Synthesis and characterisation of complexes of Group 13 metal amidinate heterocycles with the CpFe(CO)₂ fragment†

Cameron Jones,* Simon Aldridge,* Timo Gans-Eichler and Andreas Stasch

The first examples of complexes between a 4-membered amidinato–Group 13 metal(III) heterocycle and a transition metal fragment are formed in salt elimination reactions between $Na[CpFe(CO)_2]$ and $[MX_2(amid)]$, M = Al, Ga or In; X = Cl or Br; amid$^-$ = $[(RN)_2CBu^t]^-$; R = Pr^i or cyclohexyl (Cy). The formed complexes, $[CpFe(CO)_2M(X)(amid)]$ (4 examples) have been crystallographically characterised and subject to halide abstraction reactions. In one case, the cationic complex, $[CpFe(CO)_2Ga(OEt_2)\{(CyN)_2CBu^t\}][BAr^f_4]$, was isolated and crystallographically characterised. A hydrolysis product of this complex, $[\{CpFe(CO)_2Ga[(CyN)_2CBu^t]\}_2(\mu\text{-}OH)][BAr^f_4]$, was also isolated in low yield from this reaction and structurally characterised.

Introduction

The amidinate class of ligand, $[RNC(R')NR]^-$, has been utilised in the formation of a multitude of complexes of metals from across the periodic table.[1] Complexes of Group 13 metals in the +3 oxidation state have received particular attention as these have found a number of applications as, for example, polymerisation catalysts and as materials precursors in chemical vapour deposition processes.[2,3] In this field we are interested in exploiting sterically bulky amidinates and related guanidinates, $[RNC(NR'_2)NR]^-$, in the stabilisation of thermally labile fragments, *e.g.* indium and gallium hydrides.[4] In addition, we have recently been successful in forming the first Group 13 metal(I) and (II) complexes incorporating amidinate and/or guanidinate ligands.[5] Of most note are the monomeric, 4-membered, N,N-chelated metal(I) heterocycles, $[:M\{(Ar)NC(NCy_2)N(Ar)\}]$, M = Ga or In, Ar = $C_6H_3Pr^i_2$-2,6, Cy = cyclohexyl. Theoretical studies on models of these compounds suggest that they should act as good σ-donor ligands to transition metal fragments, as is now well known for Group 13 metal diyls, $:M(I)R$.[6]

Although we are examining this possibility with some success,[7] an alternative synthetic route to complexes between transition metal fragments and less bulky Group 13-amidinate heterocycles would be attractive as this would allow a wider range of complex types to be accessed. It seemed that the reaction of amidinate metal(III) dihalides, $[(amid)MX_2]$, (amid = general amidinate) with anionic transition metal fragments, $[M'L_n]^-$, could give complexes of the type, $[L_nM'M(X)(amid)]$, halide abstraction from which could yield cationic complexes, $[L_nM'M(amid)]^+$. There are close parallels here with the formation of cationic iron borylene and related complexes, *e.g.* $[(C_5R_5)Fe(CO)_2BR']^+$ or $[\{(C_5R_5)Fe(CO)_2EMes^*\}_2(\mu\text{-}X)]^+$ (R = H or Me, R' = aryl or amido, E = Ga or In, X = Cl or Br, Mes* = $C_6H_2Bu^t_3$-

Centre for Fundamental and Applied Main Group Chemistry, School of Chemistry, Main Building, Cardiff University, Cardiff, UK CF10 3AT. E-mail: jonesca6@cardiff.ac.uk

† Electronic supplementary information (ESI) available: ORTEP diagrams and selected bond lengths and angles for **2(a)** and **2(c)**. See DOI: 10.1039/b611758a

2,4,6),[8,9] *via* halide abstraction from the neutral complexes, $[(C_5R_5)Fe(CO)_2E(X)R']$[8,10] using, for example, $Na[BAr^f_4]$, Ar^f = $C_6H_3(CF_3)_2$-3,5. Of note here are the significant levels of Fe–B π-bonding exhibited by the cationic iron borylene complexes. This is brought about by the presence of two empty p-orbitals at the boron centre and the cationic nature of the complexes which enhances the overlap of symmetry related orbitals on the Fe and B centres. If complexes of the type, $[L_nM'M(amid)]^+$, could be accessed, the likely empty p-orbital at the Group 13 element centre may similarly act as a π-acceptor and lead to a degree of metal–metal back bonding. Our efforts in this direction are reported herein.

