Bridging of monoanionic hydrocarbon groups between two metal centers is well established for the lighter main group elements, and is particularly broadly appreciated for aluminum. Major classes of bridging hydrocarbon ligands in aluminum complexes include alkane, aryl, and acetylide and vinyl groups. Despite the broad occurrence of bridging interactions in aluminum chemistry, there are very few examples of bridging hydrocarbons between the heavier group 13 elements gallium and indium. Structurally characterized examples for gallium are limited to [Me₂Ga(μ-C≡CPh)]₄, [(η⁵-C₅H₅)Fe(μ-C≡C(CH₃)₂GaMe₂)]₂, and a gallol dimer containing bridging alkenyl groups. For indium, the only example is [Me₂In(μ-2-C₅H₅)]. Some striking differences exist between aluminum and gallium complexes containing similar ligands. For example, triphenylaluminum is dimeric in the solid state, while triphenylgallium is a monomer in the solid state. Trimethylaluminum is dimeric in the solid state and in solution with a well-known methyl-bridged structure, while the methyl groups in solid trimethylgallium have only very weak bridge-like interactions between neighboring gallium atoms. Within this perspective, we report the synthesis, structure, bridge–terminal exchange kinetics, and molecular orbital calculations of a series of gallium–pyrazolato complexes that contain bridging phenyl ligands. The observation of bridging phenyl ligands in these complexes is particularly surprising, since triphenylgallium is monomeric. The results imply that bridging interactions in the heavier elements may be induced by appropriate choice of ancillary ligands that dispose two metal centers in close proximity. Thus, complexes of the heavier group 13 elements with bridging hydrocarbon ligands are likely to be more accessible than the current literature may suggest.

Treatment of triphenylgallium (2 equiv) with 3,5-dimethylpyrazole, 3,5-diphenylpyrazole or 3,5-di-tert-butylpyrazole afforded (C₆H₅)₂Ga(μ-Me-pz)(μ-C₆H₅)Ga(C₆H₅)₂ (1, 62%), (C₆H₅)₂Ga(μ-Ph-pz)(μ-C₆H₅)Ga(C₆H₅)₂C₂H₆ (2, 62%), and (C₆H₅)₂Ga(μ-Bu₂-pz)(μ-C₆H₅)Ga(C₆H₅)₂ (3, 40%), respectively, as colorless or off-white crystalline solids (eq 1).

\[
\text{2 Ph₃Ga + R - N - N - R → } \begin{array}{c}
\text{toluene} \\
23°C, 18h \\
\text{GaPh₃}
\end{array} \\
\text{(1)}
\]

The structural assignments for 1–3 were based on spectral and analytical data and X-ray crystal structure determinations. The \(^1\)H NMR spectra of 1–3 at ambient temperature showed three broad multiplets for the bridging phenyl groups and sharper multiplets for the terminal phenyl groups. The \(^1\)C{\(^1\)H} NMR spectra at ambient temperature exhibit broad ipso-carbon resonances for the bridging and terminal phenyl rings between 157.33 and 158.33 ppm and 146.45–148.26 ppm, respectively.

Figure 1 shows a perspective view of 1 along with selected bond lengths and angles. The molecular structure consists of a dimethylpyrazolato ligand with a diphenylgallium group bonded to each nitrogen atom. A phenyl group acts as a bridge between the gallium atoms. The two gallium atoms and the ipso-carbon atom of the bridging phenyl group define a plane, while the two nitrogen atoms lie 0.290 and 0.147 Å above and below this plane. The bridging phenyl group is slightly canted toward Ga(1), giving a distinct C–C–C–C bond lengths lie in the range 1.9597(19)-1.973(2) Å for the terminal phenyl groups and are 2.114(2) and 2.219(2) Å for the bridging phenyl group. The geometry about the gallium centers is distorted tetrahedral. For comparison, crystallographically characterized gallium complexes with bridging hydrocarbon groups have terminal gallium–carbon bond lengths that range between 1.95 and 1.99 Å, bridging gallium–carbon bond lengths between 1.992 and 2.587 Å, and gallium–carbon–gallium angles for bridging hydrocarbon groups within four-membered rings range between 74.2° and 93.3°. The related value for 1 (96.88(9)°) is larger due to geometric constraints imposed by the Ga₂CN₂ ring.

The kinetics of exchange between the terminal and bridging phenyl groups of 1–3 (0.106 M) was studied by \(^1\)C{\(^1\)H} NMR spectroscopy in toluene-\(d₆\) between ~30 and 30 °C. Details of these determinations are given in the Supporting Information. Eyring analysis of the exchange processes gave the following parameters:

**Figure 1.** Perspective view of 1. Selected bond lengths (Å) and angles (deg): Ga(1)–N(1) 1.967(16), Ga(2)–N(2) 1.979(16), Ga(1)–C(6) 2.219(2), Ga(1)–C(12) 1.964(2), Ga(1)–C(18) 1.959(19), Ga(2)–C(6) 2.114(2), Ga(2)–C(24) 1.973(2), Ga(2)–C(30) 1.964(2), N(1)–N(2) 1.376(2), N(1)–Ga(1)–C(6) 100.33(8), N(2)–Ga(2)–C(6) 103.34(8), Ga(1)–C(6)–Ga(2) 96.88(9).
This work describes the first examples of gallium complexes containing bridging phenyl ligands. Such interactions are unexpected, due to the small number of structurally characterized heavier group 13 complexes with bridging hydrocarbon ligands and the fact that triphenylgallium is monomeric in the solid state with terminal phenyl ligands. The activation parameters of the bridging-terminal phenyl exchanges in 1–3 are consistent with strict intramolecular processes, which suggests that the gallium–nitrogen bonds are sufficiently strong to maintain the structure in solution. The molecular orbital calculations predict that extended orbital overlap involving the bridging phenyl carbon atom is weak at best and thus contributes little to the stabilization of the bridging interaction. Thus, the nature of the ancillary ligand holding the two metal atoms together appears to be the key factor that leads to the unusual bridging phenyl ligands in 1–3. The results of this work suggest that many other heavier group 13 metal complexes with bridging hydrocarbon ligands should be available through appropriate choice of supporting ligands. To this end, we have synthesized and structurally characterized the indium analogue of 3. Recent reports of long, weak Ga=CHR–Ga contacts (Ga–C > 3 Å) in solid-state gallium trialkyls raise the possibility that even saturated alky groups might be induced to bridge between gallium, indium, and other heavier main group metal centers.

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Supporting Information Available: Synthetic procedures and analytical and spectroscopic data for 1–3; tables of final positional parameters for the calculations (PDF). X-ray crystallographic files for 1 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(9) Spectral, analytical, and kinetic data for 1–3 and positional parameters for 4 and 5 are contained in the Supporting Information.

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