

## Electronic Supplementary Information

### **Models for the Reactive States of Homocuprates: Syntheses, Structures and Reactivities of [Cu<sub>2</sub>Li<sub>2</sub>Mes<sub>4</sub>] and [Cu<sub>3</sub>LiMes<sub>4</sub>]**

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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.<sup>[1]</sup> CuMes was prepared according to literature procedures.<sup>[2]</sup> 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-butylcyclohexan-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 (<sup>1</sup>H, <sup>13</sup>C) and LiCl/D<sub>2</sub>O (<sup>7</sup>Li).

### Synthesis of [Cu<sub>2</sub>Li<sub>2</sub>Mes<sub>4</sub>] (5) and [Cu<sub>3</sub>LiMes<sub>4</sub>] (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**: <sup>1</sup>H NMR (400.3 MHz, toluene-D<sub>8</sub>, 298 K): δ = 6.51 (s, 8H, Ar-*H*), 2.77 (s, 24H, *ortho*-CH<sub>3</sub>), 1.93 (s, 12H, *para*-CH<sub>3</sub>) ppm. <sup>7</sup>Li NMR (155.6 MHz, toluene-D<sub>8</sub>, 298 K): δ = -9.99 ppm. <sup>13</sup>C NMR (100.7 MHz, toluene-D<sub>8</sub>, 298 K): δ = 167.2, 149.3, 126.5, 124.3, 28.5, 20.7 ppm. M.p. = 189 °C (decomp.).

**7**: <sup>1</sup>H NMR (400.3 MHz, C<sub>6</sub>D<sub>6</sub>, 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-*H*<sub>3</sub>), 2.80 (s, 12H, *ortho*-C17/19/37/39-*H*<sub>3</sub>), 2.26 (s, 6H, *para*-C8/28-*H*<sub>3</sub>), 1.88 (s, 6H, *para*-C18/38-*H*<sub>3</sub>) ppm. <sup>7</sup>Li NMR (155.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ = -11.02 ppm. <sup>13</sup>C NMR (100.7 MHz, C<sub>6</sub>D<sub>6</sub>, 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:**

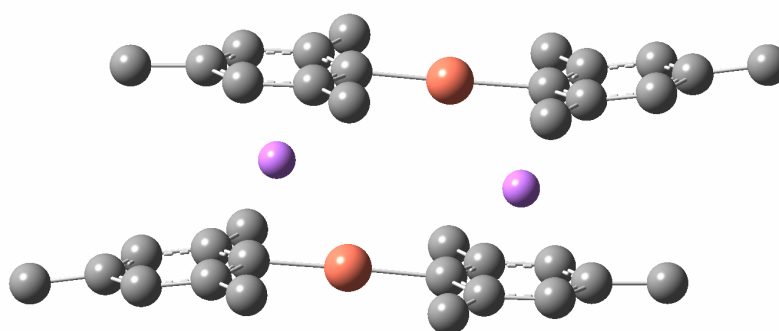
The procedure used was an adaptation of the procedure reported by Saegusa *et al.* for the addition reaction of *n*-BuLi to  $\alpha,\beta$ -unsaturated carbonyl compounds in THF using CuMes.<sup>[1]</sup> A representative cuprate reaction using CuMes is given below:

CuMes (365 mg; 2 mmol) was dissolved in 10 mL of the desired solvent (toluene, THF or Et<sub>2</sub>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  $\mu$ L; 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  $\mu$ L, 2 mmol) was also added. The organic phase was separated and the aqueous phase washed with 2 x 5 mL of Et<sub>2</sub>O. The combined organic phases were dried over MgSO<sub>4</sub> and analyzed using GC.