Results and discussion

In order to access precursors suitable for halide abstraction reactions, suspensions of $Na[CpFe(CO)_2]$ in diethyl ether were treated with the amidinato Group 13 dihalides, **1(a–d)**, to give the neutral complexes, **2(a–d)**, in moderate yields after work-up (Scheme 1). Although **1(a–c)** were prepared by literature procedures, **1(d)** has not previously been reported and its synthesis and spectroscopic details can be found in the experimental
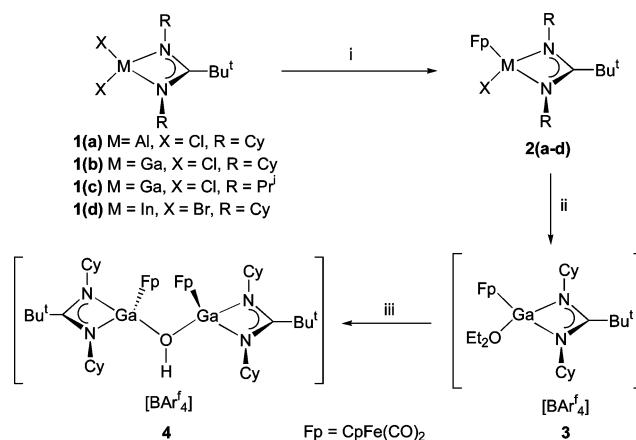
Scheme 1 i) Na[Fp], Et₂O, −NaX; ii) Na[BAr^f₄], CH₂Cl₂–Et₂O, −NaCl (M = Ga, X = Cl, R = Cy); iii) trace H₂O, CH₂Cl₂–Et₂O.

section. The spectroscopic data for **2** are consistent with their proposed monomeric structures and all display two CO stretching absorptions in their infrared spectra (*e.g.* **2(b)**: v_{CO} 1985, 1933 cm^{-1}) at wavenumbers close to those previously reported for related complexes, *e.g.* [CpFe(CO)$_2$E(X)Mes*]; E = Ga, X = Cl (v_{CO} 1999, 1952 cm^{-1}); E = In, X = Br (v_{CO} 1996, 1945 cm^{-1}).[10]

X-Ray crystal structure analyses were carried out on complexes **2(a–d)**, which are the first structurally authenticated complexes of 4-membered Group 13 metal heterocycles with transition metal fragments. An analysis of the crystallographic data revealed **2(a–c)** to be structurally similar (**2(a)** and **2(b)** are isomorphous) and thus only the molecular structure of **2(b)** is depicted in Fig. 1 (see also Table 1). The halide ligands of these monomeric complexes effectively adopt an *anti*-conformation with respect to the Fe–Cp linkage, as evidenced by their halide–M–Fe–Cp centroid torsion angles (**2(a)** 176.6°, **2(b)** 177.9°, **2(c)** 171.7°). In contrast, the In–Br bond in **2(d)** (Fig. 2, see Table 1) adopts a conformation with respect to the Fe–Cp unit which is closer to a *syn*-disposition (Br–In–Fe–Cp centroid torsion angle: 45.8°). These differences possibly occur because the increased Fe–M bond length in **2(d)** may reduce the steric interaction between the CpFe(CO)$_2$ fragment and the indium heterocycle thereby allowing a more free rotation about the M–Fe bond than is possible in the other compounds. Saying this, the effects of crystal packing forces cannot be ruled out as a reason.
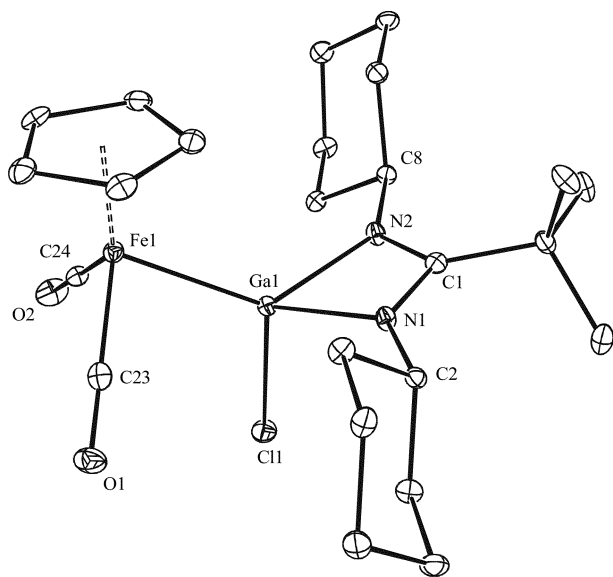

Fig. 1 Molecular structure of **2(b)** (hydrogen atoms omitted for clarity; ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): Ga(1)–N(2) 1.984(2), Ga(1)–N(1) 1.987(2), Ga(1)–Cl(1) 2.2294(8), Ga(1)–Fe(1) 2.3540(6), N(1)–C(1) 1.341(4), N(2)–C(1) 1.347(3); N(2)–Ga(1)–N(1) 66.39(9), N(2)–Ga(1)–Cl(1) 104.45(7), N(1)–Ga(1)–Cl(1) 106.18(8), N(2)–Ga(1)–Fe(1) 130.24(8), N(1)–Ga(1)–Fe(1) 124.29(7), Cl(1)–Ga(1)–Fe(1) 115.20(3), N(1)–C(1)–N(2) 108.0(2).

