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The Benzannelation Approach to Novel Gallium and Indium Heterocycles

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Main group heterocycles are of interest to the pharmaceutical, agricultural chemical, and materials science communities.[1] To date, most of the emphasis has been placed on carbocyclic systems that incorporate an element from groups 14−16. Interestingly, and with the obvious exception of boron,[2] there is a paucity of information concerning the corresponding ring systems of the heavier group 13 elements.[3] Recognizing that element−carbon bonds are significantly weaker for the heavier congeners, we have targeted group 13 ring systems in which the bonding is enhanced by conjugation and/or benzannelation. Here we report a new class of benzannelated heterocycles involving gallium and indium.

Experimental Section. General Considerations. All experiments were performed under anaerobic and anhydrous conditions using standard Schlenk techniques or a HE-493 Vacuum Atmospheres drybox. Solvents were dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. Ar*GaCl$_2$,[4,5] Ar*InBr$_2$,[4] 2,2′-dilithiobiphenyl,[6] and 2,2′-dilithiobiphenyl·2TMEDA[7] were prepared according to literature procedures. The GaCl$_3$ was used as received (Strem). NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.15 MHz; ^{13}C, 75.48 MHz; 295 K). ^{1}H and ^{13}C NMR spectra are referenced to C$_6$D$_6$ which was dried over sodium−potassium alloy and distilled prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to Si(CH$_3$)$_4$ (0.00 ppm).

Synthesis of 1. A mixture of Ar*GaCl$_2$ (768 mg, 2 mmol) and 2,2′-dilithiobiphenyl (332 mg, 2 mmol) in 10 mL of Et$_2$O was allowed to react at 25 °C for 4 h. The reaction mixture was filtered, following which the filtrate was concentrated and cooled to −20 °C. The yield of the resulting colorless crystals of **1** was 30% . MS (CI+), *m/e* (%): 467 = M$^+$ (100). HRMS (CI+), *m/e*: calcd, 467.2229; found, 467.2224. Mp (uncorrected): 181 °C. ^{1}H NMR, δ: 7.91 (d, 7.8 Hz, 2H), 7.72 (d, 6.6 Hz, 2H), 7.56 (s, 2H), 7.30 (d, 6.6 Hz of d, 7.2 Hz, 2H), 7.22 (d, 6.9 Hz of d, 7.2 Hz, 2H), 1.35 (s, 9H), 1.33 (s, 18H). ^{13}C NMR, δ: 157.8 (q), 151.0 (q), 149.7 (q), 145.1 (q), 135.6, 130.2, 121.8, 121.0, 37.8 (q), 35.1 (q), 33.3, 32.6.

Synthesis of 3. A solution of GaCl$_3$ (350 mg, 2 mmol) in 5 mL of Et$_2$O was added dropwise to a solution of 2,2′-dilithiobiphenyl (400 mg, 2.4 mmol) in 5 mL of Et$_2$O at −78 °C. Stirring was continued for 2 h at −78 °C after which the reaction mixture was allowed to warm to 25 °C. After being stirred for 1 h at 25 °C, the reaction mixture was filtered and the solvent was removed under reduced pressure to yield a pale yellow oil. Alternatively, the filtrate was treated immediately with Ar*Li (504 mg, 2 mmol) in 10 mL THF. The resulting reaction mixture was filtered, following which the filtrate was concentrated and cooled to −20 °C to afford a <10% yield of colorless powder **1**.

Synthesis of 4. A mixture of Ar*InBr$_2$ (104 mg, 0.2 mmol) and 2,2′-dilithiobiphenyl·2TMEDA (90 mg, 0.23 mmol) in 4 mL of Et$_2$O was allowed to react at −78 °C for 30 min, during which time the yellow reaction mixture became colorless and a precipitate formed. The reaction mixture was warmed to 25 °C, filtered, and the solvent was removed from the filtrate to afford colorless, microcrystalline **4** in ~13% yield. MS (CI+), *m/e* (%): 513 = M + H (57). HRMS (CI+), *m/e*: calcd, 513.2012; found, 513.2015. ^{1}H NMR, δ: 8.09 (d, 6.6 Hz, 2H), 7.90 (d, 6.6 Hz, 2H), 7.59 (s, 2H), 7.32 (m, 2H), 7.20 (d, 6.6 Hz of d, 7.5 Hz, 2H), 1.36 (s, 9H), 1.29 (s, 18H). ^{13}C NMR, δ: 157.5 (q), 155.1 (q), 150.4 (q), 149 (q), 137.6, 129.7, 129.0, 122.9, 120.9, 37.0 (q), 35.1 (q), 32.6, 31.6.

