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Complexes of Four-Membered Group 13 Metal(I) N-Heterocyclic Carbene Analogues with Metal Carbonyl Fragments

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The four-membered gallium(I) and indium(I) heterocycles, [:M(Giso)] (M = Ga or In; Giso = $\{[N(Ar)]_2CN(C_6H_{11})_2\}^-$, Ar = C_6H_3*i*Pr_2-2,6), were treated with a series of transition metal carbonyl complexes. These reactions afforded the complexes $[Fe(CO)_4\{Ga(Giso)\}]$, $[(CO)_3Co\{\mu\text{-}Ga(Giso)\}_2Co(CO)_3]$, $[Ru(CO)_2(PPh_3)_2\{M(Giso)\}]$ and $[CpMo(CO)_2\{[(Giso)Ga]_2OH\}]$, which were crystallographically and/or spectroscopically characterized. The results of the study show that the two heterocycles can act as σ-donor ligands, but they are not as nucleophilic as, for example, group 13 diyls, :MR (M = Ga or In; R = alkyl, aryl, etc.). In addition, the degree of π-back-bonding in their metal carbonyl complexes does not appear to be significant.

Introduction

The coordination chemistry of singlet group 13 metal(I) diyls, :MR (R = bulky aryl, alkyl, $C_5Me_5^-$, etc.), is extensively developed.[1] These compounds have been employed as metal donor Lewis bases in the formation of complexes with elements from every block of the periodic table. Although not as widely studied, the coordination chemistry of related group 13 metal(I) heterocycles is rapidly developing. In this field, systems that have been examined include the neutral six-membered heterocycles, [:M(Nacnac)] (M = Al[2] or Ga,[3] Nacnac = $\{N(Ar)C(Me)\}_2CH$, Ar = C_6H_3*i*Pr_2-2,6), stabilized by a β-diketiminate ligand, and the five-membered anionic gallium heterocycle, $[:Ga(dab)]^-$ (dab = $\{N(Ar)C(H)\}_2$),[4] which is a valence-isoelectronic analog of the typical N-heterocyclic carbene (NHC) class of ligands. It can also be considered as a gallyl anion, and its nucleophilicity is demonstrated by the fact that it has formed complexes with more than forty s-,[5] p-,[6] d-[7] and f-block[8] elements. It should be noted that its direct boron analog, the boryl anion $[:B\{N(Ar)C(H)\}_2]^-$,[9] is now known, and its coordination chemistry is emerging.[10] Theoretical studies have suggested that each of the metal heterocycles possesses a singlet lone pair of electrons at the group 13 center and an empty metal p-orbital orthogonal to the heterocycle plane.[11] There is, however, little experimental or theoretical evidence to suggest any significant π-back-bonding in late transition metal complexes of the heterocycles. The reasons for this include the high energy of the empty p-orbitals relative to that of filled d-orbitals of appropriate symmetry at the coordinated transition metal center.

Group 13 metal(I) heterocycle chemistry has recently been extended to the four-membered metallocycles, [:M(Giso)] {M = Ga (**1**) or In (**2**); Giso = $[\{N(Ar)\}_2CN(C_6H_{11})_2]^-$}, which are stabilized by incorporation of a very bulky guanidinate ligand.[12,13] Compounds **1** and **2** have been utilized as ligands in the preparation of a range of group 10 metal(0) complexes, e.g. $[(dppe)Pt\{M(Giso)\}_2]$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] and $[Pt\{Ga(Giso)\}_3]$,[14] and platinum(II) complexes, e.g. *cis*-$[Pt(Ar^f)_2\{Ga(Giso)\}_2]$, *trans*-$[Pt(Ar^f)_2\{In(Giso)\}_2]$ and *trans*-$[Pt(Ar^f)_2\{In(Giso)\}_3]$ [Ar^f = *p*-C_6HF_4 or *p*-$C_6(OMe)F_4$].[15] These studies have revealed **1** and **2** to be poorly nucleophilic ligands [compared to group 13 metal(I) alkyl compounds]. In addition, there was some experimental and theoretical evidence for dπ–pπ back-bonding associated with the covalent component of the Pt–Ga bonds of the homoleptic complex, $[Pt\{Ga(Giso)\}_3]$.[14] Nevertheless, as the ionic component of these bonds dominates, the degree of back-bonding was not thought substantial. Saying this, the electrophilicity of the In centers of **2** has been demonstrated by $[Pt(Ar^f)_2\{In(Giso)\}_3]$, which exhibits strong intramolecular In···F interactions in the solid state and in solution.[15] As a result, the indium heterocycles in these complexes can be thought of as being Lewis-amphoteric. In order to gain further information on the ligating properties of **1** and **2**, their reactions with sources of transition metal carbonyl fragments have been explored. Herein, we describe our efforts in this direction.

