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Phenylcopper(I) and Diphenylcuprate(I): Characterization of Aggregation States by ^{13}C NMR Spectroscopy[1]

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Structural data for organocopper compounds in the solid state has been accreting over the past two decades.[2–4] Little is known, however, about the structures of these important reagents in solution, where they are used.[5–7] Phenylcopper(I), the simplest arylcopper(I) and the first organocopper compound to be prepared,[8] is a useful reagent, especially in dimethyl sulfide (DMS).[9] In addition, organocuprates, such as lithium diphenylcuprate(I),[10] are among the most useful synthetic reagents, and among the least understood in terms of structure and mechanism.[11,12] In this paper, it is shown by variable temperature ^{13}C NMR spectroscopy that, whereas the corresponding organolithium species, PhLi, is an equilibrium mixture of "tetramer" and "dimer" in diethyl ether[13] and of "dimer" and "monomer" in THF,[14] PhCu/DMS is an equilibrium mixture of "tetramer" and "trimer". We also establish the ^{13}C NMR shifts of dimeric and monomeric Ph_2CuLi, and we rationalize the chemical shift of the "higher order" cuprate $[Ph_3CuLi_3]^+[Ph_2Cu]^-$.[5]

Table I. Dependence of $\delta(^{13}C_{ipso})$ on Aggregation

species	*n*	aggregate[a]	$N^{\text{ipso}\,b}_{\text{Cu}}$	$N^{\text{ipso}\,c}_{\text{Li}}$	$\delta(^{13}C_{ipso})$
$(PhCu)_n$	1	monomer	1	0	151.0 ppm[d]
	2	dimer			not observed
	3	trimer	2	0	149.3
	4	tetramer	2	0	146.8
$(Ph_2CuLi)_n$	1	monomer	1	0	174.5[e]
	2	dimer	1	1	163.1
	3	trimer			not observed
	4	tetramer			not observed
$[Ph_3CuLi_3]^+ X^-$		monomer[f]	1	2	169.3
$(PhLi)_n$	1	monomer	0	1	196.0[g]
	2	dimer	0	2	186.8[h]
	3	trimer			not observed
	4	tetramer	0	3	172.2

[a] Concentrations *ca.* 0.2 M in DMS. For structural data, see refs 2–4. [b] Number of Cu atoms per *ipso*-C. [c] Number of Li atoms per *ipso*-C. [d] Estimated value. [e] 12-Crown-4 (2 equiv) and HMPA present. [f] A subunit of a larger cluster, X = Ph_2Cu. [g] Pentamethyldiethylenetriamine (PMDTA, 1 equiv) present. [h] Tetramethylethylenediamine (TMEDA, 1 equiv) present.

The ^{13}C NMR spectra of PhCu in DMS (or a DMS/THF mixture) as a function of temperature reveal that two species are present, as shown by the equilibrium below.

$$\underset{\mathbf{1}}{3[(PhCu)_4 \cdot x DMS]} + y DMS \rightleftarrows \underset{\mathbf{2}}{4[(PhCu)_3 \cdot z DMS]}$$

$$K = [\mathbf{2}]^4/[\mathbf{1}]^3$$

The relative amount of **1** (δ 146.8, 143.7, 127.1, 127.5 ppm[15]) increases at the expense of **2** (δ 149.3, 143.3, 126.6, 126.2 ppm[15]) as concentration or temperature increases,[16] with coalescence occurring at *ca.* −25 °C (0.2 M). A plot of log[**1**] *vs* log[**2**] has a slope of 1.3 ± 0.1, consistent with a tetramer–trimer equilibrium (slope = 1.33). The structure of the high-temperature species is $(PhCu)_4 \cdot 2DMS$ (by X-ray crystallography[2d]); therefore, the low-temperature species is the trimer.

