Neutral organocopper(III) complexes

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Neutral organocopper(III) complexes have been prepared from organocuprate(I) reagents and alkyl halides in the presence of certain strongly electron donating ligands.

Organocuprate(III) complexes, $R_4Cu^{III}Li$, recently joined organocuprate(I) complexes, $R_2Cu^{I}Li$ ('Gilman reagents'), in the panoply of organocopper compounds.†[1–3] Before our rapid injection nuclear magnetic resonance (RI-NMR) studies,[1,2,4,5] such Cu^{III} complexes had been relegated to the realm of 'elusive' intermediates, for example, in the reactions of Gilman reagents with α-enones[6] or alkyl halides.[7]

The first such 'copper(III) intermediate' to be characterized was prepared *via* the reaction of $Me_2CuLi{\cdot}LiI$ with 2-cyclohexenone and TMSCN, namely lithium cyanobis(methyl)-(3-trimethylsiloxy-2-cyclohexenyl)cuprate(III).[1] It was followed by several more examples of anionic Cu^{III} species from reactions of methyl cuprates with alkyl halides, for example, $EtMe_3CuLi$ (**A**) and $EtMe_2Cu(CN)Li$ (**B**).[2,3]

However, the Cu^{III} analogs of the well-known organocopper(I) compounds, $RCu^{I}(L)$ (L = neutral ligand),[6,7] were still unknown. Now, by using RI-NMR techniques, we have been able to prepare the first examples of such neutral organocopper(III) complexes, $RR'_2Cu^{III}(L)$ (Chart 1).

When EtI (1 equiv., 0.5 M in THF-d_8) was injected into a THF-d_8 solution of $Me_2CuLi{\cdot}LiI/PBu_3$,‡ spinning in the probe of an NMR spectrometer at –100 °C, $EtMe_2Cu(PBu_3)$ (**1**) was formed almost exclusively with only a small amount ($<5\%$) of **A**. Above −80 °C, **1** decomposed to $MeCuPBu_3$ and propane, the expected products of reductive elimination.

The structure of **1** was assigned on the basis of two-bond couplings ^2J across Cu, which were introduced for Cu^{I} compounds,[8] but have also proven invaluable for structure assignment in Cu^{III} chemistry.[1,2] The *trans*-coupling (^2J = 130.4 Hz) between P and the methylene C atom in $CH_3{}^{13}CH_2({}^{13}CH_3)_2Cu(PBu_3)$ is much larger than the *cis*-coupling (^2J = 14.6 Hz) of P with the methyl C atoms (see Fig. 1), which is also the general case for Pt complexes.[9] The small *cis*-coupling, previously observed between methylene and methyl C atoms,[1,2] was not resolved in this case.

When $Me_2CuLi{\cdot}LiI/PMe_3$ was injected with EtI under the same conditions, the products were $EtMe_2Cu(PMe_3)$ (**2**) and **A** (6 : 1). Complex **2** was stable at −100 °C; however, the ^{31}P NMR peak was broad, and we did not observe any *J* coupling.

Injection of EtI into $Me_2CuLi{\cdot}LiI/P(OMe)_3$ under the same conditions gave $EtMe_2Cu[P(OMe)_3]$ (**3**) and **A** (1 : 1). As in the case of **2**, *J* coupling was not observed.

Injection of EtI into $Me_2CuLi{\cdot}LiI/PPh_3$ under the same conditions gave $EtMe_2Cu(PPh_3)$ (**4**) and **A** (2 : 3) along with a small amount ($<10\%$) of propane. A large *trans*-coupling (^2J = 118.0 Hz) was observed between P and the methylene C atom; however, the peaks were too broad to resolve *cis*-couplings. When the reaction mixture was warmed to −80 °C, **4** was no longer present; it had decomposed to propane and $MeCuPPh_3$ before the first scan (*ca.* 0.1 h).