In all complexes, the amidinate ligands appear to be largely delocalised while the N–M and M–Fe distances lie within the reported ranges.[11] It is of interest that the Fe–M bond length of **2(a)** is slightly longer than those of **2(b)** and **2(c)**. This is, however, in line with the now established larger covalent radius of aluminium

Table 1 Crystal data for compounds **2(a–d)**, **3** and **4**

| Compound	2(a)	2(b)	2(c)	2(d)	3	4
Empirical formula	C$_{24}$H$_{36}$AlClFeN$_2$O$_2$	C$_{24}$H$_{36}$GaClFeN$_2$O$_2$	C$_{18}$H$_{28}$GaClFeN$_2$O$_2$	C$_{24}$H$_{36}$InBrFeN$_2$O$_2$	C$_{60}$H$_{58}$BF$_{24}$FeGaN$_2$O$_3$	C$_{80}$H$_{85}$BF$_{24}$Fe$_2$Ga$_2$N$_4$O$_5$
M	502.83	545.57	465.44	635.13	1447.46	1900.47
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	8.7688(18)	8.7580(18)	16.618(3)	9.3802(19)	30.023(5)	13.873(3)
b/Å	15.849(3)	15.865(3)	9.4461(19)	10.710(2)	17.780(5)	20.005(4)
c/Å	17.550(4)	17.650(4)	13.563(3)	15.261(3)	26.410(5)	31.856(6)
α/°	90	90	90	109.94(3)	90	90
β/°	90	90	92.57(3)	92.94(3)	115.322(5)	91.50(3)
γ/°	90	90	90	91.50(3)	90	90
V/Å^3	2438.9(9)	2452.4(9)	2126.8(7)	1437.9(5)	12743(5)	8838(3)
Z	4	4	4	2	8	4
ρ_{calcd}/Mg m^{-3}	1.369	1.478	1.454	1.467	1.509	1.428
μ(Mo-K$_\alpha$)/mm^{-1}	0.787	1.822	2.087	2.715	0.766	1.025
F(000)	1064	1136	960	640	5872	3872
No. of reflns collected	32614	8770	7968	11354	44400	52383
No. of independent reflns	5035 [R(int) = 0.1256]	4965 [R(int) = 0.0318]	4176 [R(int) = 0.0227]	6198 [R(int) = 0.0295]	23061 [R(int) = 0.0504]	15894
Final R indices ($I>2\sigma(I)$) R1, wR2	0.0351, 0.0726	0.0318, 0.0656	0.0252, 0.0574	0.0304, 0.0712	0.1188, 0.3001	0.0779, 0.2024
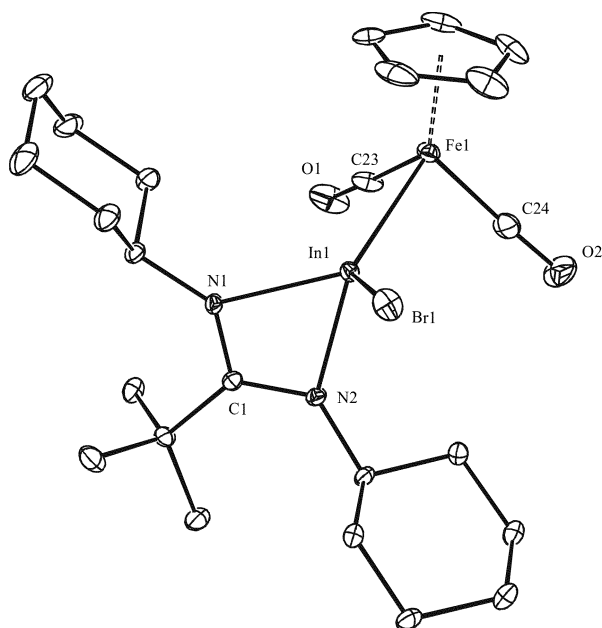
Fig. 2 Molecular structure of **2(d)** (hydrogen atoms omitted for clarity; ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): In(1)–N(2) 2.178(2), In(1)–N(1) 2.190(2), In(1)–Fe(1) 2.5151(7), In(1)–Br(1) 2.5652(11), N(1)–C(1) 1.337(3), N(2)–C(1) 1.336(3); N(2)–In(1)–N(1) 60.40(8), N(2)–In(1)–Fe(1) 129.09(7), N(1)–In(1)–Fe(1) 125.21(7), N(2)–In(1)–Br(1) 103.81(7), N(1)–In(1)–Br(1) 108.29(7), Fe(1)–In(1)–Br(1) 117.06(3), N(2)–C(1)–N(2) 110.6(2).

