Transmetalation Reaction of Dimethylzinc and (Bis(2-pyridyl)methyl)lithium

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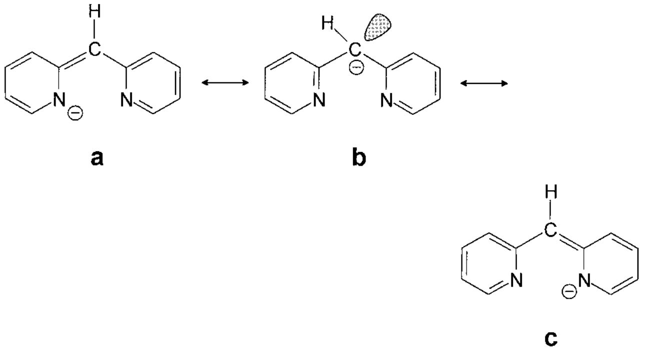
*Summary: The unexpected transmetalation reaction between the (bis(2-pyridyl)methyl)lithium compound [$(THF)_2LiPy_2CH$] (**1**) and dimethylzinc produces the novel dimer [$MeZnC(H)Py_2]_2$ (**2**), in which dimerization occurs via mutual ring N→Zn chelation between two monomers which contain Zn−C bonds. While all known (2-pyridyl)methyl anions are C(sp^2)-centered planar ligands, structural evidence in **2** shows that the central carbon atom is partially sp^3-hybridized.*

Recently we commenced a study of the coordinational behavior of chelating pyridyl-substituted anions in metal coordination.[1] In these systems the formal negative charge at the central, deprotonated Py_2CH^-, Py_2N^-, Py_2P^-, or Py_2As^- function is delocalized into the π-systems of both pyridyl rings (Py). Hence, the resulting anions are not coordinated like classical carbanions, amides, phosphides, or arsenides. The triphenylmethyl anion exhibits a contact of the central carbon atom with the small and hard lithium and sodium cations, while the large and soft cations K^+ to Cs^+ coordinate to the π-system of a single phenyl ring.[2] In contrast, the $PyPh_2C^-$ anions are carbanions only formally and behave in their coordination like amides. Alkali metals are bound to the pyridyl nitrogen atom in the plane of the ring.[3] Similarly, the Py_2P^- and Py_2As^- anions are only formally phosphides or arsenides because in their metal derivatives neither a P− nor an As−metal bond is observed.[4] The metals are exclusively chelated by the ring nitrogen atoms. Neutral pyridyl-substituted methane derivatives Py_3CR (R = H, OH), well-established in the literature, are N-chelating ligands in metal coordination.[5] The central deprotonated carbon atom in the Py_2CH^- anions did not display any accumulation of charge density.[6] In all known metal complexes both pyridyl rings are coplanar and the central carbon atom shows sp^2 character.[7] Metals are coordinated via ring nitrogen atoms, and the mesomeric resonance forms **a** and **c** contribute most in describing the bonding.[8] Metal coordination via the central carbon atom and implicit sp^3 character according to resonance form **b** has never been observed until now, even when a strong covalent M−C bond could be formed.



Only the central nitrogen atom in the Py_2N^- amide ligand could be employed in coordination toward the soft metals indium and thallium in the cationic fragments Me_2In^+ and Me_2Tl^+. Rotation about the central $N-C_{ipso}$ bond and noncoplanar arrangement of the two rings cause dimeric and polymeric structures, respectively.[9] In the Py_2CH^- anions rotation about the central $(H)C-C_{ipso}$ bond has never been observed. In order to study whether the central carbon atom in the Py_2CH^- carbanion can also be employed in coordination to “soft” metals, we metalated bis(2-pyridyl)methane with potassium hydride and elemental rubidium and cesium. Unfortunately, all resulting products are virtually insoluble, even in polar organic solvents. Thus, crystallization was not possible and characterization via X-ray single-crystal structure analysis was impossible. To examine the possibility of carbanionic coordination in accord with resonance form **b**, we carried out a 1:1 reaction between the (bis(2-pyridyl)methyl)lithium compound **1** and dimethylzinc (eq 1).

