J|A|C|S
COMMUNICATIONS

Four-Membered Group 13 Metal(I) N-Heterocyclic Carbene Analogues: Synthesis, Characterization, and Theoretical Studies

Cameron Jones,*,[†] Peter C. Junk,[‡] Jamie A. Platts,[†] and Andreas Stasch[†,‡]

School of Chemistry, Main Building, Cardiff University, Cardiff CF10 3AT United Kingdom, and School of Chemistry, Monash University, PO Box 23, Victoria 3800, Australia

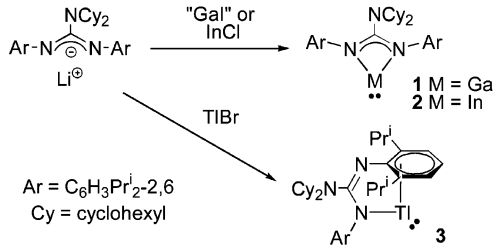
Received November 23, 2005; E-mail: jonesca6@cardiff.ac.uk

The coordination and red−ox chemistry of compounds containing an Al or Ga center in the +1 oxidation state is a fascinating and rapidly emerging field. Much of the work in this area has centered on metal diyls, :MR,[1] although more recently the chemistry of group 13 metal(I) heterocycles has begun to be explored. Of most note are the neutral six-membered β-diketiminato complexes, [:M{[N(Ar)C(Me)]$_2$CH}], Ar = $C_6H_3Pr^i{}_2$-2,6; M = Al − Tl,[2] and the very nucleophilic, anionic, five-membered gallium heterocycles, [:Ga{N(R)C(H)}$_2$]$^-$, R = Bu^t or Ar,[3] both of which possess singlet lone pairs of sp-character at the metal center. The five-membered heterocycles are valence isoelectronic analogues of N-heterocyclic carbenes (NHCs) and like NHCs, one (R = Ar) is proving its worth in the stabilization of thermally labile and/or low oxidation state main group and transition metal fragments.[4]

In consideration of this and the fact that the first example of a four-membered NHC has recently been reported,[5] we saw monomeric, four-membered group 13 metal(I) heterocycles, [:M{η^2-*N,N*′-N(R)C(R′)N(R)}], as worthwhile synthetic targets. There are considerable synthetic challenges associated with this goal as the reactive metal centers of these rings would be less sterically shielded by their N-substituents than the metal centers in five- or six-membered heterocycles. In addition, their NCN backbones will lead to significantly more acute NMN bite angles than seen for the larger rings. In initial attempts to form such heterocycles, the reaction of a bulky amidinate salt with metal(I) halides afforded either “five-membered” isomers of the objective heterocycles, viz. [M(η^1-N:η^3-Ar−Piso)], M = In or Tl, Piso$^-$ = [N(Ar)C(Bu^t)N(Ar)]$^-$,[6] or the gallium(II) dimer, [{GaI(η^2-*N,N*′-Piso)}$_2$],[7] the latter via a disproportionation process. We reasoned that four-membered heterocycles could be accessed by employing a more N-electron-rich ligand with a bulkier backbone substituent to favor *N,N*-chelation of the electron-deficient metal center.[8] A bulky guanidinate ligand has been developed for this purpose and utilized to prepare the first four-membered group 13 metal(I) heterocycles.

Treatment of group 13 metal(I) halides with the lithium guanidinate, Li[Giso], Giso$^-$ = [(Ar)NC(NCy$_2$)N(Ar)]$^-$, in toluene led to the guanidinate complexes, **1**−**3**, in moderate to good yields (Scheme 1). In the cases of the gallium and indium complexes, *N,N*-chelation is preferred over N,arene-chelation, which is the observed structural motif for the thallium complex (cf. [M(η^1-N:η^3-Ar−Piso)]). The differences here are likely due to the increasing ionic radii in the series, Ga$^+$−Tl$^+$,[9] which disfavors *N,N*-chelation of the heavier ion. All attempts to isomerize the three complexes between the two structural forms have so far been unsuccessful.

Scheme 1



Although **1**−**3** are extremely air sensitive, they are thermally very stable, and all decompose at temperatures in excess of 150 °C. The NMR spectra of **1** and **2**[10] are consistent with their formulations, while those for **3** are more symmetrical than its solid-state structure would suggest. This observation indicates a fluxional process occurring in solution at room temperature in which the thallium center exchanges between the two N-centers of the ligand. It is not known if this occurs via an *N,N*-chelated intermediate, but the exchange must be a low-energy process as the NMR spectra of **3** remain largely unchanged down to −90 °C. This contrasts with the related amidinate complex, [Tl(η^1-N:η^3-Ar−Piso)], which does not appear to exhibit fluxionality in solution. These differences likely result from the fact that the guanidinate ligand of **3** (unlike the amidinate, Piso$^-$) has a resonance structure possessing two C−NAr single bonds, viz. [Cy$_2$N$^+$ = C{−N$^-$(Ar)}$_2$], thus facilitating its isomerization via rotation about these bonds.

