10.1071/CH11193_AC

Australian Journal of Chemistry 2011, 64(8), 1173–1176

Accessory Publication

A Neutral Gallium(I) N-Heterocyclic Carbene Analogue: Synthesis, Characterisation and Theoretical Analysis

Sam L. Choong,[A] *William D. Woodul,*[A] *Andreas Stasch,*[A] *Christian Schenk*[A] *and Cameron Jones*[A,B]

[A]School of Chemistry, PO Box 23, Monash University, Melbourne, Vic., 3800, Australia.

[B]Corresponding author. Email: cameron.jones@monash.edu

X-Ray Crystallography

Crystals of **1** and **2** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[1]using all unique data. The relatively high R-factors for the crystal structure of **2** are due to high thermal displacement parameters for the C and F atoms of the aluminate anion, $[Al\{OC(CF_3)_3\}_4]^-$, of the salt. Attempts to model disorder of the CF_3 groups of this anion were not successful. The problems associated with the crystallographic refinement of this weakly coordinating anion are well recognised and have been previously discussed.[2] Despite this, the geometrical parameters for the cation of the salt, which displays no significant interaction with the anion, are reliable and of sufficient accuracy for comparison with the parameters for **1** (see main text).

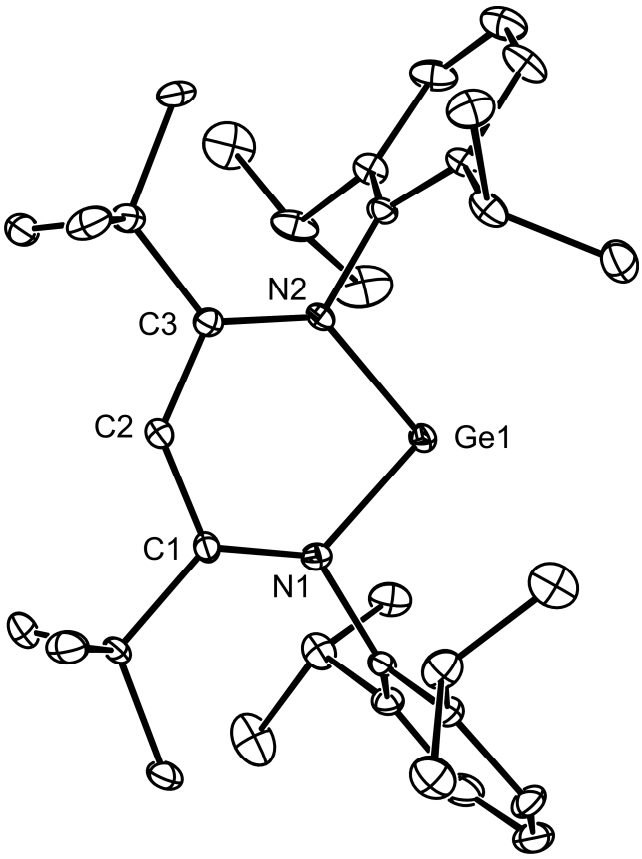

Fig. S1. ORTEP diagram of the cationic component of **2** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Ge(1)-N(2) 1.895(5), Ge(1)-N(1) 1.896(6), N(1)-C(1) 1.333(9), N(2)-C(3) 1.359(8), C(1)-C(2) 1.413(10), C(2)-C(3) 1.388(9), N(2)-Ge(1)-N(1) 93.6(2), C(3)-C(2)-C(1) 132.3(6).

Computational Studies

For quantum-chemical calculations the Turbomole[3] program package was used, employing the Becke-Perdew 86-functional[4] at RI-DFT[5] level with the def2-TZVPP basis set[6] for the Ga and N atoms and the SVP basis set[7] for the remaining C and H atoms. The molecular orbitals of the global minimum energy structure (showing zero imaginary frequencies) were visualized with the aid of molden.[8] NBO orbital analyses were performed using the program packages Gaussian09[9] and NBO 3.0[10] at the same combination of functional and basis sets as mentioned above. The population analysis was carried out according to the Ahlrichs-Heinzmann method.[11]

The optimised geometry of [:Ga(^{Buf}Nacnac)] **1a** (E = -3399.29788 Hartree) obtained using Turbomole (see above) is in good agreement with the experimental solid state structure of **1**. The calculated structure of **1a** is depicted in Figure S2.

