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Experimental charge density distribution of non-coordinating sp^3 carbanions in $[Mg\{(pz^*)_3C\}_2]^\dagger$ Daniel Kratzert,^a Dirk Leusser,^a Daniel Stern,^a Jens Meyer,^b Frank Breher^b and Dietmar Stalke^{*a}

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In this communication we present the experimental charge density distribution in $[Mg\{(pz^*)_3C\}_2]$ (**1**), ($pz^* = 3,5$ -dimethylpyrazolyl), containing two non-coordinating sp^3 carbanionic lone-pairs.

Anionic tripodal C_3 -symmetrical ligands like $[MeSi(NtBu)_3]^{3-}$,¹ $[Sb(NtBu)_3]^{3-}$,² or $[S(NtBu)_3]^{2-}$,³ were originally designed to coordinate one hemisphere of various metal cations and later turned out to be promising ligands in *e.g.* enantioselectively catalytic transformations.⁴ Hückel's tris(pyrazolyl)methane and Trofimenko's $[HB(pz^*)_3]^-$ scorpionates might be regarded as the original templates for this whole class of ligands.^{5a,b} As pyrazolyl ligands are very suitable ligands in *e.g.* bioinspired coordination chemistry⁶ this original tripodal motif was recently modified by switching the anchor atom to tin,^{7,8} germanium,⁷ silicon⁹ or carbon.¹⁰ These ligands can serve as site-selective Janus-head ligands¹¹ because they provide the N-chelating coordination site and the lone-pair (LP) at the anchor atom. Hence, they are interesting ligands for the formation of multimetallic complexes.^{10,12}

Fig. 1 Lewis formulae of **1** and **2**.

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In this communication we present the experimental charge density distribution of $[Mg\{(pz^*)_3C\}_2]$ (**1**), ($pz^* = 3,5$ -dimethylpyrazolyl)^{13a} (Fig. 1). The quantification and hence the determination of the Lewis-basicity of the related LPs would be most advantageous. Crystal packing of **1** shows no further interactions of the carbanions with other molecules, which gives rise to two undisturbed stereochemically active LPs.

1 crystallizes in the space group $R\bar{3}$ with Mg1 on the special position $x = 1/3$, $y = 2/3$, $z = 1/6$, leading to a symmetrical 6-fold coordination of the central metal atom by one nitrogen atom of each pyrazolyl group.[†] The asymmetric unit contains just one sixth of the complex.^{13b} Even though the bond lengths can give a first hint to the electronic properties of a given molecule, the method of choice is the direct investigation of the electron density distribution to elucidate the structure–reactivity relationship. Analysis of the bond lengths alone would not explain the bond properties in **1**. Therefore we carried out a multipole refinement on a high-resolution data-set, collected at 15 K. The resulting experimental charge density (CD) distribution $\rho(r)$ was topologically analyzed according to Bader's Quantum Theory of Atoms In Molecules (QTAIM).¹⁴

Fig. 2 Laplacian distribution along various bond paths.

The central formal Mg^{2+} ion is fixed between two $C(pz^*)_3$ anions. It is coordinated by one nitrogen atom (N1) of each of the six pyrazolyl rings. The carbanionic atom C6 shows tetrahedral environment with the potential LP pointing away from the octahedrally distorted coordinated magnesium atom.

Fig. 3 Laplacian distribution of **1** in the ring plane (left) and perpendicular (right) (positive values red; negative values blue).

The bond path (BP) between Mg1 and N1 is 2.1973 Å long and the related bond critical point (BCP) has the properties commonly assigned to closed-shell interactions with low $\rho(\mathbf{r}_{\text{BCP}})$ ($0.21 \text{ e } \text{\AA}^{-3}$) and a positive $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$ ($+3.33 \text{ e } \text{\AA}^{-5}$). The spatial distribution of the Laplacian field ($L(\mathbf{r})$) is positive around the metal ion and reveals a distinct negative value at the nitrogen atom (Fig. 2 and 3), which can be attributed to the donating nitrogen LP. $L(\mathbf{r})$ along the BP (Fig. 2) is typical for a dative bond in organometallic chemistry: a distinct region of charge concentration in the vicinity of the donating atom (N1) originating from the LP density, which is not far expanded into the bond.¹⁵ More than 0.5 Å ahead of the BCP, $L(\mathbf{r})$ changes the sign and stays positive on low level, indicating charge depletion over the whole bonding region. $L(\mathbf{r})$ rises drastically when reaching the basin of the metal as expected for a cation. The closed-shell nature of the N → Mg interaction is displayed in both the distribution of $L(\mathbf{r})$ along the BP as well as the spherically shaped distribution in space (Fig. 3).

