


 Cite this: *Chem. Commun.*, 2022, 58, 4372

 Received 12th January 2022,
 Accepted 10th March 2022

DOI: 10.1039/d2cc00216g

rsc.li/chemcomm

Carbenes are known to stabilize main group element compounds with unusual electronic properties. Herein, we report the synthesis of carbene-stabilized group 13 metal radicals (cAAC)MX₂(IPr) (M = Al, X = Br **3; M = Ga, X = Cl **4**) and the corresponding cations [(cAAC)MX₂(IPr)][B(C₆F₅)₄] (M = Al, X = Br **5**; M = Ga, X = Cl **6**), which were characterized spectroscopically and by sc-XRD. Quantum chemical calculation gave insights into their electronic structures.**

Radicals are important species in organic synthesis,¹ polymer² and plasma chemistry³ and in bioorganic chemistry.⁴ They typically tend to dimerize, hence kinetic stabilization by use of sterically demanding ligands or electronic stabilization by delocalization of the unpaired electron are major stabilizing strategies. In recent years, main group element radicals received increasing interest due to their unique physical and chemical properties,⁵ and several bulky and/or π -conjugated ligands were established which allowed for the isolation of electronically and sterically stabilized reactive radicals.

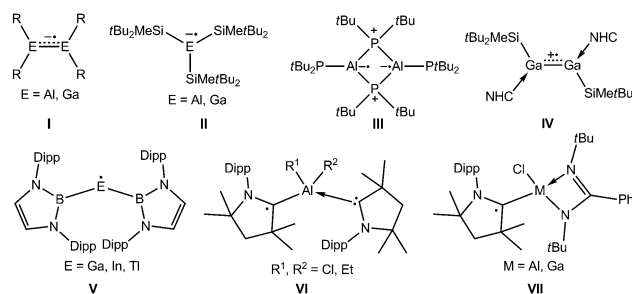
In contrast to widely known boron-based radicals,^{6f} the number of heavier group 13 metal radicals is limited (Scheme 1) to dinuclear radical anions (**I**),^{6,7} in which the unpaired electron is localized in the π_{M-M} orbital, mononuclear radical anions (**II**),⁸ cyclic Al biradical (**III**)⁹ and boryl-substituted neutral radicals (**V**, M = Ga–Tl).¹⁰ Recently, the N-heterocyclic carbene (NHC) coordinated radical cation **IV** was synthesized by one-electron oxidation reaction of the digallene.¹¹ Cyclic (alkyl)(amino)carbenes (cAAC) are also known to

stabilize main group metal radicals¹² including group 13 metal radicals (**VI**,^{13a,b} **VII**),^{13c} but reactivity studies of such radicals are yet still missing.

In view of the splendid performance of NHCs in stabilizing low-valent main group compounds¹⁴ and our general interest in main group metal radicals, we became interested in the synthesis and reactivity of group 13 metal radicals stabilized by one cAAC and one NHC, and we herein report on the syntheses of cAAC(IPr)MX₂ radicals and their oxidation reactions.

Reduction of adducts (cAAC)MX₃ (M = Al, X = Br, **1**; M = Ga, X = Cl, **2**; cAAC = C(Me)₂CH₂C(Me)₂N(Dipp)C; Dipp = 2,6-iPrC₆H₃) with two equivalents of KC₈ in the presence of 1 equivalent of IPr (IPr = [C(Me)N(iPr)]₂C) gave red crystals in 26% (**3**) and 32% (**4**) yields after workup (Scheme 2), while only mixtures of the starting reagents and **3** and **4** were obtained from equimolar reactions. **3** and **4** are air and moisture sensitive solids, which are soluble in toluene and *n*-hexane. They are stable at ambient temperature for several months, whereas they decompose upon heating to 131 °C and 124 °C, respectively.

Single crystals of **3** (Fig. S16, ESI†) and **4** (Fig. 1) were obtained from concentrated toluene solutions upon storage at 4 °C. Both compounds crystallize in the monoclinic space group *P*2₁/*c*.



Scheme 1 Examples of heavier group 13 elements containing radicals. R = CH(SiMe₃)₂, 2,4,6-iPr₃C₆H₂; Dipp = 2,6-iPrC₆H₃.

