

## 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. Part II

**Experiment****number:**

CH-1058

<b>Beamline:</b> ID-24	<b>Date of experiment:</b> from: 25/04/01 to: 01/05/01	<b>Date of report:</b> August 29, 2001  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> S. Diaz-Moreno	

**Names and affiliations of applicants** (\* indicates experimentalists):

\*Sofia Diaz-Moreno, ESRF, France.

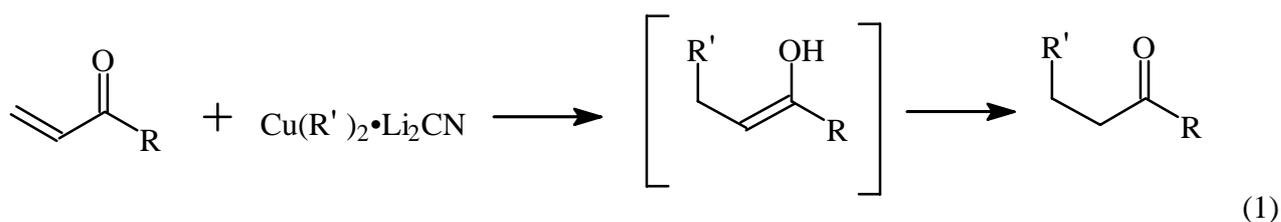
\*James Penner-Hahn, University of Michigan, U.S.A.

\*Irene Diaz, CSIC, Sevilla, Spain.

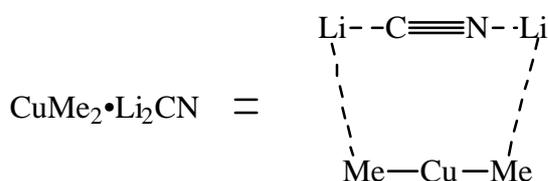
\*Daniel T. Bowron, ISIS, England.

**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).

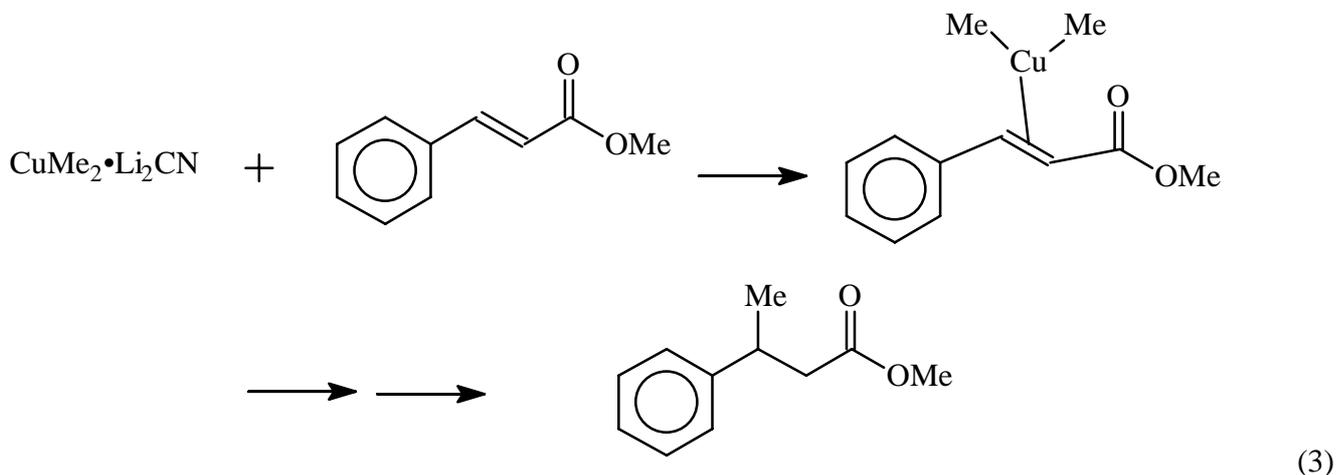


Although the reactivity of the cyanocuprate reagent was originally attributed to the formation of a three-coordinate Cu-cyanide complex<sup>1-2</sup> (sometimes referred to as a "higher-order" cuprate), a variety of recent results<sup>3-5</sup> have shown that, in fact, the Cu is two-coordinate in this species, and that it is best described by a structure such as that in (2). In particular, EXAFS spectra of  $\text{CuCN} + 2\text{RLi}$  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).<sup>5</sup>



(2)

Previous work has shown that methyl-*trans*-cinnamate (the enone substrate shown in Equation 3) reacts with cuprate reagents by initial formation of a  $\pi$ -bonded complex. NMR studies<sup>6</sup> showed that addition of methyl-*trans*-cinnamate to solutions of  $\text{Me}_2\text{CuLi}$  at low temperature resulted in formation of a stable intermediate arising from  $\pi$ -complexation of the enolate to the copper center. The XANES spectrum<sup>7</sup> of this solution was found to be dramatically different from that of either  $\text{Me}_2\text{CuLi}$  or  $\text{Me}_2\text{CuLi} + \text{CN}^-$ . The  $1s \rightarrow 4p$  transition was significantly reduced in intensity on formation of the  $\pi$ -complex, consistent with an increase in the copper coordination sphere from two to three (counting the  $\pi$ -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 3.



