

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/239948461>

First X-Ray Crystal Structure and Internal Reference Diffusion-Ordered NMR Spectroscopy Study of the Prototypical Posner Reagent, $\text{MeCu(SPh)Li(THF)}(3)$

ARTICLE in CHEMISTRY - A EUROPEAN JOURNAL · JULY 2013

Impact Factor: 5.73 · DOI: 10.1002/chem.201301415 · Source: PubMed

CITATIONS

2

READS

66

8 AUTHORS, INCLUDING:



Thomas Heavey

Boston University

3 PUBLICATIONS 5 CITATIONS

SEE PROFILE

Michael D Murphy

University of North Carolina at Charlotte

25 PUBLICATIONS 487 CITATIONS

SEE PROFILE

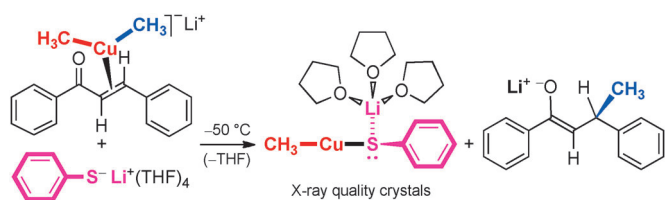


Craig Alan Ogle

University of North Carolina at Charlotte

84 PUBLICATIONS 1,384 CITATIONS

SEE PROFILE



Grow slow: The usual direct treatment of MeLi and CuSPh did not yield X-ray quality crystals of MeCu(SPh)Li. An indirect method starting from Me₂CuLi·LiSPh and chalcone afforded the desired crystals by the slow reaction of the intermediate π -complex

(see scheme). This strategy produced the first X-ray crystal structure of a Posner cuprate. A complementary NMR study showed that the contact ion pair was also the main species in solution.

Cuprates

S. H. Bertz,* R. A. Hardin,
T. J. Heavey, D. S. Jones, T. B. Monroe,
M. D. Murphy, C. A. Ogle,*
T. N. Whaley ■■■■-■■■■

First X-Ray Crystal Structure and Internal Reference Diffusion-Ordered NMR Spectroscopy Study of the Prototypical Posner Reagent, MeCu(SPh)Li(THF)₃



First X-Ray Crystal Structure and Internal Reference Diffusion-Ordered NMR Spectroscopy Study of the Prototypical Posner Reagent, $\text{MeCu}(\text{SPh})\text{Li}(\text{THF})_3$

Steven H. Bertz,* Richard A. Hardin, Thomas J. Heavey, Daniel S. Jones, T. Blake Monroe, Michael D. Murphy, Craig A. Ogle,* and Tara N. Whaley^[a]

Dedicated to Professor Gary Posner, an organocopper pioneer, a gentleman and a scholar, on the occasion of his 70th birthday

Heterocuprates, $\text{R}(\text{Het})\text{CuLi}$, are a successful solution to the efficiency problem of homocuprates, R_2CuLi ("Gilman reagents"), which only transfer one equivalent of R in most applications.^[1,2] The non-transferred ligand, Het, in these mixed cuprates^[3] is bonded to copper via a heteroatom (e.g., $\text{Het}=\text{SPh}$, NCy_2 , PPh_2). The first synthetically useful heterocuprates were the phenylthiocuprates, introduced by Posner et al.^[4] They were followed by more stable and more reactive amidocuprates^[5] and phosphidocuprates,^[5–7] nevertheless, thiocuprates are still very useful, as the usual precursor (CuSPh) is stable and commercially available; moreover, they are key intermediates in some interesting reactions of homocuprates.^[2] By using a novel preparative procedure (**1**; Scheme 1), we have been able to obtain the first X-ray crystal structure of a Posner cuprate, $\text{MeCu}(\text{SPh})\text{Li}(\text{THF})_3$ (**1**; Figure 1), and by using diffusion-ordered NMR measurements, we have found that this structure persists in solution.

