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[20] Crystal data of $Ba_2Ag_{10}S_7$: black needle crystal, monoclinic, space group *C2/m* (no. 12), $a = 14.460(3)$, $b = 4.295(2)$, $c = 13.467(3)$ Å, $\beta = 103.88(3)^\circ$, $V = 812.1(5)$ Å^3, $Z = 2$.

NMR Spectroscopic Structural Determination of Organozinc Reagents: Evidence for "Highly Coordinated" Zincates**

T. Andrew Mobley and Stefan Berger*

In an interesting series of papers from the laboratories of Uchiyama and Sakamoto,[1] differences in the reactivity between stoichiometrically formulated $[Me_3Zn]Li$ and $[Me_4Zn]Li_2$ led the authors to postulate the existence of a tetracoordinated zinc complex in solution. ^1H NMR studies indicate that only one type of methyl resonance exists in these species, even at very low temperatures. However, as noted by the authors the NMR spectra observed could be the result of a rapid equilibrium of different complexes. Based upon our recent success in using fully ^{13}C-labeled material to identify the number of methyl groups bound to the central copper atom in analogous cuprate complexes,[2] we undertook a structural investigation of the above mentioned organozincates.

The use of fully ^{13}C-labeled material results, in the absence of ^1H-decoupling irradiation, in magnetic inequivalence of chemically equivalent carbon atoms. This result is a consequence of the difference in the C,H coupling between a carbon atom and those protons directly attached and those protons attached to another ^{13}C-labeled methyl group in the same molecule. Since the magnetic inequivalence of the carbon atoms allows the observation of the carbon–carbon coupling constant over two bonds, analysis of the spectra provides an easy method of counting the number of labeled methyl groups attached to the metal center.

As a base compound, the neutral $(^{13}CH_3)_2Zn$ species (**1**) was synthesized by heating $^{13}CH_3I$ and Zn powder in the presence of a small amount of Cu catalyst in a sealed glass system.[3] Vacuum transfer of the volatile material from the solid residue to a liquid-nitrogen cooled flask resulted in the isolation of **1** contaminated by a small amount of $^{13}CH_3I$ starting material. A small amount of **1** was dissolved in $[D_8]$THF or $[D_{14}]$hexane and the ^1H and ^1H-coupled ^{13}C NMR spectra were obtained at 400 and 600 MHz, respectively. Expansions of the methyl regions of the ^{13}C NMR spectra are shown for **1** in hexane and **1** in $[D_8]$THF (Figure 1a and 1b, respectively). For comparison the spectrum of the analogous compound $[(^{13}CH_3)_2Cu]Li$ (**2**) in $[D_8]$THF is also shown (Figure 1c). All three spectra show a similar coupling pattern with only slight changes in the coupling constants. The spectra were modeled on the basis of the higher-order coupling pattern of an $A_3XX'A'_3$ system and the calculated coupling constants are summarized in Table 1. Dimethylzinc synthesized by treatment of ZnI_2 with two equivalents of $^{13}CH_3Li$ resulted in identical spectra when the concentration of the zinc species was low.

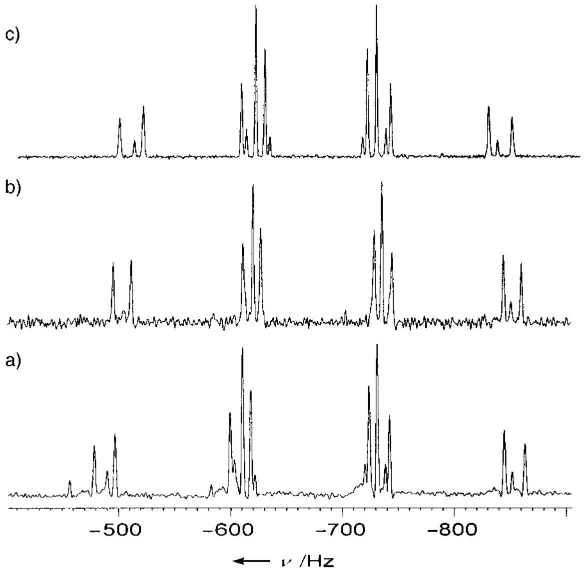

Figure 1. ^1H coupled ^{13}C NMR spectra at −80 °C: a) **1** (0.08 M) in hexane; b) **1** (0.35 M) in $[D_8]$THF; c) **2** (0.26 M) in $[D_8]$THF.