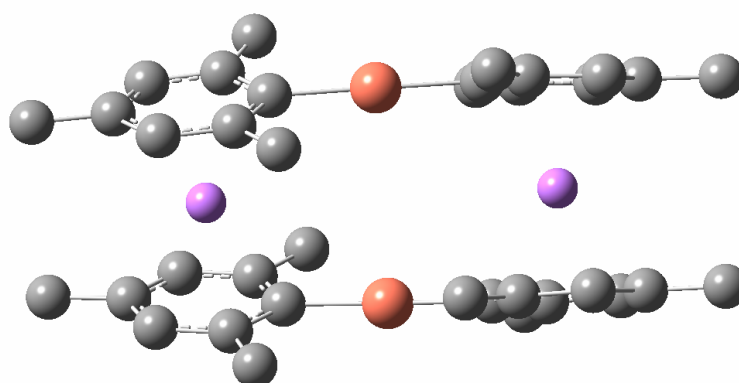
- [1] N. S. Nudelman and F. Doctorovich, *Tetrahedron*, 1994, **50**, 4651.  
[2] T. Tsuda, T. Yazawa, K. Watanabe, T. Fujii and T. Saegusa, *J. Org. Chem.*, 1981, **46**, 192.

### Theoretical Calculations

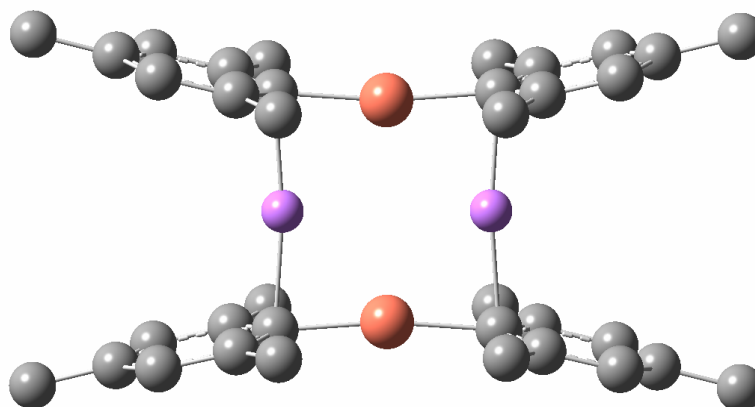
All calculations were carried out with a Gaussian 03 package.<sup>[1]</sup> The density functional theory method was employed using the B3LYP hybrid functional.<sup>[2]</sup> Structures were optimised with a basis set consisting of the all electron SVP basis set by Horn and Ahlrichs<sup>[3]</sup> for copper and 6-31G(d)<sup>[4]</sup> 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.<sup>[5]</sup> Natural charges were calculated by natural population analysis at the same level used for geometry optimization.<sup>[6]</sup> 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).  $C_i$ -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*,  $\eta^6$ ) -0.483, C(*ipso*,  $\eta^6$ ) -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.