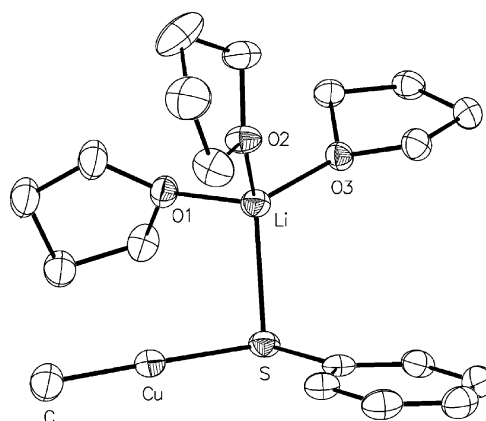
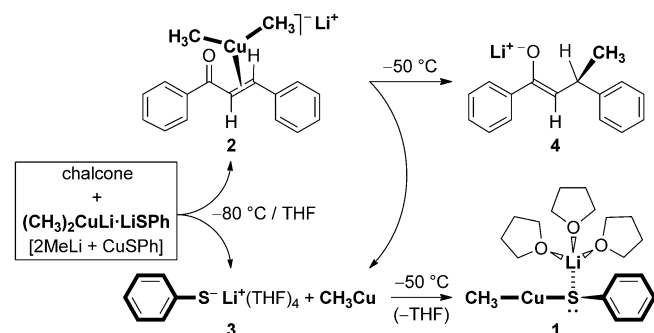


Figure 1. ORTEP plot (50% ellipsoids) for **1**. Selected bond distances [Å] and angles [°]: Cu–C, 1.914(3); Cu–S, 2.1797(7); Li–S, 2.431(4); Li–O1, 1.920(5); Li–O2, 1.914(5); Li–O3, 1.914(4); C–Cu–S, 176.15(12); Cu–S–Li, 98.94(10).



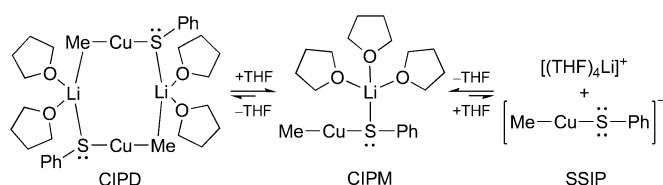
Scheme 1. Slow synthesis of **1** by an indirect method.

Crystals of **1**, grown from solutions that had been prepared by adding MeLi (1 equiv) to CuSPh as usual,^[4] were not suitable for X-ray crystallography, as they grew too quickly. Therefore, we set out to prepare $\text{MeCu}(\text{SPh})\text{Li}$ by an alternative procedure, which involved the treatment of MeCu with PhSLi , both formed in situ. To generate MeCu slowly, we developed a modification of the method that Bertz et al.^[8] used to prepare halide-free MeCu , which was based on the observation by House et al.^[9] that the 1,4-addition of Me_2CuLi to α -enones yielded MeCu and a lithium enolate. Instead of 2-cyclohexenone, we used chalcone for the current application, as its conjugate addition reaction with organocuprates is much slower.^[10]

Accordingly, chalcone was added to a solution of $\text{Me}_2\text{CuLi} \cdot \text{LiSPh}$, prepared from MeLi (2 equiv) and CuSPh , and the resulting solution, which contained cuprate–olefin π -complex **2**^[10] and $\text{PhSLi}(\text{THF})_4$ (**3**), was stored at approximately -50°C . The ensuing "slow synthesis" proceeded via the usual 1,4-addition reaction to give soluble enolate **4** and MeCu , which was intercepted efficiently, as no amorphous yellow precipitate was observed. Instead, we obtained the desired product **1** as exquisite, X-ray quality crystals, which allowed us to determine its structure.^[11]

[a] Prof. Dr. S. H. Bertz, R. A. Hardin, T. J. Heavey, Prof. Dr. D. S. Jones, T. B. Monroe, Dr. M. D. Murphy, Prof. Dr. C. A. Ogle, T. N. Whaley
Department of Chemistry
University of North Carolina–Charlotte
Charlotte, NC 28223 (USA)
Fax: (+1) 704-687-0960
E-mail: sbertz1@uncc.edu
cogle@uncc.edu

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201301415>; including lists of bond lengths and angles for **1** and details of M_w determinations.



