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σ-Carbon versus π-Arene Interactions in the Solid-State Structures of Trimeric and Dimeric Copper Aryls $(CuAr)_n$ (n = 3, Ar = 2,6-$Ph_2C_6H_3$; n = 2, Ar = 2,6-$Mes_2C_6H_3$)

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Reaction of $LiC_6H_3Ph_2$-2,6 or $LiC_6H_3Mes_2$-2,6 with CuO*t*-Bu in pentane or toluene yields the unsolvated copper aryls $(CuC_6H_3Ph_2\text{-}2,6)_3$ (**2**) and $(CuC_6H_3Mes_2\text{-}2,6)_2$ (**3**). Addition of another equivalent of lithium aryl to **3** affords the lithium cuprate $LiCu(C_6H_3Mes_2\text{-}2,6)_2$ (**4**). The new compounds **2**−**4** were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy, mass spectrometry, and X-ray crystallography. The X-ray structure shows **2** to be trimeric in the solid state. The bridging terphenyl ligands exhibit two different coordination modes. Two of them connect two copper atoms via their *ipso* C_6H_3 carbons, while the third bridges two copper centers by either a σ-C (*ipso* C_6H_3) or a π-arene (*ipso*/*ortho* phenyl) interaction. A dimeric unit is observed in the solid-state structure of **3**, in which the two aryl groups are linked by two bridging coppers. The copper atoms mainly interact with the *ipso* carbons of the C_6H_3 group. The quasi-linear coordination is completed by two *ipso* and *ortho* carbons of a mesityl group. Molecular weight determinations of the copper aryls **2** and **3** by cryoscopy in benzene solution show an equilibrium between monomers and dimers. Compound **4** is the first example of a structurally characterized, monomeric, nonsolvated lithium cuprate. It crystallizes with two independent molecules, showing C−Cu−C angles of 171.1° and 173.8°, respectively. The lithium ions are accommodated between two adjacent mesityl groups of the terphenyl ligands.

Introduction

Organocopper reagents are of major importance for the carbon−carbon bond formation in organic synthesis.[1] This is part of the reason why their solution and solid-state structures[2] have attracted considerable interest for the last two or three decades. Most of the attention has been given to the structural characterization of the synthetically important lithium diorganocuprates[3] and higher order cuprates.[4] A lot of interest has been focused also on alkyl or aryl copper complexes stabilized by either heteroatom donor substituents in the *ortho* position[5] or coordination to donor solvents such as dimethyl sulfide (DMS) or tetrahydrothiophene (THT).[6] However, structural reports on simple homoleptic alkyl or aryl copper compounds are relatively rare and currently limited to tetra- and pentameric species.[7,8] Smaller aggregates, namely, mono-,[6d,e] di-,[5d,g,6d] and trinuclear[5b,9] compounds, have been obtained only by using chelating heteroatom-containing ligands and/or coordinating solvents. In this paper, the synthesis and structural characterization of aryl copper derivatives of the bulky terphenyl ligands 2,6-$Ph_2C_6H_3$ and 2,6-

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[1] (a) Bähr, G.; Burba, P. *Houben-Weyl Methoden der Organischen Chemie*; Müller, E., Ed.; Georg Thieme: Stuttgart, 1970; Vol. 13/1, pp 735−761. (b) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980. (c) Taylor, R. J. K., Ed. *Organocopper Reagents: A Practical Approach*; Oxford University Press: Oxford, 1994. (d) Lipshutz, B. H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, Chapter 3.2.

[2] (a) van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283. (b) Power, P. P. *Progr. Inorg. Chem.* **1991**, *39*, 75. (c) Holloway, C. E.; Melnik, M. *Rev. Inorg. Chem.* **1995**, *15*, 147. (d) van Koten, G.; James, S. L.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 3, Chapter 2.

[3] Examples for neutral contact-ion-paired compounds: (a) $Li_2Cu_2(C_6H_4CH_2NMe_2\text{-}2)_4$: van Koten, G.; Jastrzebski, J. T. B. H.; Muller, F.; Stam, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 697. (b) $Li_2Cu_2Ph_4(OEt_2)_2$: Lorenzen, N. P.; Weiss, E. *Angew. Chem.* **1990**, *102*, 322; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 300. (c) $Li_2Cu_2Ph_4(DMS)_3$: Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 8008. Examples for solvent-separated species: (d) $[Cu(dppe)_2][CuMes_2]$ (dppe = bis(diphenylphosphino)ethane): Leoni, P.; Pasquali, M.; Ghilardi. C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. (e) $[Li(thf)_4][Cu(CH_2SiMe_3)_2]$: Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23. (f) $[Li(12\text{-crown-}4)_2][CuMe_2]$ or $[CuPh_2]$: Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337.

[4] (a) $Li_3(CuPh_2)(CuPh_3)(DMS)_4$ and $Li_5(CuPh_2)_3(CuPh_3)(DMS)_4$: see ref 3c. (b) $Li_6(OEt_2)_3Cu_4(CCPh)_{10}$: Olbrich, F.; Kopf, J.; Weiss, E. *Angew. Chem.* **1993**, *105*, 1136; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1077.

[5] (a) $(CuC_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4$: Guss, J M.; Mason, R.; Søtofte, I.; van Koten, G.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1972**, 446. (b) $\{CuCH(PPh_2)_2\}_3$: Camus. A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39. (c) $(CuC_6H_4OMe\text{-}2)_8$: Camus. A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1979**, *174*, 121. (d) $\{CuC(SiMe_3)_2C_5H_4N\text{-}2\}_2$: Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1419. (e) $(CuCHSiMe_3C_5H_4N\text{-}2)_4$: Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 3085. (f) $(CuC_{10}H_6NMe_2\text{-}8)_4$: Wehman, E. van Koten, G.; Knotter, M.; Spelten, H.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *J. Organomet. Chem.* **1987**, *325*, 293. (g) $(CuOxl)_2$ (Oxl = 2-(4,4-dimethyl-2-oxazolinyl)-5-methylphenyl): Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Rotteveel, M. A.; Stam, C. H. *Organometallics* **1988**, *7*, 1477. (h) $(CuC_6H_4CH_2NMe_2\text{-}2)_4$: cited in ref 2d.

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$Mes_2C_6H_3$ is reported. Especially the latter has been used successfully in the past few years for the stabilization of low coordination numbers,[10] compounds free of Lewis donors,[11] and new multiple-bond systems.[12] It is shown that the presence of these sterically encumbered ligands enables the isolation of previously uncharacterized types of lowly aggregated copper compounds.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of purified argon. Solvents were freshly distilled under argon from Na wire or $LiAlH_4$. The compounds $2,6\text{-}Ph_2C_6H_3I$ **(1)**,[13] $(2,6\text{-}Mes_2C_6H_3Li)_2$,[11a] and $(CuO\textit{t}\text{-}Bu)_4$[14] were synthesized by known literature procedures. NMR spectra were recorded on Bruker AM 200 and AC 250 spectrometers and referenced to solvent resonances. IR spectra (Nujol mull, CsBr plates) were obtained in the range 4000−200 cm^{-1} with a Perkin-Elmer Paragon 1000 PC spectrometer.

