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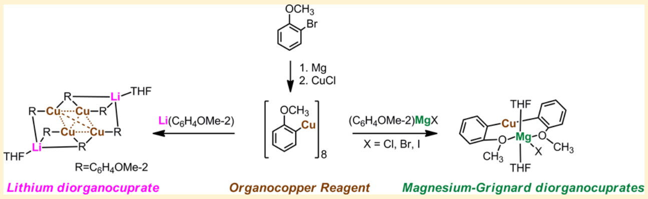
Functionalized Organocuprates: Structures of Lithium and Magnesium Grignard 2-Methoxyphenylcuprates

Roberta Bomparola, Robert P. Davies,* Steven Lal, and Andrew J. P. White

Department of Chemistry, Imperial College London, South Kensington, London, U.K. SW7 2AZ.

S *Supporting Information*

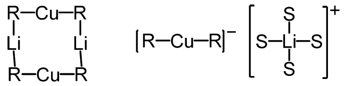
ABSTRACT: Lithium and magnesium Grignard diorganocuprates incorporating the functionalized aryl group 2-methoxyphenyl have been prepared and structurally characterized in the solid state. $[Cu_4Li_2(C_6H_4OMe\text{-}2)_6(THF)_2]$ (**2**) and $[Cu(C_6H_4OCH_3\text{-}2)_2Mg(THF)_2X]$ (**3-X**; X = Cl, Br) all exhibit coordination of the s-block metal center by the methoxy oxygen, resulting in the formation of novel aggregates and favoring contact ion pair structures. In contrast, separate ion pair structures had previously been observed under similar conditions for nonfunctionalized arylcuprates. The magnesium organocuprates **3-Cl** and **3-Br** are of particular interest, being rare examples of structurally characterized Grignard-derived organocuprates and the first examples of functionalized Grignard organocuprates. All reported organocuprates undergo oxidative aryl coupling in the presence of O_2 or $PhNO_2$ to give 2,2′-dimethoxybiphenyl.



INTRODUCTION

Organocuprates are excellent reagents for the formation of carbon−carbon bonds and have been extensively employed in synthetic methodology since the 1960s for a number of important reactions, including conjugate addition, substitution reactions, coupling reactions, and carbocupration.[1,2] However, it is only relatively recently that significant insights have been obtained into the mechanism of operation of these reagents and the origin of their unique reactivity,[3−5] including recent evidence of the important role played by Cu(III) intermediates.[6]

One of the first key steps in building the current understanding of organocuprates was identification of the structural forms adopted by these complex species.[3] Thus, the resting state and also reactive form of lithium organocuprates ("R_2CuLi", R = organo group) in a nonpolar or weakly coordinating solvent such as diethyl ether is now commonly accepted to be the dimeric contact ion pair (CIP) species **I** (Figure 1). However, in a more strongly coordinating solvent, such as THF, the less reactive solvent-separated ion pair (SSIP) species **II** is predominant. Studies on the structures of analogous magnesium Grignard derived organocuprates ("R_2CuMgX", X = halide) are far less developed, despite the fact that the heritage and synthetic usage of these reagents rival that of their lithium-based analogues.[1] We have recently reported the first structural characterizations of magnesium Grignard organocuprates, revealing $[Ph_4Cu_2(Mg(OEt_2)I)_2]$ to adopt a dimeric CIP structure in diethyl ether which is analogous to that of lithium diorganocuprate CIPs (**I**) but with MgI formally replacing Li in the ring.[7] Larger "inverse crown" type aggregates[8] were observed when employing the bulkier mesityl ($C_6H_2Me_3$-2,4,6) aryl group, and similar to the case for lithium organocuprates, solvent-separated species were discerned when more strongly coordinating THF solvent molecules were present.[7]



I **II**

Figure 1. CIP (**I**) and SSIP (**II**) structures of lithium homocuprates.

Most structural studies on organocuprates to date have employed simple nonfunctionalized aryls (such as phenyl[9−14] or mesityl[15−17]) as the organo R group. However, many organocuprate synthetic protocols employ aryl or alkyl groups with additional functionalization such as amine, ether, alkenyl, and alkynyl groups[18] and it is still unclear how closely the structures and behavior of these species match those of their unfunctionalized cousins. A small number of lithium organocuprates containing dimethylamino-functionalized aryl groups have been studied, including the lithium homocuprate $[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ (**III**), which was shown to adopt a CIP structure with dimethylamino substituents coordinating to the lithium atoms via their nitrogen lone pairs (Figure 2).[19] An additional advantage to studying such species is the demonstrated ability of intramolecular Lewis donor groups to stabilize reagents or aggregates which are otherwise too reactive or unstable to be isolated. Hence, the aforementioned dimethylamino-substituted aryl was also employed by van Koten and co-workers to prepare $[(C_6H_4(CH_2NMe_2)\text{-}2)_2CuLi_2(CN)(THF)_4]_\infty$ (**IV**), which

