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"Give me five" – an amino imidazoline-2-imine ligand stabilises the first neutral five-membered cyclic triel(1) carbenoides[†]

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We present the first cyclic five-membered triel(i) carbenoides E(AmIm) for E = Ga, In, Tl; AmIm = amido imidazoline-2-imine, which fill the current gap between four- and six-membered triel(i) carbenoides supported by HGiso and HNacNac. Ga(AmIm) can act as a strong σ -donor ligand in transition metal complexes, while the intermediacy of the Al(i) carbenoide Al(AmIm) is rationalised based on the isolation of an Al(iii) insertion product.

N-Heterocyclic carbenes (NHCs, e.g. IDipp, I)¹ have significantly stimulated the area of σ -donor ligands with applications in main group² or transition metal chemistry, Fig. 1.³ Their cyclic nature allows for a careful control of the ring size, which commonly spans from three- to six-membered cycles and provides systematic variation of the N-C-N bent angle as a sensitive tool to tune the σ -donating and π -acidic behaviour of NHCs. The dianionic diamido backbone in NHCs was later employed for neutral carbenoides of heavier group 14 elements,⁴ but also for anionic species containing group 13 elements, i.e. five-membered Ga(1) anions of type II.5,6 In contrast, monoanionic N,N'-chelating scaffolds opened up routes towards neutral triel(I) species A and C, which can be considered as true carbenoides isolobal to NHCs. While guanidinate ($Giso^{-}$) stabilizes four-membered rings in A (for E = Ga, In), in the case of thallium the formation of four-membered cycles is prevented in favour of a η^3 -coordination by the arene group. In particular, Ga(I) carbenoide A was demonstrated as a strong σ -donor in transition metal complexes.⁷ Neutral sixmembered triel(I) species C were obtained for E = Al, Ga, In, Tl employing the monoanionic β -diketiminate (NacNac⁻),⁸ and Al(I) and Ga(I) carbenoides C are widely used in coordination

chemistry or substrate activation.⁹ The interest in Al(1) or Ga(1) donors can be traced back to the softer and more electron releasing behaviour towards transition metals compared to NHCs. That said, and in view of the predominance of five-membered cycles in the chemistry of NHCs, we were surprised at the lack of five-membered triel(1) carbenoide *vs.* the existing systems **A** and **C** set out to fill this current gap with compounds of type **B**.

The stabilisation of triel(1) carbenoides **A** and **C** was facilitated by the parent scaffolds HGiso (**A**) and HNacNac (**C**), which upon deprotonation afford monoanionic *N*,*N*'-coordinating ligands providing σ/π -donation *via* the amide and imine entities, Fig. 2. For new five-membered *N*,*N*'-chelated triel(1) species we present compound **1** (HAmIm), the deprotonation of which yields the monoanionic amido imidazoline-2-imine ligand (AmIm⁻). The incorporation of the imidazoline-2-imine entity is a key advantage of HAmIm **1** and leads to improved σ/π -donation of the imine compared to HGiso and HNacNac.^{10,11}

The route towards HAmIm **1** employs the reaction of diamino compound 2^{12} with 2-chloro imidazolium salt 3^{13} according to previous protocols.¹⁴ Compound **1** was fully characterised including X-ray crystallography, Fig. 4 and ESL⁺ In approaches towards five-membered triel(I) carbenoide HAmIm **1** was deprotonated and reacted with triel(I) precursors, Fig. 3.



Fig. 1 A representative example of NHCs (I) and the nucleophilic Ga(i) anion II. Neutral triel(i) carbenoide are reported for four-(**A**) and sixmembered cycles (**C**). Novel five-membered species **B** are presented in this work. Dipp = $2,6-(iPr)_2C_6H_3$.

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Fig. 3 (i) 4: benzyl potassium, then GaCp*. (ii) 5: nBuLi, then InCp. 6: nBuLi, then TlBF₄. Insert: Crystals of compound 6.

