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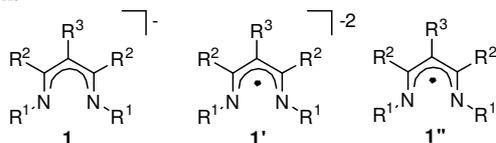
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Paramagnetic aluminium β -diketiminate†

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The β -diketiminate ligand framework is shown to undergo reduction to form a neutral main group radical stabilized by spiroconjugation of the unpaired electron over the group 13 element centre. The synthesized paramagnetic complex was characterized by EPR spectroscopy and computational chemistry.

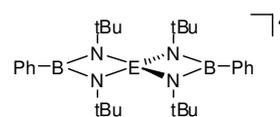
The chemistry of monoanionic, N,N'-chelating β -diketiminate (NacNac) ligand **1** is currently well established.¹ Nevertheless, only very few investigations have detailed its redox properties. Lappert and co-workers were the first to report the synthesis of novel Yb complexes of **1** whose structures were rationalized on the basis of different oxidation states for different NacNac ligands, including the dianionic radical state **1'**.² The same group also presented the X-ray crystal structure of a paramagnetic dilithium complex of **1'**, but its chemistry was not investigated further.³ In addition to experimental studies, Clyburne *et al.* have published a computational treatment of the reaction of a β -diketiminatoaluminium(I) complex with a hydrogen atom and an electron.⁴



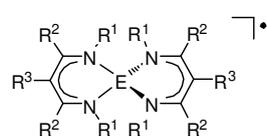
From this background, we set out to explore the hitherto unknown radical chemistry of the NacNac ligand in its main group complexes. This represents an attractive objective as the extreme versatility and tunability of the ligand framework is ideal for the generation of a new family of paramagnetic coordination compounds.⁵ During the course of our investigations, Wiegardt and Khusniyarov published spectroscopic and computational data on a cationic Ni^{II} complex featuring a neutral, mono-oxidized, NacNac radical **1''**.⁶ They attributed the stability of the compound to the interaction of the radical ligand with the high-spin metal centre, giving rise to an overall doublet ground state. This conclusion was supported by the fact that the zinc analogue of the cation, with a completely filled d-shell, was unstable. While these results add further evidence on the wider redox non-innocent behaviour of the NacNac ligand, they also cast some doubt on the feasibility of our objective in achieving the first paramagnetic p-block metal complexes of this particular framework.

The spirocyclic structural motif, two mutually perpendicular π -ligands held by a tetrahedrally coordinated central element,⁷ has

been of recurring importance in the field of paramagnetic coordination compounds.⁸ Our investigations on this scaffold have centred on its ability to stabilize main group ligands in atypical oxidation states via spiroconjugation *i.e.* delocalization of the unpaired electron over both ligands.⁹ Recently, this approach has allowed *e.g.* capturing the fleeting boraamidinate radical as stable and persistent group 13 complexes, **2**, via one electron oxidation of their lithium salts.¹⁰ In a similar fashion, the synthesis of analogous compounds incorporating the formally dianionic NacNac radical, **3-6**, could proceed via reduction of the corresponding cationic precursors. However, cationic 2:1 complexes of NacNac ligand with group 13 elements are virtually nonexistent, the sole characterized member being [**4d**]⁺.¹¹ A survey of the published data revealed that a straightforward metathetical reaction between the lithiated ligand **1** and group 13 halides fails to proceed beyond 1:1 stoichiometry.¹²



