Oxidative Coupling of an Anionic Gallium(I) Carbene Analogue: Synthesis and Structural Characterization of an Unprecedented π-Cyclopentadienyl-Bridged Digallane Complex

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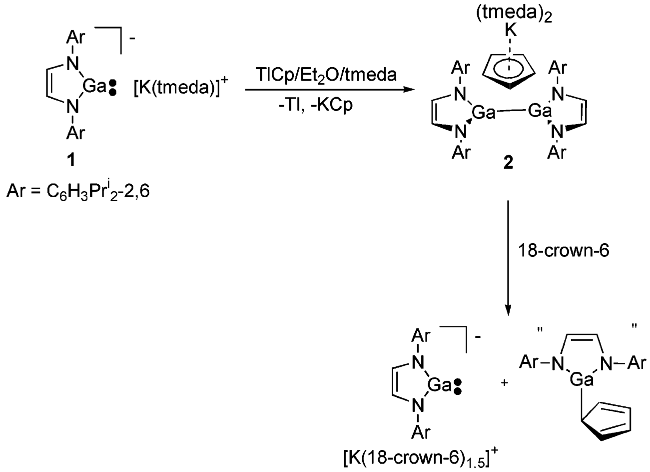
Summary: An unprecedented π-cyclopentadienyl-bridged digallane complex, $[\{Ga[N(Ar)C(H)]_2\}_2\{\mu\text{-}CpK(tmeda)_2\}]$ ($Ar = C_6H_3Pr^i{}_2$-2,6), incorporating the first structurally characterized π-interaction with a Ga(II) center, results from the oxidative coupling of an anionic gallium(I) heterocycle with cyclopentadienylthallium(I). This compound can be regarded as an intermediate in the nucleophilic attack of a digallane by the Cp^- anion.

Two different synthetic routes to the anionic gallium(I) heterocycles $[:Ga\{N(R)C(H)\}_2]^-$ ($R = C_6H_3Pr^i{}_2$-2,6 (Ar) (**1**), Bu^t) have been developed by our group[1] and that of Schmidbaur.[2] The facile nature of the route to **1** has allowed us to begin an exploration of its coordination chemistry by examining its reactions with metallocenes,[3] metal carbonyls,[4] and group 13 hydrides.[5] Throughout this work, **1** has proved to be a very nucleophilic σ-donor and has exhibited parallels with the important N-heterocyclic carbene (NHC) class of ligand. For example, its reaction with nickelocene leads to Cp^- displacement and the formation of the anionic complex $[CpNi(\mathbf{1})_2]^-$,[3] in much the same way that Cowley et al. have shown NHCs to react with nickelocene to form cationic complexes of the type $[CpNi(NHC)_2]^+$.[6] Considering this similarity and the evolving area of NHC main-group-metal cyclopentadienyl chemistry,[7] we wished to begin an investigation of the interaction of **1** with p-block cyclopentadienyl complexes. The preliminary and unexpected results of this study are reported herein.

Treatment of [K(TMEDA)][**1**] with 1 equiv of TlCp led to thallium metal deposition and the formation of the cyclopentadienyl-bridged digallane complex **2**, in moderate yield (46%) (Scheme 1).[8] A similar yield of **2** resulted from the reaction of [K(TMEDA)][**1**] with InCp. The mechanism of these reactions seemingly involves an oxidative coupling of anionic **1** to form the digallane $[\{Ga^{II}[N(Ar)C(H)]_2\}_2]$ (**3**), which complexes half of the generated KCp to form **2**. It is noteworthy that the digallane **3** has been reported by Jutzi et al.[9] to be formed by photolysis of the galladiazole $[(\eta^1\text{-}Cp^*)Ga\{N(Ar)C(H)\}_2]$. It should also be mentioned that one other closely related digallane, $[\{Ga^{II}[N(Bu^t)C(H)]_2\}_2]$, has been reported by Cowley et al.[10] We have shown that **3** can alternatively be prepared in high yield via oxidative coupling of **1** with $[FeCp_2]^+$ or $[Co_2(CO)_8]$.[11]

Scheme 1



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(1) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *Dalton* **2002**, 3844.