The solid-state geometry of **3** is very similar to that of [Tl(η^1-N:η^3-Ar−Piso)] and shows it to be monomeric but with weak intermolecular Tl−arene interactions (see Supporting Information for further discussion). The monomeric complexes, **1** and **2**, are isomorphous, and the structure of the gallium heterocycle is depicted in Figure 1.[11] There are no close intermolecular metal−element contacts (<3.4 Å) in either structure. In addition, there is no spectroscopic or structural evidence to suggest the presence of hydride ligands at the two-coordinate metal centers. The M−N distances of the heterocycles are slightly longer than those in related five- and six-membered rings[2,3] but the N−M−N angles are significantly more acute. Although the C−N bond lengths are indicative of considerable delocalization over the essentially planar N$_3$C guanidinate backbones of both structures, the geometries of the chelating N-centers are distorted from trigonal planar (Σ angles: **1** 350.0° mean; **2** 350.3° mean), and the planar backbone −NCy$_2$ groups are rotated out of the MN$_2$C least squares plane by 26.7° (**1**) and 27.2° (**2**). Similar observations have been made for guanidinate−Al(III) complexes,[12] and the distortions are thought to arise from steric crowding between all N-substituents.

Considering the potential that **1** and **2** have as ligands, DFT calculations were carried out on the model complexes, [:M{η^2-*N,N*′-(Ph)NC(NMe$_2$)N(Ph)}], M = Al, Ga, or In. The optimized geometries of the heterocycles are similar, and those where M = Ga or In closely resemble the structures of **1** and **2**, although with slightly over-estimated M−N bond lengths. In each, the metal’s singlet lone pair and p$_z$-orbital (orthogonal to the heterocycle plane) are associated with the HOMO and LUMO, respectively (e.g. Figure

---

[†] Cardiff University.
[‡] Monash University.

10.1021/ja057967t CCC: $33.50 © 2006 American Chemical Society

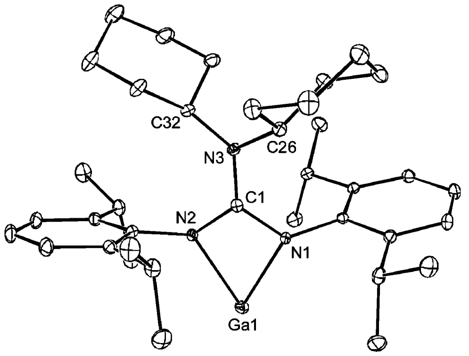


Figure 1. Molecular structure of **1**. Relevant bond lengths (Å) and angles (deg): Ga(1)−N(1) 2.087(2), Ga(1)−N(2) 2.095(2), C(1)−N(1) 1.350(3), C(1)−N(2) 1.349(3), C(1)−N(3) 1.373(3); N(1)−Ga(1)−N(2) 63.77(7), N(1)−C(1)−N(2) 109.9(2), N(1)−C(1)−N(3) 125.1(2), N(2)−C(1)−N(3) 125.1(2), Ga(1)−N(1)−C(1) 93.33(14), Ga(1)−N(2)−C(1) 93.02(14). Relevant bond lengths (Å) and angles (deg) for **2**: In(1)−N(1) 2.298(2), In(1)−N(2) 2.298(2), C(1)−N(1) 1.345(3), C(1)−N(2) 1.351(3), C(1)−N(3) 1.382(3); N(1)−In(1)−N(2) 58.06(6), N(1)−C(1)−N(2) 111.70(18), N(1)−C(1)−N(3) 124.22(19), N(2)−C(1)−N(3) 124.08(19), In(1)−N(1)−C(1) 95.17(13), In(1)−N(2)−C(1) 95.03(13).

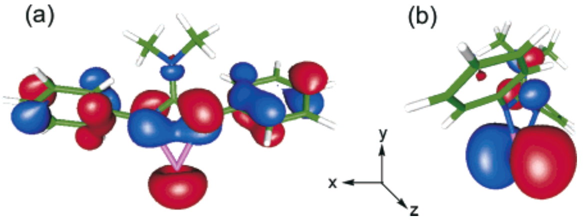


Figure 2. (a) HOMO and (b) LUMO of [:Ga{η^2-*N*,*N*′-(Ph)NC(NMe$_2$)N-(Ph)}].

