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Preparation of Copper Organometallics *via* Nucleophilic Substitution of $\mathrm{CpCuPPh_3}$: Syntheses and X-ray Structure Determinations of $\mathrm{[Li(THF)_4]^+[(fluorenyl)_2CuPPh_3]^-}$ and $\mathrm{[Cy_3PCu(\mu\text{-}C{\equiv}C^tBu)_2Cu(PPh_3)_2]}$ (THF = Tetrahydrofuran, Fluorenyl = $\mathrm{C_{13}H_9}$)

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The ion-separated complex $\mathrm{[Li(THF)_4]^+[(fluorenyl)_2CuPPh_3]^-}$ (**2**) and the dinuclear complex $\mathrm{[Cy_3PCu(\mu\text{-}C{\equiv}C^tBu)_2Cu(PPh_3)_2]}$ (**3**) have been synthesized by nucleophilic substitution of $\mathrm{CpCuPPh_3}$ (**1**) with fluorenyllithium (1:1 or 1:2 equiv) and with *tert*-butylacetylide lithium and tricyclohexylphosphine (1:1:1 equiv), respectively. Both complexes have been characterized by elemental analyses, solid-state IR spectroscopy, ^{1}H and ^{31}P NMR spectroscopy, and low-temperature X-ray diffraction studies. Complex **2** crystallizes in the monoclinic space group *C*2/*c*, with cell dimensions a = 37.425(7) Å, b = 15.230(3) Å, c = 20.050(4) Å, β = 105.03(3)°, V = 11037(4) Å^3, and Z = 8. The distorted trigonal planar copper anion of complex **2** is the first example of a mononuclear cuprate stabilized by neutral phosphine coordination. Complex **3** crystallizes in the triclinic space group $P\bar{1}$, with cell dimensions a = 13.185(3) Å, b = 13.572(3) Å, c = 22.516(5) Å, α = 83.97(3)°, β = 77.12(3)°, γ = 66.08(3)°, V = 3590.0(14) Å^3, and Z = 2. Complex **3** is an unusual binuclear complex containing both distorted three and four coordinate copper centers bridged by acetylide ligands. It contains an extremely short Cu$\cdot\cdot\cdot$Cu distance of 2.389(1) Å. The preparation of complexes **2** and **3** demonstrates the potential of **1** as a starting point for the halide-free syntheses of copper organometallics.

Introduction

Our recent exploration of the nucleophilic attack of metal cyclopentadienyls of group 13 (E = Tl) and group 14 (E = Sn, Pb) has shown that the composition of the products is largely dependent on the nucleophilicity and steric bulk of the attacking nucleophile. Reactions with weak nucleophiles such as Cp$^-$ result in nucleophilic addition to the metal centers to produce anionic organometallic fragments.[1−4] However, use of more potent nucleophiles such as imino anions results in substitution of the Cp ligands of $\mathrm{Cp_2E}$ (E = Sn, Pb).[5,6] Thus reaction of $\mathrm{LiN{=}C(NMe_2)_2}$ with $\mathrm{Cp_2Sn}$ (1:1) produces the dimeric mixed-ligand complex $\mathrm{[(\eta^3\text{-}Cp)Sn\{\mu\text{-}N{=}C(NMe_2)_2\}]_2}$, the product of monosubstitution, and the reaction of $\mathrm{LiN{=}C(^tBu)(Ph)}$ with $\mathrm{Cp_2Pb}$ (2:1) produces the triorganoplumbate $\mathrm{Pb[\mu\text{-}N{=}C(^tBu)(Ph)]_3Li{\cdot}THF}$, the result of disubstitution and then addition.[5,6] Similarly, the interaction of the highly nucleophilic and relatively sterically unhindered fluorenyl anion with $\mathrm{Cp_2Sn}$ results in disubstitution of the Cp ligands followed by addition of a third fluorenyl group, to form a triorganostannate anion.[1] A balance is reached between steric bulk and nucleophilicity with the $\mathrm{(SiMe_3)_2N^-}$ nucleophile. Substitution of only one Cp is observed with $\mathrm{Cp_2Sn}$, but the LiCp·PMDETA biproduct remains coordinated to Sn. The product, the "loose-contact" complex $\mathrm{(Cp)(Me_3Si)_2NSn(\mu\text{-}Cp)Li{\cdot}PMDETA}$, can be viewed as a model intermediate for the substitution of $\mathrm{Cp_2Sn}$, which presumably occurs by an associative mechanism.[7]

We have now extended this work to study the reactions of the late-transition metal cyclopentadienyls. Reaction of fluorenyllithium with $\mathrm{CpCuPPh_3}$ (**1**) in THF (1:1 or 2:1 equiv) results in substitution of the cyclopentadienyl ligand and in the addition of a second fluorenyl group to form $\mathrm{[Li(THF)_4]^+[(fluorenyl)_2CuPPh_3]^-}$ (**2**), a Gilman reagent possessing a mononuclear cuprate center stabilized by a phosphine ligand. In contrast, the reaction of a mixture of **1** and tricyclohexylphosphine with *tert*-butylacetylide lithium (1:1:1 equiv) in THF results in substitution of the Cp by the acetylide and in the formation of the acetylide-bridged complex $\mathrm{[Cy_3PCu(\mu\text{-}C{\equiv}C^tBu)_2Cu(PPh_3)_2]}$ **3**.