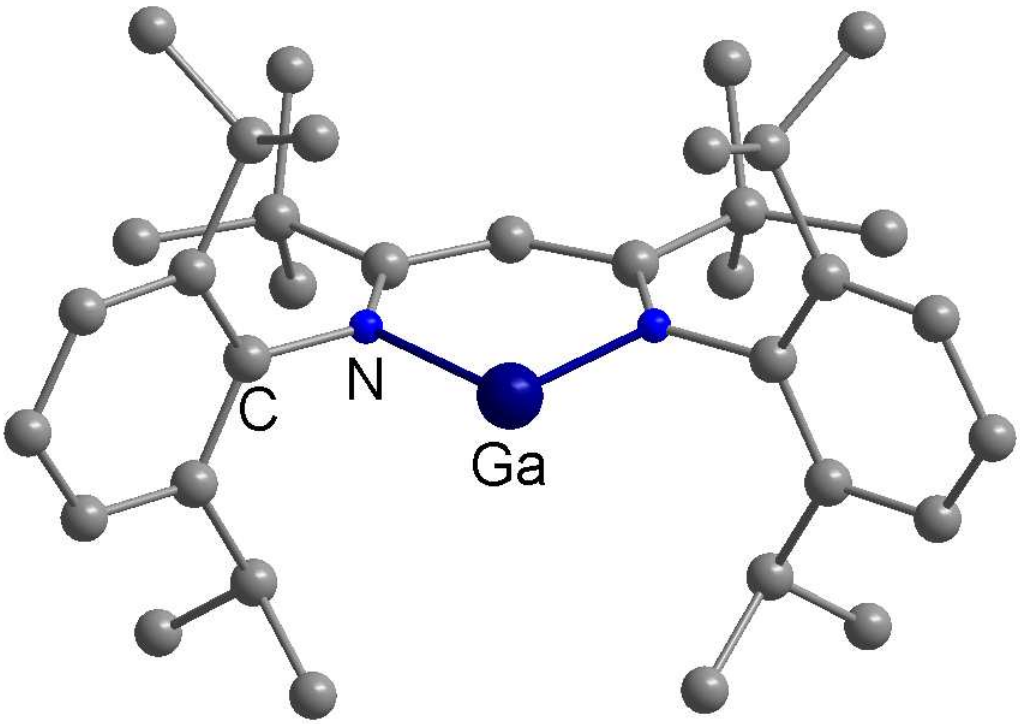

Fig. S2. Calculated structure of [:Ga(^{But}Nacnac)] **1a** (hydrogen atoms are omitted for clarity).

Table S1. Cartesian coordinates for the calculated structure of **1a**.

Ga	-0.00100	-1.27400	-0.00200
N	1.50500	0.23700	0.01000
N	-1.50500	0.23800	-0.01000
C	2.74800	-0.47600	0.00300
C	-2.74800	-0.47500	-0.00500
C	1.30900	1.56300	0.01800
C	-1.30800	1.56400	-0.01400
C	3.29800	-0.94500	1.23500
C	3.32400	-0.87400	-1.24200
C	-3.29800	-0.94200	-1.23700
C	-3.32300	-0.87600	1.24000
C	2.44400	2.66300	0.04900
C	0.00000	2.11700	0.00300
C	-2.44300	2.66400	-0.04200
C	4.44500	-1.76300	1.19400
C	2.67100	-0.60900	2.59100
C	4.46900	-1.69400	-1.22400
C	2.72000	-0.46100	-2.58700
C	-4.44400	-1.76100	-1.19700
C	-2.67200	-0.60200	-2.59300