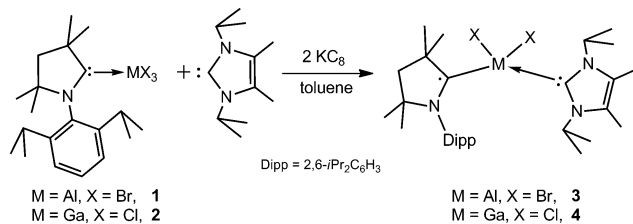
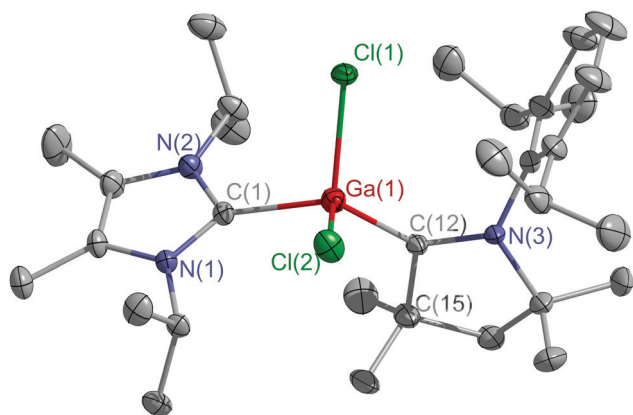
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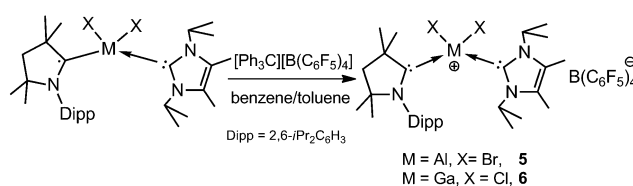
† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic characterization (NMR, EPR and IR spectra), cyclic voltammograms, elemental analysis and details of theoretical study of **3**–**6**. For ESI and crystallographic data in CIF or other electronic format. CCDC 2129477 (**3**), 2129478 (**4**), 2129479 (**5**), 2129480 (**5S**) and 2129481 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d2cc00216g



Scheme 2 Synthesis of radical species **3** and **4**.Fig. 1 Molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

The C–M–C bond angles (**3** 113.20(5)°, **4** 116.78(13)°) are wider than the Br–Al–Br (101.08(2)°) and Cl–Ga–Cl (100.68(5)°) bond angles (Table S2, ESI†). The Al–C_{cAAC} bond length in **3** (1.941(1) Å) is typical for an Al–C σ-bond and comparable to other cAAC-coordinated aluminum radicals (**VI**, **VII**).¹³ The Al–C_{IPr} bond length is far longer (2.078(1) Å) but similar to that reported for (IPr)Al(Si*t*Bu₂Me)Br₂ (2.062(3) Å),¹⁵ while the Ga–C_{cAAC} bond length in **4** (1.932(3) Å) is shorter than the Ga–C_{IPr} bond length (2.059(3) Å) and that in **2** (2.039(2) Å).¹⁶ Similar distances were found in (IPr)GaCl₃ (2.011(4) Å),¹⁷ (IPr)Ga(Mes)Cl₂ (1.978(2) Å)¹⁸ and (IPr)GaCl₂(cAACH) (2.065(15) Å).¹⁹

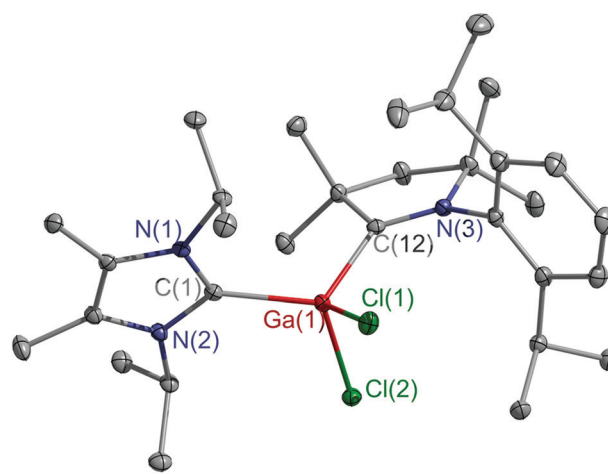
Reactions of radicals **3** and **4** with [Ph₃C][B(C₆F₅)₄] yielded the cationic species **5** and **6** (Scheme 3). Although [R₂ML₂]⁺ cations (R = H, alkyl) are well known, knowledge of group 13 metal dihalide cations are still in their infancy. Compound **6** is soluble in polar solvents (THF, CH₂Cl₂), while **5** decomposes with formation of [cAACH][B(C₆F₅)₄] (Fig. S19, ESI†). Cyclic voltammetry (CV) analyses demonstrate the redox reversibility between neutral radicals and cations (Fig. S23, ESI†). ¹H NMR

