Platinum Complexes

DOI: 10.1002/anie.200702726

Interaction between d- and p-Block Metals: Synthesis and Structure of Platinum–Alane Adducts**

Holger Braunschweig, Katrin Gruss, and Krzysztof Radacki*

Dative bonds between transition metals and the archetypal Lewis acid BF_3 were proposed as early as 1966,[1] but were called into question 30 years later.[2] However, more recent work by Hill,[3] Parkin,[4] Bourissou,[5] and Rabinovich[6] and respective co-workers has demonstrated that borane complexes of the type $[L_nM{-}BR_3]$[7] can be obtained from a range of late Lewis basic transition metals, and the nature of the dative metal–boron bond has been elucidated by experimental and computational studies. In addition, the metal–phosphine fragments $\{M(PCy_3)\}$ (M = Pd, Pt) have proven to act as versatile metal bases towards a range of coordinated boryl[8] and borylene ligands.[9]

The heavier Group 13 elements are also known to form a variety of transition-metal complexes, in analogy to boron.[10] Despite the plethora of complexes with transition-metal–aluminum bonds, however, corresponding alane complexes $[L_nM{-}AlR_3]$ are exceptionally rare. Structural evidence for an unsupported dative transition-metal–aluminum bond is to our knowledge restricted to the ionic species $[NEt_4][(\eta^5\text{-}C_5H_5)(OC)_2Fe{-}AlPh_3]$.[11] Bergman and co-workers reported the synthesis of $[(\eta^5\text{-}C_5Me_5)(Me_3P)IrH_2(AlPh_3)]$, which, according to structural data, has a certain amount of Ir–Al interaction. This metal–metal bond, however, is supported by two bridging hydrogen atoms.[12] Given the pronounced propensity of zerovalent platinum to add to three-coordinate boron centers, we initiated studies to extend this chemistry to the higher homologue, aluminum. Herein we report the first neutral alane complexes with an unsupported dative bond.

The reaction of $AlCl_3$ with an equimolar amount of $[Pt(PCy_3)_2]$ (**1**) in C_6D_6 was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A new resonance at $\delta = 53.5$ ppm ($^1J_{PtP} = 3032$ Hz) was observed that is shifted only marginally upfield with respect to that of **1** ($\delta = 62.3$ ppm, $^1J_{PtP} = 4161$ Hz).[13] Corresponding reactions between Pt^0 species and BCl_3 or other boron halides usually proceed by oxidative addition of the boron–halogen bond to the platinum center, which is accompanied by a significant upfield shift of the $^{31}P\{^1H\}$ NMR spectroscopic resonances.[14] Thus, the chemical shift observed herein provided a strong indication that the reaction takes a different course.

After workup, a colorless crystalline material was obtained in almost quantitative yield, for which the elemental analysis revealed a 1:1 composition with respect to the starting materials. The formulation of this compound as the platinum alane complex *trans*-$[(Cy_3P)_2Pt{-}AlCl_3]$ (**2**) was shown by a single-crystal X-ray diffraction study (Figure 1).[15] Complex **2** crystallizes in the triclinic space group $P\bar{1}$, and the platinum center adopts an unusual T-shaped geometry with a P-Pt-P angle of 162.07(2)°. Similar geometries have only been reported for the related SO_2 complex *trans*-$[(Cy_3P)_2Pt{-}SO_2]$ (P-Pt-P 165.72(4)°)[16] and the platinum(II) boryl complex *trans*-$[(Cy_3P)_2Pt\{B(Fc)Br\}][BAr^F{}_4]$ ($Fc = [(\eta^5\text{-}C_5H_4)Fe(C_5H_5)]$, $Ar^F = 3,5\text{-}C_6H_3(CF_3)_2$; P-Pt-P 162.96(3)°).[17] The most prominent structural feature of **2** is the presence of an unsupported platinum–aluminum bond with a Pt–Al separation of 2.3857(7) Å, which only slightly exceeds that of zerovalent platinum alanediyl complexes, for example, $[(dcpe)Pt(AlCp^*)_2]$ (dcpe = 1,2-bis(dicyclohexylphosphanyl)ethane, $Cp^* = Me_5C_5$; 2.327(2) and 2.335(2) Å). The diyl complex, however, has an additional Pt−Al π backdonation, thus resulting in a short Pt–Al bond.[18]