The species $[(^{13}CH_3)_3Zn]Li$ (**3**) could be synthesized by treatment of $(^{13}CH_3)_2Zn$ with one equivalent of $^{13}CH_3Li$. In practice a suitable excess of $^{13}CH_3Li$ was used to account for the presence of the $^{13}CH_3I$ contaminant. The ^1H and ^{13}C NMR spectra of this sample also show a higher order coupling pattern; however, the coupling pattern differs substantially from that of dimethylzinc (Figure 2a). These spectra could be modeled successfully with a $A_3XA'_3X'A''_3X''$ system (Figure 3).[4] The resulting calculated spectrum is shown for comparison in Figure 2b and the calculated coupling constants are summarized in Table 1.

Addition of one additional equivalent of $^{13}CH_3Li$ results in the formation of $[(^{13}CH_3)_4Zn]Li_2$ (**4**). The ^1H and ^{13}C spectra indicate that the bulk of the zinc-containing material is identical to **3**. However, in addition to one equivalent of $^{13}CH_3Li$ in its tetrahedral tetrameric form, a broad, weak resonance is observed at $\delta = -12$ (Figure 4). Furthermore, after an overnight ^{13}C NMR acquisition at high field

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[**] This work was supported by the Fonds der Chemischen Industrie.

1433-7851/99/3820-3070 $ 17.50+.50/0

Table 1. Calculated coupling constants for organocuprate and organozincate compounds.

Compound	Spin system	$^1J_{AX}$ [Hz]	$^2J_{XX'}$ [Hz]	$^3J_{AX'}$ [Hz]	$^4J_{AA'}$ [Hz]
Me_2Zn (**1**) in Hexan	$A_3XA'_3X'$	121.7	18.4	– 1.0	– 0.4
Me_2Zn (**1**) in [D$_8$]THF	$A_3XA'_3X'$	116.0	15.9	– 0.6	0.4
$[Me_3Zn]Li$ (**3**) in [D$_8$]THF	$A_3XA'_3X'A''_3X''$	110.9	14.0	0.6	0.4
$[Me_4Zn]Li_2$ (**4**) in [D$_8$]THF	$A_3XA'_3X'A''_3X''A'''_3X'''$	112.0	12.2	0.4	0.4
$[Me_2Cu]Li$ (**2**) in [D$_8$]THF	$A_3XA'_3X'$	109.5	21.0	– 0.8	–

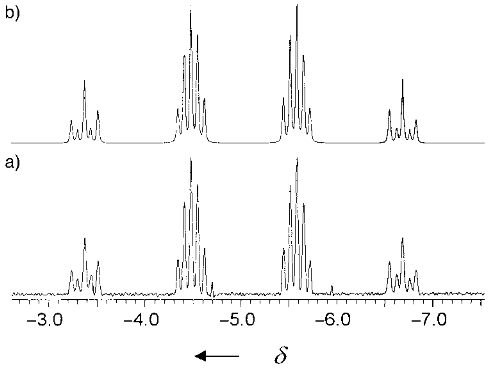

Figure 2. a) ^{1}H coupled ^{13}C NMR spectrum of **3** (0.08 M) in [D$_8$]THF at – 80 °C; b) calculated spectrum for an $A_3XA'_3X'A_3$“X” spin system (coupling constants are summarized in Table 1).

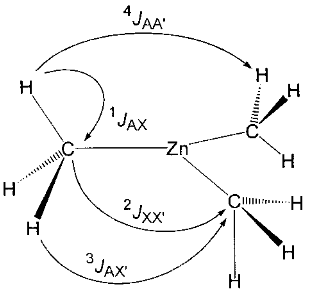

Figure 3. Trimethylzincate structure with spin couplings used in the calculation of the $A_3XA'_3X'A''_3X''$ spin system.

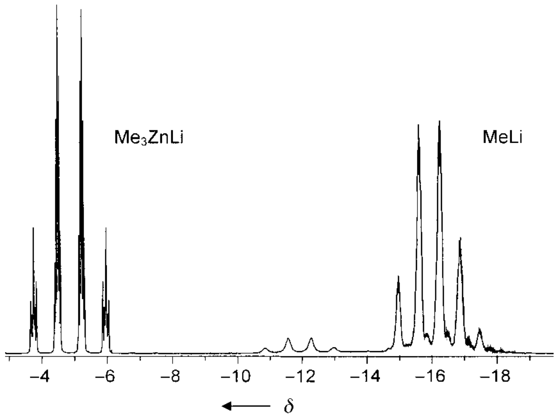

Figure 4. ^{1}H coupled ^{13}C NMR spectra of **4** (0.08 M) in [D$_8$]THF at – 80 °C.

