Synthesis and Characterization of the Organoiodocuprate Complexes $[Li(THF)_4][2,6\text{-}Mes_2H_3C_6Cu_2I_2]$ (Mes = C_6H_2-2,4,6-Me_3) and $(Et_2O)_2Li\{ICuC_6H_3\text{-}2,6\text{-}Trip_2\}$ (Trip = C_6H_2-2,4,6-*i*-Pr_3)

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Treatment of CuI with 2 equiv of LiC_6H_3-2,6-Mes_2 (Mes = C_6H_2-2,4,6-Me_3) in Et_2O/THF solution affords the species $[Li(THF)_4][2,6\text{-}Mes_2H_3C_6Cu_2I_2]$ (**1**), which was characterized by ^1H, ^7Li, and ^{13}C NMR spectroscopy and by X-ray crystallography. An analogous reaction involving CuI and 1 equiv of LiC_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3) gives the contact ion-pair species $(Et_2O)Li\{ICuC_6H_3\text{-}2,6\text{-}Trip_2\}$ (**2**), which was characterized similarly. Compounds **1** and **2** represent very rare instances of well-characterized organohalocuprate species. The unique structure of the anion in **1** features two copper iodides bound to the ipso-carbon of the *m*-terphenyl ligand $-C_6H_3$-2,6-Mes_2. The organic group interacts almost equally strongly with each copper, and there is a very short Cu−Cu distance of 2.391(3) Å. The copper in compound **2** is bound in an almost linear fashion by an iodide and an ipso-carbon atom from the ligand $-C_6H_3$-2,6-$Trip_2$. The iodide is also bound to a lithium ion (which is solvated by two ethers) such that there is an unusually narrow interligand angle Li−I−Cu = 95.5(2)° at the iodide.

Introduction

Organocopper(I) compounds[1] may exist as neutral species or as anions[2] or cations[3] which form part of an ionic salt. They are generally obtained by the reaction of an organolithium reagent with copper halide, and with 1:1 stoichiometry lithium halide is usually eliminated to afford a neutral organocopper product $(CuR)_n$ (*n* is commonly 4). When less than 1 equiv of organolithium reagent per copper halide is used, some unreacted copper halide will be available for complexation to the neutral organocopper species, and a CuR−CuX complex (R = organic ligand, X = halide) may form. Several examples of such compounds featuring various CuX:CuR ratios in neutral aggregates have been reported and structurally characterized.[1,4,5] In contrast there are very few well-characterized organohalocuprate species (e.g., of general formula $Li_xCu(X)_y(R)_z)$ in which a copper is bound to both an organo group and a halide. The existence of such complexes was originally inferred on the basis of the enhanced reactivity of CuPh in the presence of LiI.[6] In addition, NMR spectroscopy has indicated that halide ions had a significant role to play in the structure of cuprates.[7] The first organohalocuprate structure was obtained by the addition of 12-crown-4 to a mixture of CuBr and $LiCH(SiMe_3)_2$ which resulted in the formation of the solvent-separated ion-pair species $[Li(12\text{-}crown\text{-}4)_2][Cu(Br)CH(SiMe_3)_2]$.[8] Also, the addition of $(THF)_3LiSi(SiMe_3)_3$ to CuCl or CuBr has afforded the unusual silylhalocuprate compounds $[Li(THF)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$[9] and $(THF)_3LiBrCu_2\{Si(SiMe_3)_3\}_2$.[10] In this paper it is shown that the use of the bulky terphenyl ligands readily allows the crystallization of two new organohalocuprates, one of which has a previously unobserved anionic structural type.

Experimental Section

General Procedures. All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed immediately before use. The compounds $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$[11] and (Et_2O)-LiC_6H_3-2,6-$Trip_2$[12] were synthesized by literature procedures; CuI was purchased commercially (Aldrich) and was used without further purification. ^1H, ^7Li, and ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument and refer-

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enced to the deuterated solvent. The ^{13}C NMR spectra were used to establish the purity of the compounds in solution since they are subject to desolvation when isolated.

