

Chemical bonding and electron localization in a Ga(I) amide.

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Common to almost all metal amides including a terminal M-N(R)R' moiety is that they possess a trigonal planar N geometry. The reason for this particular geometry has been widely discussed, and one of the explanations presented has previously been multiple M-N bonding.¹ In an attempt to shed more light on this situation, we present here a study of the chemical bonding and electronic properties in a monovalent one-coordinate Ga-amide² (**1**, Figure 1) with particular emphasis on the chemical reactivity and the geometry around the N atom. For this purpose, the electron density in **1** has been determined theoretically from a single point B3LYP/6-311G** calculation and experimentally from multipole modelling³ of X-ray data collected at 90 K. There is no strong evidence for multiple bonding involving the N atom. Instead, the topology of both the Laplacian distribution and the ELI-D⁴ describe a situation with a N atom having a tetrahedral arrangement of two single σ -bonds (to C and Si) and two lone pairs pointing towards Ga in a scissor grasp (Figure 2). This behavior, in combination with the evidence found for significant ionicity in the Ga-N bond, suggests that the trigonal planar N geometry is rather the result of a partly electrostatic interaction between the positively charged Ga and an sp^3 hybridized N atom in ($::N(R)R'$).

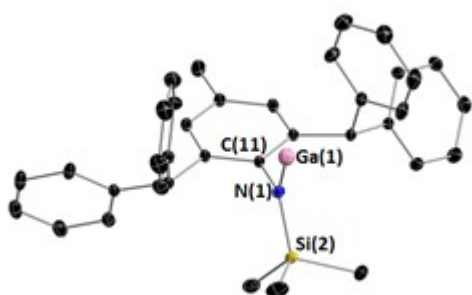


Figure 1: ORTEP drawing of the molecular unit of **1**. Hydrogen atoms have been omitted for clarity.

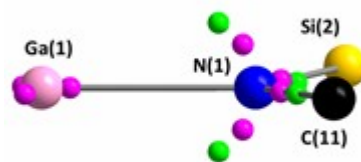


Figure 2: $-\nabla^2\rho(\mathbf{r})$ maxima from the B3LYP/6-311G** electron density (pink) and B3LYP/6-311G** ELI-D maxima (green) around N(1) and Ga(1) in **1**.

1. See for example: a) R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 12498-12509; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463-3503; c) M. Lappert, P. P. Power, A. Protchenko, A. Seeber, *Metal Amide Chemistry*, John Wiley & Sons Ltd, Chichester, **2009**.
2. D. Dange, J. Y. Li, C. Schenk, H. Schnockel, C. Jones, *Inorg. Chem.* **2012**, *51*, 13050-13059.
3. N. K. Hansen, P. Coppens, *Acta Crystallogr. Sect. A* **1978**, *34*, 909-921.
4. a) M. Kohout, *Int. J. Quantum Chem.* **2004**, *97*, 651-658; b) M. Kohout, F. R. Wagner, Y. Grin, *Int. J. Quantum Chem.* **2006**, *106*, 1499-1507; c) M. Kohout, *Faraday Discuss.* **2007**, *135*, 43-54; d) F. R. Wagner, V. Bezugly, M. Kohout, Y. Grin, *Chem. Eur. J.* **2007**, *13*, 5724-5741; e) V. Bezugly, P. Wielgus, M. Kohout, F. R. Wagner, *J. Comput. Chem.* **2010**, *31*, 1504-1519.