Results and Discussion

The phosphine-stabilized Gilman reagent $\mathrm{[Li(THF)_4]^+[(fluorenyl)_2CuPPh_3]^-}$ (**2**) can be prepared in

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Scheme 1

$$\mathrm{CpCu{\cdot}PPh_3} + x(\mathrm{fluorenyl})\mathrm{Li} \xrightarrow{x=1,\,2} [(\mathrm{fluorenyl})_2\mathrm{Cu{\cdot}PPh_3}]^-[\mathrm{Li(THF)_4}]^+$$

2

$$\mathrm{CpCu{\cdot}PPh_3} + \mathrm{LiC{\equiv}C^tBu} \xrightarrow{\mathrm{Cy_3P}} [\mathrm{Cy_3P{\cdot}Cu}(\mu\text{-}\mathrm{C{\equiv}C^tBu})_2\mathrm{Cu{\cdot}(PPh_3)_2}]$$

3

low but reproducible yield by the reaction of fluorenyllithium with $CpCuPPh_3$ (**1**) (1:1 or 2:1 equiv) (Scheme 1). Evidently, the product results from nucleophilic substitution of the Cp ligand followed by nucleophilic addition of a second fluorenyl anion. In contrast to the synthesis of **2**, the reaction of **1** with $LiC{\equiv}C^tBu$ in the presence of Cy_3P (1:1:1 equiv) produces the unusual dinuclear copper complex $[Cy_3PCu(\mu\text{-}C{\equiv}C^tBu)_2Cu(PPh_3)_2]$ (**3**), in which two different types of neutral phosphines are present (Scheme 1).

Prior to the determination of the crystal structures of **2** and **3**, both complexes were characterized by elemental analyses (C and H), solid-state IR spectroscopy, ^1H and ^{31}P NMR spectroscopy, and their melting points. Complex **2** was initially isolated as a THF solvate, $[Li(THF)_4]^+[(fluorenyl)_2CuPPh_3]^-{\cdot}0.5THF$. This loosely bound lattice solvation is lost from complex **2** upon isolation under vacuum (10^{-1} atm, 15 min) prior to transfer to the glovebox for analysis. The spectroscopic and analytical data for **2** were obtained on the dry, unsolvated complex. Complex **3** also contains a lattice-bound THF, but this is retained upon isolation and can be detected in the spectroscopic and analytical data. These preliminary studies confirmed the basic identities of both complexes. Although the high thermal stability of complex **3** (mp 125 °C) is not unusual (such acetylide complexes have long been known to be more thermally stable than comparable copper organyls[8]), the stability of the cuprate complex **2** is worthy of note. The complex is stable up to a temperature of 55 °C and survives for several weeks under inert atmosphere with only mild surface oxidation occurring.

The identities of **2** and **3** are particularly clear from their room-temperature ^1H and ^{31}P NMR spectra. The apical hydrogens of the fluorenyl ligands of **2** appear as a singlet (δ 3.84) and are distinct from the arene protons, which appear as a collection of well-resolved multiplets in the aromatic region (δ 7.74–6.80). The ratio of the fluorenyl groups to the PPh_3 and THF ligands (2:1:4) is consistent with the later structural characterization of the complex. In the ^1H NMR spectrum of **3** the cyclohexyl group appears as a broad collection of multiplets (δ 2.1–0.8). The sharper *tert*-butyl resonance, which overlaps the cyclohexyl resonances, is easily discerned (δ 1.22). Again the ratio of the Cy_3P, Ph_3P, and $^tBuC{\equiv}C-$ ligands in **3** is consistent with the later structural characterization of the complex. The ^{31}P NMR spectrum of **3** confirms that both Cy_3P and Ph_3P are present in a 1:2 ratio. These resonances can be assigned on the basis of the similarity of the Ph_3P signal in **3** with that of **2** [δ −148.14 in **3**; cf δ −144.51 in **2**]. The $C{\equiv}C$ stretching vibration in **3**, which is characteristically very weak in this type of complex (e.g. in $[Cu_3\{S(2\text{-}Me_2NCH_2\text{-}C_6H_4)\}_2(C{\equiv}C^tBu)]_2$[9]), could not be clearly assigned.

Table 1. Crystal Data and Structure Solutions for 2 and 3[a]

	2	**3**
empirical formula	$C_{62}H_{69}CuLiO_{4.5}P$	$C_{70}H_{89}Cu_2OP_3$
M_r	987.62	1166.40
cryst size/mm^3	0.49 × 0.48 × 0.42	0.41 × 0.38 × 0.28
cryst system	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a/Å	37.425(7)	13.185(3)
b/Å	15.230(3)	13.572(3)
c/Å	20.050(4)	22.516(5)
α/deg	90	83.97(3)
β/deg	105.03(3)	77.12(3)
γ/deg	90	66.08(3)
V/Å^3	11037(4)	3590.0(14)
Z	8	2
D_c/Mg m^{-3}	1.189	1.079
θ range/deg	$3.52 \le \theta \le 20.00$	$3.51 \le \theta \le 22.50$
no. of reflcns collcd	5225	9534
no. of indpdt reflcns	5124 ($R_{int} = 0.0307$)	9132 ($R_{int} = 0.0417$)
goodness of fit	1.133	1.078
R_1, wR_2 [$F > 4\sigma(F)$][b]	0.0837, 0.2211	0.0810, 0.2327
R_1, wR_2 (all data)[b]	0.1161, 0.2678	0.1155, 0.2942
final diff peak, hole	1.152, −0.650	2.083, −0.757

[a] Details in common: $T = 153(2)$ K, $\lambda = 0.710\,73$ Å. [b] $R_1 = \sum||F_o - F_c||/\sum F_o$ and w$R_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{0.5}$.