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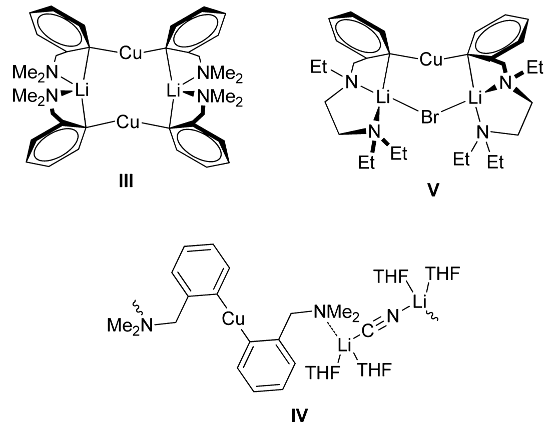


Figure 2. Organocuprates containing amine-functionalized aryl groups.

proved key in understanding the chemistry of cyano Gilman (Lipshultz) cuprates at a time when there was much controversy regarding the nature of these species.[20] In addition, a diamine-functionalized aryl was thought to play a large role in contributing to the thermodynamic stability of the lithium diorganocuprate−lithium halide complex [$Cu(C_6H_4(CH_2N(Et)CH_2CH_2NEt_2)$-2)$_2Li_2Br$] (**V**).[21] Using similar principles, Ribas et al. employed a triaza macrocyclic ligand to yield the first example of an isolable Cu(III) monoaryl species.[22]

In this work we investigate the role of ether-functionalized aryl groups in lithium and Grignard organocuprates. There are currently no structurally characterized examples of Grignard-derived organocuprates with functionalized aryls of any sort, and as discussed above, studies on functionalized lithium diarylcuprates are currently limited to just those with one or more amine donor groups. The 2-methoxyphenyl group has been selected as the organo group, since organocuprates containing this ligand are readily accessible and have previously been employed in a number of synthetic protocols, including the syntheses of dihydromultifidene,[23] hallucinogenic amphetamine derivatives,[24] and the anticancer natural product yomogin.[25]

■ EXPERIMENTAL SECTION

General Considerations. All experimental work was carried out under an inert atmosphere of nitrogen using standard Schlenk double-manifold and glovebox techniques. Purification and drying of the solvents was carried out following standard methods or using an Innovative Technologies PureSolv solvent purification system with purification-grade solvents. NMR spectra were recorded on a Bruker DPX400 spectrometer with internal standards. Melting points were measured in capillaries sealed under nitrogen, and microanalytical data were obtained from the Science Technical Support Unit, London Metropolitan University.

Synthesis of [$Cu(C_6H_4OMe$-2)]$_8$·8THF (1). A 40 mmol portion of 2-bromoanisole (5.0 mL) was added dropwise to a suspension of magnesium metal (44 mmol, 1.07 g) in THF (40 mL) at 0 °C. After complete addition the reaction mixture was brought to room temperature and stirred for 1 h. The resultant Grignard reagent was then added to a suspension of copper(I) chloride (40 mmol, 3.94 g) in THF (40 mL) at 0 °C, and the mixture was stirred overnight. A 20 mL portion of 1,4-dioxane was added to aid the precipitation of MgBrCl, which was removed by filtration, and the filtrate volume was concentrated under vacuum. Storage at −35 °C for 3 days yielded orange crystals (2.58 g, 38% yield relative to 2-bromoanisole); mp 128 °C dec. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 9.2−6.1 (m, 32 H, Ar-H), 3.70 (m, 32 H, CH_2O-THF), 3.5−2.1 (s, 24 H, $-OCH_3$), 1.52 (m, 32 H, CH_2-THF). Anal. Calcd for $C_{56}H_{56}Cu_8O_8$ (FW = 1365.3): C, 49.26; H, 4.13. Found: C, 49.15; H, 4.19 (note that the THF solvent of crystallization was lost during the isolation procedure required to prepare the sample for analysis).

Synthesis of [$Cu_4Li_2(C_6H_4OMe$-2)$_6$(THF)$_2$] (2). A solution of *n*BuLi in hexane/cyclohexane (2.5 M, 1.06 mmol, 0.43 mL) was added dropwise to a solution of 2-bromoanisole (1.06 mmol, 0.13 mL) in hexane (5 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. A solution of 2-methoxyphenylcopper (**1**; 0.182 g, 1.06 mmol) in toluene (4.6 mL) was added to give a yellow precipitate, which was dissolved with the addition of THF (0.5 mL) and then filtered over Celite. Storage at room temperature for 5 days yielded yellow blocks of **2** suitable for X-ray crystallography (85 mg, 24% yield based on 2-bromoanisole). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 8.02 (m, 6H, H6), 7.23 (m, 6H, H4), 7.05 (m, 6H, H5), 6.69 (m, 6H, H3), 3.68 (m, 8 H, CH_2O-THF), 3.40 (s, 18H, $-OCH_3$), 1.49 (m, 8 H, CH_2-THF). ^{7}Li NMR (155.6 MHz, 25 °C, C_6D_6) δ 1.46.