[Li(THF)$_4$][2,6-Mes$_2$H$_3$C$_6$Cu$_2$I$_2$] (1). (LiC$_6$H$_3$-2,6-Mes$_2$)$_2$ (1.60 g, 2.5 mmol), dissolved in an ice-cooled mixture of Et$_2$O and THF (1:2, 30 mL), was added dropwise (over ca. 1 h) to a suspension of CuI (1.90 g, 10 mmol) in THF (10 mL) at ca. −78 °C. Upon warming to room temperature, the white-colored mixture became yellow-orange. The solution was stirred for a further 3 h, and the precipitate was allowed to settle. The pale yellow supernatant liquid was filtered through Celite and placed in a freezer (ca. −20 °C) for 2 days to afford the product **1** as colorless crystals. Yield; 1.78 g (35.6%). Mp: 151−152 °C (decomposed into reddish brown liquid). ^{1}H NMR (THF-d_8, 25 °C): $\delta = 7.41$ (t, 1H, $J = 7.8$ Hz, p-C$_6$H$_3$); 7.02 (d, 2H, $J = 7.8$ Hz, m-C$_6$H$_3$); 6.84 (s, 4H, m-Mes); 2.24 (s, 12H, o-(Mes)CH_3); 1.97 (s, 6H, p-(Mes)CH_3). ^{13}C{^{1}H}NMR(THF-d_8, 25 °C): $\delta =$ 174.16 (br, i-C$_6$H$_3$); 157.94 (o-C$_6$H$_3$); 145.28 (i-Mes); 142.38 (p-Mes); 139.79 (o-Mes); 135.97 (m-Mes); 128.65 (m-C$_6$H$_3$); 126.40 (p-C$_6$H$_3$); 68.19 (THF); 67.39 (quintet, THF-d_8); 26.32 (THF); 25.27 (quintet, THF-d_8); 23.81 (p-(Mes)CH$_3$); 21.26 (o-(Mes)-CH$_3$). ^{7}Li NMR (THF-d_8, 25 °C, LiCl/D$_2$O was used as reference); $\delta = -0.68$ (br s).

(Et$_2$O)$_2$Li{ICuC$_6$H$_3$-2,6-Trip$_2$} (2). (Et$_2$O)LiC$_6$H$_3$-2,6-Trip$_2$ (2.81 g, 5 mmol), dissolved in Et$_2$O (30 mL), was added dropwise to a suspension of CuI (0.96 g, 5 mmol) in Et$_2$O (20 mL) at ca. −78 °C. The mixture was allowed to warm to room temperature, during which time it became a dark orange color. The solvent was then removed under reduced pressure, and the dark brown residue was extracted with n-hexane (30 mL) and filtered. The filtrate was stored at ca. −20 °C for 2 days to afford the product **2** as colorless crystals. Yield: 2.69 g (65%). Mp: 193−196 °C (decomposed to dark brown powder). ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = 7.29{-}7.20$ (br m, m- and p-C$_6$H$_3$, m-Trip); 7.15 (s,C$_6$D$_6$) 3.51 (br, o-(CH_2CH$_3$)$_2$); 3.23 (sept. 4H, $J = 6.6$ Hz, o-CH(CH$_3$)$_2$); 2.89 (sept. 2H, $J = 6.0$ Hz, p-CH(CH$_3$)$_2$); 1.44 (br, o-(CH$_2$CH_3)$_2$); 1.31 (d, 24H, $J = 6.6$ Hz, o-CH(CH_3)$_2$); 1.26 (d, 12H, $J = 6.0$ Hz, p-CH(CH_3)$_2$). ^{13}C{^{1}H}NMR (C$_6$D$_6$/1 μL of neat THF, 25 °C): $\delta = 173.74$ (i-C$_6$H$_3$); 149.88 (o-C$_6$H$_3$); 146.86 (o-Trip); 146.11 (i-Trip); 128.95 (p-C$_6$H$_3$); 125.01 (m-C$_6$H$_3$); 120.05 (m-Trip); 68.71 (THF); 65.92 (OEt$_2$); 34.88 (p-CH(CH$_3$)$_2$); 30.58 (o-CH(CH$_3$)$_2$); 25.29 (THF); 24.92 (p-CH(CH$_3$)$_2$); 24.72 (OEt$_2$); 24.69 (o-CH(CH$_3$)$_2$). ^{7}Li NMR (C$_6$D$_6$, 25 °C) (LiCl/D$_2$O reference), $\delta = -0.37$ (br s).