(1.30 Å) *versus* gallium (1.25 Å).[12] The difference between these radii is not reflected in the magnitudes of the N–M–N angles of the complexes, which become narrower with increasing molecular weight of the metal. An examination of the M–X bonds of the compounds showed them to be unexceptional and close to the means for previously reported terminal interactions (Al–Cl 2.13 Å, Ga–Cl 2.18 Å, In–Br 2.55 Å).[11]

In order to prepare cationic complexes with 3-coordinate Group 13 centres, **2(a–d)** were treated with one equivalent of Na[BAr$^f_4$] in dichloromethane. Although this halide abstraction methodology has proved successful for related complexes, *e.g.* [(C$_5$R$_5$)Fe(CO)$_2$E(X)Mes*] (R = H, E = Ga, X = Cl; R = Me, E = In, X = Br),[10] no reactions were observed with **2**, despite extended reaction times. It is not known why these differences occur but reasons could include the presumably more hindered 4-coordinate Group 13 centres in the latter relative to the 3-coordinate centres in the former. In addition, the M–X bonds in the latter are shorter and probably stronger than those in the former despite their 4-coordinate Group 13 metal centres. This shortening is likely a result of a negative inductive effect of the electronegative N-centres of the amidinate ligands in **2**. Saying this, a chloride abstraction from a similarly hindered 4-coordinate gallium centre (in [(nacnac)Ga–Au–Ga(Cl)(nacnac)], nacnac = (ArNCMe)CH$^−$) has recently been reported.[13]

Repeating the halide abstraction reactions in the presence of a donor solvent, diethyl ether, met with mixed success. Again, **2(a)** remained unreactive towards Na[BAr$^f_4$], presumably because of the relative strength of its M–X bond, whilst reactions with **2(b–d)** did occur. However, only in the case of the reaction with **2(b)** could products be isolated from the reaction mixture, *viz.* the ionic

complexes **3** and **4** (Scheme 1). Compound **3** doubtless results from chloride abstraction and subsequent coordination of the generated 3-ccordinate gallium centre by a molecule of diethyl ether. This is reminiscent of the formation of the Lewis base adducts, [CpFe(CO)$_2$B(L)NCy$_2$]$^+$ (L = THF or 4-picoline), which arise from the treatment of the borylene complex, [CpFe(CO)$_2$BNCy$_2$]$^+$, with the donor (L).[8a] Compound **4** was obtained in low yield (< 5%) and almost certainly arises from the hydrolysis of **3** by traces of water in the reaction mixture.

The spectroscopic data for **3** are consistent with its proposed formulation. Of most note is its infrared spectrum which exhibits CO stretching bands (ν_{CO} 2007 cm^{-1}, 1958 cm^{-1}) which are shifted to higher wavenumbers by *ca.* 20 cm^{-1} relative to those in the precursor complex, **2(b)**, as expected for a cationic complex. Because of the low yield of **4**, no meaningful spectroscopic data could be obtained for this compound.

The structures of the cationic components of **3** and **4** are depicted in Fig. 3 and 4 respectively. During the course of refinement, the asymmetric unit of **3** was found to contain two crystallographically independent cations and anions. No significant geometric differences were found between the two and, accordingly, geometric parameters for only one are reported here. A relatively high *R*-factor was obtained for this structure due to extensive disorder in the [BAr$^f_4$]$^−$ counter-ions. Despite this, the connectivity within the cations is unambiguous. The gallium centre of **3** has a distorted tetrahedral geometry, very similar to that in **2(b)**. As a result, there is no possibility of any Fe–Ga π-bonding in this complex. Its Ga–Fe and Ga–N bonds are slightly shorter than those in the precursor molecule, an observation that can be attributed to a contracted gallium radius in the cationic complex. The structure of the cation of **4** shows it also to have distorted
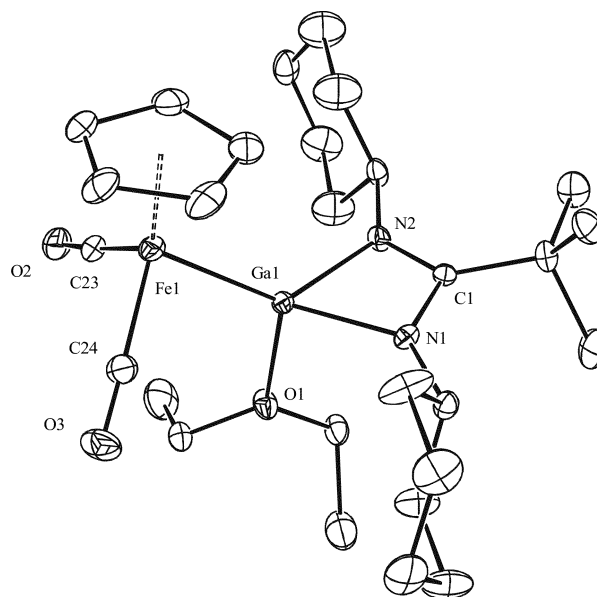