Scheme 3 Synthesis of **5** and **6**.

spectra of **5** and **6** show characteristic signals of cAAC and IPr ligands. The singlets at 2.36 (**5**) and 2.34 ppm (**6**) are assigned to the methyl groups on the IPr backbone, while the doublet at 1.54 ppm (**5**, **6**) and the septet at 5.40 (**5**) and 5.27 ppm (**6**) are assigned to the isopropyl groups of IPr. In addition, two doublets (1.38, 1.39 ppm **5**; 1.35, 1.38 ppm **6**), one septet (2.74 (**5**), 2.70 (**6**) ppm) and three singlets (1.47, 1.56, 2.15 ppm **5**; 1.48, 1.53, 2.20 ppm **6**) are assigned to cAAC. The ¹³C NMR spectrum of **6** shows resonances of both carbene carbon atoms at 153.0 and 225.1 ppm.

Single crystals of **5** and **6** were obtained by layering *n*-hexane on the top of fluorobenzene solutions at ambient temperature. Compounds **5** (Fig. S18, ESI†) and **6** (Fig. 2) crystallize in the monoclinic space group *P*2₁/*n* and *P*2₁/*c*, respectively. The coordination geometry of cations **5** and **6** and radicals **3** and **4** is similar. The C–M–C bond angles (117.12(5)° **5**, 117.59(5)° **6**) are slightly wider than those of radicals **3** and **4**, while the Al–C_{cAAC} bond in cation **5** is elongated compared to that of **3**, but close to those of adducts (cAAC)AlX₃ (X = Cl, 2.037(1) Å; X = I, 2.049(2) Å).^{13b,20} Comparable findings were observed for cation **6**, showing a longer Ga–C_{cAAC} bond (2.037(1) Å) than radical **4** (1.932(3) Å), whereas comparable bond lengths were reported for (cAAC)GaCl₃ (2.039(2) Å),¹⁶ (cAAC)GaHCl₂ (2.053(2) Å),¹⁹ and (cAAC)₂Ga₂Cl₄ (2.078(2) Å), respectively.²¹ The M–C_{IPr} bonds (2.047(1) **5**; 2.026(1) Å **6**) are slightly shorter than those of neutral radicals **3** (2.078(1) Å) and **4** (2.059(3) Å), but still fall in the typical range of Al–C_{IPr} and Ga–C_{IPr} bond lengths.^{11,15,17–20}

Electron paramagnetic resonance (EPR) spectroscopy was conducted on **3** and **4** to provide further insight into their electronic properties. The frozen solution (77 K) spectrum of **3** exhibits an isotropic *S* = 1/2 signal centred near *g*_e = 2.0023 (Fig. 3). The spectrum of **3** is split by an isotropic ²⁷Al (100% nat. abund.) hyperfine constant (HFC) of *a*_{iso}(²⁷Al) = 38 MHz, much smaller than the Al centred unpaired spin (*A*(²⁷Al) = ~1000 MHz),²² but more consistent with Al–cAAC radical species **VI** (*a*_{iso}(²⁷Al) =

Fig. 2 Molecular structure of **6**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms and the anionic part are omitted for clarity.