2 E = B, Al, Ga, In

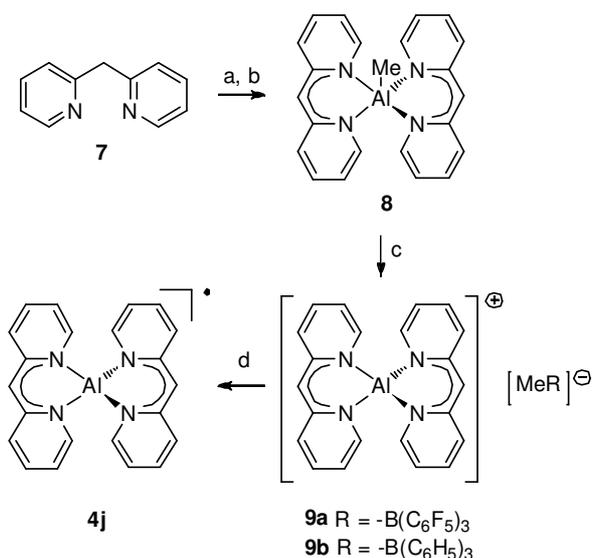


3 E = B
4 E = Al
5 E = Ga
6 E = In

a R¹ = Me, R² = R³ = H
b R¹ = tBu, R² = R³ = H
c R¹ = Ph, R² = R³ = H
d R¹ = R² = Me, R³ = H
e R¹ = Me, R² = tBu, R³ = H
f R¹ = Me, R² = Ph, R³ = H
g R¹ = tBu, R² = Me, R³ = H
h R¹ = Ph, R² = Me, R³ = H
i R¹ = R² = -CHCHCH-, R³ = H
j R¹ = R² = -CHCHCHCH-, R³ = H
k R¹ = R² = -CHCHCHCH-, R³ = Me

Taking into account the scarcity of published works on spirocyclic complexes of the NacNac ligand with group 13 elements, we turned our attention to computational pre-screening of **3-6** in order to determine the best possible candidates for synthesis (Electronic Supporting Information, ESI). Geometry optimizations and subsequent frequency analyses carried out using density functional theory (DFT) revealed that the majority of the investigated systems are stable minima on the potential energy hypersurface, thereby confirming their viability as synthetic targets. However, we note that the optimized structures of gallium and indium radicals have lower point group symmetries than their lighter group 13 analogues, indicative of either incomplete or missing spiroconjugation (ESI). Consequently, only the derivatives **3** and **4** were retained for further analyses.

The lowest unoccupied molecular orbital (LUMO) of the NacNac ligand is known to contain large contributions from $p\pi$ -type atomic orbitals at the $-NR^1$ and $-CR^2$ centers,⁶ indicating that the electronic properties of the corresponding dianionic radicals can be altered the best by varying the substituent at these positions. In contrast, the substituent at the middle carbon atom ($-CR^3$) will have a more indirect effect because the LUMO has a node at this position. Of all the different substituent combinations **a–k** investigated, the ones which delocalize the spin density the most should be preferred as this helps to prevent unwanted dimerization.⁵ In this respect, NacNac ligands with either aryl groups (**c**, **f** and **h**) or neighboring fused rings (**i–k**) at R^1 and R^2 positions are to be favored (ESI). However, having too bulky substituents at either R^1 or R^2 position could prevent conjugative interactions which are expected to be vital for the kinetic stability of the radicals. Taking all of the above, and considerations of synthetic simplicity, into account, we ultimately chose the aluminum derivative **4j** as our primary target radical.



Scheme 1 Preparation of the neutral radical **4j** from ligand **7**. a) 1 eq. *n*-BuLi, THF, -78°C , 1h; b) 0.5 eq. MeAlCl₂, THF, -40°C , 1h, 45°C , 45 min, 57%; c) 1 eq. B(C₆F₅)₃, CH₂Cl₂, RT, 2 h, 82 % / 1 eq. B(C₆F₅)₃, CH₂Cl₂, RT, 2 h, 60%; d) 1 eq. CoCp₂, CH₂Cl₂, RT, 24 h / 1 eq. CoCp₂, CH₂Cl₂, RT, 24 h / 1 eq. K, toluene, RT, 15 min.