(2) (a) Schmidt, E. S.; Jockisch, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1999**, *121*, 9758. (b) Schmidt, E. S.; Schier, A.; Schmidbaur, H. *Dalton* **2001**, 505.

(3) Baker, R. J.; Jones, C.; Platts, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 10534.

(4) Baker, R. J.; Jones, C.; Platts, J. A. *Dalton* **2003**, 3673.

(5) Baker, R. J.; Jones, C.; Kloth, M.; Platts, J. A. *Angew. Chem., Int. Ed.* **2003**, *43*, 2660.

(6) Abernethy, C. D.; Clyburne, J. A. C.; Cowley, A. H.; Jones, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 2329.

(7) (a) Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. *J. Organomet. Chem.* **2002**, *643*−*644*, 487, (b) Carmalt, C. J.; Cowley, A. H. *Adv. Inorg. Chem.* **2000**, *50*, 1 and references therein.

(8) Experimental data for **2**: to a suspension of TlCp (0.22 g, 0.82 mmol) in diethyl ether (20 cm^3) was added a solution of [K(TMEDA)][**1**] (0.50 g, 0.82 mmol) in Et_2O/TMDEA (20 cm^3/1 cm^3) at −78 °C. This mixture was warmed to room temperature and stirred for 18 h. The solvent was removed in vacuo and the orange residue washed with hexane (2 × 10 cm^3) and then extracted into DME (30 cm^3). Filtration, concentration to ca. 10 cm^3, and placement at −30 °C gave yellow-orange crystals of **2** (0.23 g, 46%), mp 75−78 °C (dec). N.B.: recrystallization of **2** from toluene afforded $\mathbf{2}.(toluene)_{0.5}$. ^1H NMR (C_7D_8, 300 MHz, 298 K): δ 0.87 (d, $^3J_{HH} = 6.5$ Hz, 24 H, CH_3), 1.13 (d, $^3J_{HH} = 6.6$ Hz, 24 H, CH_3), 2.11 (s, 24H, NCH_3), 2.32 (s, 8H, NCH_2), 3.23 (sept, $^3J_{HH} = 6.6$ Hz, 4 H, CH), 6.16 (s, 4H, NCH), 6.95−7.15 (m, 12H, ArH). $^{13}C\{^1H\}$ NMR (C_7D_8, 75 MHz, 298 K): δ 24.15 (CH_3), 24.74 (CH_3), 28.21 (CH), 45.64 (NCH_3), 58.05 (NCH_2), 116.93 (Ar), 123.03 (Ar), 125.81 (Ar), 144.09 (Ar), 144.78 (C=C). IR (ν/cm^{-1}): 1659 (m), 1624 (w), 1352 (m), 1256 (s), 1066 (w), 1056 (s), 801 (m), 760 (s). MS: *m*/*z* (APCI) 377 [100%, $\{N(Ar)C(H)\}_2{}^+$]. A reproducible microanalysis could not be obtained for **2**, due to its high air sensitivity and the fact that it slowly decomposes at room temperature.

(9) Pott, T.; Jutzi, P.; Schoeller, W. W.; Stammler, A.; Stammler, H.-G. *Organometallics* **2001**, *20*, 5492.

(10) Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421.

(11) Baker, R. J.; Jones, C. Unpublished results.

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This result is comparable to the recently reported ferrocenium-induced oxidative coupling of NHCs.[12] The proposed mechanism of formation of **2** seems feasible when it is considered that the direct reaction of **3** with KCp in the presence of excess tmeda also leads to **2** in good yield (56%).

This reaction can be compared to that of lithium alkyls with tetraorganyl digallanes, which can lead to nucleophilic attack at one gallium center to give anions of the type $[R_2R'GaGaR_2]^-$, e.g. R = $CH(SiMe_3)_2$ and R′ = C≡CPh,[13] with retention of the Ga−Ga bond. In this respect **2** can perhaps be considered as an isolated intermediate in the attack of the Cp^- anion at one of its Ga centers. To test this hypothesis, decomplexation of the K center from the Cp^- anion of **2** by treating it with 18-crown-6 led to the known potassium salt of **1**, viz. $[K(18\text{-crown-}6)_{1.5}]$[**1**],[1] and presumably $[(\eta^1\text{-Cp})Ga\{N(Ar)C(H)\}_2]$, though this could not be identified in the reaction mixture. This result probably stems from an increase in the nucleophilicity of the Cp^- anion upon potassium decomplexation, which leads to its attack at one Ga center and subsequent Ga−Ga bond cleavage.

The spectroscopic data[8] for **2** are largely consistent with its formulation, though resonances corresponding to the Cp^- anion were not observed in its ^1H or $^{13}C\{^1H\}$ NMR spectra at ambient temperature or upon cooling d_8-toluene solutions of the compound to −65 °C. Cooling below this temperature led to significant precipitation of the complex, while decomposition of the complex commenced above 30 °C. These observations presumably arise from an, as yet unknown, fluxional process which is unusually slow compared to fluxional processes in Ga(I) and Ga(III) cyclopentadienyl complexes.[14] These are generally rapid on the NMR time scale at ambient temperature. In **2**, fluxional processes may be slowed by the bridging nature of the Cp ligand and conceivably could involve sigmatropic, haptotropic, or 1,2-gallium shifts of the Cp ligand. In addition, a fluxional complexation/decomplexation of the weakly coordinated (vide infra) $K(TMEDA)_2Cp$ salt from the digallane moiety of **2** cannot be discounted.

The molecular structure of **2** is depicted in Figure 1, which shows it to sit on a 2-fold rotation axis and to incorporate a Cp ligand that is disordered over two sites.[15] To the best of our knowledge, this represents the first structural characterization of a complex in which a Cp ligand symmetrically bridges two p-block metals α to each other and thus is related to the Cp-bridged α-bimetallic transition-metal systems widely explored by Werner's group.[16] It should be noted that Uhl et al. have recently detailed a series of related digallane complexes with bridging anionic σ-donor ligands: e.g. carboxylates.[17] In addition, **2** can be compared to a complex incorporating a η^1:η^1-Cp ligand bridging two β-Sn centers: viz., $[CpNi\{SnN(Bu^t)Si(Me)_2N(Bu^t)\}_2(\mu\text{-}\eta^1\text{: }\eta^1\text{-Cp})]$.[18]

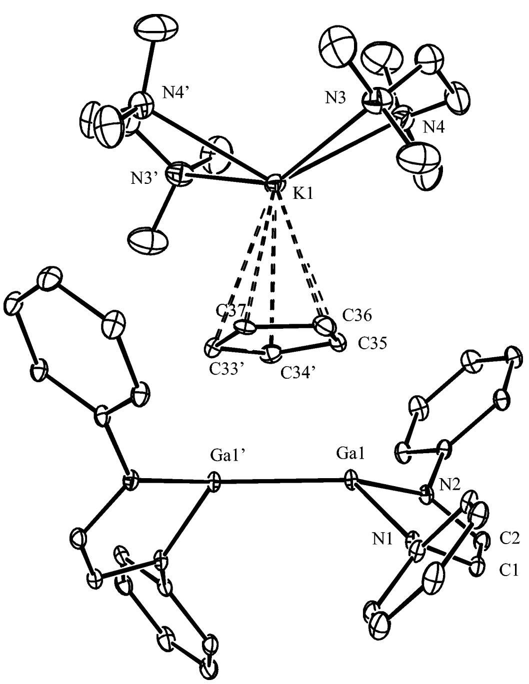

Figure 1. Molecular structure of **2** (isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)−N(1) = 1.907(3), Ga(1)−N(2) = 1.924(3), Ga(1)−Ga(1′) = 2.4461(8), Ga(1)−C(35) = 2.630(3), Ga(1)−C(36) = 2.811(4), Ga(1)−C(34′) = 3.055(3), Ga(1′)−C(33′) = 2.515(4), Ga(1′)−C(37) = 2.830(3), Ga(1′)−C(34′) = 3.106(4); N(1)−Ga(1)−N(2) = 86.66(11), N(1)−Ga(1)−Ga(1′) = 119.27(8), N(2)−Ga(1)−Ga(1′) = 140.63(8). A prime denotes the symmetry operation $-x$, y, $-z + 1/2$.

Complex **2** displays the first structurally characterized π-interaction with a Ga(II) center. In comparison, π-complexes of Ga(I) are widely known,[14] but those of Ga(III) are very rare and their chemistry is currently evolving.[19] The Cp ligand in **2** is largely delocalized (C−C distances 1.398(10)−1.423(10) Å) and sits above the Ga−Ga bond with Ga−C distances (2.515(4)−3.106(4) Å) markedly longer than normal σ-Ga−C bond lengths (ca. 2.0−2.2 Å).[7a,13] Its mode of attachment to the digallane fragment can perhaps be best described as η^1: η^1-π-bridging, as the Ga(1)−C(35) and Ga(1′)-C(33′) bond lengths are appreciably shorter than the other Ga−C interactions. It is worth noting that a dialuminane containing a toluenediyl ligand that bridges two aluminum centers in a related η^1: η^1-σ-fashion has recently been reported.[20] In comparison to the Ga−Ga bond in the free digallane **3** (2.3482(2) Å),[9] that in **2** is significantly longer at 2.4461(5) Å but close to the mean value for all structurally characterized digallane(4) compounds (2.45 Å).[21] Moreover, the Ga centers in **2** are

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[12] Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1054.

[13] Uhl, W.; Spies, T. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1059.

[14] (a) Jutzi, P.; Reumann, G. *Dalton* **2000**, 2237, (b) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969 and references therein.

[15] Crystal data for **2**: $C_{69}H_{109}Ga_2KN_8$, M_r = 1229.18, monoclinic, space group $C2/c$, a = 21.284(4) Å, b = 15.538(3) Å, c = 23.066(5) Å, β = 114.31(3)°, V = 6952(2) Å^3, Z = 4, D_c = 1.174 g cm^{-3}, $F(000)$ = 2640, μ(Mo Kα) = 0.879 mm^{-1}, 150(2) K, 6285 unique reflections (R(int) = 0.0728), R(on F) = 0.0505, R_w(on F^2) ,= 0.1159 ($I > 2\sigma(I)$). Crystal data for **2**·0.5(toluene): $C_{72.5}H_{113}Ga_2KN_8$, M_r = 1275.25, monoclinic, space group $P2_1/c$, a = 13.074(3) Å, b = 43.191(9) Å, c = 13.836(3) Å, β = 107.65(3)°, V = 7445(3) Å^3, Z = 4, D_c = 1.138 g cm^{-3}, $F(000)$ = 2740, μ(Mo Kα) = 0.823 mm^{-1}, 150(2) K, 9866 unique reflections (R(int) = 0.1177), R(on F) = 0.0997, R_w(on F^2) = 0.2377 ($I > 2\sigma(I)$).

[16] Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155.

[17] (a) Uhl, W.; El-Hamdan, A. *Eur. J. Inorg. Chem.* **2004**, 969, (b) Uhl, W. *Chem. Soc. Rev.* **2000**, *29*, 259 and references therein.

[18] Veith, M.; Stahl, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 106.

[19] (a) Baker, R. J.; Jones, C. *Chem. Commun.* **2003**, 390. (b) Pietryga, J. M.; Jones, J. N.; Mullins, L. A.; Wiacek, R. J.; Cowley, A. H. *Chem. Commun.* **2003**, 2072.

[20] Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 10784.

[21] As determined from a survey of the Cambridge Crystallographic Database, September, 2004.