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Results and Discussion

Prior studies have shown that the gallium(I) species, [:Ga(Nacnac)],[16] [:Ga(dab)]$^{-}$[17] and :GaAr* [Ar* = C_6H_3-(C_6H_2*i*Pr_3-2,4,6)$_2$-2,6],[16] readily displace CO from Fe(CO)$_5$ to give complexes with the Fe(CO)$_4$ fragment. In contrast, treatment of **1** or **2** with Fe(CO)$_5$ in toluene at room temperature led to no reaction. This is an indication of their relatively poor nucleophilicity, and likely results from the high s-character of their metal lone pairs.[12] As $Fe_2(CO)_9$ can act as a more labile source of the Fe(CO)$_4$ fragment, its reactions with **1** or **2** were carried out. No identifiable products could be isolated from the reaction with **2**, but that with **1** afforded a moderate yield of [Fe(CO)$_4${Ga(Giso)}] (**3**) as a pale yellow crystalline solid (Scheme 1). Similarly, both metallocycles were treated with $Co_2(CO)_8$, but only the reaction with **1** led to an identifiable product, viz. yellow [(CO)$_3$Co{μ-Ga(Giso)}$_2$Co(CO)$_3$] (**4**), after workup. The ruthenium complex, [Ru(CO)$_2$(PPh$_3$)$_3$], is known to exist in equilibrium with [Ru(CO)$_2$(PPh$_3$)$_2$] and free triphenylphosphane in solution.[18] This facilitated its reaction with **1** and **2**, yielding the five-coordinate red-orange complexes, [Ru(CO)$_2$(PPh$_3$)$_2${M(Giso)}] [M = Ga (**5**) or In (**6**)]. A variety of reactions of **1** or **2** with other metal carbonyl complexes, e.g. [W(CO)$_5$(thf)] and [{CpMo(CO)$_2$}$_2$], were carried out, though the only product isolated from these was [CpMo(CO)$_2${[(Giso)Ga]$_2$OH}] (**7**) (Scheme 1), obtained in very low yield ($< 5\%$) from the reaction of **1** with [{CpMo(CO)$_2$}$_2$]. This is presumably a hydrolysis product, which arose from the presence of adventitious water in the reaction mixture. Attempts to carry out rational, higher yielding syntheses of this compound were not successful.

A number of previous studies have examined the nature of the Ga–Fe bond of complexes of gallium(I) ligands with the Fe(CO)$_4$ fragment by using X-ray crystallographic and IR spectroscopic data. To allow comparisons with this prior work, compound **3** was spectroscopically and crystallographically characterized. Its molecular structure is depicted in Figure 1 and reveals it to have an Fe–Ga bond significantly shorter than those in the closely related neutral β-diketiminate complex, [Fe(CO)$_4${Ga(Nacnac)}], and the anionic diazabutadiene complex, [Fe(CO)$_4${Ga(dab)}]$^{-}$ (see Table 1). This occurs despite the apparently greater nucleophilicity of the gallium heterocycles in those complexes, and

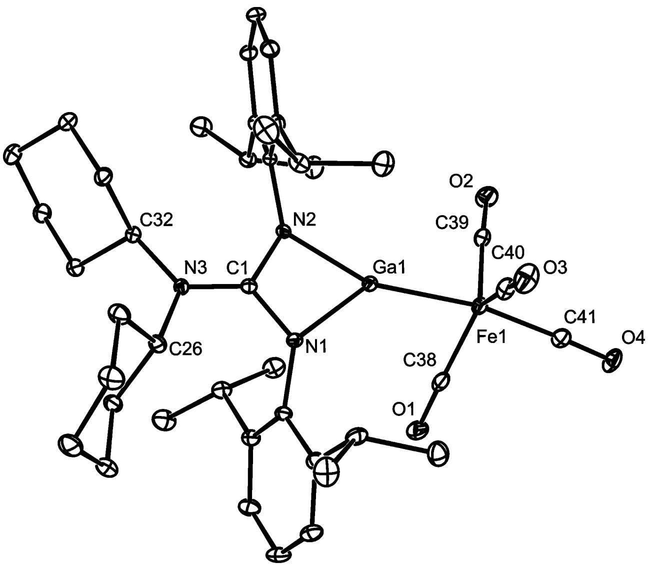
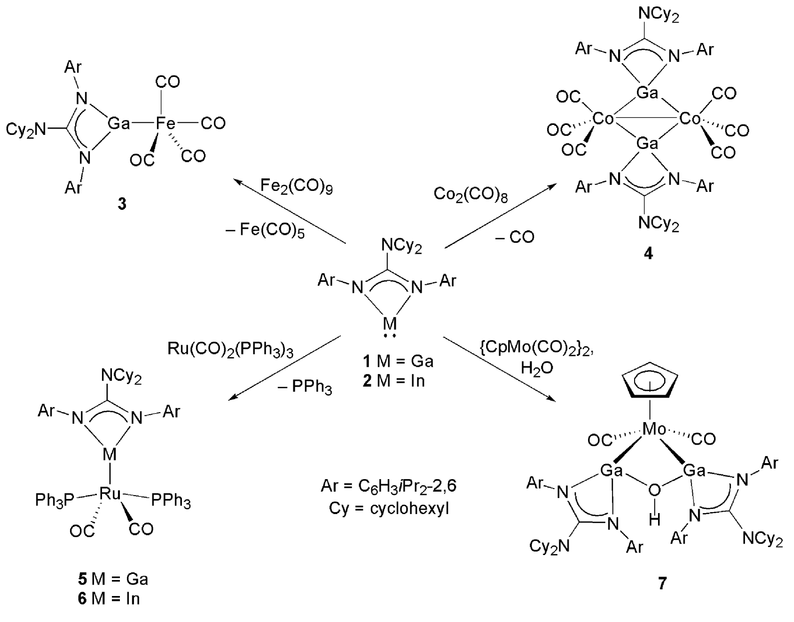