A plot of ln *K vs* 1/*T* yields the approximate thermodynamic parameters $\Delta H = -3.7 \pm 1.0$ kcal/mol and $\Delta S = -21 \pm 4$ cal/(mol·K). As in the case of Li reagents, the smaller cluster is favored by lower temperatures or concentrations.[17] The presence of a trimer in the equilibrium mixture is also supported by "stereochemistry of aggregation" studies on *o*-tolylcopper(I) in DMS, in which case the low-temperature species has methyl ^{13}C NMR peaks with an integral ratio 2.0:1.1:0.9 consistent with a trimer (theoretical ratio 2:1:1). A dimer would have a 1:1 ratio. The ^{13}C NMR spectrum of $((o\text{-tolyl})Cu)_4$ has been previously studied in chloroform-*d*, and the possible configurational isomers have been enumerated.[18] Trimeric (thiolato)copper(I)[2e] and (amido)copper(I)[2f] complexes are known, but homoleptic trimeric species with Cu–C–Cu bridging have not been reported.

The addition of 1,2-bis(diphenylphosphino)ethane (dppe, 1 equiv) to PhCu/DMS affords a set of peaks at δ 174.5, 144.7, 126.2, and 122.2 ppm which are assignable to $[Cu(dppe)_2]^+[Ph_2Cu]^-$. A very similar ^{13}C NMR spectrum (δ 174.5, 142.0, 125.5, and 122.3 ppm) is obtained when 12-crown-4 (2 equiv)[19] is added to (dimeric) Ph_2CuLi/DMS (δ 163.1, 143.6, 128.1, 127.0 ppm). It has been shown that $[Li(12\text{-crown-}4)_2]^+$-

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[4] (a) Higher order $[Ph_3CuLi_3]^+[Ph_2Cu]^-$: Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4135. (b) Higher order $[Ph_3CuLi_3]^+[Ph_6Cu_3Li_2]^-$: Reference 2d.

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[15] The peak positions are relative to cyclohexane-d_{12} at 26.4 ppm. PhCu (halide free) was prepared from CuBr. The spectra in tetrahydrofuran contain more than four lines, and their assignment is not as clear-cut as in DMS. In THF/DMS mixtures (~1:3) a pattern which is essentially indistinguishable from that seen in DMS is obtained.

[16] Temperature was varied between −100 and 0 °C, and concentration between 0.02 and 0.2 M. Representative ratios of **2** to **1** at −100, −78, −50, and −30 °C were 2.07, 1.77, 1.05, and 0.857.

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[19] HMPA (0.5 mL) must be added to 2.6 mL of DMS and 0.4 mL of cyclohexane-d_{12} in order to obtain homogeneity at 20 °C.

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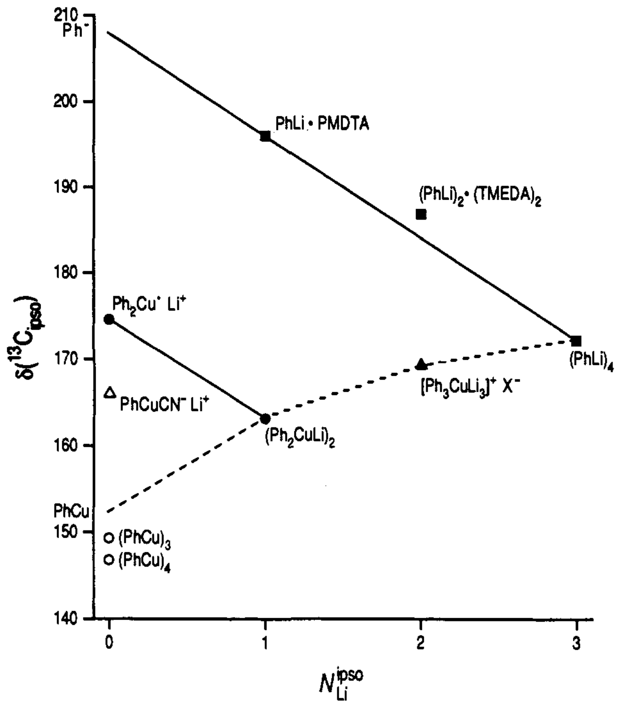

Figure 1. Plots of $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$ *vs* $N_{\mathrm{Li}}^{\mathrm{ipso}}$, the number of Li atoms per *ipso*-C. Note that the $(\mathrm{Ph_2CuLi})_n$ line (●) is parallel to the $(\mathrm{PhLi})_n$ line (■).

