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Rapid-Injection NMR Study of Iodo- and Cyano-Gilman Reagents with 2Cyclohexenone: Observation of π -Complexes and Their Rates of Formation 1

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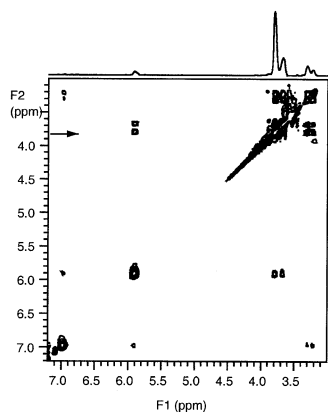


Figure 2. ^1H NMR EXSY spectrum ($\tau_{\text{mix}} = 1.0$ s) of the equilibrium mixture of **2**, **3** and **3•LiI** at -100°C in the double bond region. The arrow indicates where the trace at the top was taken.

addition. We conclude that the π -complexes have substantial enolate character, as predicted by Snyder,¹¹ and C_β appears to have higher electron density than C_α . This observation explains the anomalous β -silylation of β -aryl- α,β -unsaturated ketones (chlorosilane/ $\text{Bu}_2\text{CuLi} \cdot \text{LiCN}$) observed by Amberg and Seebach.¹²

The $[\text{LiLi}]^+$ moiety in **3•LiI** is similar to that in cuprate heterodimer **1a**, proposed in 1995,⁹ and recently buttressed by an X-ray crystal structure for $\text{Ar}_2\text{CuLi} \cdot \text{LiBr}$.¹³ The $[\text{LiCNLi}]^+$ unit in **3•LiCN** is also present in the X-ray crystal structures of cyano-Gilman reagents,¹⁴ although in the form of a SSIP, as predicted.¹⁵ At this point, we do not see any evidence for structure **3•LiCuMe₂**, which features a $[\text{MeCuMe}]^-$ bridge instead of I^- or $[\text{CN}]^-$. Nakamura et al.¹⁶ calculated a structure similar to **3•LiCuMe₂**, and it is likewise precluded under our conditions. We conjecture that the geometric fit of the bridge determines whether it is held tightly as in **3•LiI** or loosely as in **3•LiCN** (cf. exchange rates)—or not at all (ergo no **3•LiCuMe₂**).

In rapid-injection experiments with **1a** and **2**, the ^1H NMR peaks for π -complexes **3** and **3•LiI** increased until equilibrium was reached. The differential equations for various kinetic schemes were entered into the computer program MathCad, and the best fit for the measured concentrations as a function of time was determined by systematic variation of the rate constants and iteration until the residual sum of squares (RSS) was minimized. The fits were relatively insensitive to the values of k_2 and k_{-2} (eq 2); therefore, these values were determined more accurately by using exchange spectroscopy (EXSY).¹⁷ A stacked plot of the transformed ^1H NMR spectra for a typical rapid-injection experiment is included in the Supporting Information.

An EXSY experiment (Figure 2) revealed cross-peaks for the interconversion of **2** and **3•LiI**, **3** and **3•LiI** (cf. Figure 1, a and b), and **2** and **3**, as well as NOE peaks between adjacent hydrogens. The corresponding one-step exchange equilibria are given in eqs 1–3. The best fit to the experimental results is obtained with $k_3 = k_{-3} = 0$, which means that the one-step process in eq 3 is not involved to a significant degree, and the exchange observed between **2** and **3** is a two-step process, viz. eqs 1 and 2. The significant rate constants are $k_1 = 2.0 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 0.085 \text{ s}^{-1}$, $k_2 = 0.49 \text{ s}^{-1}$, and $k_{-2} = 28 \text{ M}^{-1} \text{ s}^{-1}$. These rate constants give a good fit for the rapid-injection NMR data points (Figure 3). The rates of exchange for **3** and **3•LiCN** (cf. Figure 1c) were too fast for the EXSY method to measure.