(600 MHz) with this fully labeled material, a very weak set of resonances upfield is observed whose multiplicity corresponds to **4**. An expansion with significant magnification is shown in Figure 5. A simulation based upon an $A_3XA'_3X'A''_3X''A'''_3X'''$ system confirms that identification of these resonances as $[(^{13}CH_3)_4Zn]Li_2$ is reasonable (Figure 5b).

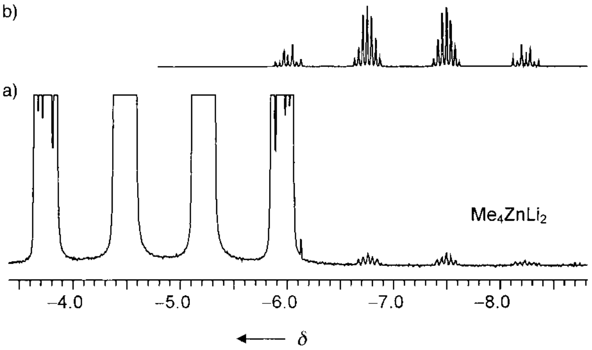

Figure 5. a) Expansion of the ^{1}H coupled ^{13}C NMR spectra of **4** (0.08 M) in [D$_8$]THF at – 80 °C showing the very weak set of resonances attributed to the tetramethylzincate species; b) calculated spectrum for the $A_3XA'_3X'A''_3X''A'''_3X'''$ spin system (coupling constants are summarized in Table 1).

Unrefined coupling constants for the species are summarized in Table 1; however, no iterative fitting of the data was possible because of limitations in the large spin system.

Compounds **3** and **4** were synthesized by a method similar to that of Uchiyama and Sakamoto et al.[1] The NMR spectra taken of concentrated samples (0.1 M) obtained by treatment of $ZnCl_2$ with three equivalents of $^{13}CH_3Li$ result in spectra similar to those obtained by Uchiyama and Sakamoto et al. However, spectra obtained of highly cooled (– 80 °C) and highly dilute (0.005 M) samples show much more complicated spectra consisting of a mixture of $[(^{13}CH_3)_3Zn]Li$, $(^{13}CH_3)_2Zn$, $(^{13}CH_3)ZnCl$, and $(^{13}CH_3)Li$. These differences are consistent with a slowing of the fast exchange processes that are present in the concentrated samples.

We interpret our results in the following way. The addition of MeLi to Me_2Zn readily occurs to form a $[Me_3Zn]Li$ species in which all three methyl groups are bound to the zinc center. All three methyl groups are chemically equivalent on the NMR timescale. This may be the result of the formation of a highly symmetrical structure (for example, C_{3v} or D_{3h}) or a rapid exchange of methyl groups in a lower symmetry structure (for example, C_{2v}). At higher temperatures intermolecular exchange of methyl groups occurs, which leads to a loss of the higher order coupling pattern. Upon addition of a second equivalent of MeLi an equilibrium with the $[Me_4Zn]Li_2$ species can be observed. However, this equilibrium lies far to the left in Equation (1).

$$[Me_3Zn]Li + MeLi \rightleftharpoons [Me_4Zn]Li_2 \tag{1}$$

These results are consistent with the results obtained in the analogous copper system and are explained by a simple coulombic repulsion model. It is easy to form the monoanionic species $[Me_3Zn]^-$ or $[Me_2Cu]^-$, but the addition of a second negative group to the metal center to form $[Me_4Zn]^{2-}$ or $[Me_3Cu]^{2-}$, respectively, results in too great a coulombic repulsion and the reaction is thermodynamically unfavored. In the solid state, however, it appears that this coulombic repulsion may be overcome; $[Me_4Zn]Li_2$ has been isolated and structurally characterized by X-ray diffraction techniques.[5] The identity of the broad resonance at $\delta = -12$ is at this time unknown. On the basis of its chemical shift and broad appearance it could be similar to MeLi in structure, with the broadness of the peaks arising from unresolved coupling between ^{6}Li and ^{13}C. Our results do not contrast those obtained in the chemical reactivity studies for these systems.[1] Even though the ground-state structures of the "higher order" zincates and cuprates appear to be monoanionic, the reactive species could of course be the higher energy tetracoordinated zincate and tricoordinated cuprate.

Further studies involving the nature of the interaction of the anion and the Li^+ counterion and studies examining the interaction of **1**, **3**, and **4** with reactive substrates are currently underway.

