



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Kinetic study of the reaction of the organocuprates compounds with enones. Characterization of Intermediates.

Experiment number:

CH-868

Beamline: ID-24	Date of experiment: from: 21/06/00 to: 27/06/00	Date of report: August 29, 2000 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): S. Diaz-Moreno	

Names and affiliations of applicants (* indicates experimentalists):

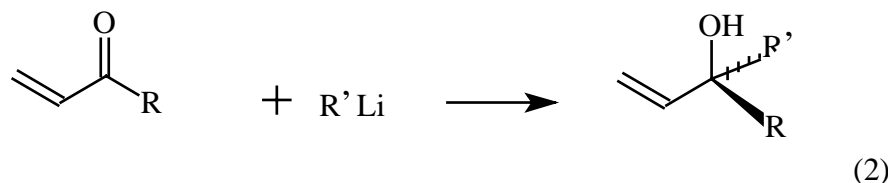
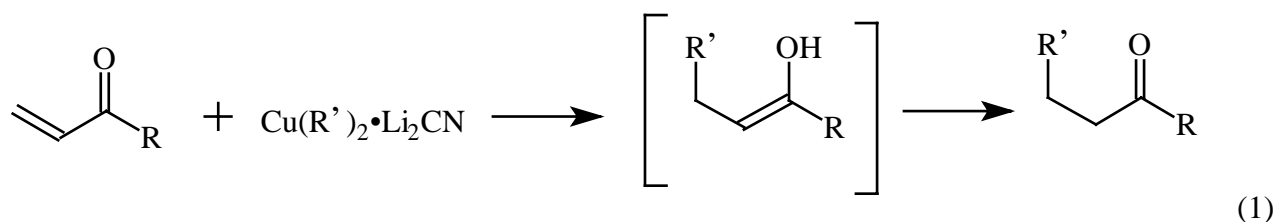
*Sofia Diaz-Moreno, ESRF

*Andrew Waltman, University of Michigan

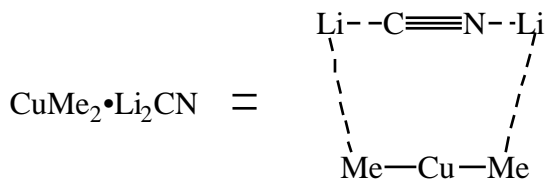
*James Penner-Hahn, University of Michigan

Report:

The addition of two equivalents of alkyl lithium to CuCN gives a so-called cyanocuprate reagent, $R_2Cu \cdot Li_2CN$. These reagents are of substantial interest in organic chemistry because of their high, yet selective, reactivity. Thus, addition of cyanocuprates to enone substrates results in rapid, but selective 1,4-addition (Equation 1). In contrast, the alkyl lithium starting material alone gives 1,2-addition (Equation 2).

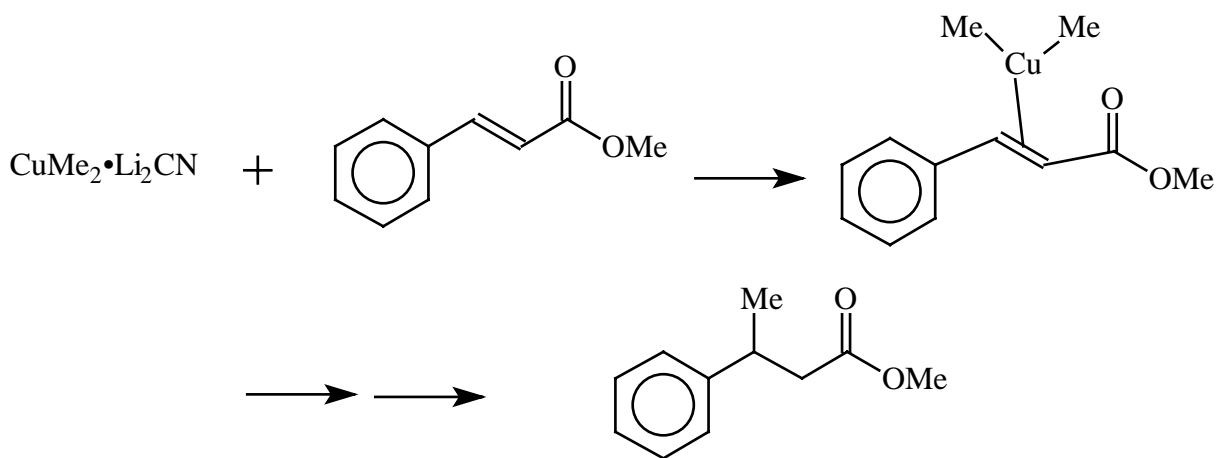


Although the reactivity of the cyanocuprate reagent was originally attributed to the formation of a three-coordinate Cu-cyanide complex¹⁻² (sometimes referred to as a "higher-order" cuprate), a variety of recent results³⁻⁵ have shown that, in fact, the Cu is two-coordinate in this species, and that it is best described by a structure such as that in (3). In particular, EXAFS spectra of CuCN + 2RLi show clear evidence only for Cu-C scattering from the alkyl groups, and XANES spectra show the intense pre-edge transition that is characteristic of two-coordinate linear Cu(I).⁵



(3)