Low-temperature single crystal X-ray crystallographic studies were performed on complexes **2** and **3**. Since both complexes were mounted for X-ray analysis directly from solution, the THF lattice solvation was retained (see Experimental Section). Details of the X-ray analyses of both complexes are given in Table 1, and Tables 2 and 3 list the atomic coordinates for **2** and **3**, respectively. Selected bond lengths and angles are given in Table 4 for complex **2** and Table 5 for complex **3**.

The X-ray crystallographic study of **2** shows it to have an ion-separated structure (Figure 1). The complex contains a diorganocuprate anion in which the copper center is rendered three coordinate by its attachment to a neutral donor triphenylphosphine molecule [Cu−P = 2.223(3) Å]. The countercation is $Li(THF)_4^+$. In addition there is a lattice-bound half THF molecule per formula unit (not shown) which is lost when **2** is placed under prolonged vacuum (10^{-1} atm, 15 min).

The fluorenyl ligands are not bonded equivalently to the Cu center of the anion [Cu−C(50) = 2.079(9) and Cu−C(70) = 2.170(9) Å]. This presumably occurs as a result of steric congestion about this Cu center. Steric crowding about this atom is also apparent from the angular distortions of the ligands around Cu. Although the geometry about the Cu center is planar (sum of angles about copper 360.0°), the bond angles at Cu are considerably distorted. The bond angle between the fluorenyl(A) ligand, Cu, and the triphenylphosphine [P−Cu−C(50) = 134.7(3)°] is far larger than the fluorenyl(B)−Cu−triphenylphosphine and fluorenyl(A)−Cu−fluorenyl(B) angles [P−Cu−C(70) = 112.6(3)° and C(50)−Cu−C(70) = 112.7(4)°].

The stabilization of Gilman reagents by use of tertiary phosphine ligands has long been employed by organic chemists, although the precise role of the phosphine has remained unknown.[10] Although a few (phosphido)cuprates, such as $[MeCuP^tBu_2Li{\cdot}2THF]$[11] and $[Li(THF)_2][CuP(^tBu_2)_2]$,[12] have been structurally characterized,

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 2

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Cu(1)	1452(1)	1543(1)	2436(1)	29(1)	C(35)	1562(3)	−1329(7)	4106(5)	49(3)
P(1)	1087(1)	446(2)	2577(1)	28(1)	C(36)	1337(3)	−667(7)	3749(5)	37(3)
Li(1)	1417(5)	−3945(13)	720(9)	56(5)	C(41)	720(2)	675(6)	3009(4)	29(2)
O(1)	1547(2)	−4065(5)	1705(4)	64(2)	C(42)	668(3)	1535(7)	3186(5)	42(3)
C(2)	1933(6)	−4100(15)	2820(11)	141(7)	C(43)	384(3)	1746(8)	3486(6)	55(3)
C(1)	1788(6)	−3490(16)	2131(11)	58(10)	C(44)	150(3)	1121(8)	3598(5)	49(3)
C(3)	1767(7)	−4774(18)	2764(12)	85(10)	C(45)	205(3)	270(8)	3442(6)	54(3)
C(4)	1509(6)	−4886(16)	2028(11)	90(10)	C(46)	482(3)	37(7)	3139(6)	52(3)
C(1A)	1955(12)	−4317(32)	2178(22)	143(19)	C(50)	1363(3)	2819(6)	2055(5)	39(3)
C(3A)	1546(7)	−4140(20)	2918(14)	56(11)	C(51)	1149(3)	3222(6)	2465(5)	37(3)
C(4A)	1318(15)	−4204(38)	2162(24)	102(22)	C(52)	1247(3)	3556(7)	3135(6)	47(3)
O(2)	1747(2)	−4689(5)	398(4)	67(2)	C(53)	971(3)	3909(7)	3410(6)	53(3)
C(5)	2151(5)	−4753(14)	782(11)	139(7)	C(54)	599(3)	3939(7)	3024(6)	54(3)
C(6)	2322(4)	−5252(10)	303(8)	91(4)	C(55)	499(3)	3620(6)	2373(6)	44(3)
C(7)	1966(11)	−5935(30)	−95(15)	83(11)	C(56)	770(3)	3265(6)	2065(5)	36(3)
C(8)	1645(9)	−5585(26)	116(23)	97(14)	C(61)	1110(2)	2679(6)	1375(5)	33(2)
C(7A)	2079(10)	−5616(25)	−125(13)	38(13)	C(62)	748(2)	2914(6)	1400(5)	35(3)
C(8A)	1711(6)	−5174(20)	−215(15)	59(12)	C(63)	451(3)	2778(6)	812(6)	43(3)
O(3)	922(2)	−4315(5)	325(4)	72(2)	C(64)	513(3)	2459(7)	211(5)	51(3)
C(10)	463(4)	−4856(8)	823(7)	73(4)	C(65)	883(3)	2266(8)	186(6)	55(3)
C(11)	390(4)	−3889(9)	629(7)	78(4)	C(66)	1169(3)	2371(7)	758(6)	46(3)
C(12)	616(4)	−3712(9)	142(7)	76(4)	C(70)	2034(2)	1211(7)	2778(5)	32(2)
C(9)	764(4)	−5103(9)	494(7)	75(4)	C(71)	2082(2)	1312(6)	2081(5)	31(2)
O(4)	1473(2)	−2736(4)	499(4)	52(2)	C(72)	2013(3)	740(7)	1507(5)	40(3)
C(13)	1574(4)	−2479(9)	−117(7)	86(4)	C(73)	2085(3)	1017(7)	908(5)	44(3)
C(14)	1555(5)	−1484(10)	−174(9)	106(5)	C(74)	2219(3)	1860(7)	834(5)	42(3)
C(15)	1387(5)	−1234(13)	350(9)	129(6)	C(75)	2291(2)	2444(7)	1387(5)	35(2)
C(16)	1455(4)	−1928(10)	884(8)	91(4)	C(76)	2237(2)	2169(6)	2024(5)	32(2)
C(21)	837(2)	−114(6)	1786(4)	30(2)	C(81)	2304(2)	2589(6)	2690(5)	32(2)
C(22)	753(2)	354(7)	1170(5)	40(3)	C(82)	2192(2)	1989(6)	3148(5)	31(2)
C(23)	542(3)	−21(8)	552(5)	53(3)	C(83)	2234(3)	2229(7)	3842(5)	38(3)
C(24)	420(3)	−896(9)	566(6)	61(3)	C(84)	2380(3)	3022(8)	4059(5)	47(3)
C(25)	508(3)	−1364(7)	1175(6)	49(3)	C(85)	2482(3)	3639(7)	3611(6)	50(3)
C(26)	715(3)	−984(6)	1775(5)	37(3)	C(86)	2443(2)	3410(6)	2923(5)	37(3)
C(31)	1346(2)	−460(6)	3080(5)	30(2)	O(100)	168(5)	−2993(12)	3419(9)	84(5)
C(32)	1589(2)	−935(6)	2776(5)	33(2)	C(101)	365(7)	−3759(18)	3455(14)	75(7)
C(33)	1805(3)	−1585(7)	3139(5)	42(3)	C(102)	689(9)	−3618(20)	3477(16)	95(9)
C(34)	1800(3)	−1788(7)	3812(6)	50(3)	C(103)	636(9)	−2738(21)	2950(17)	104(10)
C(104)	408(6)	−2473(14)	3271(11)	48(6)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonolized $\mathbf{U}_{ij}$ tensor.

