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Note

The unusual reaction of $Ga(C_5Me_5)_3$ with a nucleophilic carbene

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Dedicated to François Mathey in recognition of his many outstanding contributions to main group and organometallic chemistry

Abstract

Treatment of $Ga(C_5Me_5)_3$ with tetramethylimidazol-2-ylidene affords the carbene complex, $Ga(C_5Me_5)_2H$·carbene (**1**). The structure of **1** was determined by X-ray crystallography. Possible mechanisms for the formation of **1** are discussed.

Keywords: Pentamethylcyclopentadienyl; Gallium; Hydride; Carbene complex

1. Introduction

There has been considerable recent interest in the reactions of nucleophilic carbenes with main group Lewis acids [1]. In the context of aluminum and gallium chemistry, it has been demonstrated that imidazol-2-ylidenes will form 1:1 complexes with MMe_3 (M = Al, Ga) [2] and MH_3 (M = Al, Ga) [3]. In related chemistry, it has been shown that the outcome of the reaction of homoleptic cyclopentadienylaluminum compounds with isonitriles is dependent upon the cyclopentadienyl ring substituents. Thus, while $AlCp_3$ forms a 1:1 complex with *t*-BuNC [4], the more sterically hindered alane $(1,2,4\text{-}Me_3C_5H_2)_3Al$ undergoes an insertion reaction with this isocyanide to form a heterometallacycle [5]. Attempts to prepare the fully methylated alane, $Al(C_5Me_5)_3$, have not been successful thus far [6]; however, the gallium analogue, $Ga(C_5Me_5)_3$, is known [7] and does not form complexes with Et_2O or THF. Herein, we report that the latter gallane undergoes an unprecedented reaction with tetramethylimidazol-2-ylidene.

Treatment of $Ga(C_5Me_5)_3$ with an equimolar quantity of tetramethylimidazol-2-ylidene [8] in toluene solution results, after isolation and recrystallization, in a 54% yield of $Ga(C_5Me_5)_2H$·carbene (**1**). A preliminary structure assignment for **1** was based on ^1H- and ^{13}C-NMR spectroscopic data, which evidenced the presence of two C_5Me_5 rings, a carbene, and a hydride. However, the hapticities of the C_5Me_5 rings were not clear from the NMR data hence an X-ray crystallographic study was undertaken. Compound **1** crystallizes in the $P\bar{1}$ space group with $Z = 2$ and there are no unusually short intermolecular contacts. The molecular structure (Fig. 1) features a four-coordinate gallium atom bonded to two η^1-attached C_5Me_5 rings along with the carbene and hydride ligands. The geometry at gallium is distorted tetrahedral. Thus, the bond angle between the two C_5Me_5 ring carbons, C(11) and C(21), is 121.9(2)°, while that between C(11) and the carbenic carbon, C(31), is 105.2(2)°. The hydride ligand was located and refined isotropically and the Ga–H bond distance of 1.62(5) Å is comparable to those reported [3b] for the GaH_3 complex of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (1.58(5) and 1.62(3) Å). The Ga–C (carbene) bond distance of 2.057(5) Å in **1** is also similar to that reported [3b] for the latter GaH_3 complex (2.071(5) Å). The Ga–C(C_5Me_5) bond distances in **1**, which average 2.110(5) Å, are slightly longer than those reported [7] for $Ga(C_5Me_5)_3$ [average 2.038(4) Å], presumably due to the increase in the gallium coordination number from 3 to 4.

A plausible mechanism for the formation of **1** (Scheme 1) involves the initial displacement of a $[C_5Me_5]^-$ anion and formation of a carbene adduct of the decamethylgallocenium cation **2** [9]. Support for

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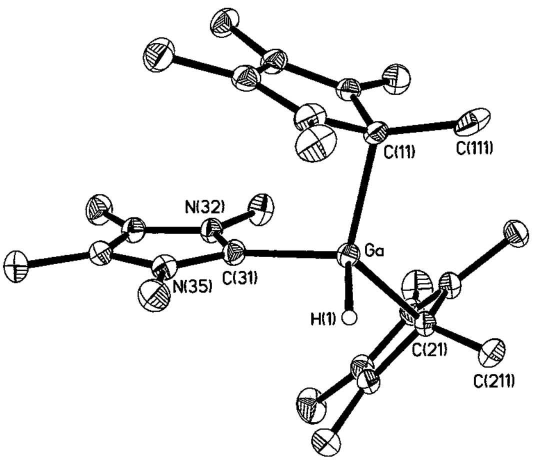


Fig. 1. View of the molecular structure of **1**. Important bond distances (Å) and angles (°), Ga–C(11) 2.102(5), Ga–C(21) 2.119(5), Ga–C(31) 2.057(5), Ga–H(1) 1.62(5), C(11)–Ga–C(21) 121.9(2), C(11)–Ga–C(31) 105.2(2), C(21)–Ga–C(31) 114.8, C(11)–Ga–H(1) 112(2), C(21)–Ga–H(1) 95(2), C(31)–Ga–H(1) 107(2).

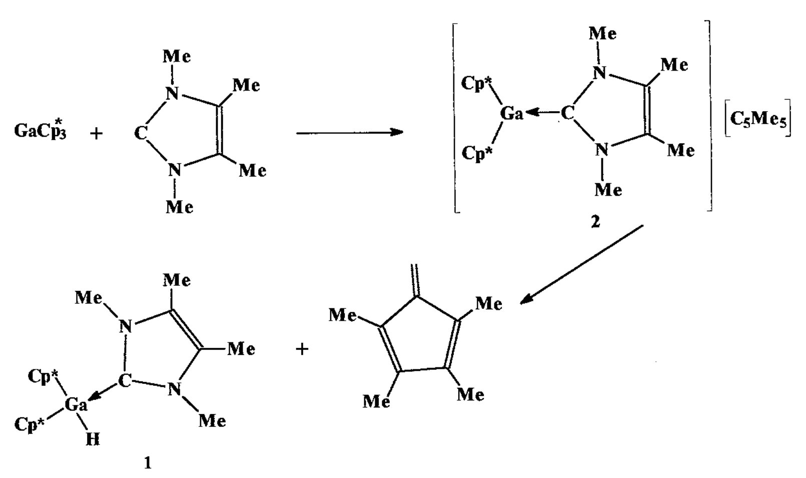
this view is provided by the fact that a similar $[C_5H_5]^-$ displacement/carbene coordination reaction has been observed previously with d-block metallocenes [10]. However, in the case of the gallocenium cation the carbene adduct is evidently unstable and undergoes reaction with the $[C_5Me_5]^-$ counterion via hydride transfer to form **1** and tetramethylfulvene [11]. An alternative mechanism that leads to the same products involves the elimination of the $[C_5Me_5]^\bullet$ radical upon treatment of $Ga(C_5Me_5)_3$ with tetramethylimidazol-2-ylidene to form a carbene adduct of the (unknown) gallyl radical $[Ga(C_5Me_5)_2]^\bullet$. The observed products would then be formed by transfer of a hydrogen atom from $[C_5Me_5]^\bullet$ to the carbene adduct of the $[Ga(C_5Me_5)]^\bullet$ radical. As pointed out by Jutzi and Reumann [12], the $[C_5Me_5]^-$ anion and the $[C_5Me_5]^\bullet$ radical are rather stable entities and hence either or both of them can serve as leaving groups.

2. Experimental

All reactions were performed under a dry, oxygen-free argon atmosphere utilizing Schlenk manifold techniques or a drybox. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on a General Electric QE 300 spectrometer at 295 K (^1H 300.16 MHz; ^{13}C, 75.48 MHz) and chemical shifts are reported relative to $SiMe_4$ ($\delta = 0.00$). High-resolution mass spectra were obtained using a VG Analytical ZABZ-E mass spectrometer operating in the chemical ionization mode with methane as the ionizing gas. Melting points were obtained in capillaries sealed under argon.

2.1. Preparation of (η^1-C_5Me_5)$_2$GaH carbene complex (1)

A solution of 1,3,4,5-tetramethylimidazol-2-ylidene [8] (0.074 g 0.60 mmol) in toluene (20 ml) was added dropwise to a stirred solution of $Ga(C_5Me_5)_3$ [7] (0.280, 0.59 mmol) in 20 ml of toluene at −78 °C. While warming to room temperature (r.t.) over an 8-h period, the color of the reaction mixture darkened slowly from pale yellow to amber. After being stirred at r.t. for a further 24 h, the dark amber solution was filtered through Celite®, and the filtrate was concentrated to a volume of 2 ml. The resulting red oil was cooled to −20 °C to afford a crop of amber crystals, 0.15 g, 54% yield, m.p. 112–113 °C (dec.). HRMS (CI^+, CH_4), Anal. Calc. for $C_{27}H_{42}GaN_2$, $(M–H)^+$, 463.2604; Found: 463.2615. ^1H-NMR (500.00 MHz, 295 K, C_6D_6): δ 7.13 (m, 3H, $o+m$-Ar), 7.02 (m, 2H, p-Ar),



Scheme 1.

3.17 (s, 6H, N–Me), 2.10 (s, 3H, Ar–Me), 1.96 (s, 30H, C_5Me_5), 1.28 (s, 6H, NCMe), 0.20 (s, 1H, Ga–H). $^{13}C\{^1H\}$-NMR (125.8 MHz, 295 K, C_6D_6): δ 140.40 (s, N*C*N), 137.48 (s, *ipso*-Ar), 129.27 (s, *o*-Ar), 128.51 (s, *p*-Ar), 128.29 (N*C*CN), 127.50 (s, *m*-Ar), 119.18 (s, C_5Me$_5$), 34.96 (s, N–Me) 21.50 (Ar–CH_3), 13.30 (s, C$_5$$Me_5$), 7.83 (s, NC*Me*).

2.1.1. Crystal data

$C_{27}H_{43}GaN_2$, $M = 465.35$, triclinic, space group $P\bar{1}$, $a = 8.6290(3)$, $b = 9.9040(3)$, $c = 17.8440(3)$ Å, $\alpha = 91.477(1)$, $\beta = 78.984(1)$, $\gamma = 75.105(1)°$, $V = 1442.07(7)$ Å^3, $D_{calc} = 1.072$ g cm^{-3}, $Z = 2$, $\lambda(\text{Mo–K}_\alpha) = 0.71073$ Å, $\mu(\text{Mo–K}_\alpha) = 9.68$ cm^{-1}. A total of 6616 independent reflections was collected on a Nonius Kappa diffractometer at 153(2) K with 2θ between 5.84 and 55.08°. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to R_1 and wR_2 values of 0.0944 and 0.1195, respectively. Compound **1** crystallizes with one disordered toluene molecule per formula unit.

Acknowledgements

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