Synthesis, structural and theoretical studies of an iron–gallium(I) heterocycle complex: Analogies with *N*-heterocyclic carbene chemistry †

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The first iron complex of an anionic gallium *N*-heterocyclic carbene analogue, [Fe(CO)₄{Ga[N(Ar)C(H)]₂}]⁻ Ar = C₆H₃-Prⁱ₂-2,6, has been prepared and shown to have an unusual polymeric structure in the solid state; theoretical studies have pointed toward minimal Fe → Ga back-bonding in this complex.

Group 13 metal(I) diyls, :MR, which contain sp-hybridised lone pairs are increasingly finding use as strong σ-donor ligands in the formation of novel transition metal complexes.[1] In addition, they possess two empty valence p-orbitals which can potentially participate in π-back-bonding interactions with suitable transition metal d-orbitals. The magnitude of this back-bonding has been studied in a number of complexes and has generated considerable controversy in the literature. This is exemplified by the complex, [(Ar*Ga)Fe(CO)₄] **1**, Ar* = C₆H₃(C₆H₂Prⁱ₃-2,4,6)₂-2,6, which has alternately been described as having an iron–gallium triple bond[2] or a single dative interaction.[3] Recent sophisticated theoretical studies on models of **1** and related compounds[4] have led to a general acceptance that the level of metal–metal π-interactions they exhibit is not substantial but also not insignificant. It is noteworthy that this increases in homoleptic transition metal-group 13 diyl complexes, *e.g.* [Ni{GaC-(SiMe₃)₃}₄].[5]

Group 13 metal(I) diyls can be thought of as carbene analogues in their coordination chemistry. In light of the explosive growth in the use of highly nucleophilic *N*-heterocyclic carbenes (NHCs) as ligands in the formation of stable p-, d- and f-block metal complexes,[6] we have become interested in preparing anionic group 13 isoelectronic analogues of NHCs and exploring their coordination chemistry. To this end we have recently reported a facile synthesis of the gallium(I) NHC analogue, **2**, [:Ga{N(Ar)C(H)}₂]⁻, Ar = C₆H₃Prⁱ₂-2,6.[7] Theoretical studies have been carried out on the model anion of **2**, [:Ga{N(H)-C(H)}₂]⁻, which show that its lone pair is associated with the HOMO and resides in an sp-like gallium orbital.[8] The nucleophilicity of **2** has recently been demonstrated with the formation of the anionic group 13 hydride complexes, [MH₂(**2**)₂]⁻, **3**, M = Ga or In, which show remarkable thermal stability in the solid state.[9] In addition, when nickelocene is treated with two equivalents of **2**, Cp⁻ displacement occurs and the formation of the anionic complex, [CpNi(**2**)₂]⁻, **4**, results.[10] It is noteworthy that this reaction mimics that of the NHC, :C{N(Me)C(Me)}₂, IMe, with nickelocene which affords the cationic complex, [CpNi(IMe)₂]⁺.[11] We wished to extend the coordination chemistry of **2** to the formation of transition metal carbonyl complexes as spectroscopic studies on these could potentially probe the degree of M–Ga π-bonding they exhibit. Our preliminary efforts in this direction are reported herein.

The reaction of **2** with an excess of Fe(CO)₅ at room temperature led to a moderate yield of the iron complex, **5**, after recrystallisation of the crude product from diethyl ether (Scheme 1). The facile nature of this CO displacement reaction is consistent with **2** being a strong σ-donor (*cf.* NHCs) and is related to the formation of the recently reported neutral gallium heterocycle-iron complex, [Fe(CO)₄{Ga[N(Ar)C(Me)]₂-CH}] **6**.[12] When **5** was treated with an excess of **2** no reaction occurred, as was the case when it was treated with an excess of the unhindered NHC, :C{N(Me)C(Me)}₂.
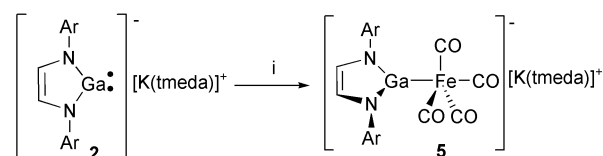
Scheme 1 *Reagents and conditions: i, Fe(CO)₅, Et₂O, 25 °C, –CO.*