Fig. 3 Structure of the cationic component of **3** (hydrogen atoms omitted for clarity; ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.958(7), Ga(1)–N(2) 1.963(6), Ga(1)–O(1) 2.042(6), Ga(1)–Fe(1) 2.3183(15), N(1)–C(1) 1.340(11), N(2)–C(1) 1.335(10); N(1)–Ga(1)–N(2) 66.8(3), N(1)–Ga(1)–O(1) 98.0(3), N(2)–Ga(1)–O(1) 100.1(3), N(1)–Ga(1)–Fe(1) 130.1(2), N(2)–Ga(1)–Fe(1) 131.1(2), O(1)–Ga(1)–Fe(1) 117.78(17), N(2)–C(1)–N(1) 107.7(7).
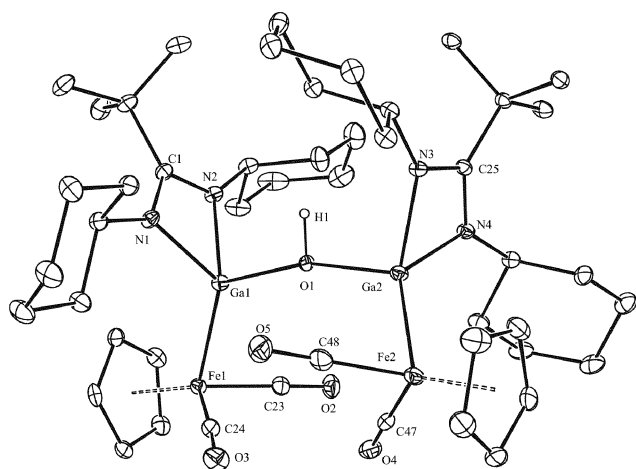
Fig. 4 Structure of the cationic component of **4** (hydrogen atoms omitted for clarity; ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): Ga(1)–O(1) 1.971(3), Ga(1)–N(2) 1.986(5), Ga(1)–N(1) 1.998(5), Ga(1)–Fe(1) 2.3354(11), Ga(2)–O(1) 1.975(3), Ga(2)–N(3) 1.987(4), Ga(2)–N(4) 1.993(5), Ga(2)–Fe(2) 2.3148(12), N(1)–C(1) 1.341(8), N(2)–C(1) 1.330(8), N(3)–C(25) 1.347(7), N(4)–C(25) 1.335(7); O(1)–Ga(1)–N(2) 96.29(19), O(1)–Ga(1)–N(1) 103.29(19), N(2)–Ga(1)–N(1) 66.1(2), O(1)–Ga(1)–Fe(1) 122.83(12), N(2)–Ga(1)–Fe(1) 126.86(15), N(1)–Ga(1)–Fe(1) 126.20(15), O(1)–Ga(2)–N(3) 97.90(18), O(1)–Ga(2)–N(4) 105.04(19), N(3)–Ga(2)–N(4) 66.37(19), O(1)–Ga(2)–Fe(2) 116.22(12), N(3)–Ga(2)–Fe(2) 130.03(14), N(4)–Ga(2)–Fe(2) 129.49(15), N(2)–C(1)–N(1) 108.9(5), N(4)–C(25)–N(3) 108.6(5).

tetrahedral gallium centres with iron–gallium separations similar to those in **3**. These centres are effectively symmetrically bridged by a hydroxide ligand with a Ga–O–Ga angle of 163.0(2)° and Ga–O distances similar to those previously reported for hydroxy bridged digallium fragments, *e.g.* 1.965 Å (mean) in $(Me_3Si)_3CGa(Me)(OH)(\mu\text{-}OH)GaC(SiMe_3)_3(Me)(OH_2)$.[14]

Conclusion

In summary, the first examples of complexes in which 4-membered amidinato–Group 13 heterocycles act as ligands towards transition metal fragments have been described. Neutral examples of the form $[CpFe(CO)_2M(X)(amid)]$ have been readily accessed *via* salt elimination reactions between $Na[CpFe(CO)_2]$ and $[MX_2(amid)]$. Halide abstraction from one example has yielded the cationic complex, $[CpFe(CO)_2Ga(OEt_2)\{(CyN)_2CBu^t\}][BAr^f_4]$, the gallium centre of which is coordinated by a molecule of diethyl ether, thus precluding any Fe–Ga π-backbonding in this complex.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Hexane and toluene were distilled over potassium whilst diethyl ether was distilled over Na/K then freeze/thaw degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DXP400 or a JEOL Eclipse 300 plus spectrometer and were referenced to the residual ^1H or ^{13}C resonances of the solvent used. Mass spectra were obtained from the EPSRC National Mass