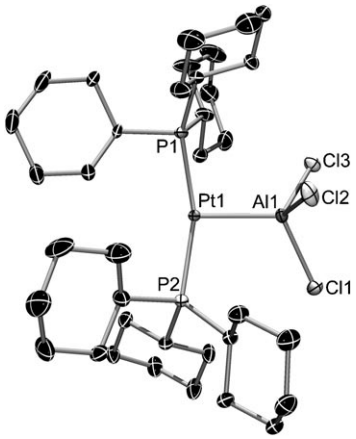


Figure 1. Molecular structure of **2** (hydrogen atoms omitted; thermal ellipsoids are set at 50% probability). Selected bond lengths [Å] and angles [°]: Pt1-Al1 2.3857(7), Al1-Cl1 2.1548(10), Al1-Cl2 2.1511(10), Al1-Cl3 2.1576(9); P1-Pt1-P2 162.07(2).

Since the compound **2** represents the first example of a platinum–alane complex, it is instructive to compare the geometry of the $AlCl_3$ moiety with that of corresponding adducts $[Cl_3Al{-}D]$ (D = main-group-element base). For these systems, a correlation of the Cl-Al-Cl angles and Al−Cl bond lengths with the stability of the appropriate adducts has been

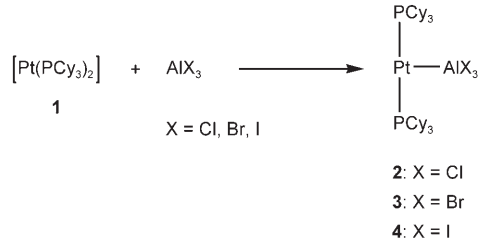
[*] Prof. Dr. H. Braunschweig, K. Gruss, K. Radacki
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de

[**] Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

established from computational[19] and experimental studies. Although monomeric $AlCl_3$ has trigonal-planar geometry, formation of the adduct $[AlCl_3(C_3N_3Cl_3)]$ imposes a significant decrease of the Cl-Al-Cl angles (113.2°) associated with an increase of the Al–Cl bond lengths (from 2.06 to 2.107 Å).[20] Similar trends were also observed for $[AlCl_3$-(dmap)] (dmap = 4-(dimethylamino)pyridine; 111.6°, 2.116 Å).[21] In comparison, complex **2** displays even more acute Cl-Al-Cl angles (105.91° mean) and notably elongated Al–Cl bonds (2.1545 Å mean), thus suggesting a strong dative Pt–Al bond.

Analogous reactions of **1** with $AlBr_3$ and AlI_3 resulted in the formation of the related alane complexes *trans*-$[(Cy_3P)_2Pt{-}AlBr_3]$ (**3**) and *trans*-$[(Cy_3P)_2Pt{-}AlI_3]$ (**4**; Scheme 1), which were isolated in almost quantitative yields



Scheme 1. Synthesis of platinum alane complexes **2**–**4**.

as pale orange (**3**) or red-brown (**4**) solids. The formulations were supported by $^{31}P\{^1H\}$ NMR spectroscopy data (**3**: $\delta =$ 51.2 ppm, $^1J_{PPt} = 3046$ Hz; **4**: $\delta = 46.8$ ppm, $^1J_{PPt} = 3062$ Hz). Alane complexes **2**–**4** are all extremely sensitive towards air and moisture. Although all the compounds are stable in the solid state, **3** and **4** tend to decompose after 1–2 days in solution to yield *trans*-$[(Cy_3P)_2PtX_2]$ and *trans*-$[(Cy_3P)_2Pt(H)X]$ (X = Br, I), as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.[22]

In conclusion, the first platinum alane complexes are reported, which display an unsupported bond between a d-block and a p-block metal. From the structural data of *trans*-$[(Cy_3P)_2Pt{-}AlCl_3]$ (**2**) the presence of a strong dative Pt–Al bond can be concluded.