$[\mathrm{Ph_2Cu}]^-$ and $[\mathrm{Cu(dppe)_2}]^+[\mathrm{Mes_2Cu}]^-$ contain ion pairs in the solid state.[3a,b] Thus, we are confident that δ 174.5 ppm characterizes the *ipso*-C in monomeric $\mathrm{Ph_2Cu^-}$, which we have now prepared by two independent routes. The ^{13}C NMR spectra of $\mathrm{Ph_2CuLi}$/pyridine-d_5 (δ 173.6, 141.8, 125.9, 122.7 ppm) and $\mathrm{Ph_2CuLi/CD_2Cl_2}$ (δ 162.3, 142.2, 128.4, 126.8 ppm) reported by Ullenius et al.[12] are in harmony with our data. On the basis of the correlation of NMR and X-ray results, we assign the former a monomeric structure, whereas the latter signals are indicative of a dimeric formulation (vide infra).

The data in Table I thus enable the characterization of the aggregation of organocopper compounds by ^{13}C NMR spectroscopy. In general, aggregation decreases the value of $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$, i.e., shielding increases with the number of Li or Cu atoms coordinated to the *ipso*-C, as in the sequence PhLi to $(\mathrm{PhLi})_2$ to $(\mathrm{PhLi})_4$ (11.5 ppm/Li) or $\mathrm{Ph_2CuLi}$ monomer to dimer (11.4 ppm). This is attributable to the paramagnetic shielding term.[20] (Note that the Li in $\mathrm{Ph_2CuLi}$ monomer is not bonded to Ph, and there are three Li atoms per *ipso*-C in PhLi tetramer and two in PhLi dimer.) The effect of coordinating a second Cu atom to the *ipso*-C in going from the putative monomeric "PhCu" (vide infra) to $(\mathrm{PhCu})_3$ (~2 ppm) is much less than the effect of adding a Li atom (11.5 ppm), suggesting that the bonding is more covalent in the case of Cu. In general, the larger downfield shift corresponds to the more ionic carbon–metal bond, due to mixing of ground σ states into π^* excited states.[21]

The effect of increasing the number of Li atoms per *ipso*-C, symbolized as $N_{\mathrm{Li}}^{\mathrm{ipso}}$, is shown in Figure 1 for $(\mathrm{PhLi})_n$ and $(\mathrm{Ph_2CuLi})_n$. For PhLi, the decrease in $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$ with the increasing $N_{\mathrm{Li}}^{\mathrm{ipso}}$ can be calculated to within 1% by using the linear relationship $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 208 - 11.5N_{\mathrm{Li}}^{\mathrm{ipso}}$. There is a parallel decrease in $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$ between monomeric diphenylcuprate(I) and dimeric lithium diphenylcuprate(I) in DMS, which provides support for our assignment of $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 163$ ppm for the dimer. (Ullenius et al. suggested that $\mathrm{Ph_2CuLi}$ is dimeric in dichloromethane.[12])

Crystals of "$\mathrm{Ph_2CuLi}$" grown from DMS reveal a $(\mathrm{Ph_2CuLi})_2 \cdot 3\mathrm{DMS}$ structure with each Ph group bridging a Cu and a Li,[3e] whereas the crystals grown from THF are $[\mathrm{Ph_6Cu_3Li_2}]^-[\mathrm{Li(THF)_4}]^+$.[3f] It appears that the $[\mathrm{Ph_6Cu_3Li_2}]^-$ cluster is an artifact of the crystallization process, since $\mathrm{Ph_2CuLi}$ in THF solution has $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 174.1$ ppm.[6] This anionic cluster has also been crystallized from DMS as a counterion for our "higher order" cuprate $[\mathrm{Ph_3CuLi_3}]^+$.[2d]

The higher order $[\mathrm{Ph_3CuLi_3}]^+$ subunit of $\mathrm{Ph_5Cu_2Li_3}$ is joined to the lower order $[\mathrm{Ph_2Cu}]^-$ subunit via 2 bridging Li atoms in the solid state,[4a] and the NMR results reported herein suggest that this is also true in solution, as $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 164.1$ ppm is much closer to the dimer chemical shift than the monomer shift.