Figure 1. Molecular structure of **3** (ORTEP, thermal ellipsoids shown at 25% probability level). Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga(1)–N(1) 1.9614(18), Ga(1)–N(2) 1.9710(18), Ga(1)–Fe(1) 2.271(1), N(1)–C(1) 1.359(3), N(2)–C(1) 1.370(3), N(3)–C(1) 1.348(3); N(1)–Ga(1)–N(2) 67.94(7), C(41)–Fe(1)–Ga(1) 169.84(8), N(3)–C(1)–N(1) 126.36(18), N(3)–C(1)–N(2) 126.39(18), N(1)–C(1)–N(2) 107.24(17).



Scheme 1. Syntheses of compounds **3**–**7**.

Table 1. Ga–Fe distances and selected infrared data for crystallographically characterized complexes of the type, $[Fe(CO)_4\{Ga(L)\}]$.[a]

Ga(L)	Ga coord. no.	Ga–Fe [Å]	ν(CO) [cm^{-1}]	Ref.
GaAr*	2	2.248(7)	2032, 1959, 1941, 1929	[16]
Ga(Giso)	3	2.271(1)	2026, 1970, 1945, 1916	this work
$[Ga(dab)]^-$	3	2.3068(8)	1988, 1965, 1876	[17]
Ga(Nacnac)	3	2.2851(4)	2010, 1940, 1915, 1900	[16]
GaCp*	4	2.2731(4)	2037, 1966, 1942	[24]
$Ga(TpMe_2)$[b]	4	2.315(3)	2011, 1919, 1890	[25]

[a] The carbonyl stretching frequencies for $[Fe(CO)_4(PPh_3)]$ are 2052, 1979 and 1947 cm^{-1}.[23] [b] $TpMe_2 = [HB(3,5\text{-}Me_2pz)_3]^-$ (pz = pyrazolyl).

presumably results from the lesser steric shielding of the gallium center in **3**. All three Fe–Ga distances are, however, longer than that in the two-coordinate complex, $[Fe(CO)_4(GaAr^*)]$, which was originally formulated as possessing an iron–gallium triple bond.[19] Subsequent theoretical and experimental studies challenged this view, and it is now generally accepted that there is no substantial π-back-bonding in $[Fe(CO)_4(GaAr^*)]$ and that its gallium diyl fragment is predominantly acting as a strong σ-donor ligand.[20–22] Indeed, it has been pointed out that the carbonyl stretching bands in the infrared spectrum of $[Fe(CO)_4(GaAr^*)]$ are found at lower wavenumbers than those in the spectrum of $[Fe(CO)_4(PPh_3)]$, the phosphane ligand of which is not considered as a strong π-acid.[23] This holds true for all the other gallium–iron complexes in Table 1, including compound **3**. It must, therefore, be concluded that there is negligible Fe→Ga back-bonding occurring in this complex.