$(CuC_6H_3Ph_2\text{-}2,6)_3$ (2). CuO*t*-Bu (0.62 g, 4.53 mmol) was added at ambient temperature to a solution of $LiC_6H_3Ph_2\text{-}2,6$ in 60 mL of toluene, freshly prepared from *n*-BuLi (1.81 mL hexane solution, 4.53 mmol) and $2,6\text{-}Ph_2C_6H_3I$ (1.61 g, 4.53 mmol). The reaction was allowed to stir overnight, whereupon the solvent was removed under reduced pressure. The remaining solid was extracted with ca. 20 mL of a *n*-hexane/toluene (1:1) mixture. Cooling of the filtered solution in a −25 °C freezer afforded **2** as pale yellow polycrystalline material. It was dried overnight by pumping at ca. 10^{-3} Torr to remove cocrystallized toluene. Yield: 0.82 g (62%). Mp: crystals turn gray at ca. 130 °C and decompose to a black liquid between 182 and 185 °C. ^1H NMR (C_6D_6): δ 6.85−7.17 (m, aryl-*H*). ^{13}C NMR (C_6D_6): δ 124.3 (*p*-Ph), 126.2 ($m\text{-}C_6H_3$), 126.8 (*o*-Ph), 128.3 ($p\text{-}C_6H_3$), 128.8 (*m*-Ph), 147.6 ($i\text{-}C_6H_3$), 149.0 (*i*-Ph), 155.6 ($o\text{-}C_6H_3$). IR (Nujol, cm^{-1}): 1949 w 1867 vw, 1798 vw, 1593 m, 1568 m, 1544 m, 1304 w, 1275 w, 1233 w, 1171 m, 1153 m, 1093 w, 1070 ms, 1025 ms, 974 w 963 w, 914 m, 841 m, 833 m, 804 s, 749 vs, 730 vs, 719 sh, 699 vs, 629 w, 612 s, 557 m, 533 m, 525 ms, 517 m, 483 w, 465 ms, 421 w, 394 ms, 363 w, 344 w, 331 w. MS (70 eV): *m*/*z* (%) 686.2 (1) [$C_{54}H_{38}{}^+$], 458.2 (51) [$C_{36}H_{26}{}^+$], 230.1 (100) [$C_{18}H_{14}{}^+$], no Cu-containing fragment detected. Anal. Calcd for $C_{18}H_{13}Cu$: C, 73.83; H, 4.47; Cu, 21.70. Found: C, 74.18; H, 4.76. Molar mass (cryoscopically in C_6H_6, c = 61.4 mmol/L, crystals of **2**·C_6D_6, obtained by crystallization from benzene, were used) calcd for monomer 292.8; found 560.

$(CuC_6H_3Mes_2\text{-}2,6)_2$ (3). A solution of $LiC_6H_3Mes_2\text{-}2,6$ (0.96 g, 3.0 mmol) in 30 mL of pentane was added at ambient temperature to CuO*t*-Bu (0.41 g, 3.0 mmol) in 10 mL of *n*-pentane, and the mixture was stirred for 1 h. The formed off-white precipitate was isolated by filtration over a glass filter frit. Cooling of the filtrate to 0 °C afforded a small amount of **4** as colorless plates (0.08 g, 4%). The remaining solid was extracted into toluene, and the resulting amber solution was concentrated under reduced pressure. After cooling in a −25 °C freezer colorless crystals (0.62 g, 55%) of **3** were obtained. Mp: crystals change color to orange at ca. 140 °C and decompose to a brown liquid at 185 °C. ^1H NMR (C_6D_6): δ 2.01 ($o\text{-}CH_3$), 2.19 ($p\text{-}CH_3$), 6.70 (*m*-Mes), 6.80 (d, $m\text{-}C_6H_3$), 7.12 (t, $p\text{-}C_6H_3$). ^{13}C NMR (C_6D_6): δ 21.1 ($o\text{-}CH_3$), 21.8 ($p\text{-}CH_3$), 124.6 ($m\text{-}C_6H_3$), 126.6 ($p\text{-}C_6H_3$), 127.2 (*m*-Mes), 134.2 (*o*-Mes), 134.8 (*p*-Mes), 143.5 (*i*-Mes), 152.3 ($o\text{-}C_6H_3$), 159.6 ($i\text{-}C_6H_3$). IR (Nujol, cm^{-1}): 1723 vw, 1606 sh, 1579 m br, 1304 w, 1232 m, 1168 m, 1097 w, 1077 m, 1027 m, 1010 w, 887 w, 852 sh, 848 s, 794 s, 7735 w, 740 sh, 726 vs, 588 w, 571 m, 556 w, 545 w, 458 w, 329 m. MS (70 eV): *m*/*z* (%) 752.2 (95) [M^+ (dimer) with ^{63}Cu], 377.1 (100) [$M^+/2+H$ with ^{63}Cu], 376.1(54) [$M^+/2$ (monomer) with ^{63}Cu]. Anal. Calcd for $C_{24}H_{25}Cu$: C, 76.46; H, 6.68; Cu, 16.86. Found: C, 75.87; H, 6.77; Cu, 16.50. Molar mass (cryoscopically in C_6H_6, c = 38.2 mmol/L) calcd for monomer 377.0; found 440.

$LiCu(C_6H_3Mes_2\text{-}2,6)_2$ (4). CuO*t*-Bu (0.28 g, 2.05 mmol) was added at ambient temperature via a solids-addition tube to a solution of $LiC_6H_3Mes_2\text{-}2,6$ (1.31 g, 4.1 mmol) in 60 mL of *n*-pentane. The mixture was allowed to stir overnight, whereupon the volume was reduced to ca. 30 mL. The white precipitate was separated by filtration over a glass filter frit and washed two times with small portions of cold *n*-pentane. Yield: 1.04 g (73%). Mp: crystals change color from yellow to gray between 145 and 215 °C and decompose to a dark red liquid between 215 and 220 °C. ^1H NMR (C_6D_6): δ 1.92 ($o\text{-}CH_3$), 2.15 ($p\text{-}CH_3$), 6.80 (*m*-Mes), 6.84 (d, $m\text{-}C_6H_3$), 7.17 (t, $p\text{-}C_6H_3$). ^{13}C NMR (C_6D_6): δ 21.1 ($p\text{-}CH_3$), 22.0 ($o\text{-}CH_3$), 124.6 ($m\text{-}C_6H_3$), 125.6 ($p\text{-}C_6H_3$), 128.5 (*m*-Mes), 135.1 (*p*-Mes), 136.5 (*o*-Mes), 146.5 (*i*-Mes), 151.1 ($o\text{-}C_6H_3$), 165.9 ($i\text{-}C_6H_3$); ^7Li NMR (C_6D_6): δ −8.3. IR (Nujol, cm^{-1}): 1610 m, 1569 w, 1540 w, 1231 m, 1206 sh, 1168 w, 1094 w, 1075 m, 1029 m, 1010 m, 960 w, 866 m, 848 vs, 797 ms, 779 w, 755 w, 731 s, 715 ms, 576 m, 560 m, 547 m, 463 w. MS (70 eV): *m*/*z* (%) 752.3 (1.7) [$(CuAr)_2{}^+$ with ^{63}Cu], 696.3 (0.3) [M^+ with ^{63}Cu and ^7Li], 689.3 (1.1) [$CuAr_2{}^+$ with ^{63}Cu], 314.1(100) [Ar^+]. Anal. Calcd for $C_{48}H_{50}CuLi$: C, 82.66; H, 7.22; Cu, 9.11; Li, 0.99. Found: C, 82.80; H, 7.32.

Reaction of 3 and 4 with Oxygen. A solution of **3** in toluene was stirred at ambient temperature for ca. 4 h under an atmosphere of dry oxygen. The solvent was removed under reduced pressure, and the dark brown residue was treated with a mixture of 5% hydrochloric acid and diethyl ether. The organic layer was separated, dried over K_2CO_3, and filtered, whereupon the solvent was removed in vacuum. The remaining material was shown by NMR spectroscopy to consist of $HOC_6H_3Mes_2\text{-}2,6$ (68%) and $C_6H_4Mes_2\text{-}1,3$ (32%).[11c] In a

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(6) (a) $(CuMes)_4(THT)_2$: Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067. (b) $(CuPh)_4(DMS)_2$: in ref 3c. (c) $(CuC_6H_4Me\text{-}2)_4(DMS)_2$: Lenders, B.; Grove, D. M.; Smeets, W. J. J.; van der Sluis; P.; Spek, A. L.; van Koten; G. *Organometallics* **1991**, *10*, 786. (d) $(CuC_6H_2Ph_3\text{-}2,4,6)_2(DMS)_2$ and $(CuC_6H_2\textit{t}Bu_3\text{-}2,4,6)(DMS)$: He, X.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 9668. (e) $(CuC_6H_3Trip_2\text{-}2,6)(DMS)$ (Trip = $C_6H_2\text{-}\textit{i}\text{-}Pr_3\text{-}2,4,6$): Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(7) (a) $(CuCH_2SiMe_3)_4$: Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999. (b) $(CuMes)_5$: see refs 6a and 7e. (c) $(CuC_6H_2\text{-}\textit{i}\text{-}Pr_3\text{-}2,4,6)_4$: Nobel, D.; van Koten, G.; Spek, A. L. *Angew. Chem.* **1989**, *101*, 211; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 208. (d) $(CuC_6H_4CH{=}CH_2\text{-}2)_4$: Eriksson, H.; Örtendahl, M.; Håkansson, M. *Organometallics* **1996**, *15*, 4823. (e) $(CuMes)_4$: Eriksson, H.; Håkansson, M. *Organometallics* **1997**, *16*, 4243. (f) $(CuC_6Me_5)_4$: Eriksson, H.; Håkansson, M. *Inorg. Chim. Acta* **1998**, *277*, 233.

(8) The copper compound $CuC_6H_2Ph_3\text{-}2,4,6$ was reported to be monomeric in the solid state: Lingnau, R.; Strähle, J. *Angew. Chem.* **1988**, *100*, 409; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436. However, this result has been contested, as the crystal used for the X-ray structure determination seems to have contained a considerable amount of cocrystallized $BrC_6H_2Ph_3\text{-}2,4,6$: Haaland, A.; Rypdal, K.; Verne, H. P.; Scherer, W.; Thiel, W. R. *Angew. Chem.* **1994**, *106*, 2515; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2443.

(9) Trinuclear heteroleptic copper complexes: (a) $Cu_3(Mes)(O_2CC_6H_5)_2$: Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1252. (b) $Cu_3(Mes)(SC_6H_4CH_2NMe_2\text{-}2\text{-}Cl\text{-}3)_2(PPh_3)$: Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400. (c) $Cu_3Br(C_6H_4CH_2N(Me)CH_2CH_2NMe_2\text{-}2)_2$: cited in ref 2d.

(10) (a) Ellison, J. J.; Ruhlandt-Senge, K.; Hope, H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 49. (b) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920. (c) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1997**, *36*, 4688.

(11) (a) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353. (b) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 7264. (c) Niemeyer, M.; Power, P. P. *Organometallics* **1997**, *16*, 3258.

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Table 1. Selected Crystallographic Data for Compounds 1−4[a]

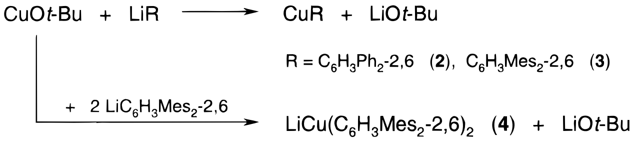
	1	$2\cdot C_6D_6$	3	4[b]
formula	$C_{18}H_{13}I$	$C_{60}H_{39}Cu_3D_6$	$C_{48}H_{50}Cu_2$	$C_{96}H_{100}Cu_{2.09}Li_{1.91}$
fw	356.2	962.7	754.0	1400.0
color, habit	colorless, plate	pale yellow, block	colorless, plate	colorless, plate
cryst size (mm)	0.50 × 0.50 × 0.08	0.60 × 0.35 × 0.25	0.45 × 0.22 × 0.05	1.00 × 0.60 × 0.10
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.472(4)	23.211(4)	10.009(3)	10.701(2)
b (Å)	7.178(3)	10.475(2)	11.328(4)	37.010(7)
c (Å)	21.966(6)	19.862(5)	17.650(6)	19.474(4)
α (deg)			103.34(3)	
β (deg)	95.06(3)	111.96(2)	99.34(3)	94.20(3)
γ (deg)			97.08(3)	
V (Å^3)	1487.6(9)	4479(2)	1894(1)	7692(3)
Z	4	4	2	4
d_{calc} (g/cm^3)	1.590	1.419	1.322	1.209
μ (cm^{-1})	21.36	14.52	11.55	6.25
2θ range (deg)	3−54	3−54	3−50	2−48
unique data	3168	9188	6672	12 090
data with $I > 2\sigma(I)$ (N_o)	2617	6137	4528	7224
no. of params (N_p)	221	772	511	1024
R1 ($I > 2\sigma(I)$)[c]	0.0372	0.0450	0.0591	0.0643
wR2 (all data)[d]	0.0958	0.1096	0.1423	0.1368
GOF[e]	1.193	1.010	1.135	1.198
resd dens (e/Å^3)	0.88/−0.84	0.56/−0.46	0.83/−0.52	0.54/−0.38

[a] All data were collected at 173 K using Mo Kα (λ = 0.710 73 Å) radiation. [b] Two independent molecules; for Cu/Li disorder see experimental part. [c] $R1 = \sum(||F_o| - |(F_c||)/\sum(|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [e] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

similiar experiment the oxidation of **4** yielded a mixture of 55% ROH and 45% RH. NMR data for $HOC_6H_3Mes_2$-2,6: ^1H NMR (C_6D_6) δ 2.11 (*o*-CH_3), 2.17 (*p*-CH_3), 6.84 (*m*-Mes), 6.93 (d, *m*-C_6H_3), 6.93 (t, *p*-C_6H_3). ^{13}C NMR (C_6D_6) δ 20.5 (*o*-CH_3), 21.1 (*p*-CH_3), 121.0 (*p*-C_6H_3), 128.8 (*m*-Mes), 129.9 (*m*-C_6H_3), 133.9 (*i*-Mes), 137.1 (*o*-Mes), 137.2 (*p*-Mes), 150.3 (*i*-C_6H_3).

X-ray Crystallography. X-ray-quality crystals were obtained as described in the Experimental Section. Crystals were removed from Schlenk tubes and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature N_2-stream.[15] All data were collected at 173 K using either a Syntex $P2_1$ (**1**, **3**, **4**) or a Siemens P4 (**2**) diffractometer. Crystal data are given in Table 1. Calculations were carried out with the SHELXTL PC 5.03[16a] and SHELXL-97[16b] program systems installed on a local PC. The structures were solved by direct methods and refined on F_o^2 by full-matrix least-squares refinement. An absorption correction was applied by using semiempirical ψ-scans (**2**, **3**) or the program XABS2[17] (**1**, **4**). Anisotropic thermal parameters were included for all non-hydrogen atoms. The C atoms of the solvate benzene in **2** showed rotational disorder (occupancy 0.5/0.5) and were constrained to a regular hexagon. The copper atom Cu(3) in **2** is disordered and was sucessfully modeled with two split positions (occupancy 0.93/0.07). The preliminary refinement of **4** revealed a substantial residue electron density (2.3 e/Å^3) in one of the two independent molecules. This Fourier peak was assigned to a partially occupied (0.092) copper atom of a cocrystallizing copper cuprate moiety. The corresponding lithium atom Li(2) was refined with a site occupation factor of 0.908. Positions and isotropic thermal parameters for most H atoms in **1** and **2** were allowed to refine. All other H atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. Their isotropic thermal parameters were either allowed to refine or constrained to 1.2 (aryl H) or 1.5 (methyl groups) times U_{eq} of the bonded carbon. Final R values are listed in Table 1. Important bond distances and angles are given in Table 2. Further details are provided in the Supporting Information.

Scheme 1. Synthesis of Compounds 2−4



Results and Discussion

Synthesis. The preparation of organocopper compounds of the type RCu usually involves the reaction of a copper(I) halide with an organolithium or -magnesium reagent in donor solvents such as Et_2O, THF, or DMS. A commonly encountered problem of this method is the contamination of the desired copper compounds with lithium or magnesium halides and the formation of stable mixed organocopper copper halide aggregates.[2d] Therefore, it seemed advantageous to us to use copper *tert*-butoxide as a halide-free starting material.[18] The good solubility of this complex permitted the reaction with lithium aryls in nonpolar solvents such as *n*-pentane or toluene according to Scheme 1. Thus, the pale yellow $CuC_6H_3Ph_2$-2,6 (**2**) and the colorless complex $CuC_6H_3Mes_2$-2,6 (**3**) were obtained in moderate yields of 62 and 55%, respectively. They show considerable thermal stability with decomposition points in the range 130−185 °C. The lithium cuprate $LiCu(C_6H_3Mes_2\text{-}2,6)_2$ (**4**) was synthesized in good yield of 73% by the reaction of CuO*t*-Bu with 2 equiv of $LiC_6H_3Mes_2$-2,6. Compounds **2**−**4** are air sensitive and possess good solubility