An X-ray crystal structure analysis ‡ of **5** was carried out and its molecular structure is depicted in Fig. 1. This shows it to be polymeric through bridging potassium centres which are unusually coordinated by a molecule of tmeda, the O(4) and O(2) centres of equatorial carbonyl ligands and an η²-interaction to one of the heterocycle's arene substituents. The Fe–Ga bond length is shorter than the mean for such inter-
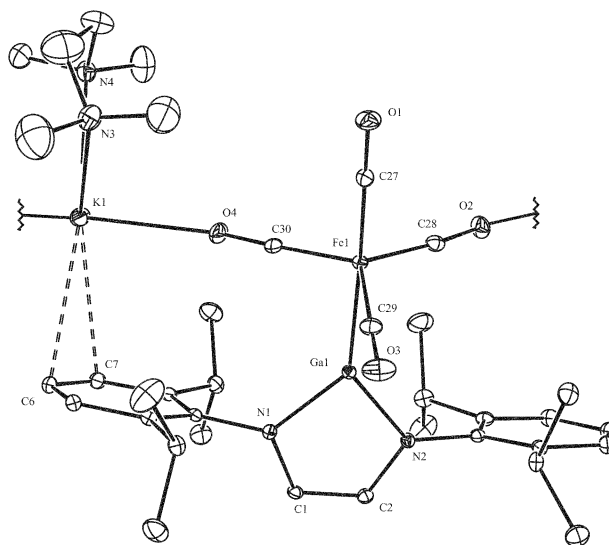

Fig. 1 Molecular structure of **5** (ellipsoids shown at the 30% probability level). Selected bond lengths (Å) and angles (°): Ga(1)–Fe(1) 2.3068(8), Ga(1)–N(1) 1.882(3), Ga(1)–N(2) 1.872(3), N(1)–C(1) 1.405(4), N(2)–C(2) 1.399(5), C(1)–C(2) 1.342(5), K(1)–N(4) 2.798(4), K(1)–N(3) 2.851(4), K(1)–O(4) 2.626(3), K(1)–O(2)′ 2.739(3), K(1)–C(6) 3.185(4), K(1)–C(7) 3.346(4), N(1)–Ga(1)–N(2) 88.17(13), N(2)–Ga(1)–Fe(1) 139.33(9), N(1)–Ga(1)–Fe(1) 132.07(9), Ga(1)–Fe(1)–C(27) 174.13(13), Ga(1)–Fe(1)–C(30) 82.66(12), Ga(1)–Fe(1)–C(28) 87.33(13), Ga(1)–Fe(1)–C(29) 81.04(13). symmetry operation ′: −x + 3/2, y + 1/2, −z + 1/2.

actions (2.397 Å [13]) but significantly longer than that in **1**, 2.248(7) Å, and **6**, 2.2851(4) Å, which contain 2 and 3 co-ordinate gallium centres respectively. As has been seen in **3** and **4**, the Ga–N bond lengths and N–Ga–N angle of the planar, localised gallium heterocycle are respectively shorter and more obtuse than in uncoordinated **2**. This is likely due to the loss of electron density from the gallium centre upon coordination which would lead to a significantly greater positive charge on it than in the free anionic ligand (*vide infra*). In this respect **5** could be viewed as the first anionic gallyl–iron complex which is related to known boryl complexes, *e.g.* [Fe(CO)$_4$(BCat)]$^-$, BCat = catecholboryl.[14]

The spectroscopic data§ for **5** are consistent with its solid state structure. Most informative of these come from its solution (THF/18-crown-6) infrared spectrum which displays carbonyl stretching absorptions at significantly lower frequencies (*ca.* 20–30 cm^{-1}) than those in the neutral complexes **1** and **6**, as would be expected for an anionic complex. The positions of these absorptions in **5**, combined with its relatively long Fe–Ga(3-coordinate) bond length, suggest little back-bonding from the iron centre into the gallium p-orbital which is orthogonal to the heterocycle plane and is associated with the LUMO of the free ligand.[8] This situation resembles that in NHC-transition metal complexes in which there is little back-bonding into the carbene centres p-orbital.[6]

It has been suggested, however, that CO stretching frequencies and Fe–Ga bond lengths are not reliable probes for the degree of back-bonding in complexes such as **1** (and by inference, **5**).[4] Therefore, we have investigated the bonding situation in the model anion, [Fe(CO)$_4${Ga[N(H)C(H)]$_2$}]$^-$, **7**, and for comparison the neutral NHC complex, [Fe(CO)$_4${C[N(H)-C(H)]$_2$}], **8**, and Fe(CO)$_5$ using the BP86/6-31G(d) density functional method† followed by Charge Decomposition Analysis (CDA)[4] for determining the σ (dative) and π (back-bonding) components of the Fe–Ga(or C) bond and Natural Bond Orbitals (NBO)[15] for assessing charge distribution within the molecules. The CDA studies have given a dative/back-bonding ratio (d/b) of 3.40 for **7** (Fe–Ga bond) which is very close to that in the NHC complex, **8** (3.39, Fe–C$_{carbene}$ bond), and is indicative of negligible back-bonding in both complexes (*cf.* a d/b ratio of 1.75 (Fe–C$_{axial}$) for Fe(CO)$_5$). It is worth noting that the model compound of **1**, *viz.* [(PhGa)Fe(CO)$_4$], exhibits a significantly greater degree of back-bonding than **7**, *i.e.* d/b = 1.51 for its Fe–Ga bond.[4c]