X-ray Crystallography. Crystals of **1** and **2** were coated with hydrocarbon oil, mounted on a glass fiber, and quickly placed in the N$_2$ cold stream on the diffractometer.[13] Data for **1** were collected with Cu Kα radiation ($\lambda = 1.541\,78$ Å) at 130 K on a Siemens P4 diffractometer equipped with a rotating anode, and data for **2** were collected at 130 K with Mo Kα radiation ($\lambda = 0.710\,73$ Å) on a Siemens R3m/v diffractometer. Both diffractometers were equipped with a low-temperature device, and the radiation was monochromated with either a nickel (P4) or graphite (R3m/v filter). Calculations were carried out with the SHELXTL-Plus program system.[14] Scattering factors and the correction for anomalous scattering were taken from common sources.[15] The structures were solved by direct methods and refined by full-matrix least-squares refinement. An absorption correction was applied using the program XABS.[16] Crystal data for **1** and **2** are provided in Table 1. The higher than usual R value and residuals for **1** probably resulted from the extreme sensitivity of the complex to desolvation and the fact that a copper X-ray source was used. In addition there is disorder in some of the THF carbon atoms coupled with large thermal motion, as described in the CIF file. A potential solvent value of 97.5 Å^3 was reported by PLATON. However, no recognizable molecule could be assembled from the difference map peaks.

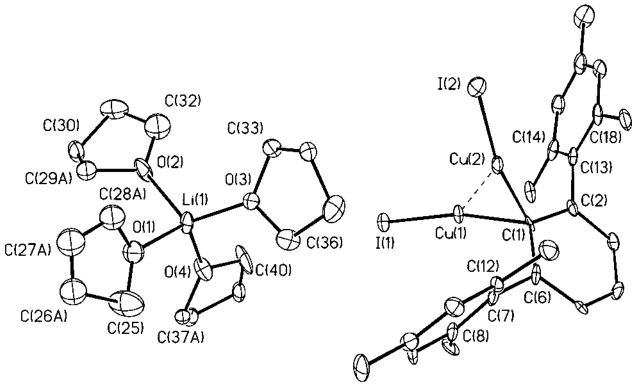

Figure 1. Thermal ellipsoid plot (30%) of **1**. H atoms are not shown for clarity.

Table 1. Crystallographic Data for Compounds 1 and 2

	1	2
formula	C$_{40}$H$_{57}$Cu$_2$I$_2$LiO$_4$	C$_{44}$H$_{69}$CuILiO$_2$
fw	989.68	827.37
color, habit	colorless, block	colorless, block
cryst syst	orthorhombic	monoclinic
space group	$Pbca$	$P2_1/n$
a, Å	12.351(2)	12.348(3)
b, Å	20.307(4)	16.564(3)
c, Å	33.867(5)	21.705(4)
α, deg	90	90
β, deg	90	92.75(3)
γ, deg	90	90
V, Å^3	8494(2)	4434(2)
Z	8	4
d, g cm^{-3}	1.548	1.239
cryst dimens, mm	0.40 × 0.22 × 0.08	0.32 × 0.28 × 0.14
μ cm^{-1}	12.922	1.22
no. of unique data	5614	8574
no. of data with $I > 2\sigma(I)$	3929	5105
no. params	438	458
R ($I > 2\sigma(I)$)	0.0876	0.0529
wR$_2$, all data	0.2569	0.1147

Results and Discussion

The compounds **1** and **2** were synthesized by the reaction of the respective lithium aryls with CuI. Attempts were made to synthesize a −C$_6$H$_2$-2,6-Mes$_2$-substituted species corresponding to **2**; however, no crystals were obtained, although ^{13}C NMR evidence suggested that the [ICuC$_6$H$_3$-2,6-Mes$_2$]$^-$ ion had formed in solution. The ^{13}C NMR spectra of **1** and **2** reveal the characteristic ipso-carbon signals at low field: 174.16 ppm for **1**, 173.74 ppm for **2**. These shifts are quite similar to the 171.7 ppm reported for the dimer [Li(THF)$_2${Cu(CN)C$_6$H$_3$-2,6-Trip$_2$}]$_2$,[17] the 168.1 ppm value observed for the neutral monomer (Me$_2$S)CuC$_6$H$_3$-2,6-Trip$_2$,[12] or the ipso-C shifts in several aryl cuprates.[18]

The structures of **1** and **2** are illustrated in Figures 1 and 2. Selected structural data are provided in Table 2. It can be seen that for **1** the compound crystallizes

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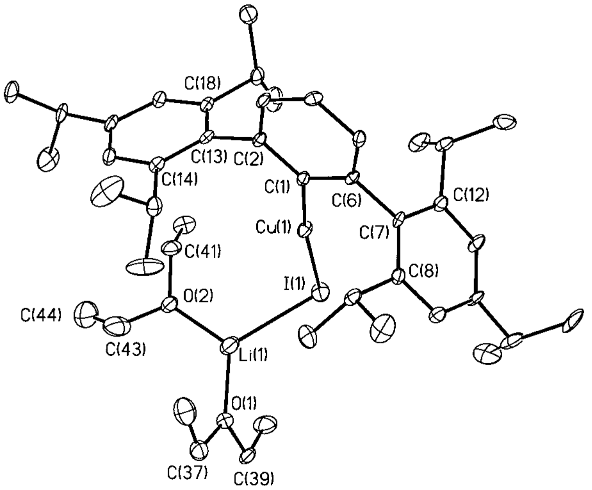

Figure 2. Thermal ellipsoid plot (30%) of **2**. H atoms are not shown for clarity.