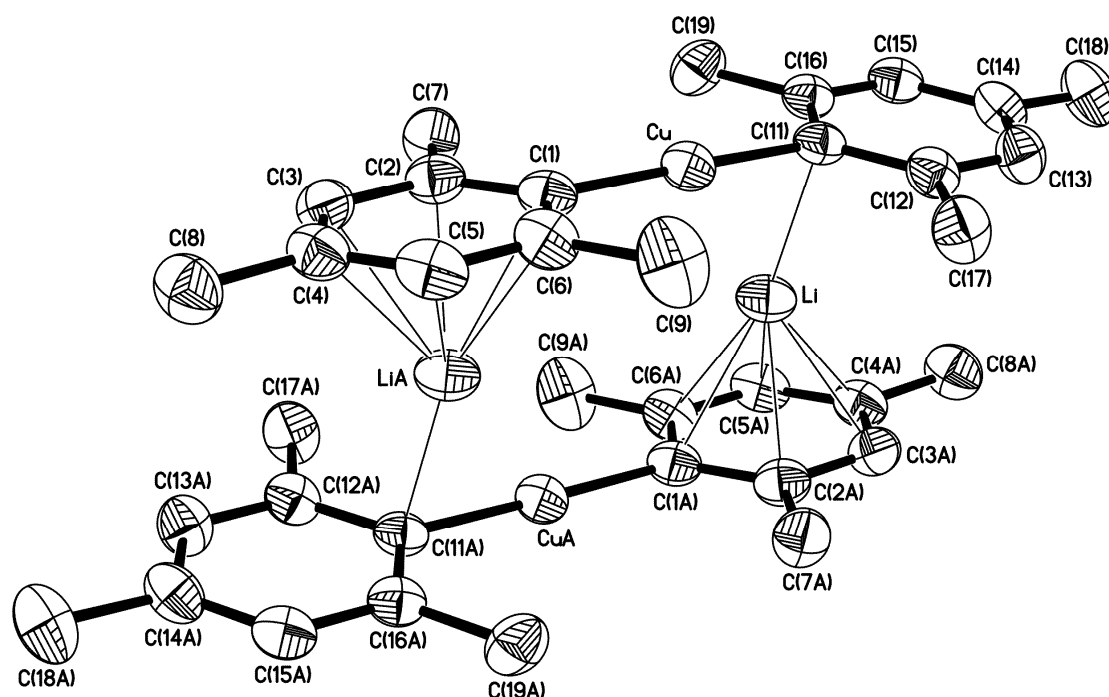


**Figure S3.** 3D optimised structure of **III** (orange = Cu; purple = Li; grey = carbon; hydrogen atoms not shown for clarity).  $C_i$ -symmetry.  $E = -4694.21637093$  au. Cu-C = 1.981 Å; C(*ipso*)-Li = 2.107, 2.109 Å; C-Cu-C = 172.07°; Natural charges: Li +0.826, Cu +0.557, C(*ipso*) -0.632

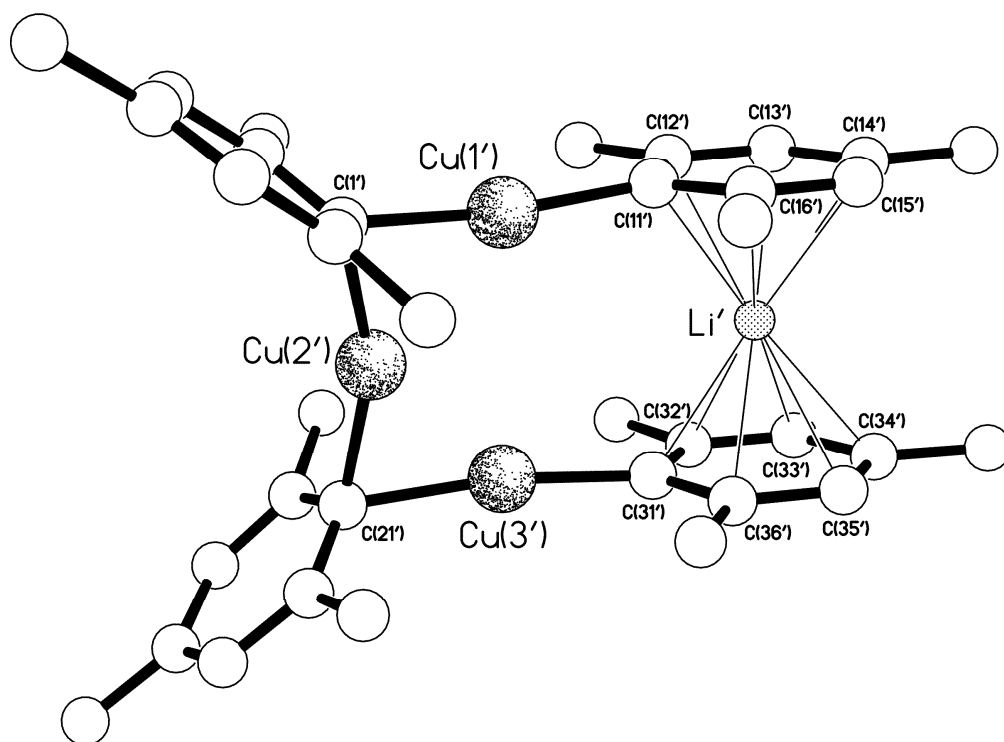
- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, revision C.02*, Gaussian Inc., Wallingford CT, 2004.
- [2] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- [3] A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571; A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.
- [4] See W. J. Hehre, L. Radom, P. con Ragué Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986 and references therein.
- [5] M. Yamanaka, A. Inagaki and E. Nakamura, *J. Comput. Chem.*, 2003, **24**, 1401.
- [6] E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO Version 3.1*.