Crystal Structure of 1. A colorless crystal of **1** suitable for X-ray diffraction study was obtained by cooling a concentrated solution of **1** in Et$_2$O to −20 °C. The crystal was mounted in a thin walled glass capillary under argon and sealed. A selection of crystal and refinement data is collected in Table 1.

The cell dimensions were determined by least-squares refinement of 25 reflections with $18 < 2\theta \leq 25°$. Molecules of **1** crystallize in the triclinic space group $P\bar{1}$ with 2 molecules per unit cell. A total of 4592 independent reflections were collected on an Enraf Nonius CAD4 diffractometer at 300 K ($2\theta - \theta$ scan technique, $4 < 2\theta < 50°$) using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Lorentz and polarization corrections were applied to the data. A total of 2703 reflections were observed ($F \geq 4.0\sigma(F)$) and used for structure solution (direct methods) and refinement. All non-hydrogen atoms were refined anisotropically and hydrogen atoms included in calculated positions and refined isotropically with a common thermal parameter. Full-matrix least-squares refinement on F using the SHELXTL-PLUS[8] program package converged to R = 6.42% and a goodness of fit of 1.23.

Results and Discussion. As reported previously for analogous main group ring systems, transmetalation reactions involving metal halides and the corresponding zirconacycles can be employed to produce metallacyclopentadiene[9] and

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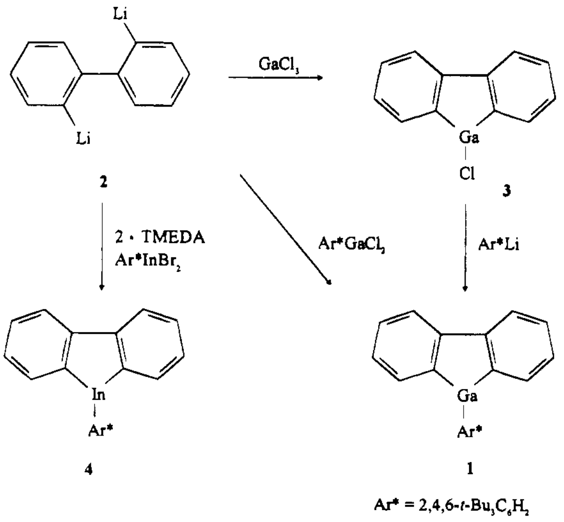
Table 1. Selected Crystallographic Data for **1**

formula	$C_{30}H_{37}Ga$
fw	467.3
cryst size, mm	0.12 × 0.18 × 0.24
cryst syst	monoclinic
space group	$P\bar{1}$
a, *b*, and *c*, Å	9.078(1), 11.257(2), 13.231(1)
α, β, and γ, deg	76.49(1), 84.59(1), 88.57(1)
V, Å3	1308.9(7)
Z	2
λ, Å	0.71073
D_{calcd}, g/cm³	1.186
μ, mm⁻¹	1.065
R(F) and R_w(F),[a] %	6.42, 6.77

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \sum[w^{1/2}||F_o| - |F_c||]/\sum[w^{1/2}|F_o|]$. $w = 1.0000/(\sigma^2(F) + 0.001000(F^2))$.

Scheme 1



metallaindene[10] compounds. Unfortunately, the "metallacycle transfer" synthetic methodology was not applicable in the present case because of the unavailability of the requisite zirconafluorene.[11]

The first benzannelated species, a gallafluorene (**1**), was prepared via the salt elimination reaction of Ar*$GaCl_2$ (Ar* = 2,4,6-*t*-$Bu_3C_6H_2$) with 2,2′-dilithiobiphenyl (**2**) (Scheme 1).