The spectroscopic data for **4** are consistent with its proposed structure. Of most note is its infrared spectrum which displays bands in the range 2031–1937 cm^{-1} that are associated with stretching modes of its terminal CO ligands {cf. $[(CO)_3Co(\mu\text{-}GaCp^*)_2Co(CO)_3]$: CO stretching bands from 2023 to 1948 cm^{-1}}.[24] No absorptions were observed in the region expected for bridging CO ligands. In addition, a single broad resonance at $\delta = 207.5$ ppm in the $^{13}C\{^1H\}$ NMR spectrum of the compound was assigned to the terminal CO ligands. An X-ray structural analysis of **4** was carried out, and its molecular structure (Figure 2) confirmed it to be a dinuclear complex with cobalt centers symmetrically bridged by gallium heterocycles. As such, it is related to $Co_2(CO)_8$[26] and the gallium diyl bridged species, $[(CO)_3Co(\mu\text{-}GaCp^*)_2Co(CO)_3]$.[24] In both those complexes the two $Co(CO)_3$ fragments are eclipsed with respect to each other, whereas those of **4** are staggered. The Co–Co distance [2.7725(9) Å] lies between those reported for $[(CO)_3Co(\mu\text{-}GaCp^*)_2Co(CO)_3]$ [2.8278(6) Å][24] and $Co_2(CO)_8$ (2.5301(8) and 2.5278(8) Å],[26] whereas the Co–Ga distances are very close to those in $[(CO)_3Co(\mu\text{-}GaCp^*)_2Co(CO)_3]$ (2.389 Å mean).

The ruthenium(0) complexes, **5** and **6**, exhibit similar NMR spectra, and the infrared spectra of Nujol mulls of solid samples of each show two CO absorptions. These occur at higher wavenumbers in the gallium complex, which, in the absence of significant Ru→M π-bonding, is indicative of the gallium heterocycle, **1**, being more nucleophilic than its indium counterpart, **2**. Indeed, this has been demonstrated in previous studies.[12,14,15] The presence of two CO stretching bands in the infrared spectra of **5** and **6** suggests

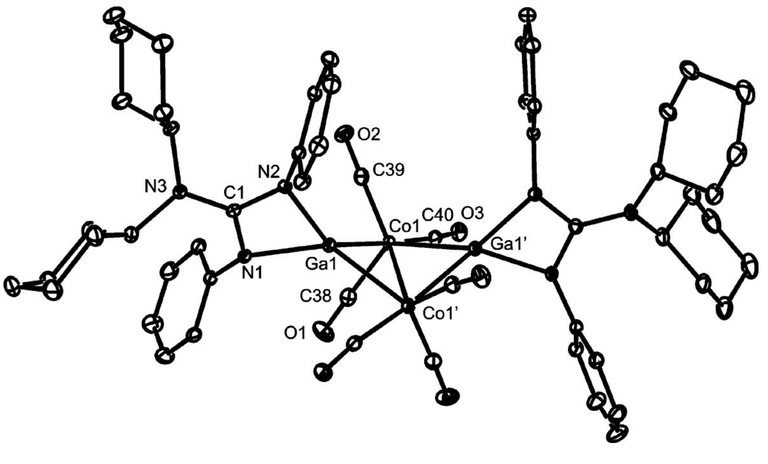


Figure 2. Molecular structure of **4** (ORTEP, thermal ellipsoids shown at 25% probability level). Isopropyl groups and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga(1)–N(2) 1.9883(19), Ga(1)–N(1) 2.0236(19), Ga(1)–Co(1) 2.3801(8), Ga(1)–Co(1)′ 2.3865(6), Co(1)–Co(1)′ 2.7725(9), N(1)–C(1) 1.361(3), C(1)–N(2) 1.365(3), C(1)–N(3) 1.371(3); N(2)–Ga(1)–N(1) 66.78(8), Co(1)–Ga(1)–Co(1)′ 71.13(3), Ga(1)–Co(1)–Ga(1)′ 96.77(3), N(1)–C(1)–N(2) 108.15(19), N(1)–C(1)–N(3) 126.1(2), N(2)–C(1)–N(3) 125.7(2). Symmetry transformation used to generate equivalent atoms: ′: $-x, y, -z + 1/2$.

that the complexes exist as one isomeric form in the solid state. This is in contrast to [Ru(CO)$_2$(PPh$_3$)$_3$], which has been structurally characterized as two isomers. The first is trigonal-bipyramidal with axial CO ligands,[27] whereas the other can be regarded as either distorted trigonal-bipyramidal with equatorial CO ligands, or as distorted square-based pyramidal with an apical phosphane ligand (C–Ru–C 139.1° mean, P$_{(ax.)}$–Ru–P$_{(ax.)}$ 155.7° mean).[28] Crystallographic characterization of **6** (Figure 3) showed it to resemble the second isomeric form, though its ruthenium coordination geometry [C–Ru–C 156.8(4)°, P–Ru–P 147.04(7)°] is closer to square-based pyramidal than in [Ru(CO)$_2$(PPh$_3$)$_3$]. The indium center takes up the apical position, and the In–Ru distance [2.5549(9) Å] is within the known range (2.51–2.68 Å).[29]