compound **2** is the first crystallographically characterized complex in which a diorganocuprate is stabilized by a neutral phosphine. The structure of **2** shows that the phosphine acts not only to electronically stabilize the copper center but also to sterically shield it. Gilman reagents are thought to commonly form polynuclear aggregates in solution.[13] Routes to simple monomeric complexes have involved either the use of sterically bulky groups such as the tris(trimethylsilyl)methyl group[14] or the use of crown ethers to complex the alkali metal cation.[13] The preparation of **2** exemplifies an alternative way by which mononuclear cuprate complexes can be stabilized (by anion solvation rather than by cation solvation).

The solid-state structure of **3** (Figure 2) consists of a Cu_2C_2 dinuclear core in which *tert*-butylacetylide ligands bridge the two Cu centers. The Cu_2C_2 core is planar, with the Cu−C−Cu bridge angles (average 69.2°) being extremely acute compared to the C−Cu−C angles [105.0(3)° at Cu(2) and 116.4(3)° at Cu(1)]. In addition, there is one THF molecule present in the lattice of **3** (not shown). Key bond lengths and angles in the core of **3** are illustrated in Figure 3.

The complex contains both distorted planar, three coordinate and pseudotetrahedral, four coordinate Cu centers [average angle about Cu(1) 119.9°; average angle about Cu(2) 109.3°]. One copper is coordinated by two triphenylphosphine ligands (average 2.272 Å) whereas the other is coordinated only by one tricyclohexylphosphine ligand [Cu−P = 2.224(2) Å]. Presumably the difference in the geometries of the two Cu centers of **3** is a result of the greater steric bulk of the tricyclohexylphosphine ligand as opposed to the triphenylphosphine ligand. Both the asymmetrically bound acetylide ligands tilt toward the four coordinate Cu center [average Cu(1)−C≡C = 152.6°, average Cu(2)−C≡C = 135.6°]. This tilting may be a consequence of the pseudotetrahedral Cu(2) being less sterically crowded in the Cu_2C_2 ring plane than the three coordinate Cu(1), where the cyclohexyl groups lie in the Cu_2C_2 plane. The tilting of the acetylide ligands toward the four coordinate Cu is also a consequence of the greater σ interaction of the sp orbitals of the acetylide groups with the three coordinate copper. This is seen by the shorter Cu−C bonds made with this center [Cu(1)−C(1A) = 2.001(9) Å and Cu(1)−C(1B) = 2.053(9) Å] compared to those made with the four coordinate Cu [Cu(2)−C(1A) = 2.203(9) Å and Cu(2)−C(1B) = 2.142(9) Å]. The acetylenic C≡C bond lengths [1.21(1) and 1.20(1) Å] are