The corresponding reaction of **2** with $GaCl_3$ resulted in the formation of an unstable oil (**3**) which was not isolated but treated *in situ* with Ar*Li to afford a low yield of **1**. The proposed formulation for **1** is consistent with the ^1H and ^{13}C NMR spectral data, the observation of an HRMS peak corresponding to M^+, and a satisfactory combustion analysis. Confirmation was provided by an X-ray crystallographic study. Individual molecules of **1** (Figure 1) crystallize in the triclinic space group $P\bar{1}$, and there are no short intermolecular contacts. The GaC_4 ring is planar within experimental error and the largest deviation is found for the gallium atom which protrudes 0.09 Å from the mean plane of the five-membered ring. Comparison of the metrical parameters for the GaC_4 ring of the benzannelated and non-benzannelated[3c] systems reveals that in the former the $C_\alpha - C_\beta$ distances are ~0.1 Å smaller due to the involvement of the double bonds in the aromatic π system. It should be noted that the metrical parameters for the biphenyl skeleton in the gallafluorene and the free hydrocarbon[12] are virtually identical. The only significant difference can be found in the distortion of the biphenyl system to accommodate the gallium atom in the five-membered ring. The angles C(24A)−C(30)−C(29) (118.0(5)°) and C(25A)−C(29)−C(30) (117.0(6)°) are notably smaller than those in the free ligand (123.8(5)°). The dihedral angle between the Ar* and gallafluorene rings is 88.7°; hence the *ortho*-*t*-Bu groups provide steric protection above and below the trigonal planar gallium center (sum of bond angles = 359.3(3)°). A further point of structural interest relates to the short contact between the gallium atom and H(9C) (2.004 Å). One of the *t*-Bu groups is oriented such that the aforementioned hydrogen atom points toward the gallium center. The Ga−aryl and Ga−C(ring) bond lengths are almost identical and fall within the single bond range.

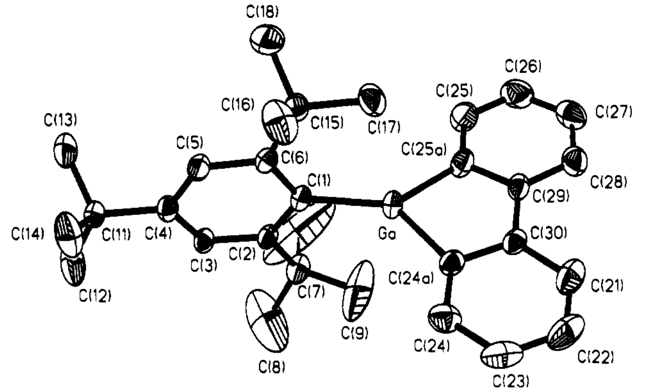


Figure 1. Crystal structure and numbering scheme for **1** at the 30% probability level, with hydrogen atoms omitted for clarity. Important bond distances (Å) and angles (°): Ga−C(1) = 1.949(6), Ga−C(24a) = 1.969(6), Ga−C(25a) = 1.954(8), C(24a)−C(30) = 1.42(1), C(29)−C(30) = 1.48(1), C(29)−C(25a) = 1.400(9); C(1)−Ga−C(24a) = 130.5(3), C(1)−Ga−C(25a) = 139.2(3), C(24a)−Ga−C(25a) = 90.2(3), Ga−C(24a)−C(30) = 106.5(4), C(24a)−C(30)−C(29) = 118.0(5), Ga−C(25a)−C(29) = 108.0(5), C(25a)−C(29)−C(30) = 117.0(6).

Interestingly, there was no evidence of reaction between **2** and Ar*$InBr_2$ and, as a consequence, it was necessary to employ the activated reagent **2**·2TMEDA (Scheme 1). We have not been successful in growing single crystals of the indafluorene **4** because of the presence of traces of LiBr·TMEDA in the product. Nevertheless, the identity of **4** is clear from the observation of the M^+ ion by high-resolution CI mass spectroscopy and also from the fact that the ^1H and $^{13}C\{^1H\}$ NMR spectra for **4** are extremely similar to those for **1**.

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Supporting Information Available: Tables of X-ray crystallographic data, bond distances, bond angles, atomic parameters, and thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

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