**X-Ray Crystallography Supporting Information**

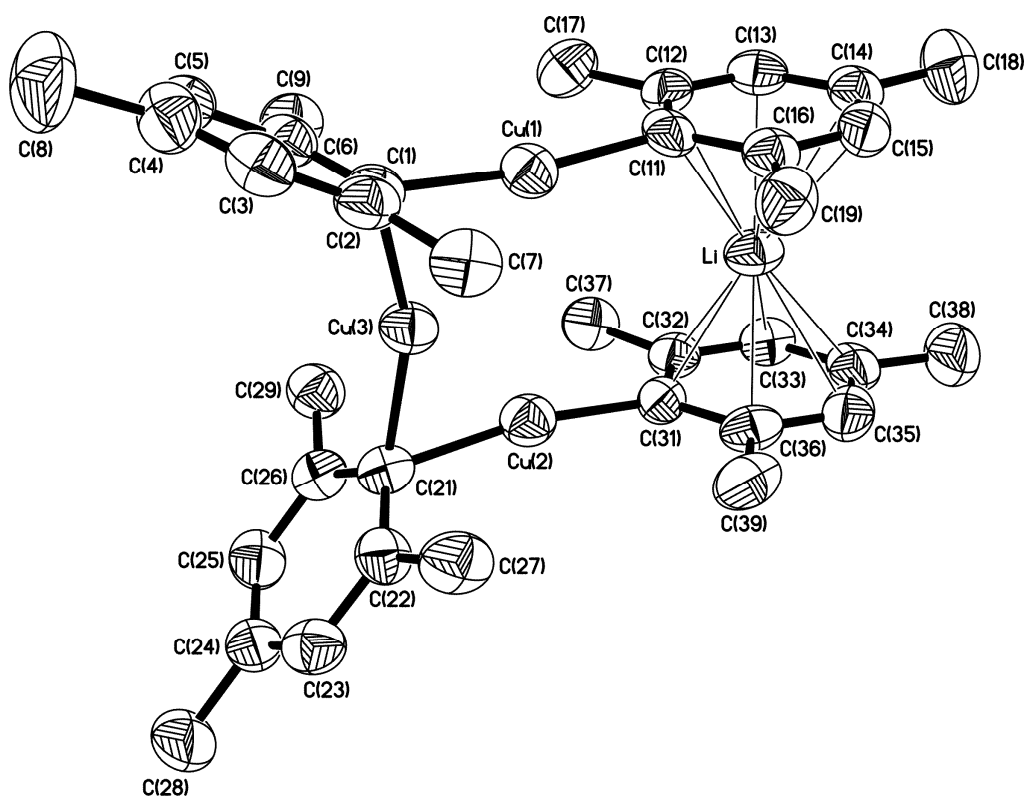
- Fig. S4** The molecular structure of **5** (50% probability ellipsoids).
- Fig. S5** The molecular structure of one (**B**) of the two independent complexes present in the crystals of **6**.
- Fig. S6** The molecular structure of one (**A**) of the two independent complexes present in the crystals 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  $\text{Cu}_3\text{Li}$  portions of the two complexes is *ca.* 0.031 Å



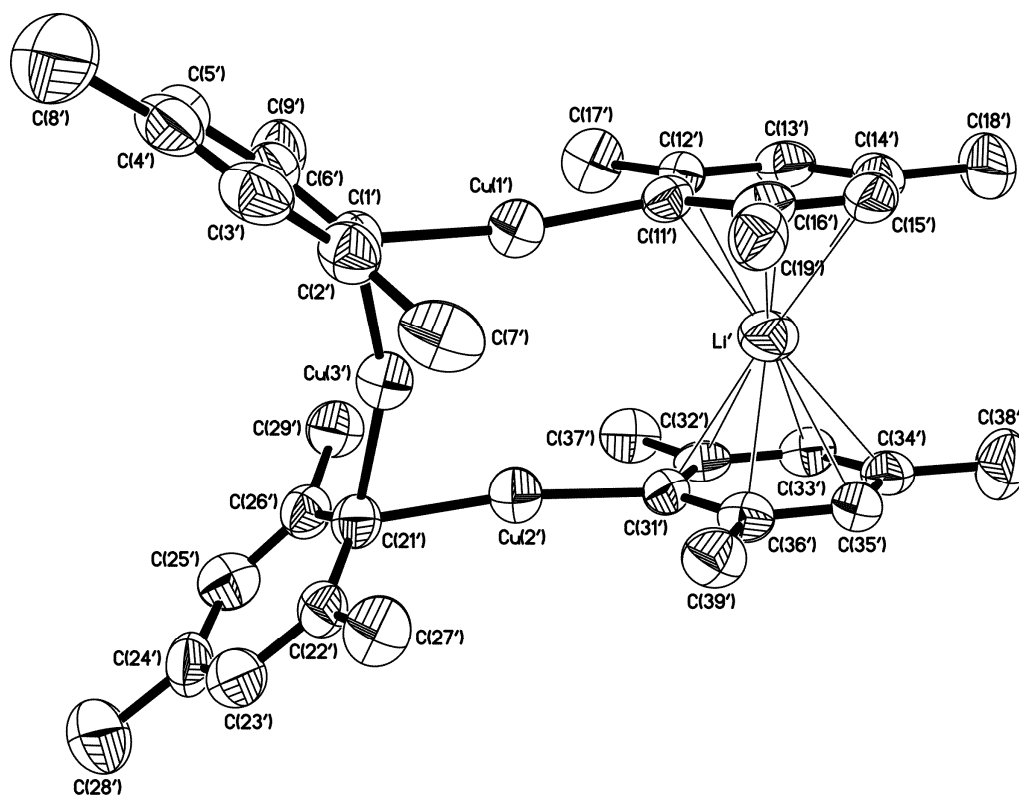
**Figure S4.** The molecular structure of **5** (50% probability ellipsoids).



