Copper Complexes

DOI: 10.1002/anie.201303783

The X-ray Crystal Structure of a Cuprate–Carbonyl π-Complex**

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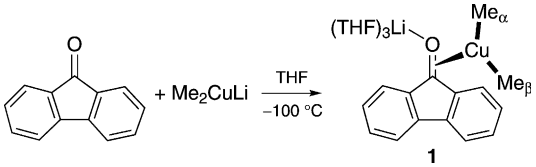
Dedicated to Professor Gerard van Koten on the occasion of his 70th birthday

Complexes between copper reagents and double-bonds have been proposed as intermediates in a number of synthetically important reactions.[1,2] Many η^2-complexes between organocuprates and carbon–carbon double-bonds, which are intermediates in 1,4-addition reactions of α,β-unsaturated carbonyl compounds, have been observed by using NMR spectroscopy.[3] Moreover, η^2-*O*,*C*-complexes between organocopper compounds and carbon–oxygen double-bonds have been proposed as intermediates in 1,2-additions to carbonyl compounds,[1] for example, copper-catalyzed asymmetric induction reactions.[4] Carbophilic additions to thiocarbonyl compounds, mediated by organocuprates, have been explained in terms of η^2-*S*,*C*-complexes of carbon–sulfur double-bonds.[5] However, there has been no report of an X-ray structure for any of these π-complexes.

Therefore, we applied our rapid-injection techniques, which were previously used to prepare several important intermediates,[5–8] to screen a number of typical aldehydes and ketones for complex formation with Me_2CuLi,[9] and we discovered such a species with unusual stability, which has allowed us to prepare it on a larger scale and grow high-quality crystals (see the Supporting Information). We now report the first X-ray crystal structure[10] of a cuprate–carbonyl π-complex, **1** (Scheme 1 and Figure 1).



Scheme 1. Preparation of Me_2CuLi–fluorenone π-complex **1**.

The most significant feature of **1** is the doubly complexed carbonyl group involving the relatively rare side-on π-bonding to the copper atom, as well as the more common end-on σ-bonding to the lithium atom via a lone pair.[11] The Me_α-Cu-Me_β angle in **1** (C1-Cu-C2 104°) is considerably distorted from the linear arrangement in $[Li([12]crown\text{-}4)_2]^+[MeCuMe]^-$ (C-Cu-C 180°, Cu–C 1.935(8) Å).[12] The Me_α–Cu bond is significantly longer than the Me_β–Cu bond (see Figure 1 caption). The carbon–oxygen bond in **1** (C3–O1 1.326(2) Å) is significantly longer than in fluorenone (1.220(2) Å).[13] A Ni^0 η^2-*O*,*C*-complex of fluorenone has the same carbon–oxygen bond length (1.326(5) Å) as **1**.[14]

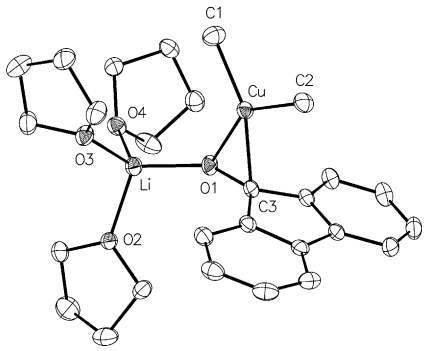


Figure 1. ORTEP representation of **1** (ellipsoids set at 50% probability, hydrogen atoms omitted for clarity). Selected bond distances [Å]: Cu–C1 1.957(2), Cu–C2 1.934(1), Cu–C3 1.977(1), C3–O1 1.326(2), Cu–O1 1.958(1), Li–O1 1.864(3), Li–O2 1.958(3), Li–O3 1.915(3), Li–O4 1.960(3).

Another salient feature of **1** is the essentially coplanar arrangement of the two methyl groups and the three atoms of the copper–carbonyl bond. Specifically, C1 is −0.068 Å from the O1-Cu-C3 plane and C2 is 0.047 Å from it. This geometry represents an approximately 2° clockwise twist of the C1–C2 axis relative to the O1–C3 bond. Therefore, dialkyl cuprate complexes of double-bonds can be described as pseudo square-planar, which was originally proposed on the basis of NMR spectroscopy.[7,8]

Also noteworthy is the approximately tetrahedral lithium atom, bonded to the cuprated carbonyl group as well as three tetrahydrofuran (THF) ligands. The former lithium–oxygen bond length is significantly less than the latter bond lengths (see Figure 1 caption). Lithium methyl(di-*tert*-butylphosphido)cuprate(I)[15] and lithium methyl(phenylthio)cuprate(I)[16] also have structures in which a lone pair of electrons is donated from a heteroatom to a $(THF)_3Li^+$ moiety in the solid state; they can be considered contact ion pairs.[2]

Rapid-injection NMR involves impelling a substrate solution from a capillary tube into a reagent solution in a spinning NMR tube, mixing them in a fraction of a second in the spectrometer probe at a controlled temperature.[17] Thus, **1** was first prepared by injecting a solution of fluorenone (60 μL, 0.5 M) in $[D_8]$THF into a solution of $Me_2CuLi{\cdot}LiI$ (30 μmol/420 μL) in $[D_8]$THF/$[D_6]$benzene (7:1) at −100 °C. New peaks appeared at $\delta = -0.66$ and −1.54 ppm

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[**] This work was supported by National Science Foundation (USA) grants 1012493 and 0321056.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303783.

for the methyl groups in the ^{1}H NMR spectrum of **1** (Figure 2, >95% conversion after 0.5 h). The corresponding peaks in the ^{13}C NMR spectrum appeared at $\delta = -8.40$ and 6.04 ppm. The ^{13}C resonance for the carbonyl carbon moved dramatically upfield from $\delta = 193.87$ ppm in fluorenone to $\delta =$ 99.94 ppm in **1**.