The treatment of ligand **7**¹³ with 1 equivalent of *n*-BuLi and 0.5 equivalent of MeAlCl₂ gives the 2:1 complex **8** in 57% yield (Scheme 1, ESI). The crystallization of **8** from CH₂Cl₂ resulted in orange single crystals suitable for X-ray diffraction (Figure 1).[‡] The molecular structure is as expected and shows a distorted penta-coordination geometry around aluminum, along with two significantly puckered ligand frameworks. The average Al–N [1.989(3) Å] and Al–C [1.977(5) Å] bond lengths are comparable to those found in analogous complexes involving monoanionic *N,N'*-chelating amidanate ligands.¹⁴ The methyl group can easily be removed (as methanide) by reacting **8** with a stoichiometric amount of either tris(pentafluorophenyl)- or trisphenylborane. This affords the salts **9a** and **9b** as orange powders in good yields, 82 and 60%, respectively.

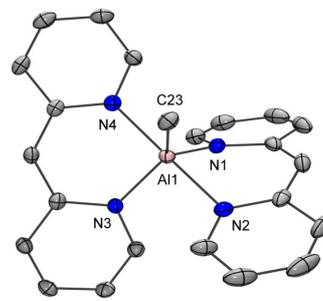


Fig. 1 ORTEP-like plot of **8** with 30% probability level thermal ellipsoids (hydrogen atoms omitted). Selected bond distances [Å] and angles [°]: C23–Al1 1.977(5), Al1–N1 1.934(3), Al1–N2 2.045(3), Al1–N3 1.931(3), Al1–N4 2.048(3), N1–Al1–N2 88.8(1), N2–Al1–N3 92.7(1), N3–Al1–N4 88.7(1), N1–Al1–N4 92.8(1), N1–Al1–C23 127.7(2), N2–Al1–C23 87.7 (2), N3–Al1–C23 127.0(2), N4–Al1–C23 89.9(2).

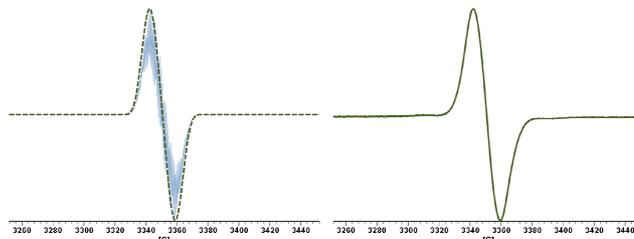


Fig. 2 Isotropic EPR-spectrum of **4j** (in toluene) as obtained from the reduction of **9a** with potassium. Experimental (right; $T = 295\text{ K}$, mod. amp. = 1.0 G) and simulated (left; line width = 0.3 G or 1.0 G (dashed)).

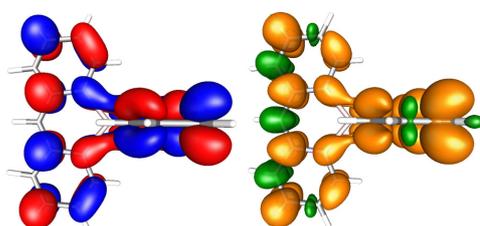
The conversion of **9** to the desired radical **4j** was accomplished by treating it with a stoichiometric amount of potassium, decamethylcobaltocene or cobaltocene. Upon mixing, the initially orange red solutions of **9** turned intensively dark. Evaporation of the solvent under vacuum yielded a solid residue that was soluble in organic solvents such as toluene, THF and CH₂Cl₂. Despite valiant efforts, all crystallization attempts yielded stacked parallel layers of plate-like red crystals, presumably of **4j**, which were unsuitable for X-ray analysis. However, the expected reaction by-product, the cobaltocenium salt of trisphenylmethylborate, was recovered from the reaction mixture as yellow crystals and its identity confirmed by crystallography (ESI).