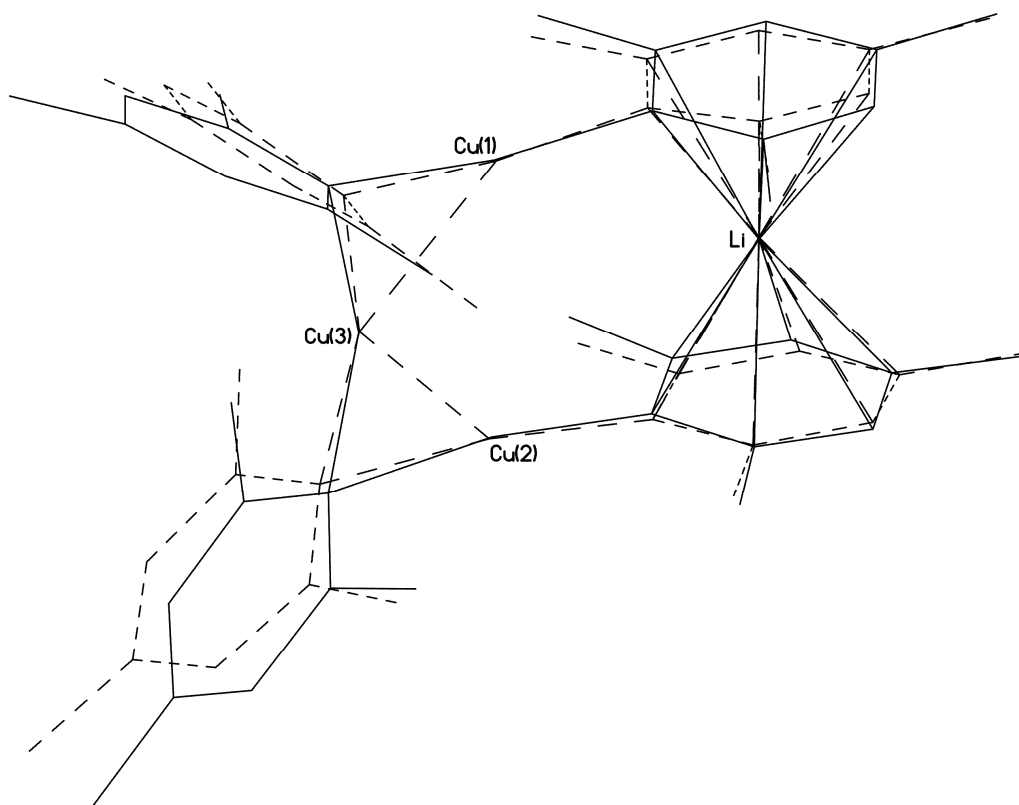
**Figure S5.** The molecular structure of one (**B**) of the two independent complexes present in the crystals of **6**.



**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  $\text{Cu}_3\text{Li}$  portions of the two complexes is *ca.* 0.031 Å.