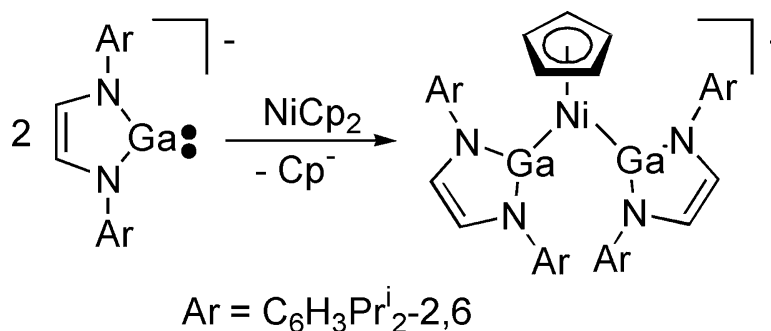Communication

Analogies between the Reactivities of an Anionic Gallium(I) Heterocycle and N-Heterocyclic Carbenes Toward Metallocenes

Robert J. Baker, Cameron Jones, and Jamie A. Platts

$$Ar = C_6H_3Pr^i_2\text{-}2,6$$

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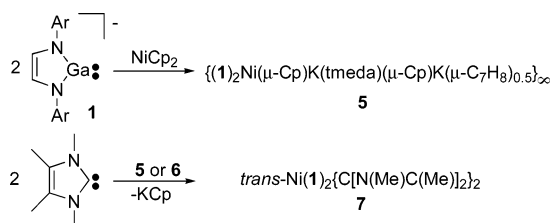Robert J. Baker, Cameron Jones,* and Jamie A. Platts

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Since the isolation of the first thermally stable N-heterocyclic carbene (NHC) in 1991,[1] this class of ligand has become ubiquitous in the formation of p-, d- and f-block metal complexes, many of which have found application in synthesis and catalytic processes.[2] We have recently developed a high-yield synthetic route to the anionic gallium(I) heterocycle, **1**, Ar = $C_6H_3Pr^i_2$-2,6,[3] which is a valence isoelectronic analogue of NHCs and therefore has significant potential for use as a novel ligand in inorganic synthesis. This analogy has been demonstrated with the formation of the anionic group 13 hydride complexes, [MH$_2$(**1**)$_2$]$^-$ **2**, M = Ga (dec 128 °C) or In (dec 116 °C), the high thermal stabilities of which are similar to those of group 13 hydride−NHC complexes and are presumably derived from the highly nucleophilic nature of the gallium centers in **1**.[4] In this respect, theoretical studies have shown that the gallium lone pair of the model anion, [:Ga{N(H)C(H)}$_2$]$^-$, is effectively sp-hybridized and is associated with the HOMO of the heterocycle.[5] It is noteworthy that significant nucleophilicity has also been ascribed to the closely related neutral six-membered gallium(I) heterocycle, :Ga{N(Ar)C(Me)}$_2$CH, **3**,[6] which, to date, has only been utilized in the formation of one transition metal complex, [Fe-(CO)$_4$(**3**)].[7] In the present study we further compare the reactivity of **1** to that of NHCs by examining its interaction with nickelocene. This has led to the first transition metal complexes of an anionic gallium(I) heterocycle. The described chemistry can be compared to the work of Cowley et al. who have shown that NHCs react with transition metal metallocenes forming 1:1 or 2:1 adducts, [Cp$_2$M(NHC)$_{1or2}$], which display varying degrees of Cp ring slippage or, more relevant to this study, complete Cp$^-$ ring displacement, as in the formation of [CpNi{C[N(Me)C(Me)]$_2$}$_2$]$^+$[Cp]$^-$, **4**.[8]

The reaction of 2 equiv of **1**[K(tmeda)] with nickelocene led to the displacement of one Cp$^-$ ligand from the nickel center and the moderate yield formation of the polymeric complex, **5**, which unusually incorporates the eliminated KCp salt (Scheme 1).