The X-band EPR spectrum of **4j** was recorded in toluene (Figure 2) and in solid state (powder spectrum, ESI) and it shows a broad singlet with $g_{\text{iso}} \sim 2.00$, the location of which is typical for organic π -type radicals containing only light *p*-block heteroatoms.¹⁵ We stress that the measured spectrum is identical irrespective of the reducing agent or solvent used. This indicates that the radical species present is the same in each case and that it is not likely to arise from e.g. reduction of solvent molecules or from other paramagnetic impurities in the reaction mixture. Furthermore, a ¹H NMR spectrum measured from paramagnetic samples revealed complete disappearance of signals assigned to the organic ligand framework, which supports the identification of the observed paramagnetic species as the purported radical **4j**.

The EPR signal observed for **4j** remains essentially unchanged even after months of storage of the solid residue in an inert atmosphere. Due to the featureless nature of the measured spectrum, the frontier orbital structure, spin density and hyperfine coupling constants of **4j** were modeled using DFT (Figure 3). The calculations revealed the presence of spriconjugation and subsequent delocalization of the unpaired electron -and spin

density- over the entire π -type scaffold, confirming that **4j** is a ligand centered delocalized radical (cf. structurally similar spirocyclic group 13 diazabutadiene radicals which have localized electronic structures).¹⁶ Consequently, very little s-wave contribution exists on the spin-active heavy nuclei (¹⁴N, ²⁷Al) or on the hydrogen nuclei of the flanking aromatic rings. This leads to the presence of multiple small hyperfine coupling constants (Table 1) that, together with a slightly broadened lineshape, succeed in masking all characteristic hyperfine information from the experimental data; a featureless singlet signal has also been observed for the lithium salt of **1'** by Lappert *et al.* Even so, a simulation of the EPR spectrum (Figure 2) using the calculated hyperfine coupling constants as estimates of the true couplings perfectly reproduces both the width and the shape of the experimental signal.

Fig. 3 The singly occupied molecular orbital (left) and spin density (right) of **4j**. Color code: orange = α spin density, green = β spin density.



β spin density.

Table 1 Calculated hyperfine coupling constants (HFCCs, in MHz) of **4j**

Nucleus	HFCC ^b	Nucleus	HFCC ^b
4 x ¹ H	4.54	2 x ¹ H	4.59
4 x ¹ H	-0.03	4 x ¹⁴ N	1.51
4 x ¹ H	-3.64	1 x ²⁷ Al	-7.71
4 x ¹ H	-10.96		

In summary, we report the theory-aided design and synthesis and spectroscopic characterization of a first p-block complex incorporating paramagnetic anionic ligands based on the ubiquitous β -diketiminato framework. The work constitutes a significant addition to the redox chemistry of this ligand system which has been largely unexplored until now. The persistence of **4j** in the solid state indicates that, through spiroconjugation, the NacNac ligand can support a singly reduced paramagnetic state in its main group complexes, which opens up a route for the generation of a new family of radicals. These results are of particular importance as the extensive modifiability of the NacNac framework allows for efficient fine-tuning of both electronic and steric properties of the radicals thus formed. We are currently extending our research to characterization of other derivatives **3-6** as well as investigating the redox properties of the NacNac ligand in other main group architectures.

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Notes and references

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- 50 Crystal data for **8**: C₂₃H₂₁AlN₄, M_r = 380.42, monoclinic, $P2_1/c$, a = 13.381(9), b = 9.413(2), c = 15.604(1) Å, α = 90.00, β = 90.54(2), γ = 90.00°, V = 1965.3(2) Å³, Z = 4, ρ_{calcd} = 1.286 g cm⁻³, μ = 0.119 mm⁻¹, T = 173(2) K, 5851 reflections collected, 3399 unique (R_{int} = 0.0534), R_1 = 0.0739 [$I > 2\sigma(I)$], wR_2 = 0.1555 (all data). CCDC-86833. See <http://dx.doi.org/10.1039/b000000x> for crystallographic data in CIF or other electronic format.
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