An intriguing feature is the orientation of the pyrazolyl rings to the central magnesium atom. Their planes are rotated along the C6–N2 bond which results in a 0.52 Å shift of the Mg atom from the mean plane. Compared to $[\text{Mg}(\text{pz}^*_3\text{CH})_2]^{2+} \cdot 2\text{Otf}^-$ (**2**), the at C6 protonated analogue of **1**, we find the C6–N2 bonds slightly elongated, the CN_3 cap with a more acute angle, and the rings rotated about the C6–N2 bond, which results in a more pronounced dislocation of Mg1 from the plane (0.52 vs. 0.23 Å).^{13a} However, the Mg...C distance is even slightly larger for **1** and DFT calculations previously performed on a lithium derivative of **1** revealed only small electrostatic interactions between the cation and anionic carbon atom.^{10h} Therefore, we assumed the reason might be related to the favourable coupling of the lone-pair at C6 to the π -density of the pyrazolyl rings (indicated by a quite appreciable ellipticity close to the $\text{BCP}_{\text{C6-N2}}$, Fig. 4). This might cause a propeller-like torsion about the C6–N bonds and the dislocation of the metal from the ring plane. The integrated atomic charge of N1 within the ring (-0.62 e) as well as the bonding criteria for N1–C1 (Table 1) are comparable to those found for other nitrogen heterocycles¹⁵ and do not support any non-typical electronic situation.

Related to the question of the electronic state at N1 is the charge density distribution in the pz^* -rings. One might expect the bonds in the heteroatomic C_3N_2 -perimeter either to display 6π -aromatic character or to exhibit localized double bonds.

Table 1 Topological analysis of the bond critical points

Bond ^a	$d(\text{A-B})/\text{\AA}$	$d(\text{A-BCP})^b/\text{\AA}$	$\rho(\mathbf{r}_{\text{BCP}})^c/\text{e } \text{\AA}^{-3}$	$\nabla^2\rho(\mathbf{r}_{\text{BCP}})^d/\text{e } \text{\AA}^{-5}$	$\lambda^3/\text{e } \text{\AA}^{-3}$
Mg–N1	2.1973	0.9402	0.208	+3.327	6.06
C6–N2	1.4422	0.5793	1.792	−15.033	12.14
N1–N2	1.3755	0.6758	2.335	−5.633	31.96
N1–C1	1.3360	0.7688	2.434	−23.221	15.66
C3–N2	1.3534	0.5528	2.286	−21.501	14.92
C2–C3	1.3870	0.6911	2.154	−17.775	13.04
C1–C2	1.4079	0.7147	2.069	−16.483	12.73
C3–C5	1.4871	0.7612	1.806	−14.591	10.86
C1–C4	1.4918	0.7389	1.873	−12.922	12.68

^a $d(\text{A-B})$: distance between atoms A and B along the bond path.

^b $d(\text{A-BCP})$: distance between the atom A and the BCP. ^c $\rho(\mathbf{r}_{\text{BCP}})$: charge density at the BCP. ^d $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$: Laplacian at the BCP. ^e λ^3 : eigenvalue of the Hessian along the bond at the BCP.

Consideration of the bond lengths alone would not provide a decisive picture since the differences in the BP lengths are only marginal (Table 1). C2–C3 (1.3870 Å) and N1–C1 (1.3360 Å) are the anticipated double bonds, but they are only 0.02 Å shorter than C1–C2 (1.4079 Å) and N2–C3 (1.3534 Å), respectively. The differences are much more pronounced in the topological descriptors at the BCPs and even more along the BPs. The density and $L(\mathbf{r})$ at the BCPs correlate with the lengths of the BPs. The shorter bonds reveal higher $\rho(\mathbf{r}_{\text{BCP}})$ values and more negative $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$. Further insight into the bond properties gains the inspection of the whole BP. For both C–C bonds in the heteroaromatic ring we found increased ellipticities over a wide range in the interatomic region. The ellipticity along the BP of C2–C3 is constantly twice as high as that of C1–C2 and very close to the value known from double bonds (Fig. 4). Less eye-striking, but suiting the chemical intuition, are the findings for the C–N bonds. $\rho(\mathbf{r}_{\text{BCP}})$ and $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$ correlate to the bond lengths differences. $L(\mathbf{r})$ along the BPs are typical for shared interactions (Fig. 2).

Fig. 4 Ellipticity along selected bond paths.