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Cu(1)	765(1)	3991(1)	2183(1)	22(1)	C(314)	478(9)	−837(8)	763(4)	40(2)
Cu(2)	824(1)	2203(1)	2357(1)	21(1)	C(315)	1193(9)	−853(8)	1128(5)	42(3)
P(1)	2359(2)	965(2)	2696(1)	23(1)	C(316)	860(8)	−42(7)	1550(4)	32(2)
P(2)	562(2)	5705(2)	2086(1)	22(1)	C(321)	−1775(7)	2961(6)	1928(4)	23(2)
P(3)	−603(2)	1812(2)	2181(1)	22(1)	C(322)	−2872(8)	3015(8)	2059(4)	37(2)
C(111)	3417(7)	1465(7)	2793(4)	28(2)	C(323)	−3726(9)	3882(9)	1850(5)	48(3)
C(112)	4568(8)	832(9)	2694(5)	49(3)	C(324)	−3493(9)	4714(8)	1511(5)	42(3)
C(113)	5326(9)	1217(10)	2834(6)	54(3)	C(325)	−2401(9)	4658(8)	1386(4)	38(2)
C(114)	4930(9)	2218(9)	3071(5)	48(3)	C(326)	−1551(8)	3794(7)	1592(4)	28(2)
C(115)	3789(9)	2860(8)	3162(5)	44(3)	C(331)	−1363(7)	1290(7)	2835(4)	26(2)
C(116)	3043(8)	2492(8)	3021(5)	39(2)	C(332)	−1408(8)	280(7)	2851(4)	33(2)
C(121)	2070(7)	363(7)	3454(4)	27(2)	C(333)	−1969(9)	−76(8)	3365(4)	40(2)
C(122)	2867(9)	−56(8)	3831(4)	41(3)	C(334)	−2494(8)	571(8)	3872(5)	41(3)
C(123)	2622(10)	−562(9)	4372(5)	51(3)	C(335)	−2442(8)	1581(8)	3861(4)	38(2)
C(124)	1595(10)	−660(8)	4547(5)	45(3)	C(336)	−1875(8)	1930(8)	3357(4)	35(2)
C(125)	811(9)	−250(8)	4185(4)	39(2)	C(1A)	1398(7)	2944(7)	1501(4)	25(2)
C(126)	1040(8)	266(7)	3637(4)	30(2)	C(2A)	1629(7)	2680(7)	972(4)	29(2)
C(131)	3230(7)	−232(7)	2222(4)	27(2)	C(3A)	1845(8)	2395(7)	318(4)	30(2)
C(132)	3564(8)	−38(7)	1601(4)	33(2)	C(4A)	1458(22)	3489(17)	−51(9)	39(6)
C(133)	4205(9)	−894(9)	1215(5)	48(3)	C(5A)	3097(19)	1839(22)	81(11)	59(8)
C(134)	4470(9)	−1953(8)	1431(5)	47(3)	C(6A)	1183(22)	1817(22)	222(10)	45(6)
C(135)	4109(8)	−2146(8)	2036(5)	40(2)	C(4A′)	2069(29)	3203(22)	−100(12)	51(8)
C(136)	3486(8)	−1278(7)	2442(5)	36(2)	C(5A′)	2856(20)	1287(21)	181(11)	45(8)
C(211)	1492(7)	6016(7)	1411(4)	29(2)	C(6A′)	788(26)	2243(27)	200(12)	46(7)
C(212)	1217(8)	5820(7)	824(4)	32(2)	C(1B)	113(7)	3466(7)	3010(4)	28(2)
C(213)	2016(9)	6009(8)	264(5)	44(3)	C(2B)	−238(7)	3582(7)	3549(4)	24(2)
C(214)	3251(9)	5326(9)	294(5)	52(3)	C(3B)	−565(9)	3724(8)	4209(4)	36(2)
C(215)	3536(8)	5532(9)	884(5)	46(3)	C(4B)	−1231(16)	3071(15)	4509(9)	65(6)
C(216)	2738(7)	5303(8)	1431(5)	37(2)	C(5B)	−1147(18)	4937(15)	4341(9)	68(6)
C(221)	−911(8)	6558(7)	1982(4)	33(2)	C(6B)	565(15)	3286(15)	4480(9)	66(6)
C(222)	−1795(8)	6335(8)	2475(5)	48(3)	C(4B′)	−1957(33)	4236(34)	4321(19)	65(12)
C(223)	−2960(9)	6938(9)	2355(6)	59(3)	C(5B′)	−290(32)	4609(28)	4400(16)	47(10)
C(224)	−3257(9)	8157(9)	2275(6)	57(3)	C(6B′)	−168(38)	2616(35)	4532(20)	69(13)
C(225)	−2393(10)	8385(9)	1781(6)	59(3)	O(1)	4908(19)	1317(18)	5189(10)	96(6)
C(226)	−1181(8)	7769(7)	1903(5)	39(2)	C(1)	4155(20)	1398(20)	5729(11)	59(6)
C(231)	730(8)	6324(7)	2745(4)	33(2)	C(2)	3039(27)	2153(26)	5608(14)	88(9)
C(232)	1476(9)	5496(8)	3134(4)	40(2)	C(3)	3283(26)	2437(26)	4897(14)	85(9)
C(233)	1513(10)	5982(8)	3697(5)	47(3)	C(4)	4415(27)	1881(26)	4722(15)	88(9)
C(234)	1860(10)	6944(9)	3533(5)	52(3)	O(2)	5116(14)	−2219(14)	−1158(8)	66(4)
C(235)	1114(10)	7770(8)	3164(15)	48(3)	C(5)	4641(23)	−2711(22)	−623(13)	71(7)
C(236)	1075(9)	7301(7)	2591(4)	35(2)	C(6)	3503(24)	−1902(22)	−349(13)	76(8)
C(311)	−211(7)	791(7)	1603(4)	24(2)	C(7)	3331(20)	−932(19)	−725(11)	57(6)
C(312)	−929(8)	798(8)	1230(4)	34(2)	C(8)	4209(22)	−1127(21)	−1120(12)	68(7)
C(313)	−568(9)	−22(8)	813(4)	39(2)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths and Angles for Complex 2