Although only a low yield of the presumed hydrolysis product, **7** (Figure 4), was obtained, it was spectroscopically and crystallographically characterized. Its molecular structure shows it to be monomeric with the molybdenum center coordinated by one cyclopentadienyl and two terminal carbonyl ligands. In addition, an anionic hydroxide bridged digallium ligand, [{(Giso)Ga}$_2$OH]$^-$, chelates the metal atom, yielding Mo–Ga distances well within the known range (2.52–2.74 Å).[29] The two gallium centers of this fragment have a close non-bonding interaction (ca. 2.83 Å). There is little precedent for the unusual digallium ligand in this complex, but there are some parallels with an iron carbonyl species that contains the cationic fragment, [Fe(CO)$_3$-{κ^2-Ga,Ga′-(RGa)$_2$OH}]$^+$ [R = Si(SiMe$_3$)$_3$], the two gallium centers of which are additionally coordinated by two oxygen atoms from the anion, [RGa(OH)$_3$]$^-$.[30] As is the case in **7**, the transition metal center of the cation is chelated by a formally anionic hydroxide bridged digallium ligand. Moreover, the gallium centers of this fragment also have a close interaction (ca. 2.91 Å).

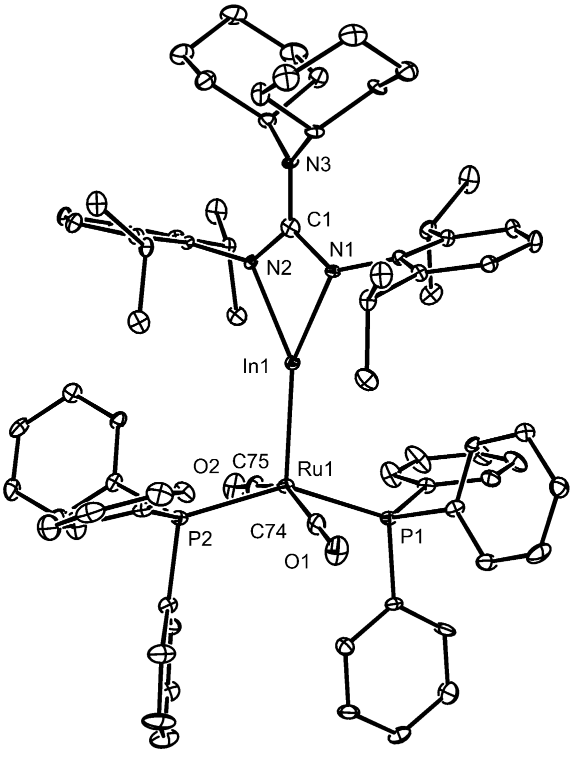


Figure 3. Molecular structure of **6** (ORTEP, thermal ellipsoids shown at 25% probability level). Isopropyl groups and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: In(1)–N(1) 2.243(5), In(1)–N(2) 2.285(5), In(1)–Ru(1) 2.5549(9), Ru(1)–C(75) 1.906(9), Ru(1)–C(74) 1.920(8), Ru(1)–P(2) 2.337(2), Ru(1)–P(1) 2.338(2), N(1)–C(1) 1.383(9), N(2)–C(1) 1.362(9), N(3)–C(1) 1.324(9); N(1)–In(1)–N(2) 58.82(19), C(75)–Ru(1)–C(74) 156.8(4), P(2)–Ru(1)–P(1) 147.04(7), C(75)–Ru(1)–In(1) 100.5(3), C(74)–Ru(1)–In(1) 102.8(2), P(2)–Ru(1)–In(1) 106.28(6), P(1)–Ru(1)–In(1) 106.61(6), N(2)–C(1)–N(1) 108.2(6).