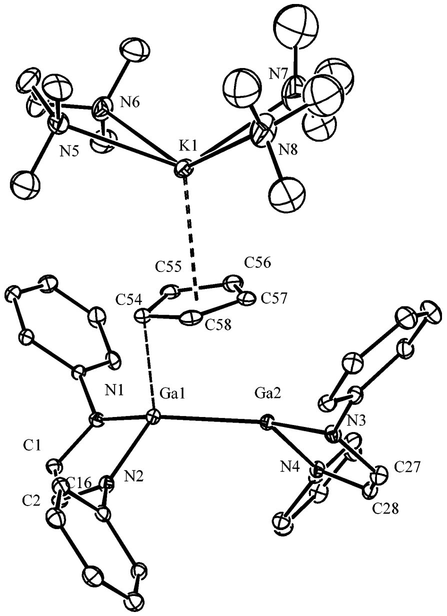

Figure 2. Molecular structure of **2** (recrystallized from toluene, isopropyl groups omitted for clarity). Selected bond lengths (Å) and angles (deg): Ga(1)−N(1) = 1.910(7), Ga(1)−N(2) = 1.907(7), Ga(2)−N(3) = 1.910(7), Ga(2)−N(4) = 1.912(7), Ga(1)−Ga(2) = 2.4549(13), Ga(1)−C(54) = 2.328(8), Ga(1)−C(55) = 2.737(8), Ga(1)−C(58) = 2.903(9), Ga(2)−C(56) = 3.082(8), Ga(2)−C(57) = 2.882(8), Ga(2)−C(58) = 3.217(8), C(54)−C(55) = 1.414(12), C(54)−C(58) = 1.415(13), C(55)−C(56) = 1.375(13), C(56)−C(57) = 1.406(14), C(57)−C(58) = 1.371(13); N(1)−Ga(1)−N(2) = 86.9(3), N(1)−Ga(1)−Ga(2) = 135.3(2), N(2)−Ga(1)−Ga(2) = 116.26(19), N(3)−Ga(2)−N(4) = 87.1(3), N(3)−Ga(2)−Ga(1) = 138.3(2), N(4)−Ga(2)−Ga(1) = 124.8(2).

more pyramidal (∑(angles at Ga) = 346.6°) than those in **3** (∑(angles at Ga) = 359.6°, average), which would be expected if there is partial donation of Cp π-electron density into the empty Ga p orbitals of the digallane fragment in **2**.

An indication of the nature of the observed fluxionality of **2** in solution comes from an isomeric crystalline form of this compound grown from toluene and incorporating that solvent in its lattice (Figure 2). Although of poor quality, the structure shows significant differences from the aforementioned described isomer in that the Cp ligand has moved considerably toward being localized and having an σ-η^1-interaction with Ga(1) (Ga(1)−C(54) = 2.328(8) Å, ∑(angles at Ga(1)) = 338.5°) while having a π-interaction with Ga(2) (∑(angles at Ga(2)) = 350.2°). A similar bonding mode for a Cp* ligand has been described for the mixed-oxidation-state compound ((η^5-Cp*)Ga^{I}Ga^{III}(μ-η^1-Cp*)Cl$_2$).[22] The fact that the Ga−Cp bondings in the two "polymorphs" of **2** are significantly different and their solution NMR spectra are identical shows that their interconversion must be a low-energy process: i.e., on the order of crystal-packing forces.

So as to obtain a preliminary indication of the nature of the interaction between the Cp ligand and the Ga$_2$ fragment in **2**, DFT calculations were carried out on the model complex [{Ga[N(Me)C(H)]$_2$}$_2${μ-CpK(NH$_3$)$_4$}] at the BP86/6-31G(d) level of theory.[23] The fully optimized geometry of this complex is similar to that of the symmetrical isomer of **2** but appears to show a weaker interaction between the Cp$^-$ anion and the digallane fragment, as evidenced by longer Ga−C distances (2.733−3.330 Å) and less pyramidalized gallium centers (∑(angles at Ga) = 353.9° average). The theoretical study also indicates a charge transfer of 0.209 electron between the CpK(NH$_3$)$_4$ and digallane fragments, which is consistent with the small overall energy required (28.7 kJ/mol) to dissociate and fully relax these fragments.

In conclusion, we have reported novel oxidative coupling reactions of an anionic gallium(I) heterocycle which have led to the first example of a symmetrically bridged Cp−digallane complex, which exhibits the only known π-interaction to a Ga(II) center. Full theoretical and experimental studies of the fluxional processes displayed by **2** in solution are underway and will be reported on in a future publication.

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Supporting Information Available: Crystallographic data as tables and CIF files for **2**, details of computational studies of [{Ga[N(Me)C(H)]$_2$}$_2${μ-CpK(NH$_3$)$_4$}], and the ^{1}H NMR spectrum of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **2001**, *20*, 2854.

[23] A full description of the theoretical methods employed and the results obtained in this study are included as Supporting Information.