Natural population analysis shows that there is a significant development of positive charge at the gallium centre of **7** (+1.110) relative to the free anionic heterocycle (+0.204) whilst the iron centre has a build up of negative charge (−0.513) relative to the iron centres in **8** (−0.403) and Fe(CO)$_5$ (−0.463). Finally, we have found that the Fe–Ga bond in **7** is much stronger (bond dissociation energy, D_e = 94.0 kcal mol^{-1}) than the Fe–C bonds in **8** (D_e = 64.9 kcal mol^{-1}) and Fe(CO)$_5$ (D_e = 52.2 kcal mol^{-1}) which is consistent with the facile formation of **5** by CO displacement and its lack of reactivity toward NHCs. The latter observation could, however, have a kinetic contribution to its origin.

In conclusion, we have prepared the first iron complex of an anionic gallium NHC analogue and have shown it to have an unusual polymeric structure in the solid state. In addition, theoretical studies have pointed toward minimal Fe → Ga back-bonding in this complex. We are currently systematically exploring the coordination chemistry of **2** and its analogy with NHCs in this respect. The results of these investigations will appear in forthcoming publications.

Notes and references

‡ *Crystal data* for **5**: C$_{36}$H$_{52}$FeGaKN$_4$O$_4$ *M* = 769.49 monoclinic, space group *P*2$_1$/*n*, *a* = 14.558(3), *b* = 14.257(3), *c* = 19.171(4) Å, *β* = 94.50(3)°, *V* = 3966.7(14) Å^3, *Z* = 4, *D*$_c$ = 1.288 g cm^{-3}, *F*(000) = 1616, *μ*(Mo-Kα) = 1.19 mm^{-1}, 150(2) K, 7785 unique reflections [*R*(int) 0.0767], *R* (on *F*) 0.0513, *wR* (on *F*^{2}) 0.1128 (*I* > 2σ*I*). CCDC reference number 211975. See http://www.rsc.org/suppdata/dt/b3/b308616j/ for crystallographic data in CIF or other electronic format.
§ *Synthesis and data for* **5**: To a solution of [K(TMEDA)][:Ga-{N(Ar)C(H)}$_2$] (1.00 g, 0.82 mmol) in Et$_2$O (30 cm^3) held at −78 °C was added Fe(CO)$_5$ (0.40 cm^3, 3.04 mmol). The resulting red/orange solution was warmed to room temperature and stirred for 12 h after which time volatiles were removed *in vacuo* affording a yellow residue. This was extracted with Et$_2$O (50 cm^3), filtered, concentrated to *ca.* 20 cm^3 and placed at −30 °C to yield yellow crystals of **5** (yield 0.34 g, 54%). Mp 152–155 °C (dec); ^{1}H NMR (400 MHz, CD$_3$CN, 300 K) δ 1.16 (d, $^3J_{HH}$ = 8 Hz, 12H, CH$_3$), 1.22 (d, $^3J_{HH}$ = 8 Hz, 12H, CH$_3$), 1.93 (s, 12H, NCH$_3$), 2.29 (s, 4H, NCH$_2$), 3.56 (v. sept, $^3J_{HH}$ = 8 Hz, 4H, CH), 5.95 (s, 2H, C$_2$H$_2$), 7.0–7.2 (m, 6H, Ar); ^{13}C NMR (100 MHz, CD$_3$CN, 300 K) δ 24.1 (CH$_3$), 25.2 (CH$_3$), 28.3 (CH), 45.2 (NCH$_3$), 57.2 (NCH$_2$), 120.6 (NCH), 122.6 (*m*-Ar), 124.1 (*p*-Ar), 145.9 (*o*-Ar), 146.9 (*i*-Ar), 217.4 (CO); IR (THF/18-crown-6) *v*/cm^{-1} 1988 (m), 1965 (w), 1876 (s); MS (-ve ion ES): *m/z*: 393 [100%, {N(Ar)C(H)}$_2^+$].

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