Electronic Supplementary Information

Models for the Reactive States of Homocuprates: Syntheses, Structures and Reactivities of \([\text{Cu}_2\text{Li}_2\text{Mes}_4]\) and \([\text{Cu}_3\text{LiMes}_4]\)

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Experimental Procedures ...........................................................p2
Theoretical Calculations .............................................................p4
X-ray Crystallography Supporting Information..........................p6
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Experimental Procedures

General Remarks:
Decane (Aldrich, anhydrous 99+%), n-butyllithium (Sigma-Aldrich, 2.5M in hexanes) and 2-cyclohexene-1-one (Sigma-Aldrich 95+%) were used without further purification. Pure, halogen-free MesLi was synthesized prior to use by reaction of equimolar amounts of MesBr with n-butyllithium in hexane at room temperature for 24h.[1] CuMes was prepared according to literature procedures.[2] THF and diethylether were dried by distillation over sodium/benzophenone. Toluene was distilled from over sodium. Unless otherwise stated, all manipulations were carried out under nitrogen using either a glove box or double-manifold vacuum line. Dry ice 2-propanol baths were used for reactions at -78 °C. GC analyses were performed with an HP GC 5890 gas chromatograph equipped with FID detector and a 25m SGE BP1 capillary column (0.22 mm i.d., 0.25 micron film, dimethyl polysiloxane). The GC was calibrated with authentic product (3-butylocyclohexan-1-one, 1-butyl-cyclohexan-1-ol) and dodecane (Aldrich 99%) as an internal standard. NMR spectra were recorded on a Bruker AV-400 spectrometer. External standards used were TMS (1H, 13C) and LiCl/D2O (7Li).

Synthesis of [Cu2Li2Mes4] (5) and [Cu3LiMes4] (6):
6.12g (33.5 mmol) of CuMes was dissolved in 40 mL toluene using gentle warming, before addition to a suspension of MesLi (4.23 g; 33.5 mmol) in 40 mL toluene. The resultant reaction mixture was stirred at 70 °C for 5 min and then for a further 2 h at 25 °C. The solution was then cooled to 0 °C and the precipitate filtered off and washed with 5 mL cold toluene. The precipitate and brown filtrate contain 5 and 6 respectively and were purified according to the following procedures: the precipitate was recrystallized from hot toluene to give colourless plate-like crystals of 5 in 27% yield (2.80 g; 9.06 mmol). The brown filtrate was reduced to dryness to give a brown solid which was re-dissolved in 20 mL hexane, filtered, reduced in vacuo to 10 ml and stored at -20 °C for 1 d to give colourless needles of 6 in 34 % yield (2.60 g, 3.85 mmol) based on CuMes.

6: 1H NMR (400.3 MHz, toluene-D8, 298 K): δ = 6.51 (s, 8H, Ar-H), 2.77 (s, 24H, ortho-CH3), 1.93 (s, 12H, para-CH3) ppm. 7Li NMR (155.6 MHz, toluene-D8, 298 K): δ = -9.99 ppm. 13C NMR (100.7 MHz, toluene-D8, 298 K): δ = 167.2, 149.3, 126.5, 124.3, 28.5, 20.7 ppm. M.p. = 189 °C (decomp.).

7: 1H NMR (400.3 MHz, C6D6, 298 K): δ = 6.96 (s, 4H, C3/5/23/25*-H), 6.43 (s, 4H, C13/15/33/35*-H), 3.21 (s, 12H, ortho-C7/9/27/29-H3), 2.80 (s, 12H, ortho-C17/19/37/39-H3), 2.26 (s, 6H, para-C8/28-H3), 1.88 (s, 6H, para-C18/38-H3) ppm. 7Li NMR (155.6 MHz, C6D6, 298 K): δ = -11.02 ppm. 13C NMR (100.7 MHz, C6D6, 298 K): δ = 153.9, 140.2, 133.9, 126.53, 126.50, 126.3, 124.1, 29.1, 28.7, 21.3, 20.3 ppm. M.p. = 174 °C (decomp.).