2). Although the metal center of each has high s-character (M = Al $3s^{1.85}3p^{0.41}$, Ga $4s^{1.90}4p^{0.37}$, In $5s^{1.90}5p^{0.36}$), what p-character there is, is largely associated with the metal p_y orbital. This gives the lone pairs sp-character and their observed directionality. The heterocycles have significant HOMO−LUMO gaps (M = Al 61.8, Ga 67.4, In 63.5 kcal mol^{-1}) which, although considerably less than the energy gaps calculated for the analogous orbitals of related six-membered heterocycles (e.g. [:M{[N(Ar)C(Me)]$_2$CH}], M = Al 91.5, Ga 102.9, In 98.5 kcal mol^{-1}),[2c,13] suggest they will be good σ-donors but weak π-acceptor ligands. There is almost no overlap of the N p-orbital lone pairs with the metal p_z orbitals, and the N−M bonds have a high ionic character (e.g. NBO charges Ga +0.71, N −0.75; Wiberg Ga−N bond index 0.23).

In summary, the first examples of four-membered group 13 metal(I) N-heterocyclic carbene analogues have been prepared. Theoretical studies suggest they will make novel ligands and that the corresponding Al(I) heterocycle may be experimentally accessible.

Acknowledgment. We thank The Leverhulme Trust for funding (A.S.) and the EPSRC mass spectrometry service.

Supporting Information Available: Full details of the X-ray crystallographic studies of **1**−**3**, full details of the DFT calculations, and full synthetic details for **1**−**3**.

References

(1) (a) Gemel, G.; Steinke, T.; Cokoja, M.; Kempter, A.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2004**, 4161 (b) Cowley, A. H. *Chem. Commun.* **2004**, 2369 and references therein.

(2) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274. (b) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 1991. (c) Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Dalton Trans.* **2005**, 273. (d) Cheng, Y.; Hitchcock, P. B.; Lappert, M. F.; Zhou, M. *Chem. Commun.* **2005**, 752.

(3) (a) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *Dalton Trans.* **2002**, 3844. (b) Schmidt, E. S.; Jockisch, A.; Schmidbaur H. *J. Am. Chem. Soc.* **1999**, *121*, 9758.

(4) Baker, R. J.; Jones, C. *Coord. Chem. Rev.* **2005**, *249*, 1857.

(5) Despagnet-Ayoub, E.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 10198.

(6) Jones, C.; Junk, P. C.; Platts, J. A.; Rathmann, D.; Stasch, A. *Dalton Trans.* **2005**, 2497.

(7) Jones, C.; Junk, P. C.; Kloth, M.; Proctor, K. M.; Stasch, A. *Polyhedron.* In press.

(8) The use of bulky backbone substituents to facilitate *N*,*N*-chelation of amidinate ligands is well-known; see for example: Schmidt, J. A. R.; Arnold, J. *Organometallics* **2002**, *21*, 2306 and references therein.

(9) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1995.