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1−4

Compound **1**			
I−C(1)	2.122(4)	C(3)−C(4)	1.379(6)
C(1)−C(2)	1.393(5)	C(4)−C(5)	1.391(6)
C(1)−C(6)	1.404(5)	C(5)−C(6)	1.398(6)
C(2)−C(3)	1.399(6)		
C(2)−C(1)−C(6)	122.5(3)	C(6)−C(1)−I	118.6(3)
C(2)−C(1)−I	118.9(3)		
Compound **2**·C_6D_6			
Cu(1)−C(1)	2.047(3)	C(19)−C(20)	1.418(5)
Cu(1)−C(19)	1.989(3)	C(19)−C(24)	1.421(5)
Cu(2)−C(19)	2.085(3)	C(20)−C(21)	1.404(5)
Cu(2)−C(37)	1.924(3)	C(21)−C(22)	1.380(6)
Cu(3)−C(1)	1.989(4)	C(22)−C(23)	1.386(6)
Cu(3)−C(43)	2.158(3)	C(23)−C(24)	1.408(5)
Cu(3)−C(44)	2.232(4)	C(25)−C(26)	1.395(5)
Cu(1)···Cu(2)	2.3758(7)	C(25)−C(30)	1.401(5)
Cu(1)···Cu(3)	2.4224(10)	C(31)−C(32)	1.399(5)
Cu(2)···Cu(3)	2.9136(11)	C(31)−C(36)	1.398(5)
C(1)−C(2)	1.428(5)	C(37)−C(38)	1.425(5)
C(1)−C(6)	1.421(5)	C(37)−C(42)	1.426(5)
C(2)−C(3)	1.393(5)	C(38)−C(39)	1.403(5)
C(3)−C(4)	1.381(6)	C(39)−C(40)	1.383(6)
C(4)−C(5)	1.374(6)	C(40)−C(41)	1.376(6)
C(5)−C(6)	1.405(5)	C(41)−C(42)	1.399(5)
C(7)−C(8)	1.392(5)	C(43)−C(48)	1.408(5)
C(7)−C(12)	1.403(5)	C(43)−C(44)	1.416(5)
C(13)−C(18)	1.395(6)	C(49)−C(54)	1.396(5)
C(13)−C(14)	1.401(6)	C(49)−C(50)	1.401(6)
C(19)−Cu(1)−C(1)	170.83(14)	C(1)−C(6)−C(13)	121.0(3)
C(19)−Cu(2)−C(37)	171.32(14)	C(19)−C(20)−C(25	121.7(3)
C(1)−Cu(3)−C(43)	162.96(14)	C(19)−C(24)−C(31)	121.0(3)
C(1)−Cu(3)−C(44)	159.4(2)	C(20)−C(19)−C(24)	116.6(3)
C(1)−Cu(3)···X	177.5	C(20)−C(19)−Cu(1)	130.1(3)
Cu(3)−C(1)−Cu(1)	73.77(12)	C(24)−C(19)−Cu(1)	111.6(2)
Cu(1)−C(19)−Cu(2)	71.30(11)	C(20)−C(19)−Cu(2)	96.1(2)
C(6)−C(1)−C(2)	117.2(3)	C(24)−C(19)−Cu(2)	118.3(2)
C(6)−C(1)−Cu(3)	130.2(3)	C(38)−C(37)−C(42)	115.4(3)
C(2)−C(1)−Cu(3)	111.6(2)	C(38)−C(37)−Cu(2)	125.9(3)
C(6)−C(1)−Cu(1)	90.7(2)	C(42)−C(37)−Cu(2)	117.8(2)
C(2)−C(1)−Cu(1)	118.9(2)	C(37)−C(38)−C(43)	121.7(3)
C(1)−C(2)−C(7)	120.6(3)	C(37)−C(42)−C(49)	119.9(3)
Compound **3**			
Cu(1)−C(1)	1.927(5)	C(7)−C(8)	1.430(6)
Cu(1)−C(31)	2.295(4)	C(16)−C(21)	1.394(7)
Cu(1)−C(32)	2.123(4)	C(16)−C(17)	1.411(6)
Cu(2)−C(25)	1.921(4)	C(25)−C(30)	1.398(6)
Cu(2)−C(7)	2.220(4)	C(25)−C(26)	1.420(6)
Cu(2)−C(8)	2.160(4)	C(26)−C(27)	1.389(7)
Cu(1)···Cu(2)	2.5953(12)	C(27)−C(28)	1.392(7)
C(1)−C(2)	1.398(6)	C(28)−C(29)	1.379(7)
C(1)−C(6)	1.406(7)	C(29)−C(30)	1.385(7)
C(2)−C(3)	1.391(6)	C(31)−C(32)	1.417(7)
C(3)−C(4)	1.384(7)	C(31)−C(36)	1.421(7)
C(4)−C(5)	1.385(7)	C(40)−C(41)	1.398(7)
C(5)−C(6)	1.395(7)	C(40)−C(45)	1.403(7)
C(7)−C(12)	1.420(7)		
C(1)−Cu(1)−C(31)	168.1(2)	C(2)−C(1)−C(6)	116.6(4)
C(1)−Cu(1)−C(32)	154.7(2)	C(2)−C(1)−Cu(1)	123.3(4)
C(1)−Cu(1)−X1	174.0	C(6)−C(1)−Cu(1)	119.9(3)
C(25)−Cu(2)−C(7)	170.6(2)	C(30)−C(25)−C(26)	116.3(4)
C(25)−Cu(2)−C(8)	151.2(2)	C(26)−C(25)−Cu(2)	122.7(3)
C(25)−Cu(2)−X2	170.5	C(30)−C(25)−Cu(2)	121.0(3)
Compound **4** Molecule 1			
Li(1)−C(7)	2.462(10)	Li(1)−C(25)	2.312(10)
Li(1)−C(8)	2.468(11)	Li(1)−C(26)	2.704(10)
Li(1)−C(9)	2.521(11)	Li(1)−C(31)	2.780(12)
Li(1)−C(10)	2.600(9)	Cu(1)−C(1)	1.922(5)
Li(1)−C(11)	2.550(11)	Cu(1)−C(25)	1.957(5)
Li(1)−C(12)	2.495(11)	Li(1)···Cu(1)	2.400(8)
C(1)−Cu(1)−C(25)	171.1(2)	C(6)−C(1)−Cu(1)	128.4(3)
C(2)−C(1)−C(6)	115.3(4)	C(26)−C(25)−Cu(1)	126.3(4)
C(26)−C(25)−C(30)	114.9(4)	C(30)−C(25)−Cu(1)	118.1(3)
C(2)−C(1)−Cu(1)	116.2(3)		

Table 2 (Continued)

Compound **4**			
Molecule 2			
Li(2)−C(55)	2.529(11)	Li(2)−C(73)	2.447(12)
Li(2)−C(56)	2.519(12)	Li(2)−C(79)	2.569(14)
Li(2)−C(57)	2.528(12)	Li(2)−C(80)	2.515(14)
Li(2)−C(58)	2.574(12)	Cu(2)−C(49)	1.925(5)
Li(2)−C(59)	2.552(14)	Cu(2)−C(73)	1.945(5)
Li(2)−C(60)	2.557(14)	Li(2)···Cu(2)	2.429(11)
C(49)−Cu(2)−C(73)	173.8(2)	C(54)−C(49)−Cu(2)	128.1(4)
C(54)−C(49)−C(50)	115.2(5)	C(74)−C(73)−Cu(2)	122.6(4)
C(74)−C(73)−C(78)	114.8(4)	C(78)−C(73)−Cu(2)	120.4(4)
C(50)−C(49)−Cu(2)	116.6(4)		
Copper cuprate			
Cu(3)−C(60)	2.065(8)	Cu(3)−C(73)	2.250(8)
Cu(3)−C(59)	2.244(8)	Cu(2)···Cu(3)	2.260(7)
C(60)−Cu(3)−C(73)	151.8(4)	X−Cu(3)−C(73)	171.6
C(59)−Cu(3)−C(73)	169.9(4)		

in aromatic solvents such as benzene or toluene, but are almost insoluble in aliphatic hydrocarbons. The reaction of organocopper compounds with molecular oxygen has been studied before[19] to give biaryls, arenes, and diaryl ethers as main products. Similarly, oxidation of mesitylcopper(I) has resulted in the isolation of the intermediate $Cu_{10}O_2Mes_6$.[20] In contrast, the reaction between toluene solutions of compound **3** or **4** and dry oxygen affords the hitherto unknown phenol HOC_6H_3-Mes_2-2,6 in a NMR yield of 68 or 55%.

Solid-State Structures. The new compounds **2**−**4** and the starting material $IC_6H_3Ph_2$-2,6 (**1**) were characterized by X-ray crystallography. The structure of **1** reveals no unusual features. The C−I bond length of 2.122(4) Å is very similiar to the values found for other aryl iodides.[21] Dihedral angles of 81.8° and 84.5° are observed between the *ortho* phenyl substituents and the central C_6H_3 ring.