Scheme 1

$$2 \begin{bmatrix} Ar \\ N \\ \| \quad Ga: \\ N \\ Ar \end{bmatrix}^- \quad \mathbf{1} \xrightarrow{NiCp_2} \{(\mathbf{1})_2Ni(\mu\text{-}Cp)K(tmeda)(\mu\text{-}Cp)K(\mu\text{-}C_7H_8)_{0.5}\}_\infty \quad \mathbf{5}$$

$$2 \begin{bmatrix} N \\ \| \quad : \\ N \end{bmatrix} \xrightarrow[-KCp]{\mathbf{5} \text{ or } \mathbf{6}} trans\text{-}Ni(\mathbf{1})_2\{C[N(Me)C(Me)]_2\}_2 \quad \mathbf{7}$$

Interestingly, the same product forms when the reaction is carried out in a 1:1 or 3:1 stoichiometry, although in lower yields. Dissolution of **5** in diethyl ether and stirring overnight leads to displacement of KCp from **5** and the formation of the monomeric contact ion pair, [(tmeda)(Et$_2$O)K(μ-η^5-Cp)Ni(**1**)$_2$], **6**. Both **5** and **6** are diamagnetic and their proposed formulations are fully supported by spectroscopic data.[9] In addition, the X-ray crystal structure[10] of **5** shows it to be a novel three-dimensional polymer
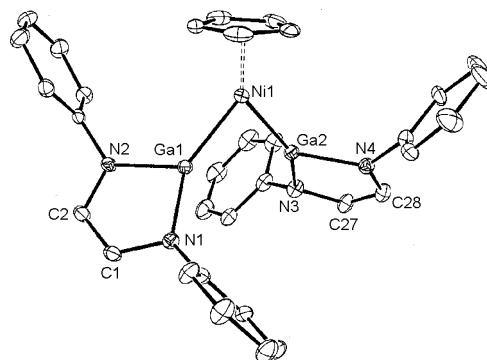

Figure 1. Structure of the anionic component of **5**. Relevant bond lengths (Å) and angles (deg): Ni(1)−Ga(1) 2.2196(11), Ni(1)−Ga(2) 2.2154(11), Ni(1)-cent. Cp 1.719(2), Ga(1)−N(1) 1.894(5), Ga(1)−N(2) 1.901(5), Ga-(2)−N(3) 1.901(5), Ga(2)−N(4) 1.900(5), N(1)−Ga(1)−N(2) 87.1(2), N(3)−Ga(2)−N(4) 87.1(2), Ga(1)−Ni(1)−Ga(2) 86.39(4). Isopropyl groups omitted for clarity.

held together with Ni(μ-η^5-Cp)K, K(μ-η^5-Cp)K, and K(μ-η^4-C$_7$H$_8$)K bridges, in addition to K-η^2-arene interactions (see Supporting Information for further discussion).

The structure of the anion of **5** is depicted in Figure 1 which shows it to be closely related to the cation of **4**. Its nickel center has a trigonal planar coordination environment (Σ angles using Cp ring centroid = 359.9°) including an acute Ga−Ni−Ga angle (86.39(4)°, cf. C−Ni−C, 97.07(2)° in **4**). The Ni−Ga (three-coordinate) bond lengths (2.2175 Å av) are significantly shorter than in nickel gallyl complexes, e.g. 2.406(1) Å in [Cp(CO)Ni-{Ga(CH$_2$Bu^t)$_2$(thf)}] (four-coordinate Ga),[11] and, indeed only longer than in one other previously reported complex, [Ni{GaC(SiMe$_3$)$_3$}$_4$] 2.1700(4) Å (two-coordinate Ga),[12] for which considerable Ni−Ga back-bonding has been suggested. Both gallium heterocycles are essentially planar although their coordination to the nickel center is asymmetric (Ni−Ga-heterocycle centroid, 166.0° av), presumably as a result of steric congestion, as has been seen for the gallium diyl coordination in [Ni(GaCp*)$_4$].[13] The geometries of the gallium heterocycles are similar to those in **2** in that their N−Ga distances and N−Ga−N angles are significantly shorter and more obtuse, respectively, than in the free anion (1.970 Å av; 83.02(11)°) due to loss of electron density from the gallium center upon coordination.