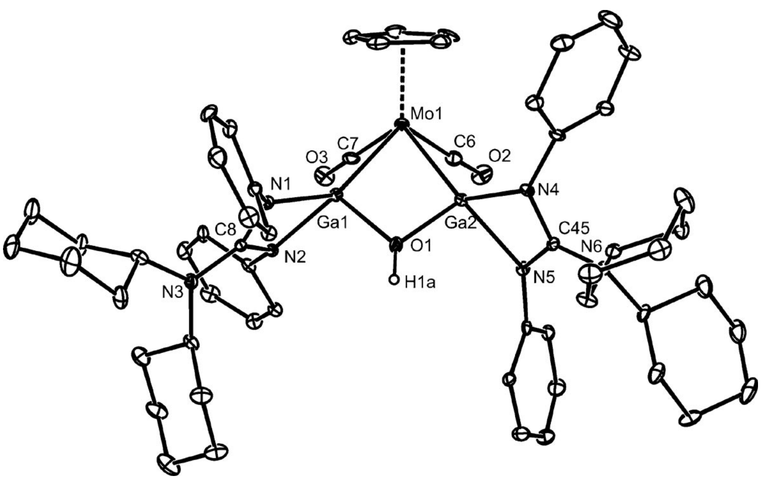


Figure 4. Molecular structure of **7** (ORTEP, thermal ellipsoids shown at 25% probability level). Isopropyl groups and hydrogen atoms (except H1a) omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo(1)–C(6) 1.944(8), Mo(1)–C(7) 1.956(8), Mo(1)–Ga(1) 2.5728(9), Mo(1)–Ga(2) 2.5896(9), Ga(1)–O(1) 1.952(4), Ga(1)–N(2) 1.986(5), Ga(1)–N(1) 2.083(5), O(1)–Ga(2) 1.963(4), Ga(2)–N(4) 2.008(5), Ga(2)–N(5) 2.071(5), N(1)–C(8) 1.353(8), N(2)–C(8) 1.339(8), N(4)–C(45) 1.350(8), N(5)–C(45) 1.344(8); C(6)–Mo(1)–C(7) 77.0(3), Ga(1)–Mo(1)–Ga(2) 66.48(3), Ga(1)–O(1)–Ga(2) 92.59(17), N(2)–Ga(1)–N(1) 65.2(2), N(4)–Ga(2)–N(5) 65.3(2), N(2)–C(8)–N(1) 109.0(5), N(5)–C(45)–N(4) 109.7(5).

Conclusions

A series of complexes of four-membered gallium(I) and indium(I) heterocycles with transition metal carbonyl fragments have been prepared. As in previous studies, these heterocycles have been shown to act as σ-donor ligands, but they appear not to be as nucleophilic as group 13 diyls, **:**MR (M = Ga or In). Moreover, the indium heterocycle is a weaker σ-donor than its gallium counterpart. A comparison of the structural and spectroscopic properties of a gallium–iron complex, [Fe(CO)$_4${Ga(Giso)}], with those of related complexes led to the conclusion that there is little Fe→Ga π-bonding in this compound, and therefore, that the gallium heterocycle is a relatively poor π-acid. We continue to explore the coordination chemistry of low-oxidation-state group 13 heterocycles.

Experimental Section

General: All manipulations were carried out by using standard Schlenk and glove-box techniques under high-purity argon. Hexane and toluene were distilled from Na/K alloy under dinitrogen. Infrared spectra were obtained as Nujol mulls by using a Perkin–Elmer 1600 series FTIR spectrometer with NaCl plates. NMR spectroscopy was carried out by using either Jeol Eclipse 300 or Bruker DPX 400 spectrometers. Mass spectra were obtained from the EPSRC Mass Spectrometry Service, Swansea. The microanalysis was carried out by Medac Ltd. UK. Melting points were determined in sealed glass capillaries under argon and are uncorrected. [**:**Ga(Giso)],[12] [**:**In(Giso)][12] and [Ru(CO)$_2$(PPh$_3$)$_3$][27] were synthesized by literature procedures. All other starting materials were purchased and used as received.

[Fe(CO)$_4${Ga(Giso)}] (3): A solution of [Ga(Giso)] (0.15 g, 0.245 mmol) in toluene (10 mL) was added to a slurry of Fe$_2$(CO)$_9$ (0.10 g, 0.275 mmol) in toluene (5 mL) at –80 °C. The mixture was slowly warmed to room temperature and stirred overnight. All volatiles were removed in vacuo, and the residue was extracted into hexane (15 mL). The extract was concentrated to ca. 7 mL and placed at –30 °C for 20 h to afford pale yellow crystals of **3** (yield 0.11 g, 58 %). M.p. > 180 °C (dec.). ^{1}H NMR (400 MHz, 296 K, C$_6$D$_6$): δ = 0.69–0.84 (br. m, 6 H, C*H*$_2$), 1.30–1.90 (br. m, 14 H, C*H*$_2$), 1.35 [br. d, 12 H, CH(C*H*$_3$)$_2$], 1.67 [br. d, 12 H, CH(C*H*$_3$)$_2$], 3.50–3.80 [br. m, 6 H, C*H*(CH$_3$)$_2$ and NC*H*], 7.05–7.30 (br. m, 6 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 298 K): δ = 22.6 [CH(*C*H$_3$)$_2$], 25.7 (*C*H$_2$), 26.8 (*C*H$_2$), 27.1 [CH(*C*H$_3$)$_2$], 29.7 [*C*H(CH$_3$)$_2$], 35.5 (*C*H$_2$), 61.0 (N*C*H), 124.6, 127.4, 139.2, 144.7 (Ar*C*), 170.1 (backbone *C*N$_3$), 215.7 (*C*O) ppm. IR (Nujol): $\tilde{\nu}$ = 2026 (s, CO), 1970 (s, CO), 1945 (s, br., CO), 1916 (s, br., CO) cm^{-1}. MS (EI 70 eV): *m*/*z* (%) = 779.2 (2) [M$^+$], 751.2 (3) [M$^+$ – CO], 695.2 (8) [M$^+$ – 3 CO], 667.3 (100) [M$^+$ – 4 CO]. EI MS: calcd. for [M$^+$] 779.2871; found 779.2872.

