Pyramidal Carbanions

A Monomeric Organolithium Compound Containing a Free Pyramidal Carbanion in Solution and in the Solid State**

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Tris(pyrazolyl)hydroborate ligands are undoubtedly among the most important face-capping, six-electron N-donor ligands in coordination chemistry.[1] Compared to these anionic species, the isoelectronic, neutral analogues $HC(R_xpz)_3$ are considerably less well developed.[2] However, interest in functionalizing the central methine carbon atom is growing, and such changes to the backbone can dramatically influence the solubility of these ligands and their metal complexes.[3] Substitution of the methine hydrogen atom is generally accomplished by deprotonation and reaction with a suitable electrophile. Nevertheless, in most cases the interesting organolithium intermediates were not isolated and characterized but were treated in situ to release the desired products.[3,4] Thus, little information is available on the constitution of such carbanion-containing species.[5,6]

The type and degree of aggregation of organolithium compounds has stimulated extensive research,[7] because lithium organyls are of fundamental interest and have important applications in many different fields ranging from synthetic chemistry to technical processes.[8] In particular, the structural elucidation of unassociated anions is important because any effects due to anion/cation interactions are minimized.[9] Carbanionic moieties attached to heterocycles or phenyl rings (e.g., $[Ph_2pyC]^-$,[10] $[py_2CH]^-$,[11] and $[Ph_3C]^-$[12] with py = pyridyl) have been structurally characterized as their alkali metal compounds. Their main structural feature is the presence of a central *trigonal-planar* carbon atom due to delocalization of the negative charge in the adjacent rings. However, no unassociated alkyl lithium compound containing a "free" *pyramidal* carbanion has been structurally characterized so far. Here we show that a

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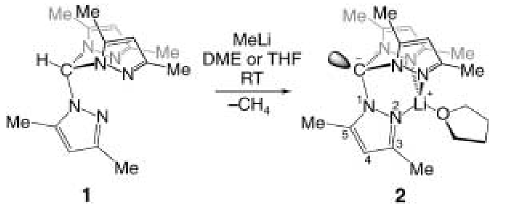
suitable bridle, created by intramolecular chelation of the lithium cation, and lack of π delocalization yields the first monomeric lithium organyl compound containing a "free" (pseudo)tetrahedral carbanion.

Reaction of tris(3,5-dimethylpyrazolyl)methane, HC(3,5-$Me_2pz)_3$ (**1**), with methyllithium in DME or THF at ambient temperature afforded a dark red solution. Title compound **2** was isolated as pale red crystals in 87 % yield by crystallization from THF/*n*-hexane (Scheme 1). The crystal-structure determination[13] of **2** (Figure 1) verified the formation of a monomeric alkyl lithium compound in which the lithium cation is tetracoordinated by three pyrazole rings and one THF molecule. Compound **2** can formally be described as zwitterion containing a spatially separated anion (C1) and cation (Li1).[14]



Scheme 1. Synthesis of **2**. DME = dimethoxyethane.