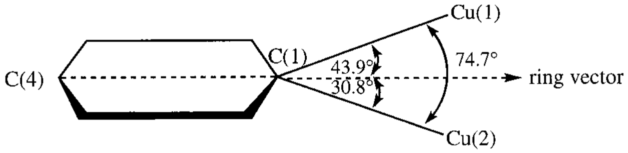

Figure 3. Schematic illustration of the aryl ring–copper bonding in **1**.

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

1		2	
Cu(1)–C(1)	1.967(12)	Cu(1)–C(1)	1.902(5)
Cu(2)–C(1)	1.974(15)	Cu(1)–I(1)	2.4512(8)
Cu(1)–I(1)	2.414(2)	Li(1)–I(1)	2.690(11)
Cu(2)–I(2)	2.423(2)	Li(1)–O(1)	1.905(11)
Cu(1)–Cu(2)	2.391(3)	Li(1)–O(2)	1.893(11)
Li(1)–O(1)	1.94(2)	C(1)–C(2)	1.417(7)
Li(1)–O(2)	1.95(3)	C(1)–C(6)	1.416(7)
Li(1)–O(3)	1.94(3)		
Li(1)–O(4)	1.84(3)		
C(1)–C(2)	1.44(2)		
C(1)–C(6)	1.43(2)		
C(1)–Cu(1)–I(1)	164.1(4)	C(1)–Cu(1)–I(1)	171.4(2)
C(1)–Cu(2)–I(2)	166.8(4)	Li(1)–I(1)–Cu(1)	95.5(2)
Cu(1)–C(1)–Cu(2)	74.7(5)	C(2)–C(1)–C(6)	115.4(5)
C(2)–C(1)–C(6)	115.5(12)	O(1)–Li(1)–I(1)	123.9(5)
O–Li–O	98.5(11)–119.1(15)	O(2)–Li(1)–I(1)	113.9(5)
		O(1)–Li(1)–O(2)	122.0(6)

as solvent-separated ion pairs. The structure of the type of anion exemplified by $[2,6\text{-Mes}_2H_3C_6Cu_2I_2]^-$ was not previously known in organocopper chemistry. As is apparent from Figure 1, it consists of a $-C_6H_3$-2,6-Mes$_2$ aryl group bridging two copper iodides through an ipso-carbon atom. The bridging is not quite symmetric, however. As shown in Figure 3, the extended C(4)–C(1) vector (i.e., C(para)–C(ipso)) does not bisect the Cu(1)-C(1)Cu(2) (74.7(5)°) angle but divides it into two unequal parts: 43.9° with respect to the Cu(1)–C(1) bond versus 30.8° with respect to the Cu(2)–C(1) bond. This suggests a slightly stronger interaction with Cu(2), but it can be seen from Table 2 that the Cu(2)–C(1) bond actually slightly longer (i.e., weaker) than Cu(1)–C(1). However, the standard deviations for these distances do not permit the attachment of much significance to this observation. The strength of the interaction of the ipso-carbon with the two coppers is approximately equal. The angle between the C(1) ring plane and the plane described by the atoms C(1)Cu(1) and Cu(2) is 87.2°.

The Cu(1)–Cu(2) separation in **1** is 2.391(3) Å. This is one of the shortest such distances observed to date in an organocopper species.[19] It may be compared to the even shorter distance of 2.369(1) Å, observed in the copper silyl compound $(THF)_3LiBrCu_2Si(SiMe_3)_3$, **3**, which features two coppers bridged by the silyl group.[10] One copper is also bound to a terminal $-Si(SiMe_3)_3$, whereas the other is bonded to a bromide, which is also complexed by a THF-solvated Li^+ ion. The $SiCu_2$ core of this molecule was described as having a three-center, two-electron bond. It has to be said that the very short Cu–Cu distances both in this molecule and in **1** are remarkable since the coppers are apparently not forced into proximity by chelating ligands with short bite distances as they are in a number of complexes with very short Cu–Cu distances, e.g., the copper(I) pentaazadienyl, $\{Cu(ArNNNNNAr)\}_3$, derivatives.[20] The close $d^{10}-d^{10}$ interactions in these and other complexes involving two copper(I) centers have been the subject of several theoretical studies.[21] The most recently reported DFT calculations[22] on copper complexes seem to imply that Cu–Cu distances as short as that seen in the molecule **1** do not necessarily mean that there is strong Cu–Cu bonding present.