Exposure of **2** to atmospheric oxygen over several days or treatment with $PhNO_2$ at room temperature produced 2,2′-dimethoxybiphenyl. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 7.49 (d, 2H, *J* = 7.4 Hz, H6), 7.28 (m, 2H, H4), 7.06 (m, 2H, H5), 6.78 (d, 2H, *J* = 8 Hz, H3), 3.39 (s, 6H, $-OCH_3$).

Synthesis of [$Cu(C_6H_4OCH_3$-2)$_2$Mg(THF)$_2$Br] (3-Br). A solution of 2-methoxyphenylcopper (**1**; 182 mg, 1.10 mmol) in toluene (2.6 mL) was added to a solution of (2-methoxyphenyl)magnesium bromide in THF (1 M, 1.10 mL, 1.10 mmol), previously prepared from the addition of 2-bromoanisole (20 mmol, 2.5 mL) to a suspension of magnesium metal (22 mmol, 0.48 g) in THF (20 mL). In order to dissolve the yellow precipitate that was formed, additional toluene (2 mL) and THF (2 mL) were added; the solution was stirred at room temperature for 15 min before filtration through Celite. Storage at −35 °C for 19 days yielded colorless crystals suitable for X-ray analysis (142 mg, 25%); mp 282 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.48 (d, 2H, *J* = 8.0 Hz, H6), 7.22 (m, 2H, H4), 7.05 (m, 2H, H5), 6.93 (m, 2H, H3), 3.82 (m, 8H, CH_2O-THF), 3.39 (s, 6H, $-OCH_3$), 1.45 (m, 8H, CH_2-THF).

Synthesis of [$Cu(C_6H_4OCH_3$-2)$_2$Mg(THF)$_2$Cl] (3-Cl). A solution of 2-methoxyphenylcopper (**1**; 182 mg, 1.10 mmol) in toluene (2.6 mL) was added to a solution of (2-methoxyphenyl)magnesium chloride in THF (1 M, 1.10 mL, 1.10 mmol), previously prepared from the addition of 2-chloroanisole (20 mmol, 2.5 mL) to a suspension of magnesium metal (22 mmol, 0.48 g) in THF (20 mL). Toluene (2 mL) and THF (2 mL) were added to dissolve the solid, and the solution was stirred at room temperature for 15 min before filtration through Celite. Storage at room temperature for 14 days yielded colorless crystals suitable for X-ray analysis (98 mg, 19%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.48 (d, 2H, *J* = 7.2 Hz, H6), 7.22 (m, 2H, H4), 7.05 (m, 2H, H5), 6.93 (m, 2H, H3), 3.69 (m, 8H, CH_2O-THF), 3.39 (s, 6H, $-OCH_3$), 1.52 (m, 8H, CH_2-THF).

Synthesis of [$Cu(C_6H_4OCH_3$-2)$_2$Mg(THF)$_2$I] (3-I). A solution of 2-methoxyphenylcopper (182 mg, 1.10 mmol) in toluene (2.6 mL) was added to a solution of (2-methoxyphenyl)magnesium iodide in THF (0.5 M, 2.20 mL, 1.10 mmol), previously prepared from the addition of 2-iodoanisole (20 mmol, 2.6 mL) to a suspension of magnesium metal (22 mmol, 0.48 g) in THF (20 mL). Toluene (2 mL) and THF (2 mL) were added, and the mixture was heated to 50 °C before filtration through Celite. Storage of the filtrate at room temperature for 12 h yielded a yellow solid, which was dried in vacuo (95 mg, yield 16%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.48 (d, 2H, *J* = 7.6 Hz, H6), 7.22 (m, 2H, H4), 7.05 (m, 2H, H5), 6.93 (m, 2H, H4), 3.71 (m, 8H, CH_2O-THF), 3.39 (s, 6H, $-OCH_3$), 1.48 (m, 8H, CH_2-THF).

X-ray Structure Determinations of 1, 2, 3-Cl, and 3-Br. The crystals were all taken directly from the mother liquor, covered with a perfluorinated ether, and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The data were collected using a Oxford Diffraction Xcalibur PX Ultra diffractometer fitted with an Oxford Cryostream low-temperature device, and the structures were refined on the basis of F^2 using the SHELXTL and SHELX-97 program systems. Table 1 provides a summary of the crystallographic

Table 1. Summary of Crystal Structure Data for **1**, **2**, **3-Br**, and **3-Cl**