Previous work has shown that methyl-*trans*-cinnamate (the enone substrate shown in Equation 4) reacts with cuprate reagents by initial formation of a π -bonded complex. NMR studies⁶ showed that addition of methyl-*trans*-cinnamate to solutions of Me_2CuLi at low temperature resulted in formation of a stable intermediate arising from π -complexation of the enoate to the copper center. The XANES spectrum⁷ of this solution was found to be dramatically different from that of either Me_2CuLi or $\text{Me}_2\text{CuLi} + \text{CN}^-$. The $1s \rightarrow 4p$ transition was significantly reduced in intensity on formation of the π -complex, consistent with an increase in the copper coordination sphere from two to three (counting the π -bond as one bond). Subsequent studies (Barnhart and Penner-Hahn, unpublished) showed that a spectroscopically identical intermediate is formed when methyl-*trans*-cinnamate is added to $\text{Me}_2\text{Cu} \cdot \text{Li}_2\text{CN}$, as shown in the first line of Equation 4.



(4)

The static EXAFS and NMR results summarized by the first line of Equation 4 provided a first glimpse into the mechanism of the reaction. The present experiments were designed to obtain a better understanding of the detailed mechanism of this reaction, and in particular to probe the structure of the intermediates represented by the two arrows in the second line of Equation 4.

Using the stopped-flow XAS equipment on ID-24, time-resolved XAS spectra were measured with 100 ms time resolution for the first 1.5 s of the room-temperature reaction of $\text{CuMe}_2 \cdot \text{Li}_2\text{CN} +$ methyl-*trans*-cinnamate, and every 0.9 sec for the first 30 s of the reaction. The resulting XANES spectra are shown in Figs. 1 and 2, respectively.

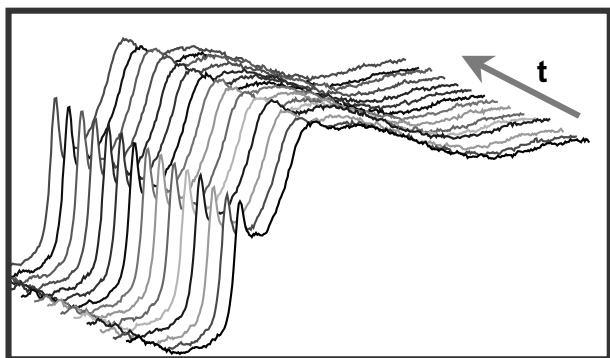


Figure 1 Series of spectra taken every 100ms for the first 1.5s of the reaction.

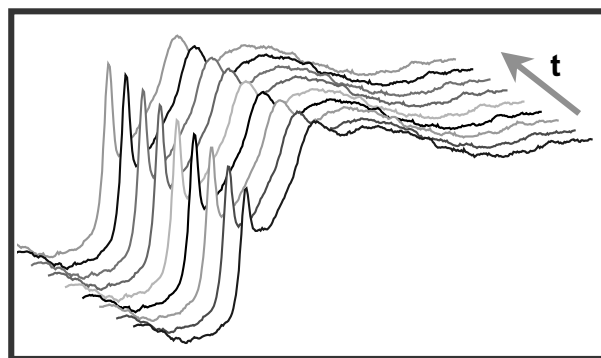


Figure 2 Series of spectra taken every 0.9s for the first 30s of the reaction.

These data show that the three-coordinate π -complex (Equation 4) is already formed at the earliest times of the reaction. This can be seen by the low amplitude of the $1s \rightarrow 4p$ transition. During the first phase of the reaction, the Cu site changes, but appears to remain 3-coordinate. The retention of an approximately 3-coordinate structure is shown by the lack of change of the $1s \rightarrow 4p$ transition, while the presence of some structural change is indicated by the increase in the intensity of the intense main edge transition. This main edge transition evolves from a nearly single peak to a pronounced double peak by 1.5 s. Subsequently structural evolution involves reformation of a two-coordinate Cu species, as indicated by the increase in the intensity of the $1s \rightarrow 4p$ transition for times > 1 s.

Detailed interpretation of these data together with interpretation of the EXAFS data is in progress. Ultimately, it should be possible to determine the rates of the different reactions and to determine the structure of the intermediates that are formed during the reaction. Already it is clear, however, that there exist at least two different 3-coordinate complexes during the reaction shown in Equation 4.

1. For reviews of cyanocuprate chemistry, see: a) Lishutz, B. H.; Sengupta, S.; *Org. React.* **1992**, *41*, 135. b) Lipshutz, B. H. *Synlett* **1990**, *3*, 119.
2. Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.
3. a) Bertz, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 5470. b) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. c) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668.
4. a) Snyder, J. P.; Spangler, D. P.; Behling, J. R.; Rossiter, B. E. *J. Org. Chem.* **1994**, *59*, 2665. b) Snyder, J. P.; Tipsword, G. E.; Spangler, D. P. *J. Am. Chem. Soc.* **1992**, *114*, 1507. c) Snyder, J.P.; Bertz, S.H., *J. Org. Chem.*, submitted.
5. Stemmler, T. L.; Barnhart, T. M.; Penner-Hahn, J. E.; Tucker, C. E.; Knochel, P.; Bohme, M.; Frenking, G. *J. Am. Chem. Soc.* **1995**, *117*, 12489-12497, and references therein.
6. Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57, and references therein.
7. Barnhart, T. M.; Hui, H.; Penner-Hahn, J. E. *J. Org. Chem.* **1995**, *60*, 4310-4311.