Spectrometry Service at Swansea University. Microanalyses were obtained from Medac Ltd. Where reproducible microanalyses could not be obtained, accurate mass spectra were obtained, except for compound **3**. The NMR spectra of this compound suggested its purity was greater than 98%. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates, or as solutions in CH_2Cl_2. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. $Na[CpFe(CO)_2]$,[15] $[AlCl_2\{(CyN)_2CBu^t\}]$,[2e] $[GaCl_2\{(RN)_2CBu^t\}]$ (R = Cy or Pr^i)[2c] and $Na[BAr^f_4]$[16] were synthesised by literature procedures whilst all other chemicals were obtained from commercial sources and used as supplied.

Syntheses

Preparation of $[InBr_2\{(CyN)_2CBu^t\}]$ 1(d). A suspension of $[Li\{(CyN)_2CBu^t\}]$ (1.30 g, 5.6 mmol) in diethyl ether (30 cm³) was added over 5 min to a suspension of $InBr_3$ (1.71 g, 4.8 mmol) in diethyl ether (30 cm³) at 0 °C. After warming to 20 °C and stirring for 2 h, volatiles were removed from the reaction mixture *in vacuo* and the residue extracted with hot toluene (50 cm³) and filtered. The filtrate was concentrated to 10 cm³ and placed at −30 °C yielding **1(d)** as colourless crystals. Mp: 190–192 °C (Yield: 2.50 g, 93%). ^1H NMR (400 MHz, C_6D_6): δ 1.10 (s, 9H, C(CH_3)$_3$), 0.92–1.60 (m, 20H, CH_2), 3.74 (m, 2H, CH); $^{13}C\{^1H\}$ NMR (75.57 MHz, C_6D_6): δ 25.2, 25.3, 38.4 (CH_2), 29.2 (C(CH_3)$_3$), 39.6 (C(CH$_3$)$_3$), 55.7 (CH), 176.4 (NCN); (MS/EI) m/z : 536 [M$^+$, 6%], 262 [M$^+$ − InBr$_2$, 100%]; acc. mass MS (EI): calc. for $C_{17}H_{31}N_2Br_2In$ 535.9887, found 535.9887.

Preparation of $[CpFe(CO)_2Al(Cl)\{(CyN)_2CBu^t\}]$ 2(a). To a suspension of $Na[CpFe(CO)_2]$ (300 mg, 1.50 mmol) in diethyl ether (20 cm³) at −78 °C was added a solution of $[AlCl_2\{(CyN)_2CBu^t\}]$ (500 mg, 1.40 mmol) in diethyl ether (20 cm³). After warming to 20 °C and stirring for 18 h, the reaction mixture was filtered and the filtrate concentrated to *ca.* 10 cm³. This was stored at −30 °C overnight, affording **2(a)** as yellow crystals. Mp: 159–161 °C (Yield: 150 mg, 21%). ^1H NMR (400 MHz, C_6D_6): δ 1.25 (s, 9H, C(CH_3)$_3$), 1.21–2.21 (m, 20H, CH_2), 3.30 (m, 2H, CH), 4.52 (s, 5H, CpH); $^{13}C\{^1H\}$ NMR (126.0 MHz, C_6D_6): δ 25.7, 26.1, 35.5 (CH_2), 29.5 (C(CH_3)$_3$), 39.4 (C(CH$_3$)$_3$), 56.0 (CH), 82.2 (Cp), 179.0 (NCN), CO resonance not observed; IR ν/cm^{-1} (CH$_2$Cl$_2$): 1974, 1914 (CO); (MS/EI) m/z : 502 [M$^+$, 15], 446 [M$^+$ − 2CO, 14], 325 [M$^+$ − CpFe(CO)$_2$, 100]; acc. mass MS (EI): calc. for $C_{24}H_{36}O_2N_2FeClAl$ 502.1625, found 502.1625; anal.: calc for $C_{24}H_{36}O_2N_2FeClAl$ C 57.33, H 7.22, N 5.57; found C 56.85, H 7.34, N 5.68.