The lithium salt of HAmIm 1 was generated *in situ* with nBuLi and the addition of InCp or TlBF₄ gave rise to the formation of In(1) or Tl(1) species 5 and 6, respectively. For compound 4 this methodology was found to be inefficient. Instead the potassium salt of HAmIm 1 was prepared employing benzyl potassium and isolated prior to the reaction with GaCp* in THF, which ultimately afforded 4. Compounds 4–6 were obtained as yellowish (4,5) or red (6) crystalline material, Fig. 4. The formation 4–6 occurs with significant structural response of the HAmIm 1. While the imidazoline-2-imine moiety in the parent 1 is in plane with the phenylene moiety and displays double bond character for the N1–C1 bond 1.304(5) Å, its orientation in 4–6 adopts a perpendicular arrangement with detectable increase of the N1–C1 bond



Fig. 4 Molecular structures of **1** and **4–6**. Hydrogen atoms (except for N–H) omitted. Thermal ellipsoids: 50% probability. Distances and angles in Å or degree (°). See also Table 1. **1**: N1–C1 1.304(5), N4–C18 1.412(5).

distance by at least 0.03 Å indicating stronger single bond character. Compounds 4-6 display planar geometry for the five-membered triel(1) cycle, *i.e.* distortions of each atom involved in the pentagonal ring lie within the experimental error. The bond distances of the triel E (E = Ga1, In1, Tl1) to the flanking nitrogen atoms N1 and N4 are unequal due to their different chemical nature, and the bond lengths E-N1 towards the iminato moiety are between 0.1-0.2 Å longer than the distances E-N4 towards the amido entity. This observation is in contrast to the four- and six-membered carbenoides A and C, in which the triel to nitrogen distances are chemically and (within the standard deviations) also crystallographically equivalent, due to resonance stabilisation of the respective anions Giso⁻ and NacNac⁻. In compounds 4-6 the bond angle N1–E–N4 is observed to fall from $79.67(7)^{\circ}$ to $70.41(5)^{\circ}$, which is in line with the longer E-N bond distances for the heavier triel. The five-membered heterocycles 4-6 fill in the currently missing gap between the four- and six-membered triel(I) carbenoides to form a consistent structural series, which is in particular reflected by an increase of the N-E-N angle for a given triel with rising ring size from A-C. The carbenoides A-C including the hypothetical Al(I) species Al(Giso) and Al(AmIm) were computed on the DFT level of theory, section ESI,† and Fig. 5.15 All computationally studied compounds display large HOMO-LUMO gaps >5.5 eV and singlet-triplet gaps >50 kcal mol⁻¹, indicating ambient temperature stability of the monomeric species from the theoretical point of view.¹⁶ A-C show triel centred lone pairs in their canonical molecular orbitals, which are presented together with the LUMOs in Fig. 5.



Fig. 5 Selected frontier molecular orbitals for A–C, which show the triel centred lone pairs and LUMOs. The levels represent the energies of HOMO or LUMO for the respective compounds unless stated otherwise. Calculations were performed with the ω B97XD functional, see section ESI.†



Fig. 6 (i) $Fe(CO)_5$. (ii) $W(CO)_5(NMe_3)$. Molecular structure of complex 7. Hydrogen atoms omitted. Thermal ellipsoids: 50% probability. Distances and angles in Å or degree (°): Ga1–Fe1 2.2716(2), Ga1–N1 1.9239(7), Ga1–N4 1.8697(7), Fe1–C30 1.7909, Fe1–C31 1.7788(10), Fe1–C32 1.7809(10), Fe1–C33 1.7872(10), N1–Ga1–N4 86.38(3). C30–Fe1–Ga1 177.67(3).

In particular, in the case of the novel five-membered systems B the lone pairs were found in the HOMO Al(AmIm), HOMO-1 (4 and 5), HOMO-2 (6) and showed strong s-character, while the LUMOs display strong p_z-character and are localised at the triel atom. Noteworthy, the energy level of the lone pair for system B is at least 0.2 eV higher compared to A or C, and the same observation also holds true for the LUMOs. This behaviour can be traced back to the properties of the AmImbackbone, and suggests system **B** to be a strong σ -donor ligands akin to A or C. We set out to probe the ligand properties of our new system and chose compound 4 as a representative example in reactions with $Fe(CO)_5$ and $W(CO)_5(NMe_3)$, Fig. 6. Ligand displacement reactions of CO and NMe3 occurred facile at ambient temperature in toluene and gave rise to complexes 7 and 8, which were fully characterised including X-ray crystallography for 7. The molecular structure of compound 7 Fe(CO)₄{Ga(AmIm)} shows a trigonal bipyramidal iron centre with three carbonyl ligands in the equatorial plane and displays structural resemblance to previously reported iron complexes $Fe(CO)_4 \{Ga(Giso)\}^7$ and $Fe(CO)_4 \{Ga(NacNac)\}^{17}$ Table 2.