	1	**2**	**3-Br**	**3-Cl**
empirical formula	$C_{56}H_{56}Cu_8O_8 \cdot 8C_4H_8O$	$C_{50}H_{58}Cu_4Li_2O_8$	$C_{22}H_{30}BrCuMgO_4$	$C_{22}H_{30}ClCuMgO_4$
fw	1942.16	1055.00	526.22	481.76
temp (K)	173	173	173	173
wavelength (λ, Å)	Cu Kα (1.541 84)	Mo Kα (0.710 73)	Cu Kα (1.541 84)	Cu Kα (1.541 84)
cryst syst	tetragonal	orthorhombic	orthorhombic	orthorhombic
space group	$P4/n$ (No. 85)	$Pbca$ (No. 61)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	18.15205(9)	17.96778(17)	8.18331(6)	7.9461(15)
b (Å)		17.60950(18)	8.43100(6)	8.5104(7)
c (Å)	13.48120(9)	30.1255(4)	33.1182(2)	33.255(3)
V (Å^3)	4442.01(4)	9531.82(18)	2284.94(3)	2248.9(5)
Z	2	8	4	4
ρ_{calcd} (g cm^{-3})	1.452	1.470	1.530	1.423
θ range (deg)	3.44−72.46	3.72−32.46	2.67−71.32	2.66−72.30
μ (mm^{-1})	2.549	1.813	3.868	2.941
no. of rflns collected	40 837	119 452	31 950	5720
no. of unique rflns (R_{int})	4398 (0.0345)	15 909 (0.0494)	4480 (0.0217)	3779 (0.0391)
no. of params	165	617	282	264
goodness of fit on F^2	1.148	1.131	1.101	1.179
R1 ($F > 4\sigma(F)$)	0.0577	0.0563	0.0163	0.0610
wR2	0.2240	0.1410	0.0434	0.1467

data for all compounds. Full details of the X-ray structure solutions, including the handling of any disorder present in the structures, is given in the Supporting Information. The absolute structure of **3-Br** was determined by a combination of *R*-factor tests ($R_1^+ = 0.0163$, $R_1^- = 0.0294$) and by use of the Flack parameter ($\chi^+ = 0.000(10)$, $\chi^- = 1.018(10)$). Similarly for **3-Cl** $R_1^+ = 0.0610$, $R_1^- = 0.0687$ and $\chi^+ = 0.00(4)$, $\chi^- = 1.00(4)$. The crystal structure data have been deposited with the Cambridge Crystallographic Data Center under deposition numbers CCDC 882792 (**1**), 882793 (**2**), 882794 (**3-Br**) and 882795 (**3-Cl**). This material can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.

■ RESULTS AND DISCUSSION

(2-Methoxyphenyl)copper(I). The synthesis of (2-methoxyphenyl)copper was first reported by Camus and Marsich in 1968, where it was observed that in comparison to phenylcopper and tolylcopper complexes it was less air and temperature sensitive and more soluble in organic solvents.[26] The reported synthesis of this complex was from the reaction of (2-methoxyphenyl)lithium with copper(I) bromide; however, the reproducibility of the reaction was poor, due in part to contamination from lithium (most likely in the form of cocomplexed (2-methoxyphenyl)lithium). We therefore adopted an alternative synthesis route via reaction of the Grignard (C_6H_4OMe-2)MgCl with copper(I) chloride in THF to give a reproducible and high-purity yield of the orange crystalline product $[Cu(C_6H_4OMe\text{-}2)]_8 \cdot 8THF$ (**1**; see the Experimental Section). Though it is somewhat complicated due to the highly aggregated nature of the complex, the ^1H NMR spectrum of **1** is fully consistent with Camus' previously reported spectroscopic analysis of this compound.[27]

A solid-state structure of (2-methoxyphenyl)copper crystallized from toluene was previously reported in 1971; however, the data were reported to be of poor quality due to "decomposition of the crystal" during the data collection and are consequently not included in the Cambridge Structural Database.[28] Hence, in order to allow comparisons to be drawn with the novel lithium and Grignard derived (2-methoxyphenyl)cuprates discussed below, a new structural analysis of **1** is briefly reported herein. Note that the crystals of **1** obtained in this work were from a THF solution and contain noncoordinating THF within the crystal lattice, whereas the 1971 structural analysis by Camus contained toluene molecules with the lattice, thus giving rise to very different crystallographic parameters. However, in both cases octomeric $[Cu(C_6H_4OMe\text{-}2)]_8$ aggregates are observed, as shown in Figure 3 for **1**.