	Distances/Å		
Cu−C(50)	2.079(9)	Cu−P	2.223(3)
Cu−C(70)	2.170(9)		
	Angles/deg		
P−Cu−C(50)	134.7(3)	C(50)−Cu−C(70)	112.7(4)
P−Cu−C(70)	112.6(3)		

Table 5. Selected Bond Lengths and Angles for Complex 3

	Distances/Å		
Cu(1)−C(1A)	2.001(9)	Cu(1)−P(2)	2.224(2)
Cu(1)−C(1B)	2.053(9)	Cu(2)−P(1)	2.273(3)
Cu(2)−C(1A)	2.203(9)	Cu(2)−P(3)	2.272(2)
Cu(2)−C(1B)	2.142(9)	Cu(1)−Cu(2)	2.3892(14)
	Angles/deg		
C(1A)−Cu(1)−C(1B)	116.4(3)	C(1A)−Cu(1)−P(2)	124.9(2)
C(1A)−Cu(2)−C(1B)	105.0(3)	C(1B)−Cu(1)−P(2)	118.4(3)
Cu(1)−C(1A)−Cu(2)	69.1(3)	C(1A)−Cu(2)−P(1)	109.1(2)
Cu(1)−C(1B)−Cu(2)	69.4(3)	C(1A)−Cu(2)−P(3)	105.2(2)
Cu(1)−C(1A)−C(2A)	155.1(7)	P(1)−Cu(2)−P(3)	123.42(9)
Cu(2)−C(1A)−C(2A)	132.1(7)	C(1B)−Cu(2)−P(1)	104.6(2)
Cu(1)−C(1B)−C(2B)	150.1(7)	C(1B)−Cu(2)−P(3)	108.2(2)
Cu(2)−C(1B)−C(2B)	139.1(7)		

longer than the *ca.* 1.17 Å found in symmetric μ_2-η^1-acetylide bridges.[15] The orientation of the acetylide ligands in **3** may suggest that there is an element of π-interaction with the four coordinate copper center. A more exaggerated form of this type of coordination has been previously observed in the hexanuclear compound $[Cu_3\{S(2\text{-}Me_2NCH_2C_6H_4)\}_2(C{\equiv}C^tBu)]_2$, in which the coordination of the alkyne is described as (μ_3-η^2).[15]

A further interesting feature in the structure of **3** is that the Cu···Cu distance [2.389(1) Å] is one of the shortest yet observed. There have been many reports concerning whether such short Cu−Cu distances represent real metal−metal bonds.[16,17] The short Cu···Cu contact in **3** may simply be due to the desire for both Cu atoms to maximize σ bonding with the sp orbitals of the acetylenic ligands, as is indicated by the very acute Cu−C−Cu bridging angles. Alternatively, by regarding the four coordinate Cu center as having a formal oxidation state of +2 and the three coordinate Cu center as having a formal oxidation state of 0, the short Cu···Cu contact can be regarded as a Cu^0−Cu^{2+} s/d bond. Although the favored model at present in acetylene-bridged Cu complexes is based upon multicenter

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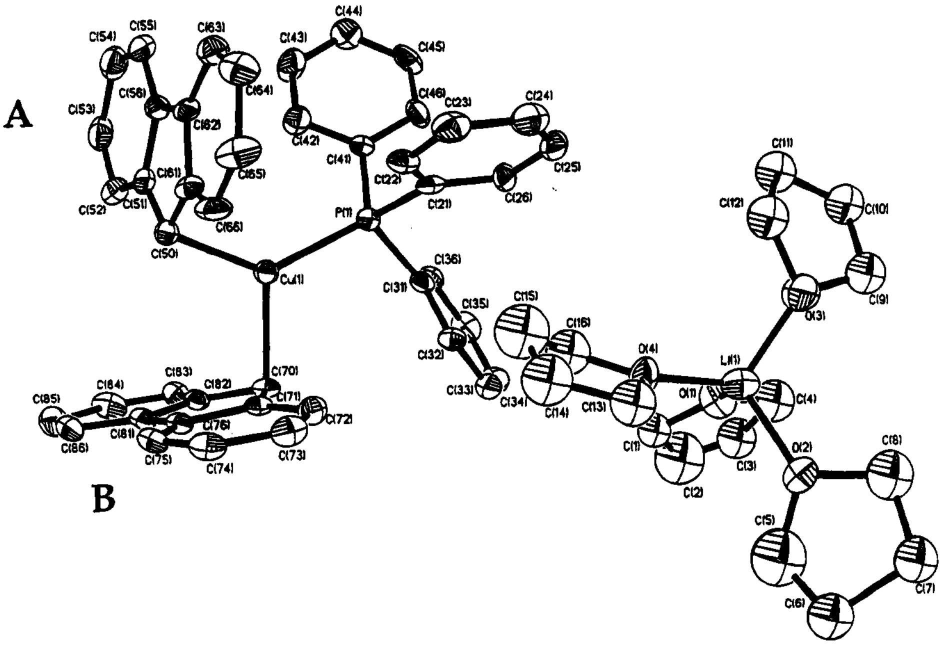

Figure 1. Solid-state structure of **2**. Thermal ellipsoids at the 40% level are shown. All hydrogen atoms have been omitted for clarity.