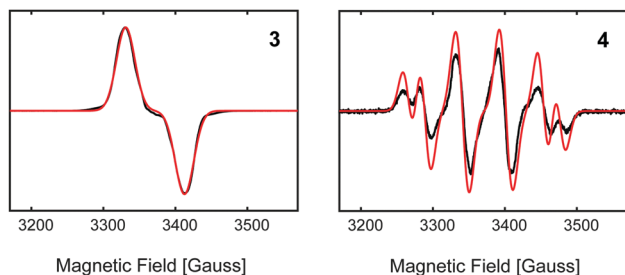


Fig. 3 EPR spectra of **3** (left) and **4** (right) at 77 K in toluene. Simulation parameters for **3**: $g = 2.0023$, $a_{\text{iso}}(\text{Al}) = 38$ MHz, line-width (peak-to-peak) = 27 Gauss. Simulation parameters for **4**: $g = 2.0025$, $a_{\text{iso}}(^{71}\text{Ga}) = 196$ MHz, $a_{\text{iso}}(^{69}\text{Ga}) = 154$ MHz, line-width (peak-to-peak) = 17 Gauss.

14.6–23.4 MHz) where the unpaired electron is localized to the cAAC ligand.^{13a,b} The room-temperature EPR of **3** (Fig. S22, ESI†) exhibits a similar broad isotropic spectrum to that of the 77 K spectrum, however, with some additional fine structure. Simulations of the room temperature spectrum estimate an Al a_{iso} value of 35 MHz, in agreement with the low estimate from simulation of the 77 K spectrum (Fig. 3) and yielding a rough error estimate of ± 5 MHz for the 77 K measurement. Additionally, a small ^{14}N hyperfine coupling of 25 MHz is estimated, consistent with the nitrogen hyperfine couplings observed in other cAAC centered radicals.^{14a,23}

The frozen solution EPR spectrum of **4** also exhibits an isotropic $S = 1/2$ signal centred near to g_e , consistent with a light-atom centred radical and unlike the significant g -shifts observed in related two-coordinate Ga centred radicals.¹⁰ The EPR spectrum of **4** is split into four dominant lines, where the two outermost lines are further split, arising from the two $I = 3/2$ isotopes of gallium (^{69}Ga (60.1%) and ^{71}Ga (39.9%)) which exhibit HFCs that scale by the nuclear gyromagnetic ratios $g_n(^{71}\text{Ga})/g_n(^{69}\text{Ga}) = 1.271$.²⁴ The hyperfine pattern is predominantly isotropic, with $a_{\text{iso}}(^{69}\text{Ga}) = 154$ MHz and simulation of the EPR spectrum with a fairly large 17 Gauss linewidth (peak-to-peak) satisfactorily reproduces the experimental spectrum. For both **3** and **4**, the relatively small Al/Ga HFCs and lack of resolvable/significant anisotropic hyperfine contributions in the frozen solution EPR spectra indicate that the unpaired electron is not Al/Ga p orbital centred but rather localized on the cAAC ligand. The small isotropic Al/Ga hyperfine coupling observed rather arises from spin polarization through the C–Al/Ga bonds, where the radical is C centred. Additionally, no significant ^{14}N hyperfine coupling is resolved, and inclusion of up to 25 MHz ^{14}N coupling by simulation remains unresolved in the broad EPR lines of the experimental spectrum (Fig. S21, ESI†). The lack of a large ^{14}N HFC further supports a C centred radical species in both **3** and **4**.

The bonding and electronic structure of radicals **3** and **4** and the cationic congeners **5** and **6** was evaluated by quantum chemical calculations.²⁵ Calculated bond lengths within the C–MX₂–C skeleton (Table S2, ESI†) are in good agreement with the experimental values. The SOMO of the parent radicals correlates well to the LUMO of cations (Fig. S24, ESI†), in line