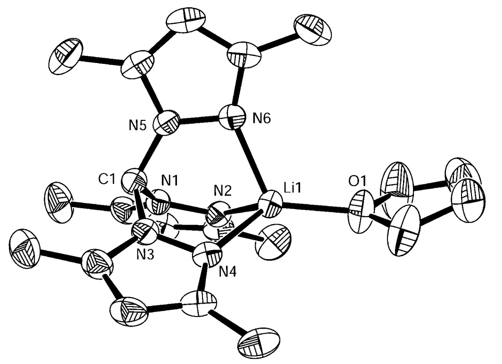


Figure 1. Molecular structure and numbering scheme for **2**; thermal ellipsoids are drawn at the 40 % probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°] (corresponding values of free pyrazole are given in brackets; superscript integers represent the ring position according to Scheme 1): C1–N1 144.9(2), C1–N3 144.6(2), C1–N5 144.6(2), Li1–N2 202.9(3), Li1–N4 203.4(3), Li1–N6 200.6(3), Li1–O1 190.8(3), N1–N2 137.4(2), N3–N4 137.3(2), N5–N6 136.6(2); N1-C1-N3 109.2(1), N1-C1-N5 109.5(1), N3-C1-N5 109.7(1), O1-Li1-N2 121.9(2), O1-Li1-N4 126.6(1), O1-Li1-N6 118.2(2), N2-Li1-N4 94.7(1), N2-Li1-N6 92.1(1), N4-Li1-N6 95.4(1). Inner ring angles C-N-N at N^1: C11-N1-N2 110.2(1), C21-N3-N4 110.9(1), C31-N5-N6 110.1(1) [109.0]. Average bond lengths within the pyrazole rings: N^1–N^2 137.1(2) [136.6], N^2=C^3 132.6(2) [132.9], C^3–C^4 138.7(3) [141.0], C^4=C^5 136.4(3) [136.9], N^1–C^5 135.3(2) [135.7].

All N-C1-N angles (109.2–109.7°) are in agreement with a (pseudo)tetrahedral environment at the carbanionic center. The hydrogen atoms of the methyl substituents in the 5-position show no tendency to form nonclassical hydrogen bonds (i.e., $C-H^{\delta+}\cdots C^{\delta-}$ contacts). The average bond lengths within the pyrazole rings, the inner ring angles (C-N-N at N^1), and the C1–N distances of about 144.7 pm clearly demonstrate the absence of charge delocalization into the pyrazole rings.[15] These geometrical features give rise to a localized carbanionic center at C1. However, one would expect an intramolecular electrostatic interaction between the regions of negative and positive charge in **2**. The degree of interaction can be estimated from the C1···Li1 distance of 289 pm, which is approximately 70 pm longer than usually observed in lithium organyl compounds with a direct Li–C bond.[16] The geometry at the lithium atom can be regarded as a stretched tetrahedron with narrow N-Li1-N angles (average 94.1°) and wide O1-Li1-N angles (average 122.2°). On the basis of equilibrium distance, the Li–N interactions appear to be stronger, as expected. The mean Li–N distance of 202.3 pm lies between those of typical Li–N donor bonds and those of lithium amides.[10,11] Apparently, the intrinsic rigidity and the steric repulsion of the lone pair of electrons at C1 and the Me substituents in the 5-position inhibit an increase in electrostatic interactions and do not allow a shorter C1···Li1 distance.

Since atom–atom equilibrium distances are not always valid bond-strength descriptors,[17] we carried out hybrid DFT (B3LYP/6-31+G(d))[18] calculations of the compliance constants in **2** to quantify the interatomic interaction strengths and possible crystal-packing effects. The gas-phase geometry was optimized by using the X-ray data as a starting point. Table 1 compares the calculated gas-phase equilibrium values of important internal coordinates with our solid-state data, and points to a realistic description of the electronic structure of **2** by the B3LYP model.

Table 1: Comparison of selected internal equilibrium coordinates of **2** in the gas phase (theoretical) and solid state (X-ray).[a]

Bond[b]	Distances [pm]		Compliance constants [pm mdyn^{-1}]	
	X-ray	Theoretical		
Li1···C1	289.0	285.2	207.5	
Li1–N	200.6–203.4	203.8–204.1	198.1	
Li1–O1	190.8	198.3	243.0	
C1–N	144.6–144.9	144.8–145.0	25.8	
				Free pyrazole
N^1–N^2	137.1	138.2	21.9	(17.5)
N^2=C^3	132.6	133.1	13.6	(13.6)
C^3–C^4	138.7	141.4	16.6	(17.3)
C^4=C^5	136.4	138.4	14.4	(14.1)
N^1–C^5	135.3	136.3	15.6	(15.2)

[a] Theoretical (B3LYP/6-31+G(d)) compliance constants are given as a measure for the interaction strengths (see text for details). [b] Superscript integers represent the ring position (see Scheme 1).