* For numbering scheme see Figures S6, S7
Addition Reactions of Lithium Organocuprate Reagents:

The procedure used was an adaptation of the procedure reported by Saegusa et al. for the addition reaction of \( n \)-BuLi to \( \alpha,\beta \)-unsaturated carbonyl compounds in THF using CuMes.[1] A representative cuprate reaction using CuMes is given below:

CuMes (365 mg; 2 mmol) was dissolved in 10 mL of the desired solvent (toluene, THF or Et\(_2\)O) and cooled to -78 °C before addition of \( n \)-butyllithium (2.5 M solution in hexanes; 0.80 mL; 2 mmol). The solution was stirred at -78 °C for 30 mins then 1.2 equivalents of cyclohexen-2-one (232 μL; 2.4 mmol) were added. After stirring for 2 h the reaction was quenched by addition of 8 mL of a saturated ammonium chloride solution and an internal standard of decane (390 μL, 2 mmol) was also added. The organic phase was separated and the aqueous phase washed with 2 x 5 mL of Et\(_2\)O. The combined organic phases were dried over MgSO\(_4\) and analyzed using GC.

Theoretical Calculations

All calculations were carried out with a Gaussian 03 package.\textsuperscript{[1]} The density functional theory method was employed using the B3LYP hybrid functional.\textsuperscript{[2]} Structures were optimised with a basis set consisting of the all electron SVP basis set by Horn and Ahlrichs\textsuperscript{[3]} for copper and 6-31G(d)\textsuperscript{[4]} for the rest. The method and basis set used here (denoted as B3LYP/631AS) have been applied to the optimisation of other lithium cuprates and are known to give reliable results.\textsuperscript{[5]} Natural charges were calculated by natural population analysis at the same level used for geometry optimization.\textsuperscript{[6]} Frequency analysis was carried out after geometry optimization to confirm the models were true energy minima with no imaginary frequencies.

**Figure S1.** 3D optimised structure of I (orange = Cu; purple = Li; grey = carbon; hydrogen atoms not shown for clarity). $C_7$-symmetry. $E = -4694.22338740$ au. Cu-C = 1.971; 1.980 Å; C(ipso)-Li = 2.146 Å; C(Ar)-Li = 2.347 to 2.399 Å; C-Cu-C = 178.70°. Natural charges: Li +0.945, Cu +0.568, C(ipso, η\textsuperscript{6}) -0.483, C(ipso, η\textsuperscript{6}) -0.622

**Figure S2.** 3D optimised structure of II (orange = Cu; purple = Li; grey = carbon; hydrogen atoms not shown for clarity). $C_2$-symmetry. $E = -4694.21905607$ au. Cu-C = 1.967 Å; C(Ar)-Li = 2.402 to 2.517 Å; C-Cu-C = 179.38°; dihedral angle between Mes rings = 27.19°. Natural charges: Li +0.885, Cu +0.570, C(ipso) -0.481.
**Figure S3.** 3D optimised structure of III (orange = Cu; purple = Li; grey = carbon; hydrogen atoms not shown for clarity). $C_{i}$-symmetry. $E = -4694.21637093$ au. Cu-C = 1.981 Å; C(ipso)-Li = 2.107, 2.109 Å; C-Cu-C = 172.07°; Natural charges: Li +0.826, Cu +0.557, C(ipso) -0.632


**X-Ray Crystallography Supporting Information**

**Fig. S4**  The molecular structure of 5 (50% probability ellipsoids).

**Fig. S5**  The molecular structure of one (B) of the two independent complexes present in the crystals of 6.

**Fig. S6**  The molecular structure of one (A) of the two independent complexes present in the crystals of 6 (50% probability ellipsoids).

**Fig. S7**  The molecular structure of one (B) of the two independent complexes present in the crystals of 6 (50% probability ellipsoids).

**Fig. S8**  Overlay of the two independent complexes (A and B) present in the crystals of 6. The r.m.s. fit of the Cu$_3$Li portions of the two complexes is ca. 0.031 Å

*Figure S4.* The molecular structure of 5 (50% probability ellipsoids).
Figure S5. The molecular structure of one (B) of the two independent complexes present in the crystals of 6.

Figure S6. The molecular structure of one (A) of the two independent complexes present in the crystals of 6 (50% probability ellipsoids).
**Figure S7.** The molecular structure of one (B) of the two independent complexes present in the crystals of 6 (50% probability ellipsoids).

**Figure S8.** Overlay of the two independent complexes (A and B) present in the crystals of 6. The r.m.s. fit of the Cu$_3$Li portions of the two complexes is ca. 0.031 Å.