Noteworthy, the coordination of **4** occurs with a strong contraction of the Ga1–N1 and Ga1–N4 bond lengths by *ca*. 0.1 Å and an increase of the bond angle N1–Ga1–N4 by *ca*. 6°. Complex 7 displays a remarkably short Ga–Fe distance indicating a strong interaction of ligand **4** with the iron centre, while the structural metrics of the carbonyl ligands at the iron centre are similar for all three complexes.

An inspection of the carbonyl stretch frequencies ν (CO) shows the Ga(I) carbenoides to be stronger σ -donors compared

Table 2 Carbonyl stretch frequencies for the complexes $Fe(CO)_4(L)$ and their Ga–Fe distances (if applicable)

$Fe(CO)_4(L)$	Ga–Fe Å	ν (CO) cm ⁻¹
$L = Ga(Giso)^{7}$ $L = Ga(AmIm)$ $L = Ga(NacNac)^{17}$ $L = PPh_{3}^{18}$ $L = PPh_{3}^{19}$	2.273(1) 2.2716(2) 2.2851(4)	2026, 1970, 1945, 1916 2019, 1944, 1913, 1889 2010, 1940, 1915, 1900 2052, 1979, 1947

Table 1 Key structural parameters for compounds of type $\mathbf{A}_{,}^{7} \mathbf{B}$ and $\mathbf{C}_{,}^{8}$ Bond lengths and angles stated in Å or degree (°)

Compounds A		Compounds B (4-6)		Compounds C	
Ga–N	2.087(2) 2.095(2)	Ga1–N1 Ga1–N4	2.0611(19) 1.9595(18)	Ga-N	2.053(1) 2.056(1)
N–Ga–N In–N	63.77(7) 2.299(2)	N1–Ga1–N4 In1–N1	79.67(7) 2.3196(16)	N–Ga–N In–N	87.53(5) 2.268(3)
N–In–N	2.298(2) 58.06(6)	In1–N4 N1–In1–N4	2.1677(16) 73.23(6)	N-In-N	2.276(3) 81.12(10)
_		Tl1-N1 Tl1-N4 N1-Tl1-N4	$2.4534(16) \\ 2.2678(16) \\ 70.41(5)$	TI-N N-Tl-N	$2.428(4) \\ 2.403(4) \\ 76.67(15)$

to triphenylphosphine and NHCs and reveals an intermediate position for the new ligand **4**, Table 2. We rank the σ -donor strength in the order of Ga(Giso) < Ga(AmIm) < Ga(NacNac) with the neglect of π -backbonding. The absence of the latter was previously documented for Ga(Giso) and for Ga(NacNac) complexes^{7,20} and also holds for the new Ga(AmIm) **4**, as indicated by the high lying computed LUMO and similar the carbonyl stretch frequencies ν (CO) for all three carbonyl complexes. The buried volume (% V_{bur}) of the ligands in the iron carbonyl complexes correlates with the ring-size in the order Ga(Giso) (25.1%) < Ga(AmIm) (26.0%) < Ga(NacNac) (32.6%).²¹ Stimulated by the known six-membered Al(NacNac) of type **C** we also attempted approaches towards the five-membered carbenoide Al(AmIm) **9**, Fig. 7 and section ESI.[†]

The reaction of deprotonated HAmIm 1 with AlI₃ afforded complex 10. Since the reduction of Al(III) diiodide precursors affords Al(NacNac), albeit in low yield,⁸ we also treated compound 10 with reducing agents at similar conditions but were not able to achieve the desired complex 9. The alternative elimination of cyclopentadienide from Al(I) precursors was investigated in reactions of the sodium salt of 1 with (AlCp*)₄, which led to few colourless crystals of compound 11 as