Boche et al. have shown that the conjugate addition reaction of organocuprates proceeds via the CIP, heterodimer $\text{R}_2\text{CuLi} \cdot \text{LiI}$ or homodimer $(\text{R}_2\text{CuLi})_2$, even though the SSIP is the predominant species in THF.⁸ The identification of **3•LiI** as the initial product

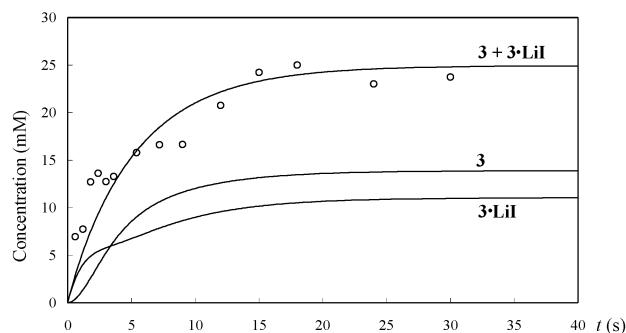


Figure 3. Rapid-injection ^1H NMR data points for the reaction of **1a** with **2** at -100°C , where the curves for the predicted rates of appearance of π -complexes are calculated from the EXSY rate constants.

from the iodo-Gilman reagent and **2** suggests that heterodimer **1a** is the reactive species as far as conjugate addition in THF is concerned, especially in light of the fact that we do not detect a π -complex (e.g., **3•LiCuMe₂**) that would implicate the homodimer, **1c**. Finally, we surmise that the halide-containing complex **3•LiI** is the one that undergoes facile conjugate addition, as the reaction mixture with 2 equiv of LiI contains a significant amount of enolate product (cf. Figure 1b), even at -100°C .

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Supporting Information Available: Rapid injection ^1H NMR stacked plot (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) a) New Copper Chemistry, part 30. For part 29 see (b) Bertz, S. H.; Chopra, A.; Eriksson, M.; Ogle, C. A.; Seagle, P. *Chem. Eur. J.* **1999**, *5*, 2680–2691.
- (2) (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980. (b) Taylor, R. J. K., Ed. *Organocopper Reagents-A Practical Approach*; Oxford University Press: Oxford, 1994. (c) Krause, N., Ed. *Modern Organocopper Chemistry*; Wiley-VCH: Weinheim, 2002.
- (3) Christenson, B.; Olsson, T.; Ullenius, C. *Tetrahedron* **1989**, *45*, 523–534.
- (4) Bertz, S. H.; Smith, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 8276–8277.
- (5) Krause, N.; Wagner, R.; Gerold, A. *J. Am. Chem. Soc.* **1994**, *116*, 381–382.
- (6) (a) McGarrity, J. F.; Prodollet, J. *J. Org. Chem.* **1984**, *49*, 4465–4470. (b) McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H. R. *J. Am. Chem. Soc.* **1985**, *107*, 1810–1815.
- (7) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425–434.
- (8) John, M.; Auel, C.; Behrens, C.; Marsch, M.; Harms, K.; Bosold, F.; Gschwind, R. M.; Rajamohanam, P. R.; Boche, G. *Chem. Eur. J.* **2000**, *6*, 3060–3068.
- (9) Bertz, S. H.; Vellekoop, A. S.; Smith, R. A. J.; Snyder, J. P. *Organometallics* **1995**, *14*, 1213–1220.
- (10) The methyl shifts for **3** were -5.9 and -1.6 ppm. For **3•LiI** the olefinic ^{13}C NMR shifts were 74.3 and 62.8 ppm, and the methyl shifts were -6.5 and -3.4 ppm; however, the S/N was not as good for this complex.
- (11) (a) Snyder, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 11025–11026. See also (b) Snyder, J. P.; Bertz, S. H. *J. Org. Chem.* **1995**, *60*, 4312–4313.
- (12) Amberg, W.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1718–1719.
- (13) Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Boersma, J.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 11675–11683.
- (14) (a) Boche, G.; Bosold, F.; Marsch, M.; Harms, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1684–1686. (b) Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1998**, *120*, 9688–9689.
- (15) (a) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031–4032. See also (b) Bertz, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 5470–5471. (c) Bertz, S. H.; Dabbagh, G.; He, X.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11640–11641. (d) Bertz, S. H.; Nilsson, K.; Davidsson, Ö.; Snyder, J. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 314–317. (e) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668–3670.
- (16) Nakamura, E.; Mori, S.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 4900–4910.
- (17) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935–967. JA027744S