Table 1 also lists the compliance constants for these coordinates.[19] Since compliance constants measure the displacement of a specific coordinate due to a unit force acting on it, a higher value is associated with a weaker interaction. The large separation between C1 and Li1 leads to a weak (electrostatic) interaction, as measured by the compliance constant of 207.5 pm mdyn^{-1}.[20] Nevertheless, the Li1–O1 compliance constant (243.0 pm mdyn^{-1}) measuring the Li···THF interaction points to an even weaker interaction, which should result in a pronounced Li1···O1 displacement on going from the theoretical gas-phase structure to the solid-state geometry. Indeed, the crystal-packing effects appear to be most severe for the Li1···O1 distance ($\Delta d = 7.4$ pm). This is interesting since Li–O contacts are normally regarded as strong interactions. Although the Li–N compliance constant of 198.1 pm mdyn^{-1} alone points to a moderate bond strength, the synergism of three Li–N contacts leads to an effective encapsulation of the Li ion. Comparing the B3LYP/6-31+G(d) compliance constants for free pyrazole with those of the pz rings in **2** reveals no major differences in bond strengths, with the exception of the N–N bonds. This bond weakening can be attributed to the increased coordination number at the nitrogen atom. Additionally, one might expect a release of electrons from the pyrazole rings to the N–Li bonds, which should give rise to short N–Li bonds, as observed in the X-ray crystal structure. Altogether, the results are in line with a "localized" methanide carbon atom (a graphical representation is given in the Supporting Information).

In view of the characteristics of **2** in the solid state, that is, a "free" tetrahedral carbanion in a monomeric compound without any significant intermolecular interactions, it seemed worthwhile to investigate its nature in solution. 1D ^{1}H and ^{13}C NMR spectroscopy showed the expected resonances of intact and equivalent pyrazolyl groups and a methanide carbon atom only slightly shifted to lower frequency, from 81.0 to 73.6 ppm with respect to **1**.[21] For trigonal-planar carbanions, such signals are generally shifted to higher frequency; for example, the methanide C atoms of $[(Me_3Si)Ph_2C]^-[Li(tmeda)_2]^+$ (tmeda = *N,N,N′N′*-tetramethylethylenediamine) and $(Me_3Si)Ph_2CH$ resonate at 66.0 and 45.9 ppm, respectively.[22] In contrast to many organolithium compounds, the methanide chemical shift did not show a large temperature dependence, and the absence of detectable coupling to lithium in the entire temperature range suggests weak Li–C interactions if at all. This unassociated character of the carbanion was substantiated by solid-state ^{13}C NMR spectroscopy, which, within experimental error, revealed identical values for the methanide chemical shift in the solid state and in solution. The fate of the cationic part was first addressed by ^{7}Li and ^{1}H NMR diffusion measurements, which revealed identical hydrodynamic radii for the cationic and anionic moieties. This result is consistent with either 1) a tight ion pair without direct Li–C interaction or 2) a zwitterionic structure as found in the solid state. These two alternatives were discriminated by recording a high-resolution ^{15}N,^{1}H correlation spectrum (Figure 2), which for one of the two nitrogen atoms revealed a quartet fine structure due to an $I = 3/2$ nucleus (i.e., ^{7}Li) with a coupling constant of $^{1}J(^{15}N,^{7}Li) = 10$ Hz.

Furthermore, a ^{15}N,^{7}Li correlation spectrum clearly demonstrated that the lithium cation in **2** is fixed in the N_3 pocket of the tris(pyrazolyl)methanide ligand, fully in agreement with its solid-state structure. Therefore, the title compound is stable towards inversion[8c,d] due to the rigid encapsulation of the lithium ion, and owing to the absence of lithium–carbon contacts no "classical" aggregation is apparent.[7]