[(CO)$_3$Co{µ-Ga(Giso)}$_2$Co(CO)$_3$] (4): A solution of [Ga(Giso)] (0.16 g, 0.261 mmol) in toluene (10 mL) was added to a solution of Co$_2$(CO)$_8$ (0.10 g, 0.288 mmol) in toluene (5 mL) at –80 °C. The resultant mixture was warmed to room temperature and stirred for 2 h. All volatiles were then removed in vacuo and the residue extracted with hexane (10 mL). The extract was concentrated to ca. 8 mL and placed at –30 °C for 1 week to afford yellow crystals of **4** (yield 30 mg, 15 %). M.p. 180–190 °C (dec.). ^{1}H NMR (400 MHz, 296 K, C$_6$D$_6$): δ = 0.68–0.98 (br. m, 12 H, C*H*$_2$), 1.22–1.93 [br. m, 76 H, CH(C*H*$_3$)$_2$, C*H*$_2$], 3.62–3.80 [br. m, 4 H, C*H*(CH$_3$)$_2$], 3.92–4.12 [br. m, 8 H, C*H*(CH$_3$)$_2$, NC*H*], 7.02–7.38 (br. m, 12 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 298 K): δ = 24.0 [CH(*C*H$_3$)$_2$], 25.3 (*C*H$_2$), 26.5 (*C*H$_2$), 27.0 [CH(*C*H$_3$)$_2$], 28.1 [*C*H(CH$_3$)$_2$], 35.0 (*C*H$_2$), 60.0 (N*C*H), 124.3, 126.0, 139.7, 145.4 (Ar*C*), 167.5, (backbone *C*N$_3$), 207.5 (*C*O) ppm. IR (Nujol): $\tilde{\nu}$ = 2031 (s, CO), 1992 (s, CO), 1955 (s, br., CO), 1937 (s, br., CO) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 544.5 (100) [GisoH$^+$].

[Ru(CO)$_2$(PPh$_3$)$_2${Ga(Giso)}] (5): A solution of [Ga(Giso)] (90 mg, 0.15 mmol) in toluene (7 mL) was added to a stirred slurry of [Ru(CO)$_2$(PPh$_3$)$_3$] (139 mg, 0.15 mmol) in toluene (5 mL) at –80 °C over 10 min. The reaction mixture was warmed to room temperature overnight, with constant stirring. A change in solution color to orange was noted. Volatiles were removed in vacuo, and the residue was extracted with hexane (8 mL), giving an orange solution. Concentration of the solution to ca. 5 mL and subsequent cooling to –30 °C overnight yielded red-orange crystals of **5** (yield 87 mg, 45 %); m.p. > 150 °C (dec.). ^{1}H NMR (400.13 MHz, 300 K, C$_6$D$_6$): δ = 0.83 (m, 8 H, C*H*$_2$), 1.34–1.57 (m, 12 H, C*H*$_2$), 1.52 [2 overlapping d, $^3J_{HH}$ ≈ 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$], 3.77 (m, 2 H, *CH*N), 4.02 [sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$], 6.85–8.01 (m, 36 H, Ar*H*) ppm. ^{31}P{^{1}H} NMR (121.65 MHz, 300 K, C$_6$D$_6$): δ = 56.85 ppm. IR (Nujol): $\tilde{\nu}$ = 1948 (s, CO), 1884 (s, CO) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 544.5 (100) [GisoH$^+$].