No complex was observed with tri(*t*-butyl)phosphine, presumably owing to steric hindrance. Furthermore, no complex was observed with triphenylarsine (*vide infra*).

The amine complexes in Chart 1 exhibited a wide range of stabilities at −100 °C. In the presence of pyridine (py, 1 equiv.) as the neutral ligand, $Me_2CuLi{\cdot}LiI$ and EtI gave $EtMe_2Cu(py)$

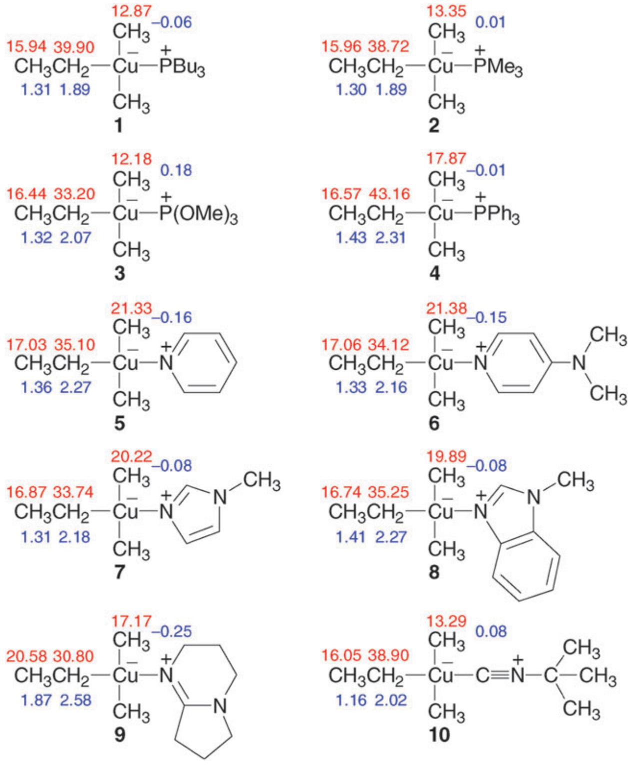

Chart 1 Organocopper(III) compounds prepared in this study with chemical shifts (ppm) at −100 °C in THF-d_8 for ^{13}C (red) and ^1H (blue).

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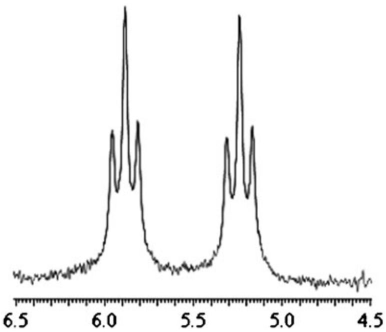

Fig. 1 ^{31}P NMR spectrum of $CH_3{}^{13}CH_2({}^{13}CH_3)_2Cu(PBu_3)$ (ppm scale) at -100 °C in THF-d_8. See text for coupling constants.

(**5**) as a short-lived intermediate (0.5 h to max. concentration). In addition to propane, which increased continuously, the final products were **A** and Me_3Cu_2Li.[10]

With 4-dimethylaminopyridine (DMAP) under the same conditions, $EtMe_2Cu(DMAP)$ (**6**) was formed in high yield (*ca.* 90%). A small amount of propane (*ca.* 10%) was also produced. Most significantly, **A** and Me_3Cu_2Li were not observed in this case.

When the cyano-Gilman reagent, $Me_2CuLi{\cdot}LiCN$, was treated sequentially with py or DMAP (0.1 or 1 equiv.) and then EtI, neither **5** nor **6**, respectively, was observed. Instead, the product in virtually quantitative yield was $EtMe_2Cu(CN)Li$ (**B**). In the reaction without amine, which we studied previously,[2] the yield of **B** (*ca.* 65%) was significantly lower, owing to the competing formation of **A** and propane.

It appears that cyanide stabilizes the Cu^{III} center significantly more than a strongly electron donating amine such as DMAP. While not incorporated into the product, py and DMAP nevertheless play an important role in the elimination of side-products. This route appears to be the best preparation of a lithium cyanocuprate(III) complex to date.

1-Methylimidazole (MI), 1-methylbenzimidazole (MBI) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) also formed stable complexes, $EtMe_2Cu(MI)$ (**7**), $EtMe_2Cu(MBI)$ (**8**) and $EtMe_2Cu(DBN)$ (**9**), respectively. In contrast, quinuclidine and triethylamine did not give complexes.

Under our RI-NMR conditions, *t*-butyl isocyanide gave $EtMe_2Cu(CNBu^t)$ (**10**) as a transient complex (0.1 h to max. concentration). The final products in essentially quantitative yield were $EtMe_3Cu^{III}Li$ (**A**) and $MeCu^I(CNBu^t)$, while the formation of propane ($<5\%$) was effectively suppressed. This route appears to be the best preparation of a lithium tetraalkylcuprate(III) complex to date.

The most stable of these new organocopper(III)† compounds have powerfully electron donating ligands. As summarized in Chart 1, the chemical shifts for these complexes are similar to those reported previously for the anionic Cu^{III} *ate* complexes,[1,2] which suggests that the charge on Cu is approximately the same. Snyder has calculated that the atomic charge on Cu in the *ate* complexes is *ca.* $+1$,[11] consistent with the Pauling Electroneutrality Principle.[12]

According to HSAB theory,[13] the most stable complexes are formed between acids and bases of similar hardness. While Cu^I is a soft acid, Cu^{III} is much harder. Consistent with this simple theory, the qualitative order of stability of the Cu^{III} phosphine and arsine complexes is correlated with the order of base hardness in the series, $PBu_3 \sim PMe_3 > PPh_3 >> AsPh_3$.

Chemical exchange is not unexpected in coordinatively unsaturated, 16-electron, d^8 transition metal species such as **1–10**, and it appears to be manifested in the ^{31}P NMR spectra, where the peaks are broad and the expected ^{13}C–^{31}P couplings are frequently absent.

Phosphine and phosphite complexes of copper(I) salts were introduced as soluble sources of Cu^I for the preparation of organocopper reagents.[6,7] Our results suggest a more significant role for such ligands in reactions involving them. Bertz *et al.* noted the beneficial effect of pyridine on the conjugate addition reaction of organocuprates, and they proposed a pyridylcopper(III) intermediate to account for it.[14] Complex **5** provides substantial support for this suggestion.

Given the diversity of neutral ligands capable of coordinating to organocopper(III) and the resulting range of stabilities, there appears to be an abundance of possibilities for fine-tuning organocopper reactivity based upon them.

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Notes and references

† The terms organocopper and organocuprate refer to compounds with Cu–C bonds to alkyl or aryl groups R in RCu^I, R_2Cu^ILi, $R_4Cu^{III}Li$, *etc.* Following the usual convention, the superscript Roman numerals are the formal oxidation numbers (see also ref. 11).

‡ The slash in formulas such as $R_2CuLi{\cdot}LiX/L$ indicates that we make no assumption regarding interaction between $R_2CuLi{\cdot}LiX$ (X = anionic ligand) and L, a neutral ligand. $Me_2CuLi{\cdot}LiI/PBu_3$ (0.06 M) was prepared from 2 equiv. of MeLi (1 M in THF-d_8) and 1 equiv. of $CuI(PBu_3)$ in an unused NMR tube at -78 °C. Sonication at 0 °C for 0.1 h was used to complete the reaction. Ligands that might be sensitive to alkyllithiums were added in THF-d_8 solution to the preformed cuprate at -78 °C. Otherwise, they were added along with the Cu salt to the NMR tube, and then THF-d_8 and MeLi were added. The trimethylphosphine was added as a commercial 1 M solution in toluene. The chemical shift of tributylphosphine was set at -32.50 ppm *versus* 85% phosphoric acid.

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