Fig. 7 (i) *n*BuLi, toluene, then All₃. (ii) NaCH₂SiMe₃, toluene, then (AlCp*)₄. Molecular structure of **11**. Hydrogen atoms and solvent molecules (benzene) omitted. Thermal ellipsoids: 50% probability. The molecule is located on a crystallographic centre of inversion. Distances and angles in Å or degree (°): Al1–N1 1.8332(9), Al1–N1' 1.8710(10), Al1–N4 1.8782(10), Al1–C1 2.0479(11), N1–Al1–N1' 91.05(4).

indicated by X-ray crystallography.²² Compound **11** can be viewed as a mixed amide/imide species with an NHC entity coordinated to an Al(III) center, and its formation can be interpreted based on the intermediacy of the desired Al(I) species **9**, which underwent bimolecular self-activation *via* the C-N bond. The oxidative addition of Al(I) to C-N bonds in imidazoline-2-iminato moieties has recently been observed in one case.²³

We present the amino imidazoline-2-imine ligand HAmIm 1, which stabilises the first neutral five-membered triel(1) carbenoide E(AmIm) for E = Ga, In, Tl (4–6), which close the current gap to complete a series of four- to six-membered cyclic carbenoides with varying steric congestion together with previous HGiso and HNacNac systems. The strong σ -donor properties of Ga(AmIm) were demonstrated. The intermediacy of Al(1) carbenoide Al(AmIm) was rationalised with the isolation of an Al(III) insertion product. Future work will concentrate on improvements to stabilise Al(1).

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 A. J. Arduengo, R. Harlow and M. A. Kline, J. Am. Chem. Soc., 1991, 113, 36.
- 2 (a) A. Doddi, M. Peters and M. Tamm, *Chem. Rev.*, 2019, 119, 6994;
 (b) M. M. Roy and E. Rivard, *Acc. Chem. Res.*, 2017, 50, 2017.
- 3 (a) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, Chem. Rev., 2000, 100, 39; (b) P. de Frémont, N. Marion and S. P. Nolan, Coord. Chem. Rev., 2009, 253, 862; (c) N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis, ed. S. P. Nolan, Wiley-VCH, Weinheim, Germany, 2014; (d) Q. Zhao, G. Meng, S. P. Nolan and M. Szostak, Chem. Rev., 2020, 120, 1981.
- 4 NHSi: (a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, J. Am. Chem. Soc., 1994, 116, 2691; (b) M. J. Krahfuss, J. Nitsch, F. M. Bickelhaupt, T. B. Marder and U. Radius, Chem. Eur. J., 2020, 26, 11276.
- 5 (a) E. S. Schmidt, A. Jockisch and H. Schmidbaur, J. Am. Chem. Soc., 1999, 121, 9758–9759; (b) R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, J. Chem. Soc., Dalton Trans., 2002, 3844–3850; (c) I. L. Fedushkin, A. N. Lukoyanov, G. K. Fukin, S. Y. Ketkov, M. Hummert and H. Schumann, Chem. Eur. J., 2008, 14, 8465–8468; (d) R. J. Baker and C. Jones, Coord. Chem. Rev., 2005, 249, 1857–1869.
- 6 Other dianionic chelating ligands afforded Al(1) and In(1) anionic species: Al(1) anions: (a) J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, Angew. Chem., Int. Ed., 2021, 60, 1702; (b) J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, Nature, 2018, 557, 92; (c) R. J. Schwamm, M. D. Anker, M. Lein and M. P. Coles, Angew. Chem., Int. Ed., 2019, 58, 1489; (d) R. J. Schwamm,