Scheme 2. CIPD–CIPM–SSIP equilibria for MeCu(SPh)Li in THF (Note that 1 equiv of CIPD yields 2 equiv of CIPM or SSIP).

The Cu–C bond length in **1** (1.91 Å) is slightly shorter than it is in homocuprate [Me₂Cu][−][Li(12-crown-4)₂]⁺ (**5**; 1.93 Å)^[12] and phosphidocuprate [MeCu[P(*t*Bu)₂Li(THF)₃]₂][−] (**6**; 1.94 Å).^[7] The C–Cu–S angle in **1** is 176° versus 180° for the C–Cu–S angle in **5** and 179° for the C–Cu–P angle in **6**.

The Cu–S bond in **1** (2.18 Å) is marginally shorter than the Cu–P bond in **6** (2.22 Å), and the Li–S bond in **1** (2.43 Å) is significantly shorter than the Li–P bond in **6** (2.54 Å)^[7] (see the Supporting Information for lists of bond lengths and angles). It is interesting to note that the structures of these heterocuprates are very similar, with a lone

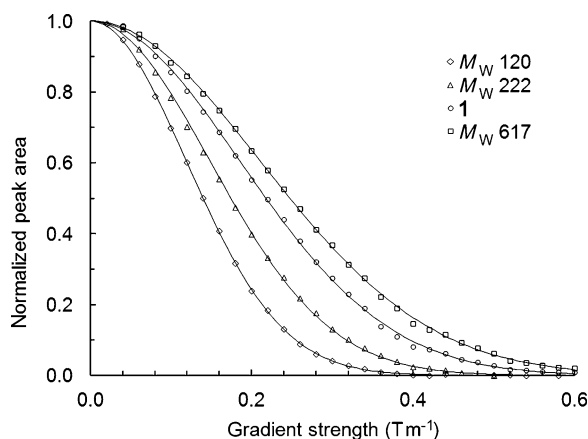


Figure 2. Diffusion attenuation curves for **1** (prepared from MeLi + CuSPh) and internal references with molecular weight (M_w) values shown in the key.

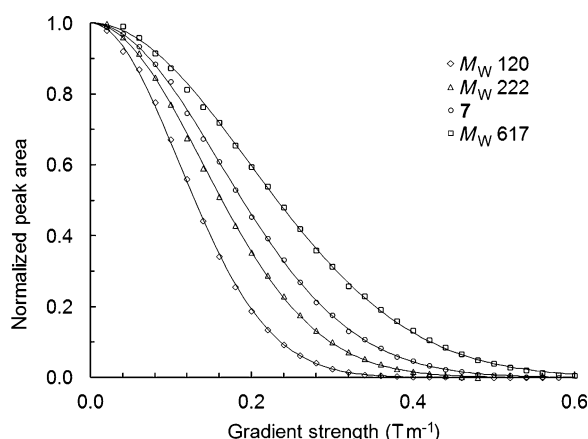


Figure 3. Diffusion attenuation curves for **7** (prepared from 2MeLi + CuSPh) and internal references with molecular weight (M_w) values shown in the key.

Table 1. Molecular weight data for selected organocopper compounds.^[a]

Reagent ^[b]	Solution species	M_{calcd}	M_{exptl}
MeCu(SPh)Li	MeCu(SPh)Li(THF) ₃ (1)	411	[CIPM]
	76 % CIPM	428	426/430
	[MeCuSPh] [−] [Li(THF) ₄] ⁺	483	[SSIP]
	[MeCu(SPh)Li(THF) ₂] ₂	648	[CIPD]
Me ₂ CuLi-LiSPh	Me ₂ CuLi(THF) ₃ (7)	317	[CIPM]
	65 % CIPM	342	342^[c]/342^[d]/337^[e]
	[Me ₂ Cu] [−] [Li(THF) ₄] ⁺	389	[SSIP]
	[Me ₂ CuLi(THF) ₂] ₂	490	[CIPD]
PhSLi	PhSLi(THF) ₃	332	[CIPM]
	14 % CIPM	395	395
	[PhS] [−] [Li(THF) ₄] ⁺ (3)	405	[SSIP]

[a] Conditions: −80 °C, 60 mM in [D₈]THF–[D₆]benzene (9:1). [b] Canonical representation. [c] The estimated uncertainty (95 % confidence level) in the mean for these three values is 340 ± 7 ($SE=1.67$, $t=4.30$). [d] Me₂CuLi from CuI. [e] Me₂CuLi from CuCN.

pair of electrons from the heteroatom coordinated to lithium, along with those from three THF ligands.