Pale yellow crystals of $\mathbf{2}\cdot C_6D_6$, suitable for X-ray crystallographic studies, were grown from a saturated C_6D_6 solution at ambient temperature. The molecular structure consists of trimeric units with a central Cu_3 core (Figure 1). The trimers possess no crystallographically imposed symmetry, and there are no close interactions with the cocrystallized C_6D_6 molecule. The copper atoms are bridged by the terphenyl ligands in two different coordination modes. Two of the ligands coordinate via their *ipso* C_6H_3 carbon atoms C(1) and C(19) to the copper atoms Cu(1), Cu(3) and Cu(1), Cu(2), respectively. The third terphenyl group acts as a bidentate bridging unit between two copper atoms. It binds to Cu(2) by the *ipso* C_6H_3 carbon C(37), while the bridging to Cu(3) is accomplished by a $\eta^2-\pi$-arene interaction to the *ipso* and *ortho* phenyl carbons C(43) and C(44). The different coordination is reflected by the dihedral angles of the C(1), C(19), and C(37) C_6H_3 rings to the central Cu_3 plane with values of 84.2°, 66.2°, and 34.1°, respectively. The displacements of the coordinating atoms C(1) (0.809 Å), C(19) (−0.493 Å), C(37) (0.555 Å), C(43) (−0.273 Å), and C(44) (−1.566 Å) show an alternating arrangement below and above the Cu(1)-Cu(2)Cu(3) plane (Figure 2). Some important bond parameters together with a view perpendicular to the Cu_3 plane are depicted in Figure 3. The copper atoms are almost linearly coordinated (C(1)−Cu(1)−C(19) = 170.8(1)°, C(19)−Cu(2)−C(37) = 171.3(1)°, C(1)−Cu(3)−X = 177.5°, where X = midpoint of C(43)−C(44)). With values of 1.924(3)−2.085(3) the $Cu-C_{ipso}$ bond lengths fall in the range of those reported for other aryl copper compounds.[2d] Shorter Cu(3)−C(1) and Cu(1)−C(19) distances and larger Cu(3)−C(1)−C(4) and Cu(1)−C(19)−C(22) angles alternate with larger and smaller values for Cu(1)−C(1), Cu(2)−C(19), and Cu(1)−C(1)−

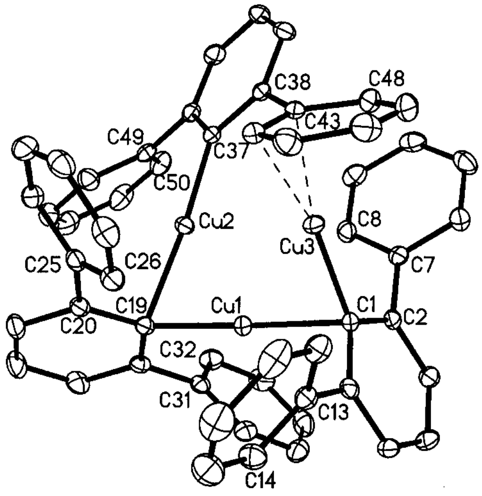

Figure 1. Molecular structure of **2**, showing 30% thermal ellipsoids and the numbering scheme. Hydrogen atoms have been omitted for clarity.

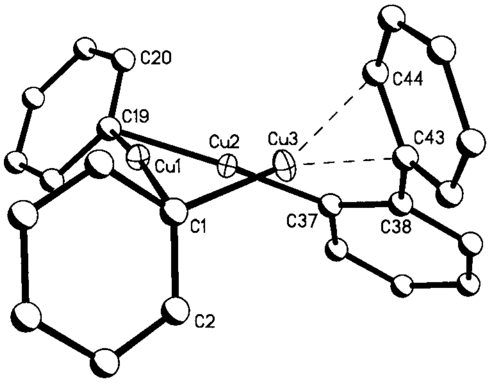

Figure 2. View of **2** along the central Cu_3 plane. Five *ortho* phenyl groups and hydrogen atoms have been omitted for clarity.

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(19) Camus, A.; Marsich, N. *J. Organomet. Chem.* **1972**, *46*, 385.

(20) Håkansson, M.; Örtendahl, M.; Jagner, S.; Sigalas, M. P.; Eisenstein, O. *Inorg. Chem.* **1993**, *32*, 2018.

(21) Recherche in Cambridge Structural Database: Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

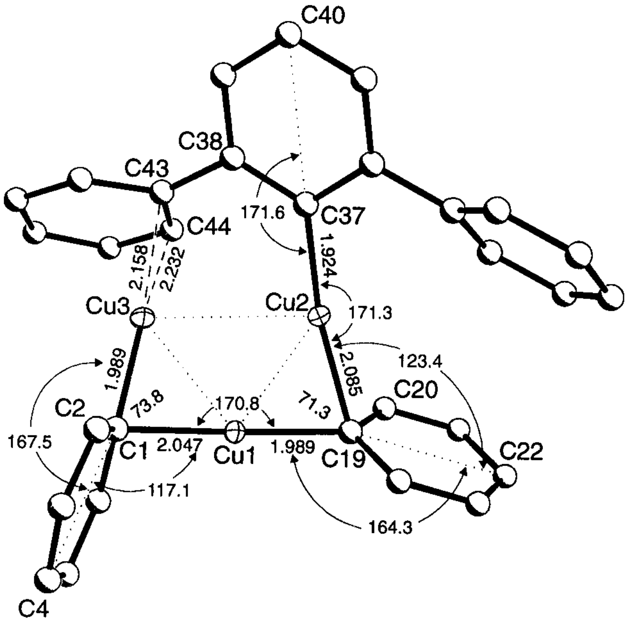

Figure 3. View of **2** perpendicular to the central Cu_3 plane showing important bond distances (Å) and angles (deg). Four *ortho* phenyl groups and hydrogen atoms have been omitted for clarity.

C(4), Cu(2)−C(19)−C(22), respectively (Figure 3). Therefore, the bonding situation can be interpreted as an alternating 2e-2c C_{ipso}−Cu and π-type C_{ipso}−Cu interaction. This kind of coordination has been noted before in $(CuC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)_4$,[7c] whereas a more symmetrical 2e-3c C_{ipso}−Cu bonding was observed in $(CuMes)_5$,[7b] $(CuMes)_4$,[7e] and $(CuC_6H_4CH{=}CH_2\text{-}2)_4$.[7d] The slightly longer Cu(3)−C(43) (2.158(3) Å) and Cu(3)−C(44) (2.232(4) Å) η^2-arene interactions are unique in aryl copper chemistry.[22] However, a similiar C=C π-coordination with Cu−C distances of 2.03−2.24 Å has been observed in the anionic cuprates $[Cu_5(C_6H_4CH{=}CH_2\text{-}2)_2Br_4]^-$ and $[Cu_5(C_6H_4CH{=}CH_2\text{-}2)_4Br_2]^-$,[7d] in the phenoxide $Cu_4(OC_6H_4CH_2CH{=}CH_2\text{-}2)_4$,[23] in the alkoxide $Cu_6(OCMe_2CH{=}CH_2)_6$,[23] and in olefin and diene complexes of copper(I) halides.[24] It is noteworthy that tetrameric *o*-vinylphenylcopper[7d] shows no π-coordination in the solid state and in THF solution. The good quality of the structure determination allows a comparison between the length of the coordinated C(43)−C(44) bond (1.416(5) Å) and the uncomplexed C(*ipso* phenyl)−C(*ortho* phenyl) distances (average 1.398 Å). With values of 2.3758(7), 2.4224(10), and 2.9136(11) Å, respectively, the rather different copper···copper interactions[25] in **2** are of the same magnitude as previously observed in other aryl copper compounds.[2d]

