighted residual (R_{wF} = 0.049). The final difference Fourier map had two residual peaks located on the threefold axis (x = −0.1898 and x = 0.4959) with densities of <0.38 e Å^{-3}, and there were no other significant features in this map. Final refinement parameters were given in Table I. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors.

Acknowledgment. We thank the National Science Foundation (Grant CHE-85-21757) for support of this work. We particularly wish to thank Dr. Scott Wilson of the University of Illinois X-ray crystallography laboratory for performing the X-ray crystal structure determination. G.S.G. is the recipient of a Sloan Foundation Research Fellowship (1988–1990).

Registry No. 1, 113507-98-5; 2, 63330-51-8; 3, 113507-99-6; 4, 113508-00-2; 5, 113508-01-3; 6, 113508-02-4; $Cu_2(O_2CMe)_4$, 142-71-2; $MgMe_2$, 2999-74-8; PMe_3, 594-09-2; $PMePh_2$, 1486-28-8; $Mg(Ch_2SiMe_3)_2$, 51329-17-0; PMe_2Ph, 672-66-2; $Mg(CH_2CMe_3)_2$, 19978-31-5.

Supplementary Material Available: A table of hydrogen atom positions for $[Cu(PMe_3)_4][CuMe_2]$ (1 page); a listing of final observed and calculated structure factors for $[Cu(PMe_3)_4][CuMe_2]$ (3 pages). Ordering information is given on any current masthead page.