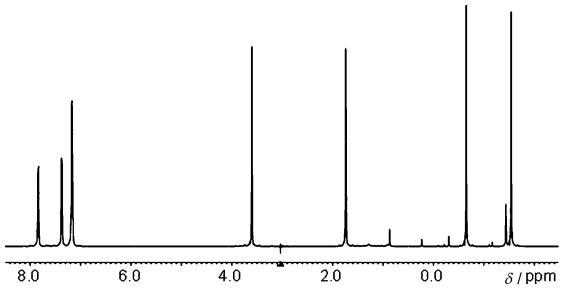

Figure 2. ^{1}H NMR spectrum of **1** from the rapid injection experiment at −100 °C (residual THF, $\delta = 1.73$ and 3.58 ppm). Also present was a small amount of Me_2CuLi ($\delta = -1.44$ ppm, compare with Figure 3).

A heteronuclear multiple bond correlation plot (HMBC, Figure 3, left) has a cross-peak (lower left quadrant) between the downfield methyl hydrogen atoms ($\delta = -0.66$ ppm), which are assigned to Me_α, and the carbonyl carbon ($\delta =$ 99.94 ppm), which is *trans* to it. *Trans* coupling across copper is typically larger than *cis*.[5–9]

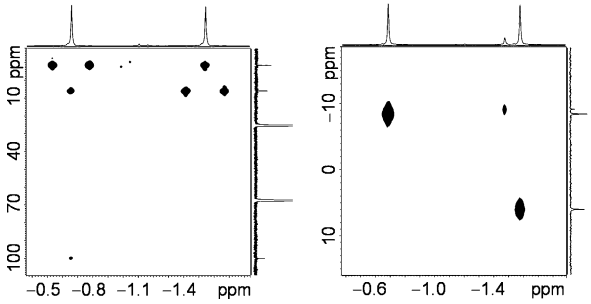

Figure 3. ^{1}H-^{13}C HMBC (left) and ^{1}H-^{13}C HMQC (right) plots for **1** at −100 °C. The minor species in the latter is Me_2CuLi (^{13}C NMR, $\delta = -9.16$ ppm, compare with Figure 2; these 2D NMR plots were from different samples).

A heteronuclear multiple quantum coherence plot (HMQC, Figure 3, right) has a cross-peak (lower right quadrant) between the upfield methyl hydrogen atoms ($\delta =$ −1.54 ppm) and the downfield methyl carbon ($\delta = 6.04$ ppm), which are assigned to Me_β. It is highly unusual for the ^{1}H NMR shift of Me_β to be the upfield signal.[8,9]

A possible explanation for the anomalous upfield shift of Me_β is shielding by an aromatic ring current, owing to the position of this methyl group vis-a-vis the central 5-membered ring (Figure 1). This aromaticity requires a cyclopentadienyl anion, which in turn requires the transfer of electron density from the dimethylcuprate moiety to the cyclopentadiene substructure, and it implies a significant degree of Cu^{III} character, as proposed by Nakamura et al.[1]

Complex **1** was stable indefinitely at −100 °C, but decomposed at a significant rate upon warming to −10 °C ($t_{1/2} = 30$ min) to afford a 9:1 mixture of 1,2-adduct and ethane, the two possible reductive elimination products. While they did not observe ethane from the reaction of $Me_2CuLi{\cdot}LiI$ with fluorenone, House et al. reported reduction products and the 1,2-adduct.[18]

To recapitulate, fluorenone formed a relatively stable cuprate–carbonyl π-complex **1** with Me_2CuLi, which allowed us to obtain the first X-ray structure of a cuprate–double-bond complex. This result supports theoretical calculations, and most importantly, establishes that such complexes are viable intermediates.

Received: May 2, 2013
Published online: August 13, 2013

Keywords: cuprates · fluorenone · NMR spectroscopy · X-ray diffraction · π-complexes

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[10] CCDC 924288 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.

cam.ac.uk/data_request/cif. Data collected with an Agilent Xcalibur Atlas Gemini Ultra diffractometer with CrysAlisPro. Refined formula, $C_{27}H_{38}CuLiO_4$; $M_r = 497.08$; crystal dimensions $0.51 \times 0.27 \times 0.12$ mm; monoclinic, space group $P2_1/n$; unit cell $10.4113(2) \times 15.4241(3) \times 16.4037(4)$ Å (2563.40(10) Å^3), $Z = 4$, calculated density 1.288 g cm^{-3}; linear absorption coefficient 0.881 mm^{-1}; 0.7107 Å $Mo_{K\alpha}$ radiation; measurement temperature 99.95(10) K; $2\theta_{max}$ 65.61°; total reflections 80374, independent reflections 9167; $R(int) = 0.0612$, $R1 = 0.0440$, $wR2 = 0.1341$; highest peak 0.85 e Å^{-3}, deepest hole −0.33 e Å^{-3}; see also the Supporting Information for solution and refinement references.

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