To probe the relative nucleophilicities of **1** and NHCs, two ligand competition reactions were carried out. First, when **4** was treated with an excess of **1**, no reaction occurred. The reactions of **5** or **6** with an excess of the NHC, :C{N(Me)C(Me)}$_2$, however, led to the unexpected elimination of KCp to give the neutral complex, **7**, in good yield. Although no conclusions can be drawn about the relative donor strengths of **1** and NHCs from these reactions, the novelty of the product from the Cp$^-$ displacement reaction warranted its further investigation.
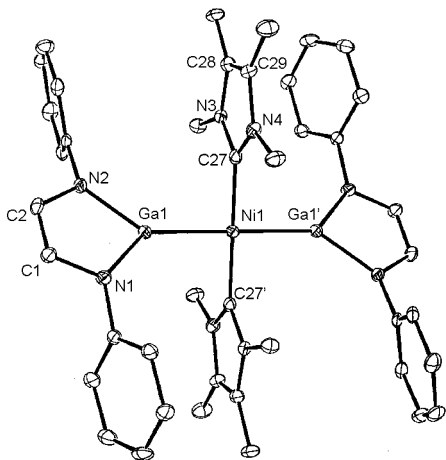
Figure 2. Molecular structure of **7**. Relevant bond lengths (Å) and angles (deg): Ni(1)−Ga(1) 2.3242(6), Ni(1)−C(27) 1.882(5), Ga(1)−N(1) 1.910-(4), Ga(1)−N(2) 1.897(4), N(1)−Ga(1)−N(2) 85.98(15), C(27)−Ni(1)−Ga(1) 93.35(13), Ga(1)−Ni(1)−C(27′) 86.65(13), Ga(1)−Ni(1)−Ga(1′) 180.00(2), symmetry operation ′: −x + 1, −y + 2, −z. Isopropyl groups omitted for clarity.

Compound **7** is diamagnetic, and its spectroscopic data are compatible with its proposed structure. This was verified by its X-ray crystal structure (Figure 2) which highlights a square planar nickel center with trans stereochemistry. The Ni−C bond lengths are close to those in related NHC complexes, e.g. 1.906 Å av in *trans*-[NiI$_2$\{C[N(Pr^i)C(Me)]$_2$\}$_2$],[14] while the Ni−Ga distances are significantly longer (ca. 0.11 Å) than in **5**, presumably because of the trans disposition of the two gallium heterocycles. Another contrast to **5** is the fact that the gallium heterocycles are symmetrically coordinated to the nickel center. As would be expected, the least-squares plane containing both NHC ligands is approximately orthogonal (87.42(16)°) to the nickel coordination plane, but surprisingly, the plane containing the gallium heterocycles bisects this plane by only 46.46(18)°. This situation presumably minimizes steric buttressing between the gallium heterocycles' Pr^i substituents and the NHCs' Me groups.

Preliminary density functional calculations were carried out on the model compound, [Ni\{C[N(Me)C(H)]$_2$\}$_2$\{Ga[N(Me)C(H)]$_2$\}$_2$], so that comparisons could be drawn with **7**. Its fully optimized geometry is *trans*-square planar, as in **7**, but in this sterically less hindered compound the least-squares planes containing the gallium heterocycles and NHC ligands are both essentially orthogonal to the nickel coordination plane. In addition, the Ni−C and Ni−Ga bond lengths and gallium heterocycle geometries are close to those in **7**. As expected, there is a significant increase in the positive charge (+0.803 av) on the gallium centers relative to that in the free heterocycle (+0.263), while the nickel center is almost neutral (+0.079).

In summary, we have demonstrated a close analogy between the reactivity of N-heterocyclic carbenes and the valence isoelectronic anionic gallium(I) heterocycle, **1**, toward nickelocene. We have embarked on a full study to examine the interaction of **1** with metallocenes and will report on this in a future publication.