Similar synthetic procedures were used for **2(b–d)**

$[CpFe(CO)_2Ga(Cl)\{(CyN)_2CBu^t\}]$ 2(b). Mp: 151–153 °C (Yield: 31%). ^1H NMR (400 MHz, C_6D_6): δ 1.30 (s, 9H, C(CH_3)$_3$), 1.21–2.29 (m, 20H, CH_2), 3.81 (m, 2H, CH), 4.47 (s, 5H, CpH); $^{13}C\{^1H\}$ NMR (126.0 MHz, C_6D_6): δ 24.4, 24.7, 35.4 (CH_2), 28.2 (C(CH_3)$_3$), 37.6 (C(CH$_3$)$_3$), 54.4 (CH), 81.1 (Cp), 173.1 (NCN), 214.8 (CO); IR ν/cm^{-1} (CH$_2$Cl$_2$): 1985, 1933 (CO); (MS/EI) m/z : 544 [M$^+$, 5], 488 [M$^+$ − 2CO, 20], 368 [M$^+$ − CpFe(CO)$_2$, 100]; acc. mass MS (EI): calc. for $C_{24}H_{36}O_2N_2FeClGa$ 544.1065, found 544.1069; anal. calc for $C_{24}H_{36}O_2N_2FeClGa$ C 52.84, H 6.65, N 5.13; found C 52.18, H 6.61, N 5.14%.

[CpFe(CO)$_2$Ga(Cl){(Pr^{i}N)$_2$CBu^t}] 2(c). Mp: 120–122 °C (Yield: 52%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.21 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CH(CH$_3$)$_2$), 1.23 (s, 9H, C(CH$_3$)$_3$), 1.49 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CH(CH$_3$)$_2$), 4.13 (sept, $^3J_{HH}$ = 6.1 Hz, 2H, CH(CH$_3$)$_2$), 4.43 (s, 5H, CpH); ^{13}C{^{1}H} NMR (126.0 MHz, C$_6$D$_6$): δ 24.5, 24.7, (CH(CH$_3$)$_2$), 28.1 (C(CH$_3$)$_3$), 37.6 (C(CH$_3$)$_3$), 45.7 (CH), 81.1 (Cp), 173.7 (NCN), 215.0 (CO); IR ν/cm^{-1} (Nujol): 1980, 1921 (CO); (MS/EI) m/z: 465 [M$^+$, 5], 437 [M$^+$ − CO, 26], 408 [M$^+$ − 2CO, 35]; anal.: calc for C$_{18}$H$_{28}$O$_2$N$_2$FeClGa C 46.45, H 6.06, N 6.02; found C 45.85, H 5.98, N 5.73%.

[CpFe(CO)$_2$In(Br){(CyN)$_2$CBu^t}] 2(d). Mp: 96–98 °C (Yield: 37%) ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.34 (s, 9H, C(CH$_3$)$_3$), 1.22–2.32 (m, 20H, CH$_2$), 3.93 (m, 2H, CH), 4.43 (s, 5H, CpH); ^{13}C{^{1}H} NMR (75.6 MHz, C$_6$D$_6$): δ 25.1, 25.7, 38.2 (CH$_2$), 29.7 (C(CH$_3$)$_3$), 40.1 (C(CH$_3$)$_3$), 55.5 (CH), 81.4 (Cp), 174.0 (NCN), 215.1 (CO); IR ν/cm^{-1} (CH$_2$Cl$_2$): 1989, 1938 (CO); (MS/EI) m/z: 634 [M$^+$, 4], 606 [M$^+$ − CO, 20], 578 [M$^+$ − 2CO, 26], 368 [M$^+$ − CpFe(CO)$_2$, 100]; acc. mass MS (EI): calc. for C$_{24}$H$_{36}$O$_2$N$_2$FeBrIn 634.0343, found 634.0347.

[CpFe(CO)$_2$Ga(OEt$_2$){(CyN)$_2$CBu^t}][BAr$^f_4$] 3. To a suspension of Na[BAr$^f_4$] (270 mg, 0.30 mmol) in dichloromethane–diethyl ether (10 cm^3) at −78 °C was added a solution of **2(b)** (150 mg, 0.27 mmol) in dichloromethane (10 cm^3). After stirring for 1 h the reaction mixture was warmed to 20 °C and stirred for 17 h. The resultant suspension was filtered, the filtrate concentrated to *ca.* 2 cm^3 and layered with hexane (10 cm^3). Storage for 48 h at −30 °C afforded **3** as colourless crystals. Mp 133–135° (Yield: 200 mg, 52%). (NB: a small amount of the hydrolysis product, **4**, was also isolated. Attempts to prepare this compound by the reaction of **3** with 0.5 equivalent of H$_2$O led only to low yields (< 5%) of **4** and other unidentified products.) ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.15 (t, $^3J_{HH}$ = 3.3 Hz, 6H, CH$_3$CH$_2$O), 1.28 (s, 9H, C(CH$_3$)$_3$), 0.96–1.84 (m, 20H, CH$_2$), 3.65 (m, 2H, CH), 3.75 (q, $^3J_{HH}$ = 3.3 Hz, 4H, CH$_3$CH$_2$O), 4.81 (s, 5H, CpH), 7.41 (s, 4H, *p*-CH of [BAr$^f_4$]$^-$), 7.56 (s, 8H *o*-CH of [BAr$^f_4$]$^-$); ^{13}C{^{1}H} NMR (126.0 MHz, CD$_2$Cl$_2$): δ 14.3 (CH$_3$CH$_2$O), 25.5, 27.8, 33.9 (CH$_2$), 29.5 (C(CH$_3$)$_3$), 37.4 (C(CH$_3$)$_3$), 55.9 (CH), 65.9 (CH$_3$CH$_2$O), 83.4 (Cp), 117.9 (*p*-CH of [BAr$^f_4$]$^-$), 124.9 (q, $^1J_{CF}$ = 269 Hz, CF$_3$), 129.1 (q, $^2J_{CF}$ = 34 Hz, *m*-C of [BAr$^f_4$]$^-$), 137.6 (*o*-CH of [BAr$^f_4$]$^-$), 162.1 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C of [BAr$^f_4$]$^-$), 180.1 (NCN), 213.3 (CO); IR ν/cm^{-1} (CH$_2$Cl$_2$): 2002, 1941 (CO); (MS/EI) m/z: 262 [CyN(H)C(Bu^t)NCy$^+$, 100].