The solid state structures of copper reagents are important for theoretical reasons;^[13] nevertheless, when it comes to practical applications, the solution structures are of paramount importance.^[14,15] Solvent-separated ion pairs (SSIP) are present in THF, and contact ion pairs (CIP) are favored in diethyl ether, where the CIP is a dimer.^[14] The X-ray structure of **1** (Figure 1) shows that in the solid state, the CIP is a monomer, which suggests that it might also be monomeric in THF solution. Equilibria among contact ion pair dimer (CIPD), contact ion pair monomer (CIPM) and SSIP for MeCu(SPh)Li are shown in Scheme 2.

We have previously studied MeCu(SPh)Li and some of its π -complexes in [D₈]THF solution,^[16] but did not address the issue of solvation. To explore the solution structure of selected organocuprates, apparent molecular weights were determined by using the internal reference diffusion-ordered NMR method of Williard and co-workers.^[17] Figure 2 and Figure 3 show typical diffusion attenuation curves, and the results are summarized in Table 1 (see the Experimental Section for reference compounds).

The experimental values for the molecular weight of **1**, $M_{\text{exptl}}=426$ and $M_{\text{exptl}}=430$, fall between the calculated values, M_{calcd} , for CIPM and SSIP. The average, $M_{\text{exptl}}=428$, is consistent with 76 % CIPM and 24 % SSIP in THF solution. We round this to a 3:1 ratio of CIPM/SSIP, considering the experimental uncertainty (Table 1, footnote [c]). We cannot rule out a small amount of CIPD for this heterocuprate; nevertheless, Gschwind et al. have shown that for the homocuprate very little CIPD is present at equilibrium in THF.^[14]

The apparent molecular weight for the corresponding homocuprate, Me₂CuLi(THF)₃ (**7**), was measured starting from CuSPh, CuI, and CuCN, and all three determinations were very close to each other (<2 % difference between values). The measured molecular weight of **7** (from CuSPh) suggests that THF solutions contain 65:35 CIPM/SSIP under our conditions.

The fact that all three measured values for the homocuprate are the same within experimental uncertainty strongly suggests that the lithium salts (LiSPh, LiI or LiCN, respectively) from the metathesis reactions used to prepare the cuprate solutions are not intimately associated with the cuprate cluster. Therefore, we conclude that the corresponding anions (PhS[−], I[−] or CN[−], respectively) cannot be bonded to the copper atoms in these cuprates (i.e., they are not “higher order” cuprates).^[18]

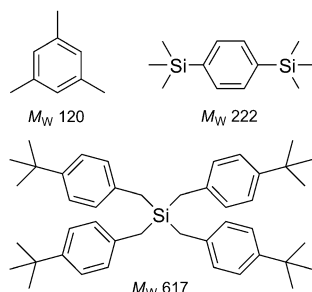
In contrast to **1** and **7**, which are mainly CIPM in solution, **3** is predominately a SSIP (ca. 86%). Interestingly, X-ray crystal structures of the 2,4,6-tri-*tert*-butyl^[19] and 2,4,6-triphenyl^[20] derivatives of **3** are CIPM with three THF ligands per lithium, as for **1** and **6**.

In conclusion, we have obtained the first single crystal X-ray structure of a Posner cuprate, MeCu(SPh)Li(THF)₃ (**1**), and shown that its solution structure in THF is largely the same (ca. 3:1 CIPM/SSIP). Finally, the solution structure of this heterocuprate is very similar to that of the Gilman reagent, Me₂CuLi(THF)₃ (**7**; ca. 2:1 CIPM/SSIP), which is independent of the cuprate precursor.