Received: May 27, 1999 [Z13472IE]
German version: *Angew. Chem.* **1999**, *111*, 3256–3258

Keywords: NMR spectroscopy · organometallic compounds · structure elucidation · zinc

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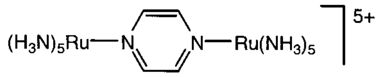
An Exceedingly Stable Diiron(II,III) Complex Ion $[(tz)\{Fe(CN)_5\}_2]^{5-}$ with Comproportionation Constants between 10^8 (in H_2O) and 10^{19} (in CH_3CN)

Markus Glöckle and Wolfgang Kaim*

Prussian Blue, formulated as cyanoiron compound $[Fe^{III}_4\{Fe^{II}(CN)_6\}_3]$ (**1**),[1] and the heterocycle-bridged Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$ (**2**, pz = pyrazine) are textbook cases for mixed-valent compounds in coordination chemistry.[2] The equilibrium constant K_c for comproportionation, which measures the stability towards disproportionation [Eqs. (1), (2)] and thus specifies the range of existence of the mixed-valent state, is about 10^{12} for **1** in water[1b] and between $10^{6.8}$ and $10^{7.3}$ for **2**, depending on the solvent.[3]



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$$M^{n-} + M^{(n-2)-} \rightleftharpoons 2\,M^{(n-1)-} \tag{1}$$

$$K_c = \frac{[M^{(n-1)-}]^2}{[M^{n-}][M^{(n-2)-}]} = e^{\Delta EF/RT} \tag{2}$$

ΔE: redox potential difference

It was therefore disappointing when the bis(pentacyanoiron) complex $[(\mu\text{-pz})\{Fe(CN)_5\}_2]^{5-}$ ($\mathbf{3}^{5-}$) with bridging pyrazine was found to exhibit only a small K_c value of $10^{1.9}$ in water, signifying very little metal–metal interaction in $\mathbf{3}^{5-}$.[4] Recent experiments in aprotic polar media, however, showed that this value for $\mathbf{3}^{5-}$ can increase up to $10^{6.5}$,[5] illustrating the crucial role of the environment for the metal–metal coupling in such highly charged systems. Using the hitherto rather neglected[6] unsubstituted 1,2,4,5-tetrazine (tz) as an excellently π-accepting bridging ligand, we have now been able to extend the stability range of such simple diiron(II,III) systems to $10^{7.9}$ in water and to $10^{19.0}$ in acetonitrile, allowing for the isolation of the corresponding ion $[(\mu\text{-tz})\{Fe(CN)_5\}_2]^{5-}$ ($\mathbf{4}^{5-}$) as a stable pentakis(tetraethylammonium) salt.[7b]

Compounds $(NEt_4)_6(\mathbf{4})$ ($Fe^{II}(tz)Fe^{II}$) and $(NEt_4)_5(\mathbf{4})$ ($Fe^{2.5}(tz)Fe^{2.5}$) were isolated[7a,b] and characterized spectroscopically and electrochemically (Figure 1, Table 1). The neighbor-

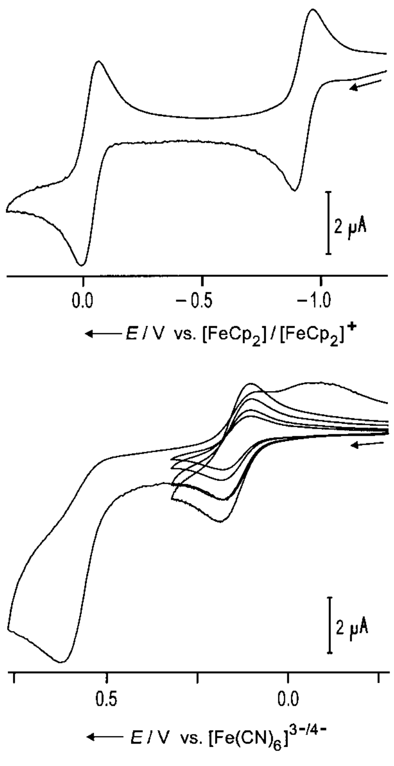

Figure 1. Cyclic voltammograms of $(NEt_4)_6(\mathbf{4})\cdot 2H_2O$ in CH_3CN/0.1 M NBu_4PF_6 at −35 °C (50 mV s^{-1}; top) and in H_2O/0.25 M Na_2SO_4 at room temperature (50 mV s^{-1} for full-scale voltammogram and 100, 50, 25, and 15 mV s^{-1} for the first oxidation wave; bottom).

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