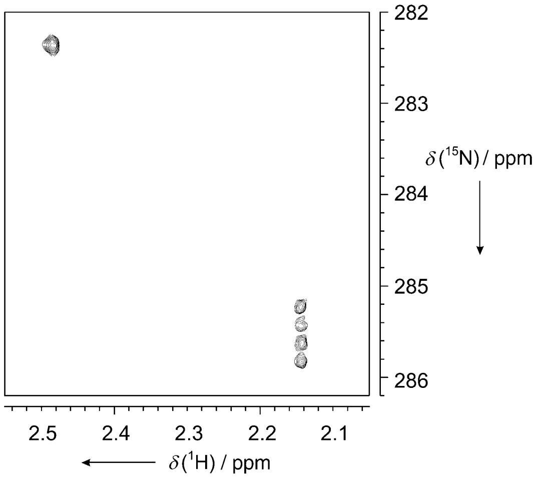


Figure 2. Section of the ^{15}N,^{1}H HMQC spectrum of **2** showing the quartet multiplicity due to the spin of ^{7}Li.

Experimental Section

All procedures were carried out under argon. Solvents were freshly distilled from sodium/benzophenone (THF, DME) or from sodium/tetraglyme/benzophenone (hexane). Compound **1** was prepared according to literature methods.[2] NMR spectra were measured on Bruker Avance spectrometers and chemical shifts are given relative to TMS (^{1}H, ^{13}C), Li^{+}(aq) (^{7}Li), and NH_3 (^{15}N).

2: Methyllithium (7.31 mL of a 1.6 M solution in diethyl ether) was added dropwise to a solution of tris(3,5-dimethylpyrazolyl)methane **1** (3.172 g, 10.63 mmol) in DME (50 mL) at room temperature. Towards the end of addition, a brown solid precipitated from the dark red solution. The reaction mixture was heated at ca. 40 °C until the brown precipitate had dissolved. After cooling to room temperature the clear red solution was stirred for 2 h. All volatile components were removed under vacuum. The dark red, oily residue was dissolved in THF (20 mL), layered with *n*-hexane (40 mL), and cooled to −30 °C. Pale red, moisture- and air-sensitive crystals of the product were isolated and dried in vacuo. A second crop of the product was isolated from the mother liquor after concentration of the solution and cooling to −30 °C. Overall yield: 3.495 g (87 %). M.p. (argon, sealed capillary) 184 °C (decomp); elemental analysis (%): calcd for $LiC_{16}H_{21}N_6{\cdot}C_4H_8O$: C 63.1, N 22.7, H 8.1; found: C 63.8, N 22.3, H 7.8; ^{1}H NMR (500.2 MHz, [D$_8$]THF): $\delta = 5.55$ (s, 3 H, CH$_{pz}$), 2.51 (s, 9 H, Me), 2.16 ppm (s, 9 H, Me); ^{7}Li NMR (194.4 MHz, [D$_8$]THF): $\delta = 9.9$ ppm; ^{13}C NMR (62.9 MHz, C$_6$D$_6$/[D$_8$]THF): $\delta =$ 144.7, 144.6 (s, pz C$_{quart}$), 101.7 (s, pz CH), 73.6 (s, C1), 14.0 (s, Me), 12.5 ppm (s, Me); ^{15}N NMR (50.7 MHz, [D$_8$]THF): $\delta = 282.3$, 285.5 ($^{1}J(^{15}N,^{7}Li) = 10$ Hz); IR (solid, ATR): $\tilde{\nu} = 2920$ m (ν(CH)), 1554 s (ν(pyrazole ring)), 1455 m, 1413 s, 1371 m (δ(CH$_2$, CH$_3$)), 1319 m, 1270 w, 1204 w, 1095 w (ν(CC), δ(CH$_2$, CH$_3$)), 1037 vs (ν(COC)), 971 w, 917 w, 897 m, 864 vs, 786 m, 766 vs, 723 s, 708 m, 691 m, 671 m, 655 cm^{-1} m (ν(LiN), ν(CC), δ(CC)); UV/Vis (THF): λ_{max} (lg ε) = 278 nm (3.05).

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