The conjugate addition reaction of organocuprate reagents with enones is much faster in less polar solvents such as hydrocarbons,[12] DMS,[9] and dichloromethane[12] than in more polar solvents such as THF or pyridine.[12] In contrast, the reaction of organocuprates with alkyl halides is much faster in polar solvents.[10] Our results suggest that the dimer is responsible for facile conjugate addition and the monomer is responsible for $\mathrm{S_N2}$-like alkylation.

As also shown in Figure 1, the magnitude of $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$ increases monotonically, but not linearly, in the series $(\mathrm{Ph_2CuLi})_2 < [\mathrm{Ph_3CuLi_3}]^+ < (\mathrm{PhLi})_4$. The change in $\delta(^{13}\mathrm{C}_{\mathrm{ipso}})$ upon going from $[\mathrm{Ph_3CuLi_3}]^+$ to $(\mathrm{PhLi})_4$ is half of that upon going from $(\mathrm{Ph_2CuLi})_2$ to $[\mathrm{Ph_3CuLi_3}]^+$. Consider now the series $[\mathrm{Ph_3CuLi_3}]^+ > (\mathrm{Ph_2CuLi})_2 >$ "PhCu", which includes the (as yet uncharacterized) "PhCu" monomer. In this series $N_{\mathrm{Li}}^{\mathrm{ipso}}$ decreases by 1 and the number of Ph groups per Cu decreases by 1 with each step. Thus, extrapolation of our data to the $N_{\mathrm{Li}}^{\mathrm{ipso}} = 0$ axis in Figure 1 leads to the estimation that $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 151$ for monomeric PhCu.

The addition of a $\mathrm{Ph^-}$ group to PhCu (monomer) to yield $\mathrm{Ph_2Cu^-}$ (monomer) results in a 23 ppm downfield shift of the ipso ^{13}C resonance. The addition of a $\mathrm{CN^-}$ group to PhCu to yield $\mathrm{PhCuCN^-}$, also a useful synthetic reagent,[22] gives a 15 ppm downfield shift.[7] We believe that back-bonding is responsible, at least in part, for the 8 ppm difference.[23,24] This analysis implies that replacement of Ph by CN in the higher order cuprate $\mathrm{Ph_3Cu^{2-}}$ to give $\mathrm{Ph_2Cu(CN)^{2-}}$ should result in a different chemical shift. In fact, the cuprate solutions prepared from PhLi (2 equiv) and CuI or CuCN both have the same $\delta(^{13}\mathrm{C}_{\mathrm{ipso}}) = 174.2 \pm 0.1$ in THF,[6] indicating that $\mathrm{CN^-}$ is not bound to Cu in these species. Our results (vide supra) suggest that both of these solutions contain monomeric $\mathrm{Ph_2CuLi}$.

To summarize, PhCu is an equilibrium mixture of "tetramer" and "trimer" in DMS. The chemical shift of the *ipso*-C atom characterizes the aggregation state of PhCu and the "Gilman reagent" $\mathrm{Ph_2CuLi}$. The data show that $[\mathrm{Ph_3CuLi_3}]^+[\mathrm{Ph_2Cu}]^-$ is a higher order cuprate as originally proposed,[5] and as confirmed by X-ray data.[4a] Finally, the so-called "higher order cyanocuprate", "$\mathrm{Ph_2Cu(CN)Li_2}$", is a variety of Gilman reagent, better represented as $\mathrm{Ph_2CuLi \cdot LiCN}$,[6,7,25] as predicted by Bertz[6] and Snyder.[26]

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