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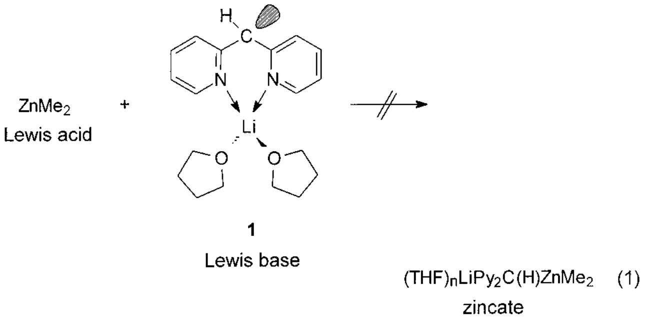

After the resulting clear solution was stirred for 12 h and the reaction mixture was stored at −35 °C for 7 days, red crystals were obtained. The result of the X-ray structure analysis[10] is shown in Figure 1.

The product was not the expected Lewis acid/base adduct; a transmetalation reaction had occurred instead. The lithium cation in the starting material $[(THF)_2LiPy_2CH]$ (**1**) was replaced by a methylzinc unit to give $[MeZnC(H)Py_2]_2$ (**2**) (eq 2).

$$\underset{\textbf{1}}{2\,[(THF)_2LiPy_2CH]} + 2ZnMe_2 \xrightarrow{\text{toluene}} \underset{\textbf{2}}{[MeZnC(H)Py_2]_2} + 2MeLi \quad (2)$$

The molecule is made up of two diorganozinc molecules chelated to each other via both ring nitrogen atoms in a head-to-tail fashion to give the overall dimer. While the Zn−methyl carbon distance of 1.974(3) Å lies in the range observed for Zn−C bonds,[11] the Zn−C(H) distance of 2.269(3) Å is remarkably longer. Without doubt, the reason for this is the considerable steric strain of two almost eclipsed pyridyl rings. The C2···N2a and C7a···N1 contacts of only 3.12 Å are in the region found in other strained ring systems, e.g., that in [2.2]paracyclophane at 3.09 Å.[12]

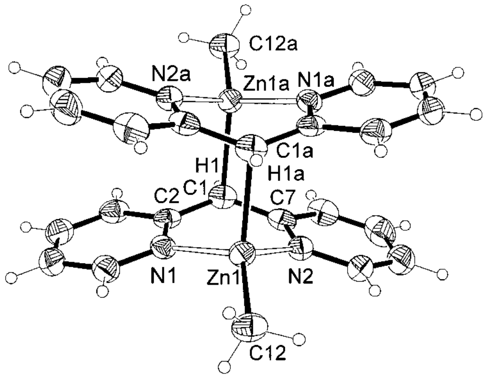

Figure 1. Solid-state structure of $[MeZnC(H)Py_2]_2$ (**2**). Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zn1−C12 = 1.974(3), Zn1−C1a = 2.269(3), Zn1−N1 = 2.044(2), Zn1−N2 = 2.035(2), C1−C2 = 1.433(4), C1−C7 = 1.440(4); N1−Zn1−N2 = 92.8(1), C12−Zn1−C1a = 113.6(1), C2−C1−C7 = 127.0(3). The noncoordinated toluene has been omitted for clarity.

The structural parameters at the central C1 atom in the dimer indicate a partial rehybridization from sp^2 to sp^3. Elongation of the central carbon bond by ca. 0.04 Å in **2** compared with the $HCPy_2$ anions containing an sp^2 carbon atom matches the increase in radii on going from an sp^2 to an sp^3 carbon. Both pyridyl rings are no longer coplanar (the ring normals intersect at an angle of 22.2°), and the sum of C−C−C and C−C−H bond angles at C1 is 351°. The hydrogen atom at C1 has been located in the difference Fourier synthesis and has been refined without application of any restraints. The angle C2−C1−C7 of 127.0(3)° in **2** is not as acute as the related angle in the neutral ligand in the complex $[H_2CPy_2LiPy_2CH]$[7] of 115.0(4)° but is considerably smaller than that in the anionic sp^2-centered ligand of 132.6(5)°. Hence, the pyramidal character of C1 in **2** is established beyond any reasonable doubt. The average Zn−N distance of 2.04 Å is located halfway between those of an amide and a dative bond.[11g,13] While the Zn−N distance of 1.82 Å in the zinc amide $[Zn\{N(SiMe_3)_2\}_2]$[14] in the gas phase is relatively short, the N→Zn bond in the $[Zn(Py_3P)_2]^{2+}$ cation[15] of 2.165(4) Å is considerably longer.

