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_4 in precision NMR tubes, sealed under Ar with rubber septa. Low-halide MeLi (1.21 M, 0.09 M residual base) was prepared in benzene-d_6/THF-d_4 solution from MeCl and 1.1 dispersion. 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_4, 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

Thus, no red points appear in Fig. 6 (Fig. 2). 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).

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

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References


Fig. 5 Concentration vs. time plots for the reaction of cyanogilman reagent 1a with 2 at −60 °C: 1a (♦), 4a† (●) and 6/7 (▲). The curves for 4a† and 6/7 are theoretical ones assuming no oscillation.

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