C	-4.46800	-1.69800	1.22000
C	-2.71900	-0.46600	2.58600
C	3.90400	2.15800	0.06200
C	2.26500	3.52300	1.33100
C	2.30400	3.56500	-1.20900
C	-3.90400	2.15900	-0.05600
C	-2.26500	3.52700	-1.32200
C	-2.30300	3.56300	1.21800
C	5.03700	-2.13300	-0.02000
C	2.04900	-1.86600	3.23900
C	3.66400	0.06400	3.56300
C	2.04200	-1.66500	-3.27600
C	3.74600	0.19800	-3.53500
C	-5.03600	-2.13400	0.01600
C	-2.05200	-1.85800	-3.24500
C	-3.66600	0.07400	-3.56200
C	-2.04200	-1.67300	3.27300
C	-3.74400	0.19200	3.53400
H	0.00000	3.21000	0.00400
H	4.88400	-2.12400	2.13900
H	1.84600	0.11300	2.40800
H	4.92700	-2.00200	-2.17900
H	1.92900	0.29100	-2.38200
H	-4.88300	-2.12000	-2.14300
H	-1.84700	0.11800	-2.40800
H	-4.92500	-2.00800	2.17500
H	-1.92700	0.28500	2.38200
H	4.57500	3.04600	0.09000
H	4.16600	1.57100	-0.84000
H	4.13800	1.53500	0.94700
H	2.35000	2.89500	2.24600
H	1.28700	4.04600	1.37100
H	3.06300	4.29900	1.37800
H	3.10600	4.33800	-1.20800
H	1.33000	4.09600	-1.25800
H	2.41100	2.96800	-2.14100
H	-4.57500	3.04700	-0.08200
H	-4.16600	1.57000	0.84400
H	-4.13800	1.53800	-0.94200
H	-2.35100	2.90200	-2.23800
H	-1.28600	4.04900	-1.36100
H	-3.06200	4.30400	-1.36600
H	-3.10500	4.33500	1.22000
H	-1.32900	4.09300	1.26800
H	-2.40900	2.96300	2.14900
H	5.93400	-2.77400	-0.03000
H	1.30000	-2.33700	2.56300
H	1.54100	-1.60700	4.19500
H	2.82600	-2.63100	3.46100
H	4.49800	-0.61900	3.84000
H	3.14800	0.35500	4.50600
H	4.11400	0.98300	3.12600

H	2.78200	-2.46300	-3.51100
H	1.55700	-1.35400	-4.22900
H	1.26200	-2.11600	-2.62200
H	4.24800	1.06900	-3.06000
H	3.24200	0.55800	-4.46000
H	4.53900	-0.51700	-3.84900
H	-5.93300	-2.77500	0.02500
H	-1.30200	-2.33100	-2.57200
H	-1.54500	-1.59600	-4.20100
H	-2.83000	-2.62200	-3.46900
H	-4.50100	-0.60700	-3.83900
H	-3.15100	0.36700	-4.50400
H	-4.11400	0.99200	-3.12200
H	-2.78300	-2.47000	3.50600
H	-1.55800	-1.36400	4.22700
H	-1.26300	-2.12300	2.61900
H	-4.24500	1.06500	3.06100
H	-3.24100	0.54900	4.46100
H	-4.53900	-0.52300	3.84700

References

[1] G.M. Sheldrick, *SHELX-97*, University of Göttingen, **1997**.

[2] I. Krossing, A. Resinger, *Coord. Chem. Rev.* **2006**, *250*, 2721. doi:10.1016/j.ccr.2005.10.023.

[3] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346. doi:10.1063/1.469408

[4] (a) J.P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822. doi:10.1103/PhysRevB.33.8822
(b) A.D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. doi:10.1103/PhysRevA.38.3098

[5] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283. doi:10.1016/0009-2614(95)00621-A

[6] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297. doi:10.1039/b508541a

[7] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571. doi:10.1063/1.463096.

[8] G. Schaftenaar, J. H. Noordik, *Mol. Design* **2000**, *14*, 123. doi:10.1023/A:1008193805436

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K.

Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Wallingford CT, **2009**.

[10] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899. doi:10.1021/cr00088a005.

[11] (a) E.R. Davidson, *J. Chem. Phys.* **1967**, *46*, 3320. doi:10.1063/1.1841219.

(b) K.R. Roby, *Mol. Phys.* **1974**, *27*, 81. doi:10.1080/00268977400100071.

(c) R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33. doi:10.1007/BF00548289.

(d) C. Erhardt, R. Ahlrichs, *Theor. Chim. Acta* **1985**, *68*, 231. doi:10.1007/BF00526774.