J|A|C|S
COMMUNICATIONS

Coordination Chemistry Umpolung: A Gallane Ligand on a Phosphine Lewis Acceptor

Neil Burford,* Paul J. Ragogna, Katherine N. Robertson, and T. Stanley Cameron

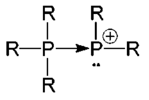
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

Ned J. Hardman and Philip P. Power

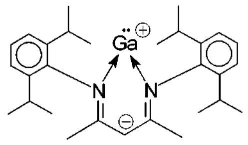
Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, California 95616

Received August 31, 2001

“Coordinate” bonds result from the interaction between electron-rich centers (Lewis base or donor) and electron-deficient (Lewis acid or acceptor) centers. As such, this bonding model is essentially restricted to the chemistry of transition metals and the elements of group 13. Reports of transition metal complexes behaving as Lewis donors (ligands) toward other metals[1] and compounds involving phosphines (bearing lone pairs) behaving as Lewis acceptors toward amines,[2−5] phosphines,[6−8] and arenes[9] highlight a new dimension in coordination chemistry. The coordinate nature of the (phosphine)-P→P(phosphenium) bond in phosphinophosphonium cations **1** has been demonstrated by phosphine ligand exchange reactions,[10] which we have now exploited to demonstrate the first (gallane)Ga→P-(phosphine) coordination.

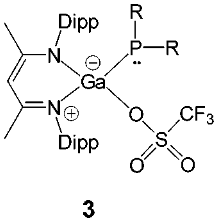


1



2

The ^{31}P NMR spectrum of the reaction mixture containing $[Ph_3P{-}PPh_2][SO_3CF_3]$ (**1**, R = Ph) and gall(I)ane[11] **2** shows two singlets, assigned to Ph_3P ($\delta = -5$ ppm) and a new complex **3** ($\delta = -57$ ppm), which has been isolated and comprehensively characterized.[12] In the context of the recently reported (gallane)-Ga→group 13 complexes[12,13] the quantitative reaction is best described as a ligand exchange of Ph_3P by **2** at the Ph_2P^+ Lewis acceptor site.



3

The solid-state structure of **3** (Figure 1) confirms the Ga−P connectivity and reveals an association of one oxygen atom of the triflate anion with the gallium center. The geometry about phosphorus is typical for a phosphine, and the C−P−C angle [105.4(5)°] is comparable with those observed in the precursor $[Ph_3P{-}PPh_2][SO_3CF_3]$, [104.25(16)°].[10] The phenyl substituents on phosphorus are apparently sterically involved with the diisopropylphenyl (Dipp) substituents, and the conformational features are retained in solution as the ^{1}H NMR data shows distinct isopropyl and methyl signals. The gallium center adopts a distorted tetrahedral geometry and is dislodged from the heterocyclic C_3N_2 plane, in contrast to the planar free ligand **2**.[11] Nevertheless, the Ga−N distances [1.950(8) Å and 1.931(8) Å] are slightly shorter [cf. **2**, 2.0528(14) Å and 2.0560(13) Å] and the N−Ga−N angle [98.3(3)°] is larger [cf. **2**, 87.56(6)°]. The Ga−O distance [1.979(6) Å] is substantially shorter than the P−O distance [3.242(7) Å], suggesting a preference for Ga−O covalency and avoiding coordinative unsaturation and electron deficiency at gallium.

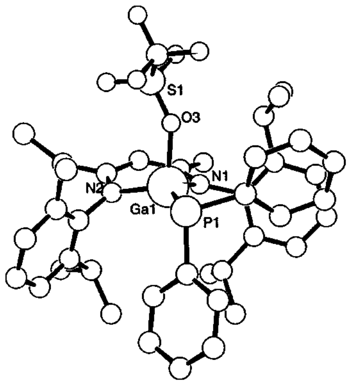


Figure 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Ga(1)−P(1) 2.312(3), Ga(1)−O(3) 1.979(6), Ga(1)−N(1) 1.950(8), Ga(1)−N(2) 1.931(8), P(1)−O(3) 3.242(7), and C(36)−P(1)−C(30) 105.4(5), C(36)−P(1)−Ga(1) 102.3(3) C(30)−P(1)−Ga(1) 108.4(4), N(1)−Ga-P(1) 132.5(3), N(2)−Ga−P(1) 122.7(3), O(3)−Ga−P(1) 97.9(2), N(2)−Ga−N(1) 98.3(3), N(2)−Ga−O(3) 102.0(3), N(1)−Ga−O(3) 95.4(3).