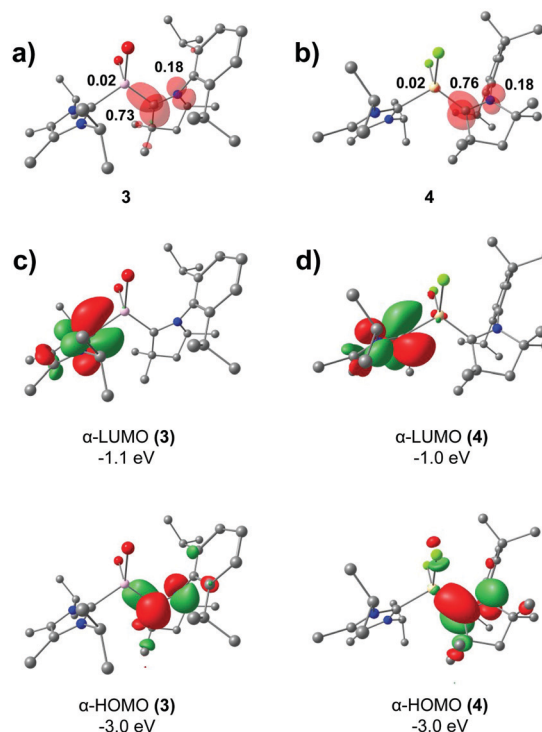


Fig. 4 Spin density plots for (a) **3** and (b) **4** (isosurface value = 0.005 a.u.) with selected Mulliken spin population values. Selected Kohn–Sham MOs for (c) **3** and (d) **4** (isosurface value = 0.05 a.u.).

with reversible reduction presented in CV. The DFT calculations at the TPSSh/def2-TZVP level of theory show that most of the spin density resides on the C atom of the coordinating cAAC ligand in both **3** (0.73) and **4** (0.76), with significant spin density present on the adjacent N atoms (0.18) (Fig. 4a and b). Only a small amount of the total spin density is located at the Al/Ga centres (0.02), which is in line with the small isotropic HFCs used to simulate the experimental spectra but in contrast with the homoleptic carbene-coordinated Al radical **VI**,^{14a,14b} in which the spin density is distributed unsymmetrically on the two carbenes, but still more than 17% spin density is located on the carbene with the minor contribution. It is noted that although the total spin density at the nitrogen is much larger than at the Al or Ga atoms, the Al and Ga hyperfine interaction dominate the EPR spectra due, in part, to their larger nuclear spins (more transitions) and their larger isotropic hyperfine coupling parameters ($a_0[^{14}\text{N}] = 1811$ MHz, $a_0[^{27}\text{Al}] = 3911$ MHz, $a_0[^{69}\text{Ga}] = 12210$ MHz).²⁴ The DFT calculated spin densities and larger a_0 values for Ga and Al in comparison to N supports the exclusion of a large N HFC (> 25 MHz) in the simulations of the experimental spectra (Fig. S21, ESI†). The magnetic orbitals for **3** and **4** are displayed in Fig. 4c and d, respectively, and show that electron density is localized to the cAAC moiety and is well represented by the $C_{\text{cAAC}}\text{--N}$ π^* -orbitals.

Upon oxidation, one electron is removed from the $C_{\text{cAAC}}\text{--N}$ π^* -orbital, resulting in increased WBIs (1.23 **3**, 1.23 **4**, 1.62 **5**, 1.63 **6**) and natural charges (-0.92 **3**, -0.87 **4**, -0.32 **5**, -0.28 **6**). In addition, the M– C_{cAAC} bond is elongated in **5** and **6** despite the



increasing charge, whereas the M–X and M–C_{IPr} bonds become slightly shorter (WBI, Tables S3–S6, ESI†) as was observed in the solid state structures. Second order perturbation analysis of **3** and **4** showed a π -type interaction between a populated C_{CAAC}-centred p-type orbital and the M–X σ^* orbitals (**3**: 9.8 kcal mol⁻¹; **4**: 9.7 kcal mol⁻¹) exclusively for the alpha spin orbitals, which is missing in the corresponding cations **5** and **6** and therefore explains the elongated C_{CAAC}–M and shortened M–X bonds in **5** and **6**. The change in charge upon oxidation also has only a negligible influence on the C_{CAAC}–M bond length as the natural charge of the metal is almost unaffected (Tables S3–S6, ESI†) and the C_{CAAC}–M bonds of **5** (2.0549(13) Å) and **6** (2.0367(12) Å) are almost identical with those of cAAC–AlBr₃ (2.055(4) Å)²⁶ and cAAC–GaCl₃ (2.039(2) Å),¹⁶ respectively. The WBI of the C_{CAAC}–Al bond is much lower compared to the C_{CAAC}–Ga bond, which might explain the lower thermal stability of **5**.

In conclusion, one electron oxidation of carbene-centred neutral radicals **3** and **4** gave cationic compounds **5** and **6**, which are rare examples of carbene-coordinated group 13 cations.

Financial support by the University of Duisburg-Essen (S. S.) and the Max Planck Society (G. E. C.) is acknowledged. We thank Mrs J. Krüger for supporting quantum chemical calculations.

Conflicts of interest

There are no conflicts to declare.

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