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Opening the 'black box': oscillations in organocuprate conjugate addition reactions† (Electronic Supplementary Information)

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Experimental methods

Solutions of the Gilman reagent **1** (0.04 M) were prepared in 0.30 mL of dry THF-d_8 in precision NMR tubes, sealed under Ar with rubber septua. Low-halide MeLi (1.21 M, 0.09 M residual base) was prepared in benzene-d_6/THF-d_8 solution from MeCl and Li dispersion.[1,2] An aliquot containing 1.95 mol equiv of MeLi was injected into a suspension of CuI (2.3 mg, 0.012 mmol) or CuCN (1.1 mg, 0.012 mmol) in 0.30 mL of THF-d_8, distilled from Na/benzophenone in a micro-still. The mixture was warmed from –78 °C to 0 °C in a sonicating bath and held there for 0.1 h to 'anneal' the reagent.[3]

The NMR tube was then re-cooled to –78 °C and inserted into the pre-cooled probe of a Varian VXR-300S spectrometer. A ^{1}H NMR spectrum was measured at –70 °C to establish the purity of the reagent, the tube was ejected, and the septum was removed in the nitrogen stream from the probe. The tube was immediately lowered into the probe again, and upon reaching temperature, the ^{1}H NMR spectrum was re-measured to make sure the cuprate solution was unchanged. A 20-µL aliquot of a 0.30-M solution of **2** (0.006 mmol) in THF-d_8, containing a known concentration of benzene (internal standard), was injected at –70 °C. The final concentration of **2** was ca. 0.02 M; it varied somewhat, owing to imprecision in the injections. The experiments were repeated at –60 and –50 °C.

One-pulse ^{1}H NMR spectra (FID) were recorded at pre-set intervals. The peaks of the transformed spectra were integrated after simulating them with Gaussians to correct the baseline. As expected from the relatively low signal-to-noise (S/N) of the one-pulse ^{1}H NMR spectra, there is significant scatter in the data, and we do not interpret small fluctuations (*e.g.*, in **7**, *vide infra*) as oscillations.

Results at various temperatures

Concentration *vs*. time plots for the reactions of **1a** and **1b** with **2** at –70 °C are given in the communication proper.

The corresponding plots for the reactions at –60 °C are given below. In the reaction with **1a** (Fig. 5), the peaks for **2** are broadened into the baseline by chemical exchange and cannot be integrated. Thus, no purple points appear in Fig. 5 (*cf*. Fig. 1). In the reaction with **1b** (Fig. 6), the peaks for **2** appear at their usual positions. Cuprate **5** is present in this reaction; however, its broad, low intensity peaks cannot be integrated accurately, owing to overlap with a broad peak at –1.1 ppm (*vide infra*). Thus, no red points appear in Fig. 6 (*cf*. Fig. 2).

At –50 °C, oscillations are hardly discernible in the scatter.

Cu enolate 7

The peak at –1.12 ppm in the reactions of **1b** is tentatively assigned to the Me group bound to Cu in **7**. This peak does not appear in the case of **1a**, perhaps because of chemical exchange with other Cu-Me groups (*cf*. **4a**$^+$). This peak does not appear to oscillate except possibly for one small oligo-oscillation in the first 100 s. Differences between NMR spectra starting from **1a** and **1b** are largely attributable to slower rates of chemical exchange when X = I *vs*. X = CN (see communication, ref. 4).

References

1 V. C. Mehta, R.C. Morrison and C.W. Kamienski, *U.S.* 5,171,467.
2 M.J. Lusch, W.V. Phillips, R.F. Sieloff, G.S. Nomura and H.O. House, *Org. Synth. Coll.*, 1990, **7**, 346-350.
3 S.H. Bertz, C.P. Gibson and G. Dabbagh, *Tetrahedron Lett.*, 1987, **28**, 4251-4254.

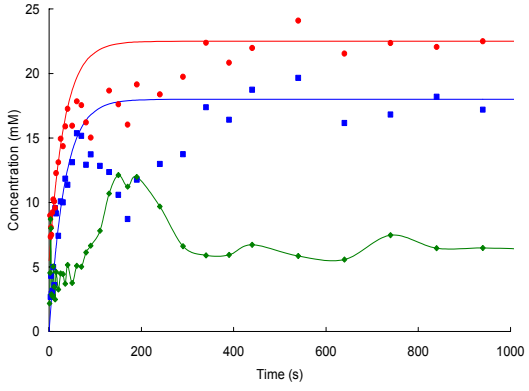

Fig. 5 Concentration *vs*. time plots for the reaction of cyano-Gilman reagent **1a** with **2** at –60 ºC: **1a** (♦), **4a**$^+$ (●) and **6**/**7** (■). The curves for **4a**$^+$ and **6**/**7** are theoretical ones assuming no oscillation.

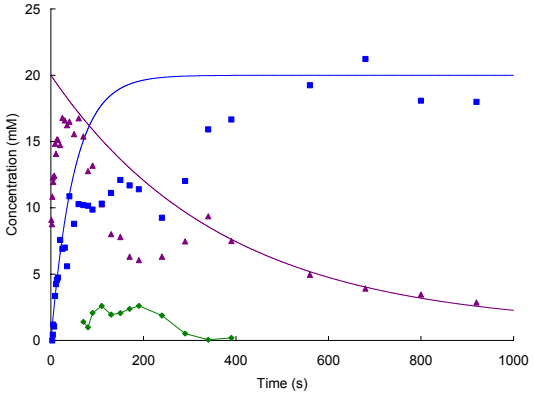

Fig. 6 Concentration *vs*. time plots for the reaction of iodo-Gilman reagent **1b** with **2** at –60 ºC: **1b** (♦), **2** (▲) and **6**/**7** (■). The curves for **2** and **6**/**7** are theoretical ones assuming no oscillation.

† Electronic supplementary information (ESI) available: experimental methods and concentration *vs*. time plots at –60 ºC. See http://www.rsc.org/suppdata/cc/b0/b000000a/