- M. P. Coles, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi and A. S. S. Wilson, Angew. Chem., Int. Ed., 2020, **59**, 3928; (e) S. Grams, J. Eyselein, J. Langer, C. Färber and S. Harder, Angew. Chem., Int. Ed., 2020, **59**, 15982; (f) S. Kurumada, S. Takamori and M. Yamashita, Nat. Chem., 2020, **12**, 36; (g) K. Koshino and R. Kinjo, J. Am. Chem. Soc., 2020, **142**, 905For the In(I) anion see: (h) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles and C. M. Fitchett, Angew. Chem., Int. Ed., 2018, **57**, 5885.
- 7 (a) C. Jones, P. C. Junk, J. A. Platts and A. Stasch, J. Am. Chem. Soc., 2006, 128, 2206; (b) S. P. Green, C. Jones and A. Stasch, Inorg. Chem., 2007, 46, 11; (c) C. Jones, A. Stasch, G. J. Moxey, P. C. Junk and G. B. Deacon, Eur. J. Inorg. Chem., 2009, 3593.
- 8 Al: (a) C. M. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. J. Hao and F. Cimpoesu, Angew. Chem., Int. Ed., 2000, 39, 4274; (b) Ga: N. J. Hardman, B. E. Eichler and P. P. Power, Chem. Commun., 2000, 1991; (c) In: M. S. Hill and P. B. Hitchcock, Chem. Commun., 2004, 1818; (d) Tl: M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, Dalton Trans., 2005, 273.
- 9 (a) M. Zhong, S. Sinhababu and H. W. Roesky, *Dalton Trans.*, 2020, 49, 1351Impressive examples of olefin activation: (b) C. Bakewell, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2019, 10, 2452; (c) C. Bakewell, M. Garçon, R. Y. Kong, L. O'Hare, A. J. P. White and M. R. Crimmin, *Inorg. Chem.*, 2020, 59, 4608.
- 10 (a) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, D. Bläser and R. Boese, Z. Naturforsch., B: J. Chem. Sci., 1995, 50, 1779;
 (b) M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones and J. Grunenberg, Org. Biomol. Chem., 2007, 5, 523.
- 11 (a) X. Wu and M. Tamm, *Coord. Chem. Rev.*, 2014, 260, 116; (b) H. Dolati, L. Denker, B. Trzaskowski and R. Frank, *Angew. Chem.*, *Int. Ed.*, 2021, 60, 2–9.
- 12 H. Liu, M. Khononov, N. Fridman, M. Tamm and M. S. Eisen, *Inorg. Chem.*, 2017, **56**, 3153.
- 13 R. A. Kunetskiy, I. Císařová, D. Šaman and I. M. Lyapkalo, *Chem. Eur. J.*, 2009, **15**, 9477.
- 14 R. A. Kunetskiy, S. M. Polyakova, J. Vavřík, I. Císařová, J. Saame, E. R. Nerut, I. Koppel, I. A. Koppel, A. Kütt, I. Leito and I. M. Lyapkalo, *Chem. – Eur. J.*, 2012, **18**, 3621.
- 15 For previous calculations on systems of type I see: C.-H. Chen, M.-L. Tsai and M.-D. Su, *Organometallics*, 2006, **25**, 2766.
- 16 The resulting large HOMO-LUMO gap (ca. 5 eV) and singlet-triplet gap (ca. 85 kcal mol⁻¹) for NHCs: (a) C. Heinemann and W. Thiel, Chem. Phys. Lett., 1994, 217, 11; (b) E. A. Carter and W. A. Goddard, J. Phys. Chem., 1986, 90, 998; (c) A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan and L. Cavallo, Organometallics, 2008, 27, 2679.
- 17 N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, J. Am. Chem. Soc., 2003, 125, 2667.
- 18 L. R. Martin, F. W. Einstein and R. K. Pomeroy, *Inorg. Chem.*, 1985, 14, 2777.
- 19 S. Warratz, L. Postigo and B. Royo, Organometallics, 2013, 32, 893.
- 20 J. Turner, J. A. B. Abdalla, J. I. Bates, R. Tirfoin, M. J. Kelly, N. Phillips and S. Aldridge, *Chem. Sci.*, 2013, 4, 4245.
- 21 L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nat. Chem.*, 2019, **11**, 872.
- 22 For previous examples of cyclopentadienide elimination form Al(i) precursors: (a) C. Dohmeier, E. Baum, A. Ecker, R. Köppe and H. Schnöckel, Organometallics, 1996, 15, 4702; (b) C. Dohmeier, D. Loos and H. Schnöckel, Angew. Chem., Int. Ed. Engl., 1996, 35, 129; (c) H. Sitzmann, M. F. Lappert, C. Dohmeier, C. Üffing and H. Schnöckel, J. Organomet. Chem., 1998, 561, 203.
- 23 T. Chu, S. F. Vyboishchikov, B. M. Gabidullin and G. I. Nikonov, J. Am. Chem. Soc., 2017, 139, 8804–8807.