The formation of methyllithium in a transmetalation reaction is uncommon but not unusual. For instance, it has been employed previously in organosilicon synthesis.[16] However, in 1917 Schlenk and Holtz confirmed in their milestone paper on alkali-metal organics[17] that the reaction of diethylzinc and lithium or sodium yields only zinc and an alkali-metal ethylzinc compound; hence, transmetalation does not occur. To favor transmetalation, they employed diorganomercury compounds instead. Nowadays there are many examples known of transmetalation reactions involving the $R_2Hg/R'Li$ system,[18] but the $R_2Zn/R'Li$ system normally yields lithium

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(10) Crystal data for **2**: $[C_{12}H_{12}N_2Zn]_2 \cdot C_7H_8$, $M_r = 591.4$, monoclinic, $P2_1/n$, $a = 9.270(2)$ Å, $b = 13.491(3)$ Å, $c = 11.000(2)$ Å, $\beta = 98.10(3)°$, $V = 1.362(1)$ nm^3, $Z = 2$, $\rho_c = 1.442$ Mg m^{-3}, $F(000) = 612$, $\lambda = 0.710\,73$ Å, $T = 153(2)$ K, μ(Mo Kα) = 1.788 mm^{-1}, crystal size 0.3 × 0.3 × 0.3 mm, 4.00° < θ < 25.00°, 2428 reflections (2393 independent) collected on a Stoe-Siemens diffractometer on a shock-cooled crystal in an oil drop.[20] The structure was solved by direct methods (SHELXS-97),[21] and 205 parameters were refined on F^2.[22] A single uncoordinated toluene molecule is located on an center of inversion and was refined anisotropically to a site occupation factor of 0.5 employing 67 ADP and distance restraints. Maximum residual electron density: 0.53 e Å^{-3}, $R1(F > 2\sigma(F)) = 0.035$ and wR2(all data) = 0.099 with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. Crystallographic data (without structure factor tables) of the structure discussed in this publication have been deposited as supplementary publication No. CCDC-132031 with the Cambridge Crystallographic Data Centre. They can be obtained free of charge from the following address: CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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zincates of general composition $Li_2ZnR_2R'_2$ or $LiZnR_2R'$.[19] In this paper a rare example of a transmetalation reaction employing a diorganozinc precursor has been presented. Apparently this reaction is not driven by the high basicity of the central carbon atom but by the coordinating periphery of the Py_2CH^- anion. To prove this reaction, we monitored the transmetalation by ^1H NMR as well as ^7Li NMR spectroscopy.[23] Complete lithiation of bis(2-pyridyl)methane gave rise to a signal at δ 3.57 in the ^7Li NMR spectrum in C_6D_6 of [$(THF)_2LiPy_2CH$] (**1**). Addition of dimethylzinc instantaneously caused the appearance of a second signal. Within approximately 3 min the original signal of **1** had disappeared. The new signal at δ 1.48 in the ^7Li NMR spectrum was identified as being due to MeLi by addition of external methyllithium to the sample of the reaction mixture. The signal increased without any change in chemical shift.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for the structure of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) **2** was prepared as follows. **1**[6] (0.70 g, 4.0 mmol) in 30 mL of toluene was reacted at −78 °C with dimethylzinc (2 mL, 2 M in toluene) by dropwise addition of dimethylzinc to **1**. Subsequently the reaction mixture was stirred for 12 h at room temperature and then was stored at −35 °C. After 7 days **2** was obtained as red crystals (0.11 g, 11%, first batch; 85% total after crystallization at −90 °C). Mp: 120 °C dec. ^1H NMR (C_6D_6, room temperature, TMS (external)): δ −0.32 (s, 3 H, CH_3), 4,91 (s, 1 H, H1), 5.79 (ddd, $^3J_{5,4} = 6.6$, $^3J_{5,6} = 6.2$, $^4J_{5,3} = 1.1$ Hz, 2 H, H5), 6.30 (dd, $^3J_{3,4} = 8.8$, $^4J_{3,5} = 1.1$ Hz, 2 H, H3), 6.55 (ddd, $^3J_{4,3} = 8.8$, $^3J_{4,5} = 6.7$, $^4J_{4,6} = 1.6$ Hz, 2 H, H4), 7.27 (d, $^3J_{6,5} = 6.2$ Hz, 2 H, H6). ^{13}C NMR (C_6D_6, room temperature, TMS (external)): δ 5.0 (s, CH_3), 87.6 (s, C1), 106.0 (s, C5), 120.3 (s, C3), 132.7 (s, C4), 146.5 (s, C6), 159.0 (s, C2). Hydrogen and carbon atoms are numbered as follows: