

Synthesis, Structure, Bridge–Terminal Exchange Kinetics, and Molecular Orbital Calculations of Pyrazolate-Bridged Digallium Complexes Containing Bridging Phenyl Groups

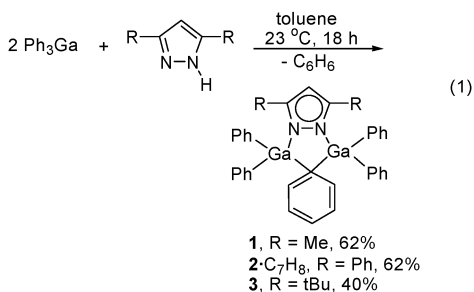
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Bridging of monoanionic hydrocarbon groups between two metal centers is well established for the lighter main group elements, and is particularly broadly appreciated for aluminum.^{1–4} Major classes of bridging hydrocarbon ligands in aluminum complexes include alkane,¹ aryl,² and acetylide and vinyl groups.³ 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.⁴ Structurally characterized examples for gallium are limited to $[\text{Me}_2\text{Ga}(\mu\text{-C}\equiv\text{CPh})_2]_2$,^{5a} $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4)\text{GaMe}_2]_2$,^{5b} and a gallole dimer containing bridging alkenyl groups.^{5c} For indium, the only example is $[\text{Me}_2\text{In}(\mu\text{-}2\text{-C}_4\text{H}_3\text{S})_2]$.⁶ Some striking differences exist between aluminum and gallium complexes containing similar ligands. For example, triphenylaluminum is dimeric in the solid state with two bridging phenyl groups,^{2a} while triphenylgallium is a monomer in the solid state.⁷ Trimethylaluminum is dimeric in the solid state and in solution with a well-known methyl-bridged structure,^{1a} while the methyl groups in solid trimethylgallium have only very weak bridge-like interactions between neighboring gallium atoms.⁸ 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 $(\text{C}_6\text{H}_5)_2\text{Ga}(\mu\text{-Me}_2\text{pz})(\mu\text{-C}_6\text{H}_5)\text{Ga}(\text{C}_6\text{H}_5)_2$ (**1**, 62%), $(\text{C}_6\text{H}_5)_2\text{Ga}(\mu\text{-Ph}_2\text{pz})(\mu\text{-C}_6\text{H}_5)\text{Ga}((\text{C}_6\text{H}_5)_2\text{C}_7\text{H}_8$ (**2**· C_7H_8 , 62%), and $(\text{C}_6\text{H}_5)_2\text{Ga}(\mu\text{-tBu}_2\text{pz})(\mu\text{-C}_6\text{H}_5)\text{Ga}(\text{C}_6\text{H}_5)_2$ (**3**, 40%), respectively, as colorless or off-white crystalline solids (eq 1).



The structural assignments for **1–3** were based on spectral and analytical data and X-ray crystal structure determinations.⁹ The ¹H

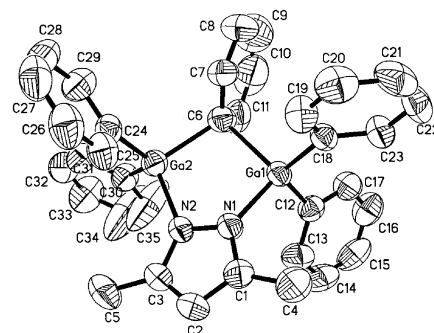


Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Ga(1)–N(1) 1.9670(16), Ga(2)–N(2) 1.9797(16), Ga(1)–C(6) 2.219(2), Ga(1)–C(12) 1.964(2), Ga(1)–C(18) 1.9597(19), Ga(2)–C(6) 2.114(2), Ga(2)–C(24) 1.973(2), Ga(2)–C(30) 1.964(2), N(1)–N(2) 1.376(2), N(1)–Ga(1)–C(6) 100.33(8), N(2)–Ga(2)–C(6) 103.34(8), Ga(1)–C(6)–Ga(2) 96.88(9).