The structures of **1**, **2**, and **3** all represent diversions from traditional p-block chemistry in terms of the environments of gallium and phosphorus, and conventional Lewis models need to evolve to appreciate the unusual bonding. Despite the Lewis acidic tradition for the chemistry of group 13 elements, the coordinatively unsaturated and lone pair-bearing nature of the gallium center in the recently reported gall(I)anes[13−15] such as **2**,[11] and the related alane,[16] identifies them as viable Lewis bases. In this context, the formation of compound **3** from **1** can be considered in terms of the introduction of a gallium ligand on a phosphenium cation and represents[17] a “coordination chemistry umpolung” (a converse of the traditional coordinate bond) in that the metal center (gallium) behaves as the donor (ligand) and the electron-rich nonmetal center (phosphorus) behaves as the Lewis acceptor. Tetracoordinate gallium bound to an electron-rich tricoordinate phosphine is unusual,

10.1021/ja012081k CCC: $22.00 © 2002 American Chemical Society

but reminiscent of the recently reported base-induced dissociation of 13/15 oligomers.[18,19] More importantly, the isolation and characterization of the gallaphosphorus triflate **3** highlights the synthetic utility of the ligand exchange process at phosphorus as a versatile approach for element−P bond formation. We are currently assessing the potential diversity of this procedure.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Killam Foundation for funding, and the Atlantic Region Magnetic Resonance Center and Dalx for the use of instrumentation.

References

(1) Liu, Y.; Leong, K.; Pomeroy, R. K. *Organometallics* **1998**, *17*, 3387−3389.
(2) Bouhadir, G.; Reed, R. W.; Reau, R.; Bertrand, G. *Heteroat. Chem.* **1995**, *6*, 371−375.
(3) Burford, N.; Cameron, T. S.; Robertson, K. N.; Phillips, A. D.; Jenkins, H. A. *J. Chem. Soc., Chem. Commun.* **2000**, 2087−2088.
(4) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Phillips, A. D.; Concolino, T. E.; Lam, K. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5413−5414.
(5) Burford, N.; Losier, P.; Bakshi, P. K.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1996**, 307−308.
(6) David, G.; Niecke, E.; Nieger, M.; Radseck, J.; Schoeller, W. W. *J. Am. Chem. Soc.* **1994**, *116*, 2191−2192.
(7) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460−5467.
(8) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712−4717.
(9) Burford, N.; Clyburne, J. A. C.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1995**, *14*, 1578−1585.
(10) Burford, N.; Cameron, T. S.; Ragogna, P. J.; Ocando-Mavarez, E.; Gee, M.; McDonald, R.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 7947−7948.
(11) Hardman, N. J.; Eichler, B. E.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **2000**, 1991−1992.
(12) Using established procedures for handling compounds under vacuum,[20] a solution of **2** (0.15 g (0.33 mmol) in C_6H_6 (60 mL) was added dropwise to a slurry of $[Ph_3P-PPh_2][OTf]$ (0.20 g, 0.33 mmol) in C_6H_6 (60 mL) over 1 h with stirring at room temperature. After 12 h, the solvent was removed from the colorless solution in vacuo, and the white solid **3** was washed with C_6H_6 (10 mL) and recrystallized from CH_2Cl_2; yield: 69%; Anal. Calcd C 61.40, H 6.26, N 3.41; Found C 61.27, H 6.46, N 3.42; IR cm^{-1} (ranked intensities): 627(11), 727(18), 736(7), 744(20), 806(17), 939(19), 1011(4), 1154(12), 1164(10), 1184(6), 1202(2), 1235(8), 1260(16), 1288(15), 1305(14), 1317(9), 1339(5), 1345(3), 1366(1), 1507(13); NMR ($CDCl_3$): $^{31}P\{^1H\}$ (rel. H_3PO_4) −57 ppm. Crystal data for $C_{42}H_{51}F_3GaN_2O_3PS$: MW = 821.63 g mol^{-1}, monoclinic, $P2_1$, $a = 10.266(1)$ Å, $b = 19.810(2)$ Å, $c = 25.714(2)$ Å, $\alpha = 90°$, $\beta = 113.41(1)°$, $\gamma = 90°$, $V = 2062.2(4)$ Å^3, $T = 293(2)$K, $Z = 2$, μ(Mo Kα) = 21.9 cm^{-1}, 3679 measured reflections, 3465 unique, 479 refined parameters, $2\theta_{max} = 127.20°$, σ limits $0 \le h \le 11$, $0 \le k \le 23$, $-12 \le l \le 11$, data were corrected for Lorentz and Polarization effects, ψ scan absorption correction, refinement using SHELX-97 full-matrix least-squares on F^2, hydrogen atoms were placed in geometrically calculated positions but not refined, largest difference peak and hole 0.424 and −0.662 e Å^3, $R[I > 2\sigma(I)] = 0.0394$, wR2($F^2$) = 0.0876; CCDC 167029.
(13) Hardman, N.; Power, P. P.; Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **2001**, 1866−1867.
(14) Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **2001**, *20*, 2854−2858.
(15) Schmidt, E. S.; Jockisch, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1999**, *121*, 9758−9759.
(16) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpesu, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 4274−4275.
(17) Arduengo, A. J.; Clyburne, J. A. C.; Carmalt, C. J.; Cowley, A. H.; Pyati, R. *J. Chem. Soc., Chem. Commun.* **1997**, 981−982.
(18) Schulz, S. *Coord. Chem. Rev.* **2001**, *215*, 1−37.
(19) Thomas, F.; Schulz, S.; Nieger, M. *Eur. J. Inorg. Chem.* **2001**, 161−166.
(20) Burford, N.; Müller, J.; Parks, T. M. *J. Chem. Educ.* **1994**, *71*, 807−809.

JA012081K