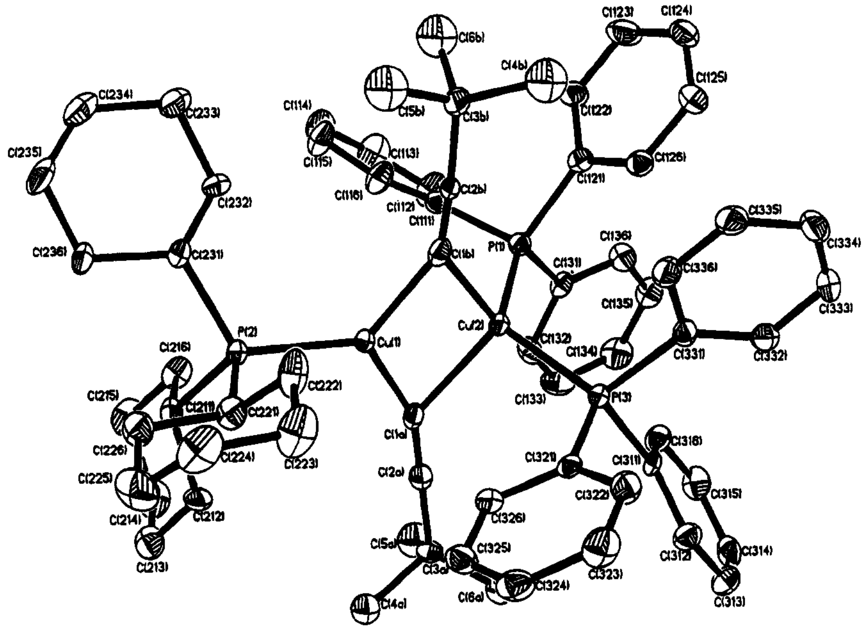

Figure 2. Solid-state structure of **3**. Thermal ellipsoids at the 40% level are shown. All hydrogen atoms have been omitted for clarity.

bonding rather than genuine metal–metal bonding,[16] Cu$\cdot\cdot\cdot$Cu bonding in **3** cannot be discounted.

The reasons for the difference in the outcome of the reactions producing the cuprate complex **2** and the neutral complex **3** are presumably the steric bulk and nucleophilicity of the nucleophiles employed. The influence of the steric bulk of the phosphine ligands present in **2** and **3** is also of importance. This can be seen from the structure of complex **3** in the solid state which can be regarded as a contact ion-pair $[(Ph_3P)_2Cu]^+$-$[(^tBuC{\equiv}C)_2Cu(PCy_3)]^-$. From this point of view, further reaction with $^tBuC{\equiv}CLi$ to produce a mixture of cuprate complexes, containing $[R_3PCu(^tBuC{\equiv}C)_2]^-$ anions akin to **2**, is intercepted by the attachment of a second Ph_3P ligand to one Cu center and by the attachment of one, more sterically demanding, Cy_3P ligand to the other.

Conclusion

The syntheses of **2** and **3** illustrate that the Cp ligand of $CpCuPPh_3$ is readily substituted to provide a halide-free route to copper organometallics that may otherwise be difficult to obtain by standard methods. Complex **2** represents the first crystallographically characterized example of a Gilman reagent stabilized by a neutral phosphine ligand. Its synthesis illustrates a potentially new method of forming such reagents containing monomeric cuprate centers. Complex **3** is an unusual asymmetric complex containing an extremely short Cu–Cu distance.

We are continuing to investigate the synthetic utility of this route in preparing a range of organometallic and mixed-metal complexes.

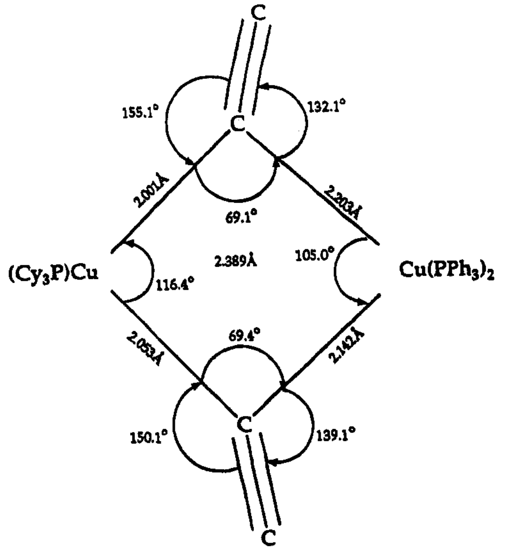

Figure 3. Core geometry of complex **3**.

Experimental Section

General Experimental Methods. Compounds **1**–**3** are air- and moisture sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[18] and under dry/oxygen-free argon. THF was dried by distillation over sodium–benzophenone and degassed prior to the reactions. Complexes **1**–**3** were isolated and characterized with the aid of an argon-filled glovebox (Faircrest Mark 4A) fitted with an O_2 and H_2O recirculation system (Type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing the samples under argon in airtight aluminium boats (1–2 mg), and C and H content was analyzed using a Perkin-Elmer 240 elemental analyzer. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry [$^2H_8$]THF (using the resonances of C_4D_7-HO as the internal reference standard). ^{31}P NMR were recorded using a Bruker WH 250 MHz spectrometer in the same solvent using a neat sample of Me_3PO as the external reference standard.

Synthesis of CpCuPPh$_3$ (1). The compound CpCuPPh$_3$ (**1**) was prepared by a variation of the literature methods.[19] To a slurry of freshly prepared CuCl (2 g, 20 mmol) and PPh$_3$ (5.24 g, 20 mmol) in 30 mL of THF was added LiCp (20 mmol in 30 mL of THF and 12.5 mL of hexane). Stirring for 30 min produced a bright yellow solution. The solution was reduced *in vacuo* to *ca.* 30 mL. Storage at 20 °C gave colorless crystals of **1** in 46% yield.

Synthesis of [Li(THF)$_4$]$^+$[(fluorenyl)$_2$CuPPh$_3$]$^-$ (2). A solution of fluorene (0.66 g, 4 mmol) in dry THF (10 mL) was treated with ^{n}BuLi (2.5 mL, 1.6 mol dm^{-3} in hexanes, 4 mmol). The resulting bright orange solution was added to a solution of **1** (0.784 g, 2 mmol) in THF (5 mL) at 25 °C under argon. Heating the resulting solution to *ca.* 50 °C produces a dark brown solution. Removal of the volatiles to *ca.* 5 mL *in vacuo* resulted in the precipitation of a light brown solid which redissolved on heating. Storage at 5 °C (12 h) gave brown cubic crystals of **2** (0.35 g, 17.5%). The X-ray crystal structure of **2** contains a half THF molecule per formula unit of **2**. This is removed when the product is isolated under vacuum (10^{-1} atm, 15 mins) prior to transfer to the glovebox for analysis. The spectroscopic and analytical data which follow are on the dry, unsolvated complex: Mp (decompn) *ca.* 55 °C to a black solid. Anal. Found: C, 75.0; H, 7.0. Calc for $C_{60}H_{65}CuLiO_4P$: C, 75.7; H, 6.8. IR (ν; Nujol): 3043 cm^{-1} (fluorenyl C–H str), 1602, 1582 cm^{-1} (C$\overset{\cdots}{-}$C aryl str). ^1H NMR (250 MHz, [$^2H_8$]THF, +25 °C): δ 7.74 (dd, 4H), 7.50 (d, 4H), 7.05 (m, 4H), 6.80 (m, 4H) [aromatic C–H, fluorenyl groups], 7.20 (m, 15H, C–H of PPh$_3$), 3.84 (s, 2H, H(50) and H(70) of fluorenyl groups), *ca.* 3.55 (m, 16H, THF) and *ca.* 1.72 (m, 16H, THF). ^{31}P NMR (101.27 MHz, [$^2H_8$]THF, +25 °C): δ −144.51 (s, PPh$_3$).

Synthesis of [Cy$_3$PCu(μ-C≡C^{t}Bu)$_2$Cu(PPh$_3$)$_2$] (3). A solution of *tert*-butylacetylene (0.25 mL, 2.0 mmol) in dry THF (10 mL) was treated with ^{n}BuLi (1.25 mL, 1.6 mol dm^{-3} in hexanes, 2.0 mmol). The resulting solution was added to a solution of **1** (0.784 g, 2 mmol) and tricyclohexylphosphine (0.560 g, 2.0 mmol) in THF (5 mL) at 25 °C under argon. Stirring the resulting solution (30 min) produces a dark brown solution. Reduction of the solution to *ca.* 5 mL *in vacuo* resulted in the precipitation of a white solid which redissolved on heating. Storage at 5 °C (12 h) gave colorless cubic crystals of **3** (0.25 g, 21.4%). Unlike complex **2**, which loses its lattice-bound THF when isolated under vacuum, complex **3** retains its lattice-bound THF, which can be clearly seen from the spectroscopic and analytical data: Mp *ca.* 125 °C to a yellow oil. Anal. Found: C, 72.0; H, 7.5. Calc for $C_{70}H_{89}Cu_2OP_3$: C, 72.1; H, 7.6. IR (ν; Nujol): 3051 cm^{-1} (aromatic C–H str), 1586 cm^{-1} (C$\overset{\cdots}{-}$C aryl str). ^1H NMR (250 MHz, [$^2H_8$]THF, +25 °C): *ca.* δ 7.43–7.21 (m, 30H, C–H of PPh$_3$), *ca.* 3.55 (m, 4H, THF) and *ca.* 1.72 (m, 4H, THF), *ca.* 2.1–0.8 (broad, m, 33H, C–H of PCy$_3$), 1.22 (s, 18H, ^{t}Bu). ^{31}P NMR (101.27 MHz, [$^2H_8$]THF, +25 °C): δ −134.82 (broad, s, PCy$_3$), −148.14 (s, PPh$_3$).

X-ray Structure Determinations of 2 and 3. Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric oxygen and moisture.[20] The oil "freezes" at reduced temperature and holds the crystals static in the X-ray beam. Data were collected on a Stoe-Siemens AED diffractometer by the θ/ω method. Details of the structure solution and refinement of both complexes are shown in Table 1. Both structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXL-93).[21] Complex **2** exhibits extensive disorder on two of the THF ligands of the Li(THF)$_4^+$ cation. This disorder occurs at three carbon atoms of one ligand [C(1), C(3), C(4)] and at two carbon atoms of the other [C(8) and C(7)]. The disorder was modeled with 50% partial occupancy over two sites at each carbon center. In complex **3**, the methyl carbon atoms of the ^{t}Bu groups were disordered over two sites about a 3-fold axis. This disorder was modeled with 50% partial occupancy over each site. Atomic coordinates, bond lengths and angles, and thermal parameters for **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre.

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Supplementary Material Available: Tables listing summaries of the crystal structure determinations, hydrogen coordinates and U values, bond lengths and angles, and displacement parameters for **2** and **3** (14 pages). Ordering information is given on any current masthead page.

OM940481T

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