Experimental Section

Crystals of **1** were prepared by adding methylolithium in diethyl ether (6.30 mL, 1.60 M, 10.1 mmol, Sigma-Aldrich) to copper(I) thiophenylate (860 mg, 4.98 mmol, Sigma-Aldrich), suspended in dry THF (25 mL, freshly distilled from Na/benzophenone) under nitrogen in a dry Schlenk flask (100 mL), cooled to −78°C in a dry ice/acetone bath. The suspension was swirled and sonicated in an ultrasonic bath at 0°C until a homogeneous solution was obtained (ca. 0.1 h). The colorless solution was cooled to −78°C, and a solution of chalcone (1.00 g, 4.80 mmol) in dry THF (10 mL) was added with magnetic stirring. The resulting solution was stored at −47°C in a low temperature refrigerator for 7 days, during which time the color lightened from orange to pale yellow with the concomitant formation of pale yellow plates. A small sample of crystals was transferred under nitrogen with a spatula to a drop of Paratone-N oil on a cold glass slide (−40°C). An oil-coated crystal was picked up with a Cryoloop (0.4–0.5 mm) and transferred using Cryotongs (80 K) to the precooled goniometer head, which was placed in the cold stream (100 K nitrogen) of the diffractometer.^[11]

Preparation of NMR samples has been described.^[10,16] For details of the molecular weight measurements, see the Supporting Information. Reference compounds (internal standards)^[21] for these diffusion-ordered NMR studies are shown below:



CCDC-928158 (**1**) 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.

Acknowledgements

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

Keywords: aggregation • cuprates • NMR spectroscopy • S ligands • X-ray diffraction

- [1] a) G. H. Posner, *Org. React.* **1972**, *19*, 1–113; b) G. H. Posner, *Org. React.* **1975**, *22*, 253–400; c) G. H. Posner, *An Introduction to Synthesis Using Organocopper Reagents*, Wiley, New York, **1980**.
- [2] Both R groups are transferred in special cases: a) G. H. Posner, D. J. Brunelle, *Chem. Commun.* **1973**, 907–908; b) S. H. Bertz, G. Dabbagh, L. M. Williams, *J. Org. Chem.* **1985**, *50*, 4414–4415; c) S. H. Bertz, Y. Moazami, M. D. Murphy, C. A. Ogle, J. D. Richter, A. A. Thomas, *J. Am. Chem. Soc.* **2010**, *132*, 9549–9551.
- [3] Mixed cuprates RR'CuLi, where R' is attached through a heteroatom or a carbon atom, have two different groups bonded to Cu. For examples of the former, see refs. [4]–[7]. For examples of the latter, see ref. [16], and references cited therein.
- [4] a) G. H. Posner, C. E. Whitten, J. J. Sterling, *J. Am. Chem. Soc.* **1973**, *95*, 7788–7800; b) G. H. Posner, D. J. Brunelle, L. Sinoway, *Synthesis* **1974**, 662–663; c) G. H. Posner, C. E. Whitten, *Org. Synth.* **1976**, *55*, 122–127. For some applications, see: d) D. M. Knotter, D. M. Grove, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1992**, *114*, 3400–3410; e) E. Sperotto, G. P. M. van Klink, J. G. de Vries, G. van Koten, *Tetrahedron* **2010**, *66*, 9009–9020.
- [5] a) S. H. Bertz, G. Dabbagh, *Chem. Commun.* **1982**, 1030–1032; b) S. H. Bertz, G. Dabbagh, G. M. Villacorta, *J. Am. Chem. Soc.* **1982**, *104*, 5824–5826.
- [6] S. H. Bertz, G. Dabbagh, *J. Org. Chem.* **1984**, *49*, 1119–1122.
- [7] S. F. Martin, J. R. Fishpau, J. M. Power, D. M. Giolando, R. A. Jones, C. M. Nunn, A. H. Cowley, *J. Am. Chem. Soc.* **1988**, *110*, 7226–7228.
- [8] S. H. Bertz, A. S. Vellekoop, R. A. J. Smith, J. P. Snyder, *Organometallics* **1995**, *14*, 1213–1220.
- [9] a) H. O. House, J. M. Wilkins, *J. Org. Chem.* **1976**, *41*, 4031–4033; b) H. O. House, W. L. Respass, G. M. Whitesides, *J. Org. Chem.* **1966**, *31*, 3128–3141.
- [10] a) S. H. Bertz, R. A. Hardin, M. D. Murphy, C. A. Ogle, J. D. Richter, A. A. Thomas, *J. Am. Chem. Soc.* **2012**, *134*, 9557–9560; b) S. H. Bertz, S. K. Cope, R. A. Hardin, M. D. Murphy, C. A. Ogle, D. T. Smith, A. A. Thomas, T. N. Whaley, *Organometallics* **2012**, *31*, 7827–7838.
- [11] a) Data were collected on an Agilent Xcalibur Atlas Gemini Ultra diffractometer with CrysAlisPro. Refined formula, C₁₉H₃₂CuLiO₃S; *M_r* = 410.99; crystal dimensions, 0.43 × 0.33 × 0.10 mm; crystal system, orthorhombic; space group, *Pna*2₁; unit cell, 18.91434(15) × 8.61215(6) × 12.91449(8) Å [*a* = 18.91434(15) Å, *b* = 8.61215(6) Å, *c* = 12.91449(8) Å]; *Z* = 4; calculated density, 1.298 g cm^{−3}; linear absorption coefficient, 2.485 mm^{−1}; radiation, CuKα 1.54184 Å; measurement temperature, 99.95(10) K; 2θ_{max}, 133.93°; total reflections, 98793; independent reflections, 3769; *R*(int) = 0.0380; *R*1 = 0.0226; *wR* = 0.0606; highest peak, 0.425 e Å^{−3}; deepest hole, −0.242 e Å^{−3}. Structure solved and refined with ShelX-97 in Olex2; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341; c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [12] H. Hope, M. M. Olmstead, P. P. Power, J. Sandell, X. Xu, *J. Am. Chem. Soc.* **1985**, *107*, 4337–4338.
- [13] a) N. Yoshikai, E. Nakamura, *Chem. Rev.* **2012**, *112*, 2339–2372; b) J. P. Snyder, *J. Am. Chem. Soc.* **1995**, *117*, 11025–11026.
- [14] a) R. M. Gschwind, *Chem. Rev.* **2008**, *108*, 3029–3053; b) M. John, C. Auel, C. Behrens, M. Marsch, K. Harms, F. Bosold, R. M. Gschwind, P. R. Rajamohanam, G. Boche, *Chem. Eur. J.* **2000**, *6*, 3060–3068.