[Ru(CO)$_2$(PPh$_3$)$_2${In(Giso)}] (6): A solution of [In(Giso)] (0.10 g, 0.15 mmol) in toluene (5 mL) was added to a stirred slurry of [Ru(CO)$_2$(PPh$_3$)$_3$] (143 mg, 0.15 mmol) in toluene (20 mL) at –80 °C over 5 min. The reaction mixture was warmed to room temperature overnight, yielding an orange solution. Volatiles were removed in vacuo, and the red/orange residue was extracted with toluene (8 mL). Concentration of the extract to ca. 5 mL and subsequent slow cooling to –30 °C overnight afforded red/orange crystals of **6** [yield 145 mg (vacuum-dried), 72 %]. ^{1}H NMR (400.13 MHz, 300 K, C$_6$D$_6$): δ = 0.87 (m, 8 H, Cy-C*H*$_2$), 1.37 [d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.43–1.65 (m, 12 H, Cy-C*H*$_2$), 1.49 [d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$], 3.73 (m, 2 H, *CH*N), 3.91 [sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$], 6.85–8.04 (m, 36 H, Ar*H*) ppm. ^{31}P{^{1}H} NMR (121.65 MHz, 300 K, C$_6$D$_6$): δ = 59.69 ppm. IR (Nujol): $\tilde{\nu}$ = 1937 (s, CO), 1869 (s, CO) cm^{-1}. MS: *m*/*z* (%) = 544.5 (100) [GisoH$^+$]. C$_{82}$H$_{94}$In$_1$N$_3$O$_2$P$_2$Ru (**6**·toluene) (1431.49): calcd. C 68.80, H 6.62, N 2.94; found C 68.27, H 6.43, N 2.86.

[CpMo(CO)$_2${[(Giso)Ga]$_2$OH}] (7): A few crystals of compound **7** were obtained from a reaction of [Ga(Giso)] with 0.5 equiv. of [{CpMo(CO)$_2$}$_2$] in toluene. M.p. 220–225 °C (dec.). ^{1}H NMR (400 MHz, 296 K, C$_6$D$_6$): δ = 0.28–0.83 (m, 12 H, C*H*$_2$), 0.90–1.89 [m, 77 H CH(C*H*$_3$)$_2$, C*H*$_2$, O*H*], 3.38–3.60 [m, 12 H, NC*H*, C*H*(CH$_3$)$_2$], 4.44 (s, 5 H, C$_5$*H*$_5$), 6.79–7.23 (m, 12 H, Ar*H*) ppm. IR (Nujol): $\tilde{\nu}$ = 3635 (OH), 1901 (s, CO), 1837 (s, CO) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 1460.7 (2) [MH$^+$], 544.5 (100) [GisoH$^+$].

X-ray Single-Crystal Structural Analyses: Crystals of **3**, **4**, **6**·(toluene)$_{1.5}$ and **7**·(hexane)$_{0.25}$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made by using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97)[31] using all unique data. Two crystallographically independent molecules were refined in the asymmetric unit of **3**. There are no significant geometric differences between them. The absolute structure parameter for the structure of **7** is 0.002(12). All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 2. CCDC-730325 (**3**), -730326 (**4**), -730327 [**6**·(toluene)$_{1.5}$] and -730328 [**7**·(hexane)$_{0.25}$] contain the supplementary crystallo-

Table 2. Crystal data and refinement details for **3**, **4**, **6** and **7**.

Compound	**3**	**4**	**6**·(toluene)$_{1.5}$	**7**·(hexane)$_{0.25}$
Empirical formula	$C_{41}H_{56}GaFeN_3O_4$	$C_{80}H_{112}Co_2Ga_2N_6O_6$	$C_{85.5}H_{98}InN_3O_2P_2Ru$	$C_{82.5}H_{121.5}Ga_2MoN_6O_3$
Formula mass	780.46	1511.06	1477.5	1480.74
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$Pna2_1$
a [Å]	10.606(2)	17.288(4)	10.631(2)	24.686(5)
b [Å]	19.359(4)	12.809(3)	32.673(7)	20.142(4)
c [Å]	20.050(4)	34.115(7)	21.742(4)	16.334(3)
α [°]	79.05(3)	90	90	90
β [°]	88.35(3)	94.02(3)	99.07(3)	90
γ [°]	78.02(3)	90	90	90
V [Å^3]	3953.5(14)	7536(3)	7458(3)	8121(3)
Z	4	4	4	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.311	1.332	1.316	1.211
μ [mm]$^{-1}$]	1.091	1.195	0.604	0.859
F(000)	1648	3192	3084	3146
Crystal size [mm]	0.40 × 0.40 × 0.15	0.25 × 0.20 × 0.10	0.20 × 0.05 × 0.02	0.09 × 0.06 × 0.04
Reflections collected/unique	28683/15380	12808/6619	24782/13050	65697/14258
R_{int}	0.0290	0.0269	0.0838	0.1251
Goodness-of-fit on F^2	1.034	1.029	1.101	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356$, $wR_2 = 0.0793$	$R_1 = 0.0346$, $wR_2 = 0.0755$	$R_1 = 0.0892$, $wR_2 = 0.1575$	$R_1 = 0.0648$, $wR_2 = 0.1205$

graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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