Colorless, X-ray-quality crystals of **3** were obtained from toluene at 0 °C. Increasing the size of the aryl substituent from $2,6\text{-}Ph_2C_6H_3$ to $2,6\text{-}Mes_2C_6H_3$ leads to

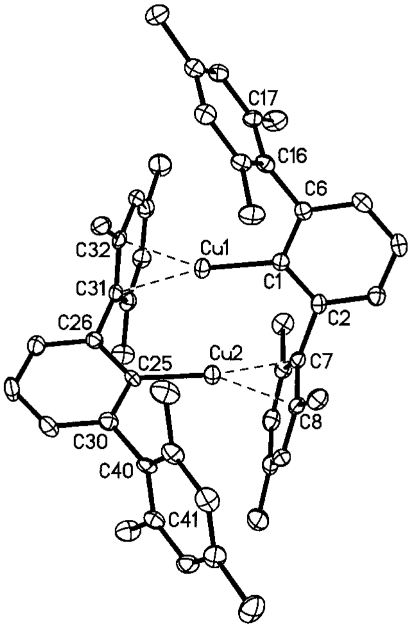

Figure 4. Molecular structure of **3**, showing 30% thermal ellipsoids and the numbering scheme. Hydrogen atoms have been omitted for clarity.

the dimeric product $(CuC_6H_3Mes_2\text{-}2,6)_2$, as depicted in Figure 4. The planes of the central C_6H_3 rings show a dihedral angle of 60.0°. Both aryl groups act as bidentate ligands, with the bridging performed by an *ipso* aryl carbon and two *ipso* or *ortho* carbon atoms of an adjacent mesityl group. With C_{ipso}−Cu−X angles of 174.0° and 170.5°, respectively, where X defines the midpoint of the C(31)−C(32) or C(7)−C(8) bonds, the coordination of the copper atoms is pseudolinear. The Cu(1)−C(1) and Cu(2)−C(25) distances of 1.927(5) and 1.921(4) Å are almost identical to the Cu(2)−C(37) bond length observed in **2**. In addition, the η^2-copper−arene interactions of 2.123(4)−2.295(4) Å (av 2.200 Å) are very similar to those in **2**. The different Cu−C_{ipso}−C_{ortho} angles of 119.9°/123.3° and 122.7°/121.0° and the Cu(1)···Cu(2) distance of 2.5953(12) can be interpreted in terms of a relatively stronger η^2-copper−arene coordination compared to the weaker copper···copper interaction.[25] Presumably, the alternative of a η^1-copper−C_{ipso}(arene) coordination, which should result in a shorter Cu−Cu distance, seems to be less advantageous.

Colorless plates of the lithium cuprate **4**, suitable for X-ray crystallographic studies, were grown from a saturated *n*-pentane solution at 5 °C. It crystallizes as contact ion paired monomers with two independent molecules in the asymmetric unit, as shown in Figure 5 for molecule 1. Compound **4** is the first example of a neutral monomeric cuprate with simple $LiCuR_2$ stoichiometry. Earlier reports of lithium diaryl cuprates are limited to dimeric complexes[3a−c] or monomeric solvent separated anionic species.[3d,f] Significant differences in the coordination of the lithium cation and the arrangement of the aryl ligands justify a separate view of both independent molecules. Interplanar angles of 77.3° (molecule 1) and 85.0° (molecule 2) are observed between the central C_6H_3 rings of the aryl substituents. The coordination of Li(1) can be described as η^1, η^6 with the lithium atom interacting most strongly with one *ipso* C_6H_3 terphenyl carbon (Li(1)−C(25) 2.312(10) Å) and

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[22] Arene−copper(I) interactions as in $(C_6H_6)CuAlCl_4$ have been known for a long time, however: Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877.

[23] Håkansson, M.; Lopes, C.; Jagner, S. *Organometallics* **1998**, *17*, 210.

[24] See for example: (a) Håkansson, M.; Jagner, S. *J. Organomet. Chem.* **1990**, *397*, 383. (b) Håkansson, M.; Wettström, K.; Jagner, S. *J. Organomet. Chem.* **1991**, *421*, 347. (c) Håkansson, M.; Jagner, S.; Walther, D. *Organometallics* **1991**, *10*, 1317; and the examples cited in: Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131.

[25] Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

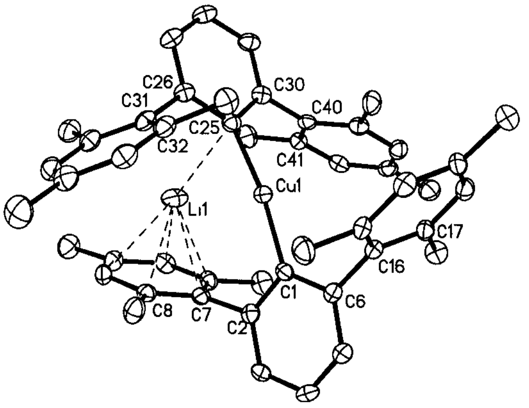

Figure 5. Molecular structure of molecule 1 in **4**, showing 30% thermal ellipsoids and the numbering scheme. Hydrogen atoms have been omitted for clarity.

with six mesityl carbon atoms of the second aryl group (2.462(10)−2.600(9) Å, av 2.516 Å). Additional weaker contacts of 2.704(10) and 2.780(12) Å are observed to the *ortho* C_6H_3 carbon C(26) and the *ipso* mesityl carbon C(31). In the case of molecule 2 the lithium atom Li(2) is bonded in a η^3, η^6 fashion. It is coordinated to the *ipso* C_6H_3 carbon C(73) (2.447(12) Å), the *ipso* and *ortho* mesityl carbons C(79) and C(80) (2.569(14) and 2.515(14) Å), and to six mesityl carbon atoms of the adjacent terphenyl ligand (2.519(12)−2.574(12) Å, av 2.543 Å). η^6−π-interactions of Li ions to arene rings are known[26,27] and usually cover a range of 2.31−2.46 Å, but may be as large as 2.57 Å.[11b] The relatively large values in **4** can be explained by steric crowding and the higher coordination of the lithium atoms taking into account the additional relatively short Li···Cu contacts of 2.400(8) and 2.429(11) Å, respectively. The copper−carbon distances of 1.922(5), 1.957(5) (molecule 1) and 1.925(5), 1.945(5) Å (molecule 2) are close to the values found for other lithium diaryl cuprates.[2b] The longer bonds to the carbon atoms C(25) and C(73) are consistent with the interactions of those atoms to the lithium centers.