In the absence of such bonding each copper may therefore be described as two-coordinate. The coordination is not linear, however, since the C–Cu–I angles are 164.1(4)° and 166.8(1)°. Moreover, the bending of the geometry at the coppers is such that the iodines appear to repel each other. On the other hand, it could be said with equal validity that the coppers are attracted toward each other. This, if true, supports the existence of a significant Cu–I interaction. The Cu–I distances, ca. 2.42 Å, are almost exactly equal to the 2.417(2) Å Cu–I distance determined for $\{2,4,6\text{-(MeO)}_3H_2C_6\}$-PCuI[23] but are marginally longer than the ca. 2.39 Å Cu–I bond length in the two coordinate linear anion $[CuI_2]^-$.[24] The Cu–C distances in **1**, which average ca. 1.97 Å, are comparable to those seen in other structures that feature aryl groups bridging two coppers.[1,2,4] However, it is somewhat shorter than the bridging Cu–C distances, ca. 2.02 Å, in 2,4,6-$Ph_3H_2C_6Cu(\mu\text{-}C_6H_2\text{-}2,4,6\text{-}Ph_3)Cu(SMe_2)_2$,[25] which features a bulky $-C_6H_2$-2,4,6-Ph_3 ligand bridging two coppers. Perhaps, the presence of two such ligands in the latter structure results in some steric congestion which lengthens the bonds.

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(19) For example, Cu–Cu distances as short as ca. 2.38 Å have been observed in chelated compounds $Cu_4(Mes)_2(SC_6H_4CH_2NMe_2\text{–}2)_2$[19a] or $Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$: Ref 1b, p 94, and in the oxo-derivative $Cu_{10}O_2$-Mes_6.[19b] (a) Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400. (b) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

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The structure of **2** (Figure 2) features an almost linearly coordinated copper (C(1)−Cu(1)−I(1) = 171.4(2)°) bound to the bulky terphenyl group $-C_6H_3$-2,6-Trip$_2$ and an iodine. The Cu−I distance ca. 2.45 Å may be contrasted with those already mentioned earlier and is marginally longer than the 2.42 Å average bond length observed in **1**. The Cu−C distance 1.902(5) Å is, however, significantly shorter than the 1.97 Å observed in **1**, which is probably due to the bridging nature of the organic ligand in the former compound. It is notable that the Cu−C bond length in **2** is essentially identical to the 1.906(4) Å found in $[(THF)_2Li\{Cu(CN)C_6H_3$-2,6-Trip$_2\}]_2$[17] and is just marginally shorter than the 1.984(6) Å found in $(Me_2S)CuC_6H_3$-2,6-Trip$_2$.[12] The slightly shorter Cu−C distance in the latter species is probably due to its neutral character, which may have less interelectronic repulsion than in the anion.

The structure of **2** is completed by an $Li(OEt_2)_2$ unit which is in contact with the anion via a Li−I interaction of 2.69 Å. The Li^+ ion is thus three-coordinate and has a planar geometry, although the interligand angles display considerable variation (cf. Table 2). The Li−I distance may be compared to the range of values 2.67−2.80 Å found in a number of LiI complexes[26] of various Lewis bases in which the Li^+ ion is four-coordinate. The Li−O distances in **2**, ca. 1.90 Å, are significantly shorter than the ca. 1.96 Å values in $(Et_2O)_2LiC_6H_2$-2,4,6-Ph$_3$,[27] which also features a three-coordinate Li^+ ion. An unusual aspect of the structure of **2** is the quite sharp angle of 95.5(2)° at the iodine. Examination of the iodine environment showed several hydrogen contacts (to H(20D), H(40B), H(41A), and H(42C)) in the range 3.23−3.48 Å. While this range of values is roughly equal to the sum of the van der Waals radii[28] of hydrogen and iodine, the apparent weakness and directionality of such interactions do not seem to account for the observed bending. Interestingly, it is notable that the K^+ interaction with an iodine from $[CuI_2]^-$ in the structures of [K(18-crown-6)]$[CuI_2]$ and [K(dicyclohexyl-18-crown-6)]$[CuI_2]$[24] also results in a relatively narrow angle at iodine. It is possible that the alkali metal−iodine interaction in all these structures does not have a strong angular dependence and that relatively weak forces such as these involved in crystal packing may be a leading cause of the observed angles.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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