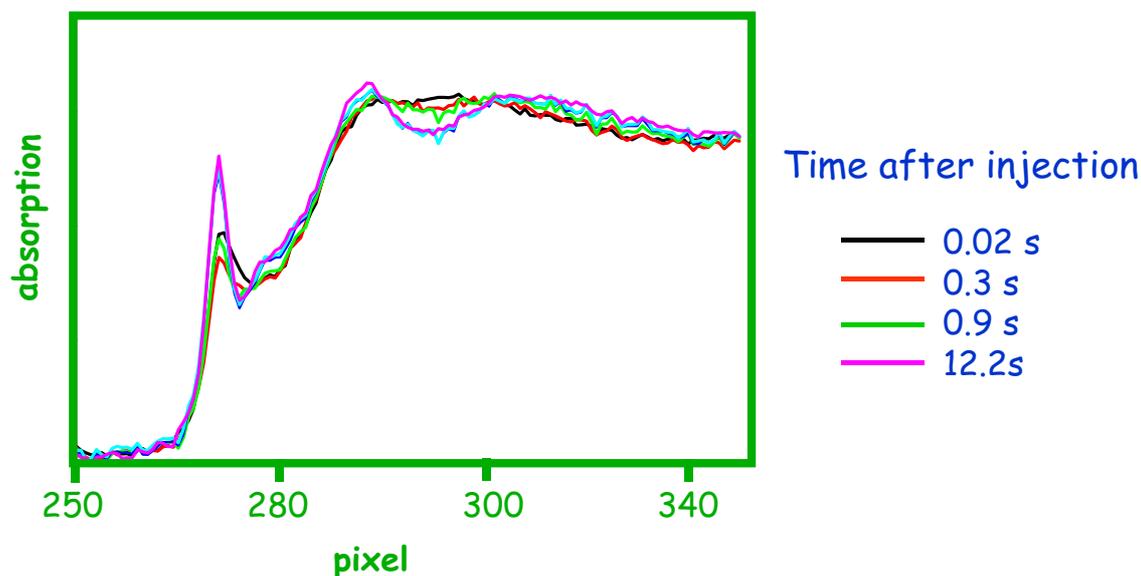
Within this framework and in order to obtain a deeper insight into the mechanism of this reaction, a previous experiment was performed by using the stopped-flow XAS equipment on ID-24 (experiment CH-868). Time-resolved XAS spectra were measured with 100 ms time resolution for the first 1.5 s of the room-temperature 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.

These earlier data showed that the three-coordinate  $\pi$ -complex (Equation 3) is already formed at the earliest times of the reaction. This can be seen by the low amplitude of the pre-peak feature present in all the spectra, and attributed to a  $1s \rightarrow 4p$  transition. Although the equipment at ID24 (detector and stopped-flow apparatus) is able to collect spectra in a much faster timescale (the fastest being 1 millisecond per spectrum) the quality of the data was very poor. This was mainly due to two reasons: in the first experiment we were forced to use a glove-bag to provide an inert atmosphere due to the sensitivity shown by the organocuprates compounds for exposed to air. This temporary solution introduced considerable noise into the data because we were not able to obtain a completely flat surface through which the X-ray beam could pass. The second reason that degraded the data quality taken in the first experiment, was that the cuvette used to measure the data had kapton windows which were impossible to keep perfectly flat during the injection of the reagents into the cell. This flexibility in the windows produced a variation in the pathlength of the x-rays when the injection of the reactants took place.

In the past year, these two difficulties have been overcome thanks to the engineering and technical support at ID24. A rigid glove-box was designed and built to be used in-situ at ID24, to enable more routine use of air-sensitive samples. Also, a new PTFE cuvette for the stopped flow cell, with rigid pyrocarbon windows has been designed and manufactured. These two new devices have been used in this second experiment (CH-1058). This has enabled us to collect considerably improved data.

The data collected in this second experiment have a much higher time resolution of 20ms per spectrum. The series of spectra are shown in Figure 1. As can be seen in the figure, the pre-peak feature decreases when passing from 20ms to 300 ms, and increase from that time up to the end of the reaction.

In this case with the improved time resolution used in this experiment, we have been able to follow the progress of the reaction including the previously unseen transformation from a two-coordinate Cu species to a three coordinate  $\pi$ -complex. This is indicated by the initial decrease in the intensity of the  $1s \rightarrow 4p$  transition. This step in the reaction is followed by the previously seen reformation to a second two coordinate Cu complex as indicated by the subsequent increase of the intensity of the same transition.



**Figure 1.** XANES region of the spectra corresponding to the reaction described above.

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.

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.