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 ¹³C{¹H} 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.⁹ 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 triphenylgallium unit containing Ga(2). The gallium–nitrogen bond lengths are 1.9670(16) and 1.9797(16) Å. The gallium–carbon 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°.⁵ 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 ¹³C{¹H} NMR spectroscopy in toluene-*d*₈ 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:

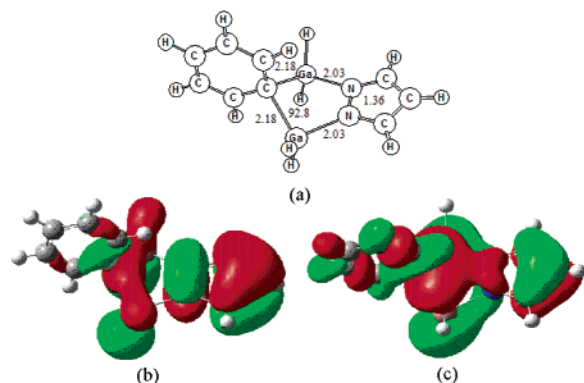
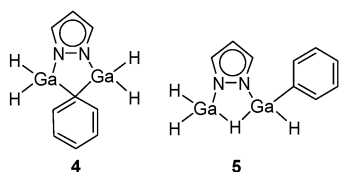


Figure 2. Calculated structure of **4**, emphasizing (a) overall structure with selected core bond lengths (Å) and angles (deg), and (b) and (c) orbital interactions involving the *ipso*-carbon atom of the bridging phenyl ligand.

1, $\Delta H^\ddagger = 7.6 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -27.2 \pm 2$ eu, and $\Delta G^\ddagger_{(298)} = 15.7 \pm 0.1$ kcal/mol; **2**, $\Delta H^\ddagger = 6.0 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -32.0 \pm 2$ eu, and $\Delta G^\ddagger_{(298)} = 15.5 \pm 0.1$ kcal/mol; **3**, $\Delta H^\ddagger = 8.9 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -23.1 \pm 2$ eu, and $\Delta G^\ddagger_{(298)} = 15.8 \pm 0.1$ kcal/mol. Analysis of 0.053 M solutions of **1–3** in toluene-*d*₈ afforded rates and activation parameters that were identical within experimental error, suggesting that the exchange processes are intramolecular. The rates of terminal–bridging phenyl exchange in **1–3** at 25 °C are calculated to be 20.1 s⁻¹ in **1**, 24.8 s⁻¹ in **2**, and 15.9 s⁻¹ in **3**. The large, negative values of ΔS^\ddagger imply ordered transition states relative to the ground states, and rotation along the N–GaPh₃ vector without gallium–nitrogen bond cleavage. The activation parameters and exchange rates at 25 °C are similar, suggesting that the size of the pyrazolato carbon substituents has only a minor effect on the exchange process.

To understand the nature of the bonding in **1–3**, the model complex **4** was optimized at the B3LYP/6-311G(d,p) level of theory.^{10,11} Model **4** showed a departure from the solid-state structure of **1** in that the nitrogen and gallium atoms reside in an approximate plane, while the phenyl *ipso*-carbon adopts an out-of-plane orientation. By contrast, **1** possesses a distorted ring with the nitrogen atoms favoring an orientation above and below the Ga₂C plane. The differences between the structures of **1** and **4** are most likely due to steric congestion associated with the phenyl substituents on the gallium atoms. The out-of-plane phenyl group orientation in **4** arises from electronic interactions, in which hybridized orbitals on the phenyl group create delocalized molecular orbitals as shown in Figure 2, b and c. However, the energy difference between a planar Ga₂N₂C ring and one with the bent carbon atom is only 1.77 kcal/mol, implying that the molecular orbitals shown in Figure 2 provide little stabilization to the structure. The isomeric complex **5** was also considered, in which the phenyl group is terminal and a hydride bridges between the gallium atoms. Model **5** is 8.1 kcal/mol lower in energy than **4**. Thus, a bridging gallium–hydrogen bond is about 4 kcal/mol stronger than a gallium–carbon bond in a bridging phenyl ligand.



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^{5,6} and the fact that triphenylgallium is monomeric in the solid state with terminal phenyl ligands.⁷ The activation parameters of the bridge–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**.¹² Recent reports of long, weak Ga–CH₂R–Ga contacts (Ga–C > 3 Å) in solid-state gallium trialkyls⁸ raise the possibility that even saturated alkyl groups might be induced to bridge between gallium, indium, and other heavier main group metal centers.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-9807269 and Special Creativity Extension thereto to C.H.W.) for support of this research.

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>.

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JA036256X