Supporting Information Available: Full details of the X-ray crystallographic studies of **5** and **7**, full details of the DFT calculations and full synthetic details for **5** − **7** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) **5**: yield 46%; mp 248−253 °C dec; ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.21 (d, $^3J_{HH}$ = 7.1 Hz, 24H, CH(CH_3)$_2$), 1.24 (d, $^3J_{HH}$ = 7.1 Hz, 24H, CH-(CH_3)$_2$), 2.09 (s, 12H, N(CH$_3$)$_2$), 2.11 (s, 1.5H, PhCH_3), 2.34 (s, 4H, NCH$_2$), 3.42 (sept, $^3J_{HH}$ = 7.1 Hz, 8H, CH(CH$_3$)$_2$), 4.62 (s, 5H, Cp-Ni), 5.25 (s, 5H, Cp-K), 6.48 (s, 4H, NCH), 6.8−7.1 (m, 14.5H, ArH); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 22.33 (PhCH$_3$), 23.43 (CH(CH$_3$)$_2$), 24.07 (CH-(CH$_3$)$_2$), 27.99 (CH(CH$_3$)$_2$), 45.86 (NCH$_3$), 58.43 (NCH$_2$), 117.02 (Cp-Ni), 118.64 (Cp-K), 122.83 (NCH), 123.14 (m-ArC), 123.69 (p-PhMe), 124.70 (p-ArC), 128.17 (o-PhMe), 128.41 (m-PhMe), 137.61 (ipso-PhMe), 142.51 (o-ArC), 163.25 (ipso-ArC); IR (Nujol) ν (cm^{-1}) 1619, 1480, 1376, 1200, 1038, 943; MS (+ve FAB) m/z: 377 [100%, (ArNCH)$_2$$^+$]. **6**: yield 42%; mp 232−235 °C dec. ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 24H, CH(CH_3)$_2$), 1.26 (d, $^3J_{HH}$ = 6.6 Hz, 24H, CH(CH_3)$_2$), 1.14 (t, 6H, $^3J_{HH}$ = 6.4 Hz, CH$_2$CH_3), 2.10 (s, 12H, N(CH$_3$)$_2$), 2.35 (s, 4H, NCH$_2$), 3.11 (sept, $^3J_{HH}$ = 6.6 Hz, 8H, CH(CH$_3$)$_2$), 3.23 (q, 4H, $^3J_{HH}$ = 6.4 Hz, OCH$_2$), 4.45 (s, 5H, Cp), 6.56 (s, 4H, NCH), 7.08 (t, $^3J_{HH}$ = 7.8 Hz, 4H, p-ArH), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 8H, m-ArH); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 22.31 (CH$_2$CH$_3$), 22.74 (CH(CH$_3$)$_2$), 23.89 (CH(CH$_3$)$_2$), 28.85 (CH(CH$_3$)$_2$), 45.74 (NCH$_3$), 58.11 (NCH$_2$), 63.63 (OCH$_2$), 121.08 (Cp), 123.18 (NCH), 123.9 (m-ArC), 124.9 (p-ArC), 139.68 (o-ArC), 163.06 (ipso-ArC); IR (Nujol) ν (cm^{-1}) 1619, 1480, 1376, 1201, 1033, 937; MS (+ve FAB) m/z: 377 [100%, (ArNCH)$_2$$^+$]; **7**: yield 63%; mp 114−117 °C dec; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 1.18 (d, $^3J_{HH}$ = 6.5 Hz, 24H, CH(CH_3)$_2$), 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 24H, CH(CH_3)$_2$), 2.22 (s, 12H, C(CH$_3$)), 3.15 (sept, $^3J_{HH}$ = 6.5 Hz, 8H, CH(CH$_3$)$_2$), 3.78 (s, 12H, N(CH$_3$)), 6.69 (s, 4H, NCH), 7.14 (t, $^3J_{HH}$ = 7.8 Hz, 4 Hz, p-ArH), 7.28 (d, $^3J_{HH}$ = 7.8 Hz, 8H, m-ArH); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 7.95 (C(CH$_3$)), 22.31 (CH(CH$_3$)$_2$), 23.51 (CH(CH$_3$)$_2$), 27.91 (CH(CH$_3$)$_2$), 31.10 (N(CH$_3$)), 122.53 (NCH), 124.52 (m-ArC), 125.71 (p-ArC), 137.69 (o-ArC), 163.64 (ipso-ArC), 176.34 (NCN); IR (Nujol) ν (cm^{-1}) 1624, 1460, 1356, 1220, 1196, 1123, 1048, 927; MS (+ve FAB) m/z: 307 [70%, Ni\{C[N(Me)C-(Me)]$_2$\}$_2$$^+$], 377 [100%, (ArNCH)$_2$$^+$], 893 [20%, \{Ga(ArNCH)$_2$\}$_2$$^+$].
(10) Crystal data for **5**·(C$_7$H$_8$)$_{0.75}$: C$_{76.75}$H$_{108}$Ga$_2$K$_2$N$_6$Ni, monoclinic, *P2$_1$/c*, a = 22.496(5) Å, b = 13.385(3) Å, c = 26.155(5), β = 99.54(3)°, V = 7767(3) Å^3, Z = 4, D$_{calc}$ = 1.190 g cm^{-3}, μ(Mo Kα) = 1.078 mm^{-1}. 12966 unique reflections were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K (3.8 <θ < 25.0°), R$_1$ = 0.084 (I > 2σI), wR$_2$ = 0.210 (all data); Crystal data for **7**·C$_7$H$_8$: C$_{73}$H$_{104}$Ga$_2$N$_8$Ni, monoclinic, *P2$_1$/n*, a = 15.991(3) Å, b = 13.198(3) Å, c = 16.475(3) Å, β = 96.27-(3)°, V = 3456.2(12) Å^3, Z = 2, D$_{calc}$ = 1.241 g cm^{-3}, μ(Mo Kα) = 1.090 mm^{-1}. 6283 unique reflections were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K (2.9 <θ < 25.3°), R$_1$ = 0.064 (I > 2σI), wR$_2$ = 0.145 (all data).
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