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# $\pi$-Complexes from acyl cyanides and lithium dimethylcuprate(I)†

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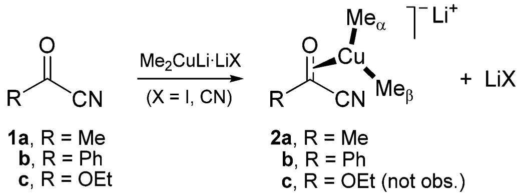
**Rapid injection of pyruvonitrile or benzoyl cyanide into solutions of $Me_2CuLi$ in THF-$d_8$ at −100 °C gave complexes that were stable at this temperature. 1D NMR with multiply labelled substrates ($^{13}C/^{15}N$) and 2D NMR ($^1H/^{13}C$) identified them as the first cuprate–carbonyl $\pi$-complexes.**

Organocuprates form $\pi$-complexes with activated alkenes and alkynes,[1–3] which are well-characterized intermediates, thanks to mechanistic studies on the conjugate addition reactions of these useful reagents.[4,5] We were able to extend our preparations of cuprate $\pi$-complexes from C–C to C–N double bonds by using isothiocyanates and azachalcones.[4] In an attempt to extend our studies to C–N triple bond complexes, we investigated acyl cyanides and serendipitously discovered the title compounds.‡

Rapid injection NMR has proven to be an outstanding method for the preparation and characterization of thermally unstable and air sensitive compounds,[6] for example, copper(I) reagents and copper(III) intermediates.[7] Thus, injection of a solution of pyruvonitrile **1a** in THF-$d_8$ into a solution of $Me_2CuLi{\cdot}LiI$ in THF-$d_8$–benzene-$d_6$ (7 : 1), spinning at −100 °C under dry nitrogen in the probe of an NMR spectrometer, gave a new species **2a** (Scheme 1), which had $^1H$ peaks (1.40, −0.08, −0.92 ppm) that grew in rapidly (<10 s), while those for the cuprate (−1.39 ppm) and substrate (2.45 ppm) disappeared. Upon irradiation of the 1.40 ppm methyl hydrogens, those at −0.08 ppm were enhanced by a NOE (*cf.* ESI†), which allowed us to assign them to $Me_\beta$.



**Scheme 1** Preparation of cuprate–carbonyl $\pi$-complexes **2**.

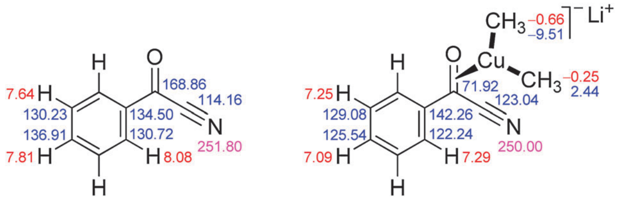
The $^{13}C$ NMR spectrum of **2a** had peaks at 124.83 ppm (cyano carbon), 68.95 ppm (carbonyl carbon), 24.41 ppm (substrate methyl), and −2.62 and −10.58 ppm (methyl groups on copper). For the methyls on copper, an HMQC plot (*cf.* ESI†) correlated the upfield $^1H$ and $^{13}C$ peaks ($Me_\alpha$) and likewise the downfield ones ($Me_\beta$).

Similar results were obtained upon injection of **1b**, which afforded **2b** (see Fig. 1 for chemical shifts). A $\pi$-complex was not observed from ethoxy derivative **1c** under our conditions.

Complex **2a**, prepared from either CuI or CuCN, decomposed at −70 °C to afford a mixture of products, including methane (from enolate formation), ethane and acetone. Complex **2b** decomposed to ethane and acetophenone at −70 °C, when prepared from CuCN, or at −20 °C, when prepared from CuI.

Triply-labelled **1b*** was prepared starting from benzoic acid-$^{13}C_1$ and $K^{13}C^{15}N$ (*cf.* ESI†). Then, triply labelled **2b*** and quintuply labelled **2b**** were prepared from **1b*** and $(CH_3)_2CuLi$ or $(^{13}CH_3)_2CuLi$, respectively (Scheme 2). The $^{15}N$ spectra were measured with a pyridine-$^{15}N_1$ external standard (0.30 M in THF-$d_8$, −100 °C) set at 318.26 ppm *versus* liquid ammonia.[8]

Scheme 2 also lists the coupling constants that could be measured directly from the $^{13}C$ and $^{15}N$ NMR spectra.



**1b** **2b**

**Fig. 1** $^1H$ (red), $^{13}C$ (blue) and $^{15}N$ (magenta) NMR shifts for **1b** and **2b** from CuI. ($^1H/^{13}C$ shifts, ppm from TMS; $^{15}N$ shifts for **2b****, see text.)

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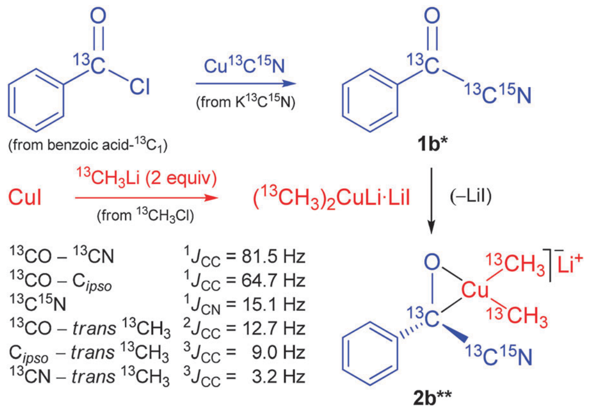

**Scheme 2** Scalar coupling constants, $J_{CC}$ and $J_{CN}$, measured for **2b****. (Note that the phenyl *ipso*-C was not labelled, *i.e.*, natural abundance.)

Several unresolved couplings appeared as shoulders or broadening, and they were calculated by using spectral simulation software (PERCH), which allowed us to estimate the 2-bond couplings between the carbonyl carbon and the cyano nitrogen, $^2J_{CN} \approx 3.7$ Hz, between the carbonyl carbon and the *cis*-methyl group (Me$_\beta$), $^2J_{CC} \approx 2.9$ Hz, and between the two methyl groups on copper (Me$_\alpha$–Me$_\beta$), $^2J_{CC} \approx 4.8$ Hz. As usual, this *cis*-coupling across Cu is much smaller than the *trans*-coupling.[4]

Collecting the measured and calculated coupling constants, the carbonyl carbon resonance at 72 ppm for **2b**** (Fig. 2) is a complex pattern with one large ($^1J_{CC}$ = 81.5 Hz), one medium ($^2J_{CC}$ = 12.7 Hz) and two small ($^2J_{CC}$ = 2.9 Hz, $^2J_{CN}$ = 3.7 Hz) couplings to the cyano carbon, the *trans*-methyl (Me$_\alpha$) carbon, the *cis*-methyl (Me$_\beta$) carbon and the cyano nitrogen, respectively.

The cyano $^{13}$C resonance at 123 ppm is a doublet of doublets of doublets with coupling to the carbonyl carbon ($^1J_{CC}$ = 81.5 Hz), the cyano nitrogen ($^1J_{CN}$ = 15.1 Hz), and the *trans*-methyl (Me$_\alpha$) carbon ($^3J_{CC}$ = 3.2 Hz, Scheme 2).

The $^{15}$N resonance at 250 ppm for **2b**** is a doublet of doublets with coupling to the cyano carbon ($^1J_{CN}$ = 15.1 Hz) and carbonyl carbon ($^2J_{CN}$ = 3.7 Hz). The magnitude of the former is much greater than the latter, which supports the assignment of the 123 ppm peak to the cyano carbon. (Note that there is no angular dependence, since the (O)C–C≡N bonding is linear).

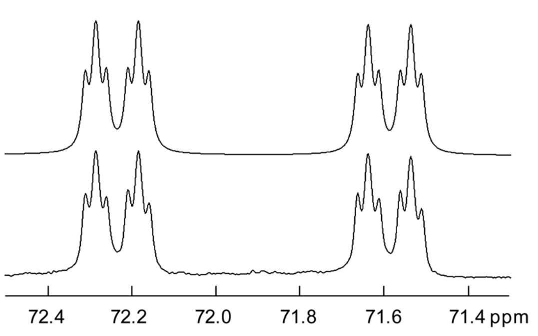

**Fig. 2** Measured (bottom) and calculated (top) $^{13}$C NMR resonances for the carbonyl region of quintuply labelled **2b****. See text for *J*-values.

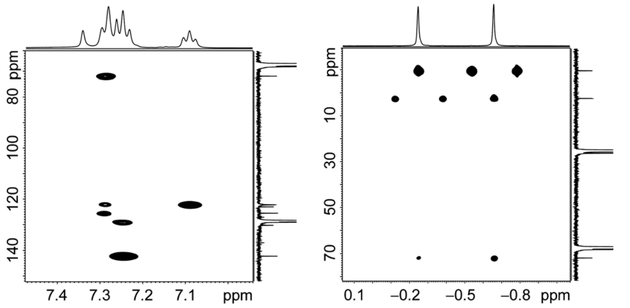

**Fig. 3** $^1$H/$^{13}$C HMBC plots for complex **2b**. See text for explanations.

Furthermore, the 1-bond coupling for the CN group in **2b**** ($^1J_{CN}$ = 15.1 Hz) is essentially unchanged (<10% difference in magnitude) from its value in **1b*** ($^1J_{CN}$ = 14.1 Hz), which indicates that the cyano group is not coordinated by copper.

Positive evidence that the carbonyl group is indeed coordinated by copper is provided by the observation of 2-bond couplings between the carbonyl carbon and the carbon atoms of Me$_\alpha$ and Me$_\beta$ ($^2J_{CC}$ = 12.7, 2.9 Hz, respectively).

Further support is provided by the large upfield change in the chemical shift of the carbonyl carbon upon complexation: $\Delta_{CO}$ = −106.52 ppm for **2a** and $\Delta_{CO}$ = −96.94 ppm for **2b**. The magnitudes (absolute values) are near the upper end of the range for C–C double bond complexes ($\Delta_{CC} \approx -40$ to −120 ppm), but near the lower end of the range for complexes of C–S double bonds ($\Delta_{CS} \approx -95$ to −180 ppm).[4] In contrast, the cyano carbon moves downfield by a relatively small amount ($\Delta_{CN}$ = 9.75, 8.88 ppm, respectively).

The conclusions from the 1D NMR studies were confirmed by 2D NMR experiments. $^1$H/$^{13}$C HMBC mapped out the 3-bond couplings, as shown in Fig. 3. The 72 ppm $^{13}$C peak was assigned to the carbonyl carbon, owing to coupling with the phenyl *ortho*-hydrogens (7.29 ppm, left-hand plot). Finally, it was possible to establish that this carbon was bonded to copper, owing to coupling with the hydrogens of Me$_\alpha$ (−0.66 ppm) and Me$_\beta$ (−0.25 ppm, right-hand plot).

Major and minor species were not observed for **2a** and **2b**, as for some cuprate–enone π-complexes.[4] Moreover, their chemical shifts are independent of the copper salt (*e.g.*, the $^1$H/$^{13}$C shifts for **2b** from CuCN are −0.64/−9.40 ppm for Me$_\alpha$ and −0.25/2.36 ppm for Me$_\beta$; see Fig. 1 for shifts from CuI). Therefore, we believe that **2a** and **2b** are not aggregates in THF.[9]

By using rapid injection NMR, it has been possible to prepare the first examples of organocuprate–carbonyl π-complexes, which were characterized by using 1D and 2D NMR. These results confirm theoretical predictions,[10] and they open up new possibilities for applications of organocopper reagents.

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## Notes and references

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