- [15] a) S. H. Bertz, K. Nilsson, Ö. Davidsson, J. P. Snyder, *Angew. Chem.* **1998**, *110*, 327–331; *Angew. Chem. Int. Ed.* **1998**, *37*, 314–317; b) S. H. Bertz, A. Chopra, M. Eriksson, C. A. Ogle, P. Seagle, *Chem. Eur. J.* **1999**, *5*, 2680–2691.
- [16] a) S. H. Bertz, R. A. Hardin, M. D. Murphy, C. A. Ogle, J. D. Richter, A. A. Thomas, *Angew. Chem.* **2012**, *124*, 2735–2739; *Angew. Chem. Int. Ed.* **2012**, *51*, 2681–2685; b) S. H. Bertz, K. L. Browder, R. A. Hardin, M. D. Murphy, C. A. Ogle, A. A. Thomas, *Organometallics* **2012**, *31*, 7809–7811.
- [17] D. Li, G. Kagan, R. Hopson, P. G. Williard, *J. Am. Chem. Soc.* **2009**, *131*, 5627–5634.
- [18] N. Krause, *Angew. Chem.* **1999**, *111*, 83–85; *Angew. Chem. Int. Ed.* **1999**, *38*, 79–81, and references cited therein.
- [19] G. A. Sigel, P. P. Power, *Inorg. Chem.* **1987**, *26*, 2819–2822.
- [20] K. Ruhlandt-Senge, P. P. Power, *Bull. Soc. Chim. Fr.* **1993**, *129*, 594–598.
- [21] L. E. Burnham, R. M. Kachlan, A. A. Thomas, C. A. Ogle, D. S. Jones, *Acta Crystallogr. Sect. E* **2010**, *66*, o2442.

Received: April 15, 2013
Published online: ■ ■ ■, 0000