The polarization in the N2–C3 bond is slightly more distinct compared to N1–C1, where we find less pronounced minima and increased charge concentration in the vicinity of the BCP. These findings are supported by the distribution of the ellipticity (ϵ) along the BP (Fig. 4). For N1–C1 it is comparable to C2–C3, but slightly more shifted to the nitrogen atoms. For N2–C3 we find a comparable absolute value for ϵ , but here it is extremely asymmetrically distributed with a well defined maximum at N2. This feature should originate in an overall increased CD perpendicular to the ring plane at N2. The same effect is evident

Fig. 5 Laplacian distribution at C6 at an isolevel of $-13.0 \text{ e } \text{\AA}^{-5}$.

between N2 and C6 on an even higher level. We determined the highest values for ε of all investigated bonds close to C6 (0.58, Fig. 4). The reason is clearly evident from $L(\mathbf{r})$. A well defined LP related charge concentration at a high level ($\nabla^2\rho_{\text{max}} = -30.55 \text{ e } \text{\AA}^{-5}$) was found in the apical position at C6 (Fig. 5).

This value is notably higher than for other quantified lone-pairs of carbanions so far with a VSCC of -23 and $-15 \text{ e } \text{\AA}^{-5}$, respectively.^{16a,b} The CD at C6 clearly indicates a carbanion with a stereochemically active LP. Interestingly, the integrated charge at C6 is $+0.64 \text{ e}$ and hence unexpectedly positive at first sight. However, it is well known that nitrogen atoms with their high electronegativity tend to contract the atomic basins of the adjacent carbon atoms.¹⁵ The distance from the nucleus position of C6 to the BCP is only $0.58 \text{ \AA}$, dividing the bond into a ratio of $2 : 3$. The same effect is present at C1 and C3 although at lower level. Taking into account that C6 is bonded to three electron withdrawing nitrogen atoms without any other bonding partners, able to compensate the polarization (e.g. CH and CH₃ at C3), the found charge at C6 is in accordance with the interpretation of C6 as a carbanion. Would there be no charge accumulated from the metallation it would clearly be considerably more positive than it actually is.

From the topological features the C6–N2 bond shows no indicators for significant bond strengthening due to π -contributions: the bond is about $0.1 \text{ \AA}$ longer, $\rho(\mathbf{r}_{\text{BCP}})$ is 20%, and $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$ is about 30% reduced, compared to the ring C–N π -bonds. Hence, the LP density at C6 is not coupling into the aromatic system of the π -acceptor pz^* ring system and the origin of the observed dislocated metal remains open.

Conclusively, the ED distribution doubtlessly shows the given Mg-complex to exhibit two carbanions. We found two well-defined LPs at the apical position suitable to act as 2-electron donor for metal coordination.^{11b} The negative charge, even though not straightforwardly reflected by the integrated values, is located at C6. This could be deduced from the lack of delocalized density from the carbanion towards the heterocycle. The pz^* -ring reveals characteristics of localized double bonds, instead of a delocalized π -system. Increased charge concentration was found at N1, but no charge transfer to the metal centre was observed, leading to the identification of the magnesium atom to be a Mg^{2+} cation and the N–Mg bond to be a typical example of a dative LP driven bond.

Notes and references

† X-Ray investigation of **1**: the data set was collected from an oil coated shock-cooled crystal on a BRUKER TXS diffractometer with D8 goniometer and INCOATEC Helios mirror optics (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) equipped with an Oxford Helijet open stream liquid helium cooling device in ω -scan mode at $15(1) \text{ K}$.¹⁷ The structure was

solved by direct methods¹⁸ and refined by full-matrix least squares methods against F^2 (XD2006).¹⁹ Crystal data for **1**: $\text{C}_{38}\text{H}_{42}\text{MgN}_{12}$, $M = 619.09 \text{ g mol}^{-1}$, rhombohedral, space group $R\bar{3}$, $a = 10.6329(10)$, $b = 10.6329(10)$, $c = 24.569(2) \text{ \AA}$, $V = 2405.6(4) \text{ \AA}^3$, $Z = 3$, $\rho_{\text{calc.}} = 1.429 \text{ Mg m}^{-3}$, $\mu = 0.107 \text{ mm}^{-1}$, 65 508 reflections measured, 5725 independent, $R_1(I > 2\sigma(I)) = 0.0291$, $wR_2(I > 2\sigma(I)) = 0.0972$. Multipole refinement of **1**: $R(F^2) = 0.016$, $R_w(F^2) = 0.034$, GoF = 2.476 after XD.¹⁹

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