A notable feature of the structure of **4** is the presence of cocrystallized $CuC_6H_3Mes_2$-2,6, as already mentioned in the Experimental Section. This is in accordance with NMR spectroscopic data for solutions of crystalline material, which always show signals for the copper aryl **3** in a ratio of less than 5%. In contrast to the dimeric structure observed for **3**, the cocrystallized $CuC_6H_3Mes_2$-2,6 species in the crystal structure of **4** can be best described as a copper cuprate moiety $Cu[CuR_2]$ (Figure 6). The formally cationic Cu(3) is coordinated in a η^1, η^2 fashion with the copper atom interacting almost equally with the *ipso* C_6H_3 aryl carbon (Cu(3)−C(73) 2.250(8) Å) and with an *ortho* and *meta* carbon of an opposite mesityl group. The copper−arene interactions of 2.065(8) and 2.244(8) Å are comparable to those in **2** and **3**. With an C_{ipso}−Cu−X angle of 171.6, where X defines the midpoint of the C(59)−C(60) bond, the coordination of the copper atom is pseudolinear.

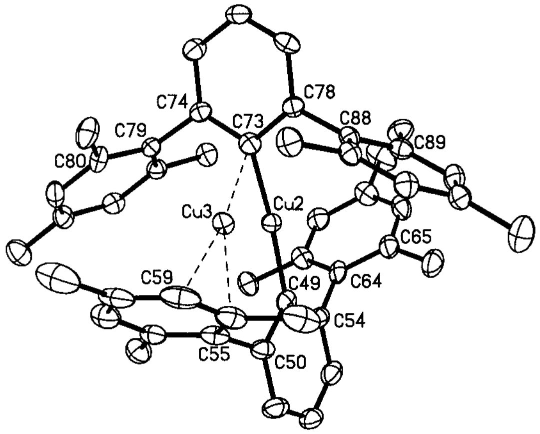

Figure 6. Molecular structure of the cocrystallized copper cuprate moiety in molecule 2 of compound **4**, showing 30% thermal ellipsoids and the numbering scheme. Hydrogen atoms have been omitted for clarity. The side occupation factor for Cu(3) is 0.092. The lithium atom Li(2) of the main $LiCuR_2$ component is not shown.

Table 3. Selected Inter- and Intramolecular Contacts (Å) for Compounds 2−4[a,b]

Compound **2**			
C(4)···C(44)′	3.637	$X_{(31-36)}$···H(47a)′′′′	2.68
C(5)···C(29)′	3.632	$X_{(13-18)}$···H(26a)	2.81
C(11)···C(51)′′	3.584	$X_{(25-30)}$···H(44a)	2.78
C(15)···C(28)′′′	3.499		
Compound **3**			
C(3)···C(44)′	3.636	C(9)···C(33)′′	3.404
C(9)···C(32)′′	3.605	C(29)···C(29)′′′	3.642
Compound **4**			
C(4)···C(42)′	3.590	C(19)···C(85)′′	3.503
C(18)···C(85)′′	3.513	C(23)···C(95)′′′	3.592

[a] Atoms marked by primes are generated by the following symmetry operations. (′): *x*, 1+*y*, *z*. (′′): 1−*x*, 0.5+*y*, 0.5−*z*. (′′′): −*x*, −*y*, −*z*. (′′′′): *x*, 0.5−*y*, 0.5+*z* for **2**. (′): −*x*, 2−*y*, 1−*z*. (′′): 1+*x*, *y*, *z*. (′′′): −*x*, 1−*y*, 2−*z* for **3**. (′): 1+*x*, *y*, *z*. (′′): *x*, *y*, −1+*z*. (′′′): −1+*x*, 0.5−*y*, +*z* for **4**. [b] $X_{(nn-mm)}$ defines the centroid of the C(*nn*)−C(*mm*) plane.

To verify the low degree of aggregation in compounds **2**−**4**, a few intermolecular contacts are stated in Table 3. No intermolecular distances shorter than 4.5 Å between copper or lithium centers and carbon atoms are observed. An interesting feature in compound **2** is the presence of a relatively short C−H π-contact[28] of 2.68 Å, which involves the midpoint of the aromatic C(31)−C(36) plane and an adjacent H(47a)′ hydrogen atom generated by the symmetry operation (*x*, 0.5−*y*, 0.5+*z*). In addition, slightly longer intramolecular C−H π-distances of 2.78 and 2.81 Å are found between the hydrogen atoms H(44a) or H(26a) and the centers of the C(25)−C(30) and C(13)−C(18) planes, respectively.

Cryoscopy and Spectroscopy. The good solubility of compounds **2** and **3** allowed the cryoscopic determination of the molecular mass in benzene. A value of 560 g mol^{-1} was obtained for $CuC_6H_3Ph_2$-2,6 (calculated for monomer, 293 g mol^{-1}). This can be interpreted in terms of either a dimeric association or an equilibrium of mono-, di-, and trimeric species in solution. The molecular mass determination for $CuC_6H_3Mes_2$-2,6 yielded a value of 440 g mol^{-1}, whereas M = 377 g mol^{-1} would be expected for monomeric **3**. This is consistent

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(26) (a) Pilz, M.; Allwohn, J.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem.* **1990**, *102*, 1085; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1032. (b) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2487. (c) Kurz, S.; Hey-Hawkins, E. *Organometallics* **1992**, *11*, 2729. (d) Schiemenz, B.; Power, P. P. *Angew. Chem.* **1996**, *108*, 2288; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2150. See also ref 11a.

(27) Tacke, M. *Eur. J. Inorg. Chem.* **1998**, 537.

(28) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669.

with an association of ca. 1.2 and the presence of monomers and dimers in benzene. In the mass spectrum of **3** intense signals of monomeric (basis peak) and dimeric units (rel intensity of 95%) are observed. This may be contrasted with the mass spectra of products **2** and **4**, which showed either no copper-containing fragments or a molecular mass peak of low intensity.

Compounds **2**−**4** were also characterized by ^{1}H and ^{13}C NMR spectroscopy. No dynamic character was observed for **2** and **3** in the range from −70 to 80 °C in toluene-d_8 solution. This is in agreement with the fast conversion of different mono-, di-, and trimeric species even at low temperatures. Relatively sharp resonances of 147.6 (**2**) and 159.6 ppm (**3**) were observed in the ^{13}C NMR for the *ipso* C_6H_3 carbons. A chemical shift of 165.9 ppm was found for the corresponding carbon in the cuprate **4**. This lies somewhere in the middle of the values reported for the lithium aryl $LiC_6H_3Mes_2$-2,6 (173.5 ppm)[11a] and the copper aryl **3**. The ^{7}Li NMR chemical shift of −8.3 ppm differs greatly from the value observed for the parent lithium aryl (+2.58 ppm)[11a] but is very close to that found for lithium cyclopentadienide.[29] This high-field shift is consistent with a well-shielded lithium ion caused by the aromatic ring current of the η^6-coordinated arene.

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Supporting Information Available: Tables of crystal data, data collection, solution, and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, hydrogen atom coordinates, and additional structure plots (48 pages). Ordering information is given on any current masthead page.

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(29) The chemical shift of LiCp in THF solution is observed at −8.37 ppm: Günther H. High Resolution ^{6,7}Li NMR of Organometallic Compounds. In *Advanced Applications of NMR to Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; John Wiley: Chichester, 1996; Chapter 9.