The structure of **1** is best considered as consisting of two tetrameric rings which lie on top of one another in a staggered conformation, so that the aryl group in one ring lies above a copper atom in the ring below. The rings are held together via coordination from anisyl methoxy oxygens in one ring to the copper centers in the adjacent ring (Cu(1)−O(7), 2.350(3) Å; Cu(2)−O(17), 2.387(3) Å), and there is no evidence of any intra-ring Cu−O interactions. Cu−C_{ipso} bond distances range from 2.013(4) to 2.051(4) Å and are therefore comparable to analogous Cu−C_{ipso} distances in tetrameric arylcuprates such as $[Cu_4Mes_4]$ (Mes = $C_6H_2Me_3$-2,4,6; 1.986(10)−1.999(9) Å)[29,30] and $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$ (1.994(2)−2.102(2) Å)[31] and are indicative of Cu−C−Cu two-electron−three-center (2e−3c) bonding. The Cu−C−Cu angles within the rings are acute (Cu(1)−C(12)−Cu(1A), 74.66(12)°; Cu(2)−C(2)−Cu(2A), 75.00(13)°) and are also typical for 2e−3c bonding of an aryl group to two copper atoms.[29−31] There is no evidence for Cu−C interactions between the tetrameric rings in **1**, the shortest Cu···C inter-ring distance being 3.130 Å. The shortest inter-ring Cu···Cu distance of 2.690 Å is shorter than the combined van der Waals radii of two copper atoms but is not thought to represent any significant bonding interaction: computational studies have shown that solid-state Cu(d^{10})−Cu(d^{10}) interactions are likely to be very weak in nature with Cu(I)···Cu(I) distances primarily governed by the presence of other supramolecular interactions within the crystal lattice.[32]

Lithium 2-Methoxyphenylcuprate 2. Reaction of (2-methoxyphenyl)copper (**1**) with (2-methoxyphenyl)lithium in toluene/THF gave a yellow solution from which crystals of $[Cu_4Li_2(C_6H_4OMe\text{-}2)_6(THF)_2]$ (**2**) were grown (Scheme 1). The solid-state structure for complex **2**, as determined using

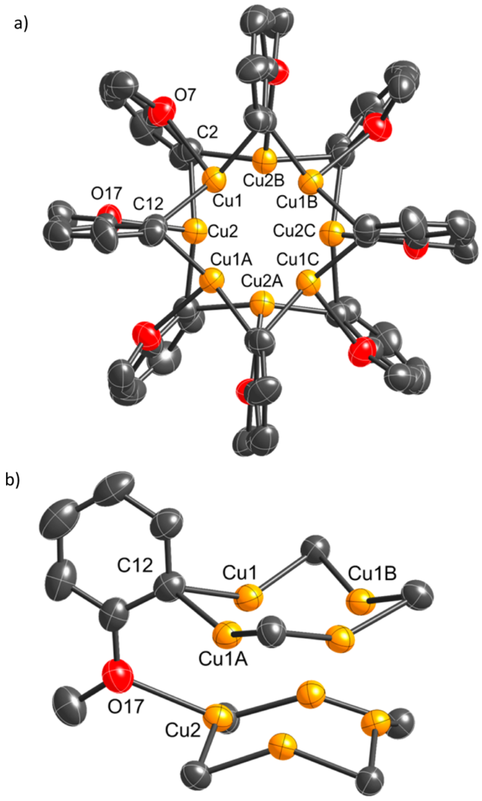
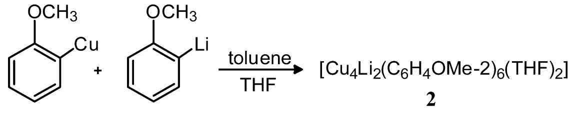


Figure 3. (a) Molecular structure of $[Cu(C_6H_4OMe\text{-}2)]_8\cdot 8THF$ (**1**). Hydrogen atoms and solvent THF molecules are omitted for clarity. (b) Simplified view of **1** showing the aryl ipso carbon atoms and just one of the methoxyphenyl groups. Thermal ellipsoids are displayed at the 30% probability level. Symmetry transformations used to generate equivalent atoms: (A) $y, -x + {}^3/_2, z$; (B) $-y + {}^3/_2, x, z$.

single-crystal X-ray diffraction, is shown in Figure 4, with key bond lengths and angles given in Table 2.

Scheme 1. Synthesis of Lithium Diarylcuprate 2



Lithium organocuprate **2** possesses a copper to lithium ratio of 2/1, despite the fact that it was formed from an equimolar mixture of its organocopper and organolithium precursors. Similar copper-rich lithium homocuprates with Cu/Li ratios greater than 1 are well-known in the literature and include the anionic clusters $[Cu_4LiPh_6]^-$ [12] and $[Cu_3Li_2Ph_6]^-$ [13] and the neutral complex $[Cu_3LiMes_4]$.[15] These species have been speculated to arise due to interaggregate exchange between $Cu_2Li_2R_4$ and Cu_4R_4 molecules in solution.[33,34]

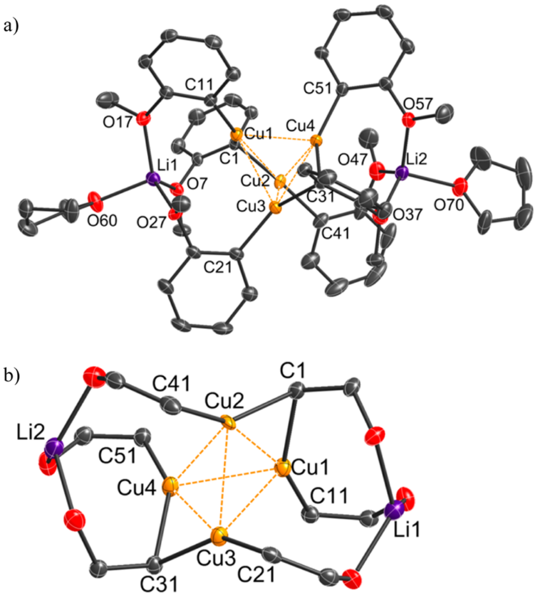


Figure 4. (a) Molecular structure of $[Cu_4Li_2(C_6H_4OMe\text{-}2)_6(THF)_2]$ (**2**), with hydrogen atoms and disorder in the THF molecules omitted for clarity. (b) Depiction of the core connectivity in **2**, omitting all other atoms. Thermal ellipsoids are displayed at the 40% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[Cu_4Li_2(C_6H_4OMe\text{-}2)_6(THF)_2]$ (2)

Cu(1)−C(11)	1.924(3)	Li(1)−O(7)	1.970(6)
Cu(1)−C(1)	1.992(3)	Li(1)−O(17)	1.953(6)
Cu(2)−C(1)	1.998(3)	Li(1)−O(27)	1.921(7)
Cu(2)−C(41)	1.922(3)	Li(1)−O(60)	1.964(6)
Cu(3)−C(21)	1.925(3)	Li(2)−O(37)	1.951(7)
Cu(3)−C(31)	1.980(3)	Li(2)−O(47)	1.940(7)
Cu(4)−C(31)	1.991(3)	Li(2)−O(57)	1.924(7)
Cu(4)−C(51)	1.911(3)	Li(2)−O(70)	1.959(7)
C(1)−Cu(1)−C(11)	141.39(13)	C(31)−Cu(4)−C(51)	139.57(14)
C(1)−Cu(2)−C(41)	144.30(13)	Cu(1)−C(1)−Cu(2)	76.71(12)
C(21)−Cu(3)−C(31)	145.05(13)	Cu(3)−C(31)−Cu(4)	77.26(12)

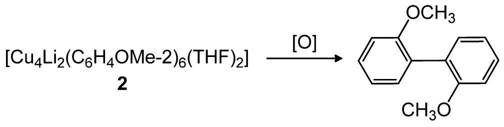
Closer analysis of the structure of **2** reveals the aggregate to be constructed from two $[Cu_2(C_6H_4OMe\text{-}2)_3]^-$ anionic organocuprate units joined together by two THF-solvated lithium cations. Within each of the $[Cu_2R_3]^-$ units there are two different types of aryl groups: the first bridges the two copper(I) atoms symmetrically to give a 3c−2e bond with Cu−C distances in the range 1.980(3)−1.998(3) Å (mean 1.990 Å). The second type of aryl group is terminal to just one Cu(I) atom, resulting in the formation of shorter Cu−C distances in the range 1.911(3)−1.925(3) Å (mean 1.920 Å) indicative of 2c−2e bonds. A similar but ion-separated $[Cu_2Mes_3]^-$ anion has previously been reported that adopts an equivalent motif, in which the two terminal mesityl groups form 2c−2e bonds with the Cu atoms (Cu−C range 1.923(8)−1.925(8) Å) and the central bridging mesityl group forms a longer 3c−2e bond (Cu−C range 2.003(8)−2.020(7) Å).[7] However, unique to **2**, the two $[Cu_2R_3]^-$ cuprate units are held together via coordination of lithium cations by the methoxy oxygen atoms with Li−O(Me) distances in the range 1.921(7)−1.970(6) Å (mean 1.943 Å). The coordination sphere of the lithium is completed by a single THF molecule (Li−O, 1.959(7) and 1.964(6) Å).

In contrast to previously reported amino-substituted homocuprates such as **III** (Figure 2), there are no $Li-C_{ipso}$ interactions evident within the solid-state structure of **2**. The bonding behavior of the methoxyphenyl groups therefore also differs significantly from that observed for the parent homometallic (2-methoxyphenyl)lithium complex, which adopts a dimeric structure in THF solution exhibiting both $Li-C_{ipso}$ and Li−OMe coordination.[35] In the case of **2** this can be rationalized by the strong carbophilicity of copper(I) in comparison to that of lithium. However, despite the absence of any Li−C_{ipso} bonding complex **2** still forms a CIP structure as opposed to a SSIP structure (Figure 1), which is rare for a lithium organocuprate in the presence of THF[17,36] and can be attributed to the strong propensity of the anisyl oxygen atoms toward lithium cation coordination.

At first glance the four copper atoms in **2** appear to from a central tetrahedron with Cu⋯Cu distances within the range 2.476(5)−2.824(6) Å and C−Cu−C bond angles distorted from linearity and pointing toward the center of the tetrahedron (mean C−Cu−C, 142.74°). However, as discussed above for **1** and on the basis of previous bonding studies,[32] this should not be automatically interpreted to support the existence of any significant copper(I)−copper(I) bonding. Nevertheless, the Cu_4 cluster does differ from previously reported $Cu(I)_4$ clusters—for example $[Cu_4I_6]^{2-}$,[37] $[Cu_4(SPh)_6]^{2-}$,[38] and $[Cu_4(SePh)_6]^{2-}$ [39]—in that in **2** only two of the six anionic ligands directly bridge copper atoms (these being the central aryl groups in the $[Cu_2R_3]^-$ units), and instead it is the peripheral Li−O(anisyl) bonding which must therefore play a large part in the supramolecular assembly of the structure.

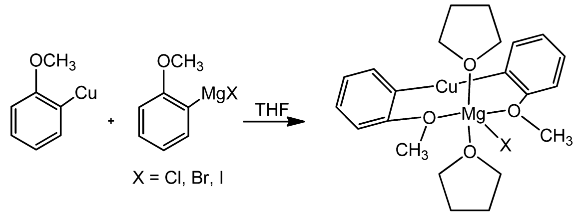
On exposure to atmospheric oxygen, the lithium organocuprate **2** was observed to decompose via oxidative coupling of the aryl groups to give small quantities of 2,2′-dimethoxybiphenyl (Scheme 2). By using the controlled introduction of nitrobenzene as the oxidizing agent in place of atmospheric dioxygen, we have been able to improve the yield of this coupling reaction to close to quantitative (>95%). In addition and as noted in Introduction, the application of lithium (2-methoxyphenyl)cuprate **2** in conjugate addition reactions is already well established in the organic chemistry literature.[23−25]

Scheme 2. Oxidative Homocoupling of 2-Methoxylphenyl



Magnesium Grignard (2-Methoxyphenyl)cuprates 3-X (X = Cl, Br, I). Despite their widespread application in synthesis,[1] studies on the structures of Grignard organocuprates (commonly prepared from the reaction of a copper(I) salt with 2 equiv of Grignard reagent) are sparse in the literature, even in comparison to lithium organocuprates. We recently reported upon the first structurally characterized examples of Grignard organocuprates: the iodo Grignard CIP organocuprate $[Ph_4Cu_2(Mg(OEt_2)I)_2]$ and bromo Grignard CIP and SSIP organocuprates $[Cu_4Mg_2Mes_6Br_2]$ and $[Cu_2Mes_3]^-[MgBr(THF)_5]^+$, respectively.[7] Two related structures derived from diorganomagnesium reagents have also been reported: $[Cu_4MgPh_6(OEt_2)]$[12] and $[Cu_4Mes_4][\mu\text{-}SAr]_2[MgSAr]_2$ (SAr = $SC_6H_4CH(Me)NMe_2$-2).[40,41] In an expansion of these previous studies, employment of the 2-methoxyphenyl ligand has led to the first structural characterization of a functionalized Grignard organocuprate. Thus, the reaction of (2-methoxyphenyl)copper with the corresponding aryl Grignard (itself prepared from the reaction of the aryl halide with magnesium metal) in THF solution gave the magnesium Grignard organocuprate complexes **3-X** (X = Cl, Br, I), as shown in Scheme 3.

Scheme 3. Synthesis of Magnesium Grignard Diarylcuprates 3-X (X = Cl, Br, I)



3-X

The preparation of **3-Br** and **3-Cl** gave crystalline products which were shown by X-ray diffraction to exist as isostructural complexes with similar crystallographic parameters (see Table 1). The molecular structure of **3-Br** is shown in Figure 5, and selected bond lengths and angles for **3-Br** and **3-Cl** are compared in Table 3.

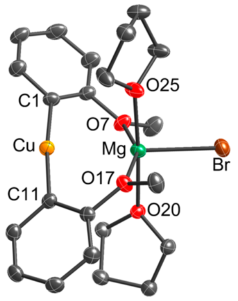


Figure 5. Molecular structure of $[Cu(C_6H_4OCH_3\text{-}2)_2Mg(THF)_2Br]$ (**3-Br**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are displayed at the 40% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in 3-X (X = Cl, Br)

	X = Br	X = Cl
Cu−C(1)	1.9176(15)	1.923(6)
Cu−C(11)	1.9190(16)	1.919(6)
Mg−O(7)	2.0756(13)	2.075(5)
Mg−O(17)	2.0973(12)	2.091(5)
Mg−O(20)	2.0771(12)	2.071(5)
Mg−O(25)	2.0559(13)	2.061(5)
Mg−X	2.5183(6)	2.352(3)
C(1)−Cu−C(11)	172.57(7)	172.6(3)
O(7)−Mg--O(17)	155.37(6)	154.1(2)
O(7)−Mg−X	101.90(4)	101.94(16)
O(17)−Mg−X	102.54(4)	103.77(16)

Both **3-Br** and **3-Cl** are monomeric but dinuclear R_2CuMgX complexes, with a 1/1 stoichiometric ratio of copper to magnesium halide. This ratio is therefore as expected from the original reaction stoichiometry but differs from that observed in the homologous copper-rich organocuprate **2**, with Cu/Li = 2/1 (vide supra). In addition, the structure of **3-X** contrasts with those of previously reported Grignard organocuprates, being the first example of a monomeric CIP complex. Although the crystals of **3-Br** and **3-Cl** were obtained from THF solutions, the organocuprates do not form THF-solvated SSIP structures, as might be initially expected (Figure 1), but rather give CIP structures, albeit with no apparent C_{ipso}−Mg bonding. Similar to the case for lithium organocuprate **2**, the formation of a CIP structure can be attributed to the strong coordination of the s-block metal by the anisole methoxy group.

Closer inspection of the makeup of **3-X** reveals two key structural components: a RCuR anionic fragment and a $MgX(THF)_2$ cationic fragment. The anionic RCuR organocuprate unit is close to linear at the copper center (C–Cu–C, 172.57(7)° (**3-Br**) and 172.6(3)° (**3-Cl**)) with mean Cu–C distances of 1.918 Å (**3-Br**) and 1.921 Å (**3-Cl**). These copper angles and distances are consistent with the presence of 2c–2e copper(I)–carbon bonds and are directly comparable in length to similar 2c–2e Cu–C bonds in **2** (mean 1.920 Å) as well as being significantly shorter than the 3c–2e bond lengths observed in **1** (mean 2.147 Å) and **2** (mean 1.990 Å). The diarylcuprate unit is connected to the Mg center via coordination of the two methoxy groups, with mean Mg–O distances of 2.086 Å (**3-Br**) and 2.083 Å (**3-Cl**). The magnesium metal centers are additionally complexed by two THF oxygens and a halide anion. The geometry at the magnesium is close to a square-based pyramid with the halide in the apical position: the sum of cis O–Mg–O bond angles is 358.57° in **3-Br** and 358.4° in **3-Cl**. The position trans to the halide is effectively shielded by the copper atom, thus preventing any additional donor coordination at this site (Cu···Mg distances are 2.7409(6) Å in **3-Br** and 2.765(2) Å in **3-Cl**). The positioning of the methyl groups as well as twisting in the THF molecules results in a chiral configuration for the molecule in the solid state, although the bulk product is racemic.

Although it was not possible to prepare crystals of the iodo Grignard derivative **3-I** suitable for X-ray diffraction analysis, the NMR data of this complex are almost identical with those observed for both **3-Br** and **3-Cl**, suggesting a similar Grignard diarylcuprate structure (see the Experimental Section). In addition, all **3-X** complexes exhibit aryl–aryl oxidative coupling, either slowly over several days in the presence of atmospheric oxygen or quantitatively over 1 h in the presence of nitrobenzene, to give 2,2′-dimethoxybiphenyl in a reaction analogous to that reported for **2** (Scheme 2).

SUMMARY AND CONCLUSIONS

Despite recent advances in the understanding of organocuprate chemistry, studies concerning the structures of organocuprates containing functionalized organo groups remain limited to a few examples of amino-functionalized diaryl lithium cuprates. Given the important role functionalized organocuprates can play in natural product and other organic synthesis protocols, we set out to explore the coordination chemistry of the 2-methoxyphenyl group in lithium and Grignard organocuprates.

In a revisitation of early work by Camus,[27,28] (2-methoxyphenyl)copper (**1**) was prepared and shown to exist in the solid state as an octameric aggregate formed from two tetrameric copper(I)–aryl rings conjoined via copper–oxygen (OMe) bonding interactions. This organocopper species was subsequently used in the preparation of the novel lithium organocuprate $[Cu_4Li_2(C_6H_4OMe\text{-}2)_6(THF)_2]$ (**2**) and the Grignard organocuprates $[Cu(C_6H_4OCH_3\text{-}2)_2Mg(THF)_2X]$ (**3-X**; X = Cl, Br, I). Solid-state structural studies show that the donor methoxy group plays a large role in determining the structures adopted by these organocuprate species, coordinating in each case to the s-block metal center with no copper–oxygen bonding present. Most notably, this intramolecular methoxy coordination to lithium or magnesium is preferred over coordination of solvent THF, thus giving contact ion pair (CIP) structures rather than THF-solvated separated ion pairs (SSIPs) as observed for nonfunctionalized arylcuprates. Previous studies have shown how a knowledge of the organocuprate structure can be key to understanding the reactivity and mechanism of reaction of these species,[3] with the balance between CIP and SSIP species being particularly important in this respect.[36] In the past such structural studies have predominately concentrated upon the role of the solvent or the steric size of the organo group. However, from this work it is apparent how the presence of additional functional groups on the organo group can also play a key role in determining the overall structure and aggregation of these reagents. It is through such studies that we are able to build a more thorough understanding of these important and widely used reagents.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files giving details of the crystal structures of **1**, **2**, **3-Br**, and **3-Cl**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: r.davies@imperial.ac.uk. Tel: +44 207 5945754.

Notes

The authors declare no competing financial interest.

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