X-Ray crystallography

Crystals of **2(a–d)**, **3** and **4** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[17] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 1.

CCDC reference numbers 617851–657856.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611758a

References

1 (*a*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*b*) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
2 (*a*) S. Dagorne, I. A. Guzei, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 274; (*b*) G. Talarico and P. H. M. Budzelaar, *Organometallics*, 2000, **19**, 5691; (*c*) S. Dagorne, R. F. Jordan and V. G. Young, *Organometallics*, 1999, **18**, 4619; (*d*) M. P. Coles, D. C. Svenson, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 4042; (*e*) M. P. Coles, D. C. Svenson, R. F. Jordan and V. G. Young, *Organometallics*, 1997, **16**, 5183.
3 J. Barker, N. C. Blacker, P. R. Phillips, N. W. Alcock, W. Errington and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1996, 431.
4 (*a*) R. J. Baker, C. Jones, P. C. Junk and M. Kloth, *Angew. Chem., Int. Ed.*, 2004, **43**, 3852; (*b*) M. L. Cole, C. Jones, P. C. Junk, M. Kloth and A. Stasch, *Chem.–Eur. J.*, 2005, **11**, 4482.
5 (*a*) C. Jones, P. C. Junk, J. A. Platts and A. Stasch, *J. Am. Chem. Soc.*, 2006, **128**, 2206; (*b*) C. Jones, P. C. Junk, M. Kloth, K. M. Proctor and A. Stasch, *Polyhedron*, 2006, **25**, 1592; (*c*) C. Jones, P. C. Junk, J. A. Platts, D. Rathmann and A. Stasch, *Dalton Trans.*, 2005, 2497.
6 G. Gemel, T. Steinke, M. Cokoja, A. Kempter and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2004, 4161 and references therein.
7 C. Jones and A. Stasch, manuscript in preparation.
8 (*a*) S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, D. L. Kays (née Coombs), N. D. Coombs and D. J. Willock, *Angew. Chem., Int. Ed.*, 2006, **45**, 6118; (*b*) D. L. Coombs, S. Aldridge, C. Jones and D. J. Willock, *J. Am. Chem. Soc.*, 2003, **125**, 6356; (*c*) D. L. Coombs, S. Aldridge, A. Rossin, C. Jones and D. J. Willock, *Organometallics*, 2004, **23**, 2911; (*d*) D. L. Kays (née Coombs), J. K. Day, L.-L. Ooi and S. Aldridge, *Angew. Chem., Int. Ed.*, 2005, **44**, 7457.
9 N. R. Bunn, S. Aldridge, D. L. Kays (née Coombs), N. D. Coombs, A. Rossin, D. J. Willock, J. K. Day, C. Jones and L.-L. Ooi, *Organometallics*, 2005, **24**, 5891.
10 N. R. Bunn, S. Aldridge, D. L. Kays (née Coombs), N. D. Coombs, J. K. Day, L.-L. Ooi, S. J. Coles and M. B. Hursthouse, *Organometallics*, 2005, **24**, 5879.
11 As determined from a survey of the Cambridge Crystallographic Database, August, 2006.
12 (*a*) R. J. Wright, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2006, **45**, 5953; (*b*) W. Uhl, *Adv. Organomet. Chem.*, 2004, **51**, 53.
13 A. Kempter, C. Gemel, M. J. Hardman and R. A. Fischer, *Inorg. Chem.*, 2006, **45**, 3133.
14 C. Schnitter, H. W. Roesky, T. Albers, H.-G. Schmidt, C. Ropken, E. Parisini and G. M. Sheldrick, *Chem.–Eur. J.*, 1997, **3**, 1783.
15 R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1967, **8**, 287.
16 D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810.
17 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.