(10) **1**: Yield 35%. Mp 158−159 °C dec. ^{1}H NMR (400 MHz, C_6D_6) δ 0.80−0.93 (m, 8 H, C*H*$_2$), 1.52 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.55 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.40−1.63 (m, 12 H, C*H*$_2$), 3.73 (overlapping m, 4 H, C*H*(CH$_3$)$_2$ and 2 H, C*H*N), 7.04−7.42 (m, 6 H, Ar*H*); ^{13}C NMR (100.6 MHz, C_6D_6) δ 22.3 (*C*H$_2$), 26.2 (CH(*C*H$_3$)$_2$), 27.6 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 33.2 (*C*H$_2$), 36.0 (*C*H$_2$), 58.8 (H*C*N), 123.9, 124.4, 143.7, 145.9 (Ar*C*), 174.2 (*C*N$_3$); IR (Nujol) ν (cm^{-1}) 1611 (s), 1583 (m), 1258 (m), 1163 (m); MS (EI/70 ev) *m*/*z*: 611.3 (M$^+$, 3%), 500.3 (GisoH$^+$ − C_3H_7, 40%); Acc. mass MS/EI, calcd for $C_{37}H_{56}{}^{69}Ga_1N_3$: 611.3725, found: 611.3725; anal. calcd (%) for $C_{37}H_{56}Ga_1N_3$: C 72.54, H 9.21, N 6.86; found: C 71.93, H 9.28, N 6.98; **2**: yield 48%. Mp 168−169 °C dec. ^{1}H NMR (400 MHz, C_6D_6) δ 0.61−0.88 (m, 8 H, C*H*$_2$), 1.23 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.33 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.13−1.50 (m, 12 H, C*H*$_2$), 3.45 (m, 2H, C*H*N), 3.55 (sept, *J* = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.83−7.20 (m, 6 H, Ar*H*); ^{13}C NMR (100.6 MHz, C_6D_6) δ 22.5 (*C*H$_2$), 26.4 (CH(*C*H$_3$)$_2$), 27.7 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 33.2 (*C*H$_2$), 36.2 (*C*H$_2$), 59.2 (H*C*N), 123.5, 124.0, 142.9, 144.3 (Ar*C*), *C*N$_3$ not observed; IR (Nujol) ν (cm^{-1}) 1609 (s), 1584 (m), 1253 (m), 1157 (m); MS (EI/70 ev) *m*/*z*: 657.4 (M$^+$, 6%), 500.3 (GisoH$^+$ − C_3H_7, 36%); Acc. mass MS/EI, calcd for $C_{37}H_{56}In_1N_3$: 657.3508, found: 657.3502; anal. calcd (%) for $C_{37}H_{56}In_1N_3$: C 67.57, H 8.58, N 6.39; found: C 67.46, H 8.75, N 6.51; **3**: yield 68%. Mp 184−185 °C dec. ^{1}H NMR (400 MHz, C_6D_6) δ 1.15−2.44 (m, 20 H, C*H*$_2$), 1.27 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.55 (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 3.34 (m, 2H, C*H*N), 3.73 (sept, *J* = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 6.92−7.43 (m, 6 H, Ar*H*); ^{13}C NMR (100.6 MHz, C_6D_6) δ 22.8 (br, *C*H$_2$), 25.1 (br CH(*C*H$_3$)$_2$), 25.8 (br, CH(*C*H$_3$)$_2$), 26.2 (br, *C*H(CH$_3$)$_2$), 26.5 (br, *C*H$_2$), 32.0 (br, *C*H$_2$), 56.9 (H*C*N), 120.5, 123.4, 141.1, 144.0 (br, Ar*C*), *C*N$_3$ not observed; IR (Nujol) ν (cm^{-1}) 1613 (s), 1583 (m), 1259 (m), 1152 (m); MS (EI/70ev) *m*/*z*: 747.3 (M$^+$, 3%), 500.3 (GisoH$^+$ − C_3H_7, 38%); Acc. mass MS/EI, calcd for $C_{37}H_{56}Tl_1N_3$: 747.4213, found: 747.4212; anal. calcd (%) for $C_{37}H_{56}Tl_1N_3$: C 59.47, H 7.55, N 5.62; found: C 59.69, H 7.73, N 5.85.

(11) Crystal data for **1**: $C_{37}H_{56}GaN_3$, triclinic, $P\bar{1}$, a = 9.6735(19) Å, b = 10.597(2) Å, c = 17.818(4) Å, α = 107.00(3)°, β = 95.17(3)°, γ = 97.82(3)°, V = 1714.1(6) Å^3, Z = 2, D_{calc} = 1.187 g cm^{-3}, μ(Mo Kα) = 0.831 mm^{-1}; 7006 unique reflections were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K ($3.0 < \theta < 26.5°$), R_1 = 0.0461 ($I > 2\sigma I$), wR_2 = 0.1071 (all data); Crystal data for **2**: $C_{37}H_{56}InN_3$, triclinic, $P1$, a = 9.787(2) Å, b = 10.556(2) Å, c = 17.863(4) Å, α = 107.14(3)°, β = 95.00(3)°, γ = 97.81(3)°, V = 1731.3(6) Å^3, Z = 2, D_{calc} = 1.262 g cm^{-3}, μ(Mo Kα) = 0.710 mm^{-1}; 7519 unique reflections were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K ($3.0 < \theta < 27.0°$), R_1 = 0.0354 ($I > 2\sigma I$), wR_2 = 0.0838 (all data); Crystal data for **3**: $(C_6H_{14})_{0.5}$: $C_{40}H_{63}TlN_3$, monoclinic, $P2_1/c$, a = 10.565(2) Å, b = 30.240(6) Å, c = 12.371(3) Å, β = 109.05(3)°, V = 3735.9(13) Å^3, Z = 4, D_{calc} = 1.405 g cm^{-3}, μ(Mo Kα) = 4.353 mm^{-1}; 7732 unique reflections were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K ($3.0 < \theta < 26.5°$), R_1 = 0.0295 ($I > 2\sigma I$), wR_2 = 0.0592 (all data).

(12) Aelts, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17*, 3265.

(13) For related theoretical studies on five- and six-membered group 13 metal(I) heterocycles see: (a) Schoeller, W. W.; Eisner, D. *Inorg. Chem.* **2004**, *43*, 2585. (b) Sundermann, A.; Reiher, M.; Schoeller, W. W. *Eur. J. Inorg. Chem.* **1998**, 305. (c) Hardman, N. J.; Phillips, A. D.; Power, P. P. *ACS Symp. Ser.* **2002**, *822*, 2. (d) Reiher, M.; Sundermann, A. *Eur. J. Inorg. Chem.* **2002**, 1854.

JA057967T