Experimental Section

2: $AlCl_3$ (0.004 g, 0.026 mmol) was added to a pale yellow solution of **1** (0.020 g, 0.026 mmol) in benzene (1 mL) in a NMR tube fitted with a Young's stopcock. The solution was kept at room temperature for 24 h to yield **2** as colorless crystals (0.021 g, 93%). ^1H NMR (500.1 MHz, C_6D_6, 25 °C): $\delta = 2.60$–0.92 ppm (m, 66 H, Cy); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 36.3$ (virtual triplet, N[23] = 26 Hz, C^1, Cy), 31.6 (s, C^3, C^5, Cy), 27.9 (m, C^2, C^6, Cy), 26.6 ppm (s, C^4, Cy); $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6, 25 °C): $\delta = 53.5$ ppm ($^1J_{PtP} =$ 3032 Hz). Elemental analysis (%) calcd for $C_{36}H_{66}AlCl_3P_2Pt$: C 48.62, H 7.48; found: C 48.34, H 7.14.

Received: June 21, 2007
Published online: September 5, 2007

Keywords: alanes · aluminum · coordination modes · Lewis bases · platinum

[1] M. P. Johnson, D. F. Shriver, *J. Am. Chem. Soc.* **1966**, *88*, 301–304.
[2] a) H. Braunschweig, T. Wagner, *Chem. Ber.* **1994**, *127*, 1613–1614; b) H. Braunschweig, T. Wagner, *Z. Naturforsch. B* **1996**, *51*, 1618–1620; c) H. Braunschweig, C. Kollann, *Z. Naturforsch. B* **1999**, *54*, 839–842.
[3] a) A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem.* **1999**, *111*, 2920–2923; *Angew. Chem. Int. Ed.* **1999**, *38*, 2759–2761; b) I. A. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2006**, *25*, 289–299.
[4] a) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny, G. Parkin, *Inorg. Chem.* **2006**, *45*, 2588–2597; b) K. Pang, S. M. Quan, G. Parkin, *Chem. Commun.* **2006**, 5015–5017.
[5] a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem.* **2006**, *118*, 1641–1644; *Angew. Chem. Int. Ed.* **2006**, *45*, 1611–1614; b) S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057.
[6] D. J. Mihalcik, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold, D. Rabinovich, *Dalton Trans.* **2004**, 1626–1634.
[7] For a recent review covering aspects of borane complexes, see: H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380–5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274.
[8] H. Braunschweig, K. Radacki, D. Rais, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1217–1219; *Angew. Chem. Int. Ed.* **2005**, *44*, 1192–1194.
[9] a) H. Braunschweig, D. Rais, K. Uttinger, *Angew. Chem.* **2005**, *117*, 3829–3832; *Angew. Chem. Int. Ed.* **2005**, *44*, 3763–3766; b) H. Braunschweig, K. Radacki, D. Rais, F. Seeler, *Angew. Chem.* **2006**, *118*, 1087–1090; *Angew. Chem. Int. Ed.* **2006**, *45*, 1066–1069; c) H. Braunschweig, C. Burschka, M. Burzler, S. Metz, K. Radacki, *Angew. Chem.* **2006**, *118*, 4458–4461; *Angew. Chem. Int. Ed.* **2006**, *45*, 4352–4355; d) H. Braunschweig, K. Radacki, D. Rais, K. Uttinger, *Organometallics* **2006**, *25*, 5159–5164; e) H. Braunschweig, K. Radacki, K. Uttinger, *Eur. J. Inorg. Chem.* **2007**, DOI: 10.1002/ejic.200700356.
[10] For a comprehensive review, see: R. A. Fischer, J. Weiss, *Angew. Chem.* **1999**, *111*, 3002–3022; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830–2850.
[11] J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, R. E. Hughes, *Inorg. Chem.* **1979**, *18*, 1097–1105.
[12] J. T. Golden, T. H. Peterson, P. L. Holland, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1998**, *120*, 223–224.
[13] S. Otsuka, T. Yoshida, M. Matsumoto, K. Nakatsu, *J. Am. Chem. Soc.* **1976**, *98*, 5850–5858; the significantly reduced Pt–P coupling observed for **2**–**4** is presumably due to the increased coordination number of the platinum center.
[14] a) Recently, *trans*-$[PtCl(BCl_2)(PPh_3)_2]$ was obtained by oxidative addition of BCl_3; $^{31}P\{^1H\}$ NMR: $\delta = 23$ ppm, $^1J_{PPt} = 3046$ Hz: J. P. H. Charmant, C. Fan, N. C. Norman, P. G. Pringle, *Dalton Trans.* **2007**, 114–123; For further examples of boron–halogen addition to Pt^0, see reviews: b) G. J. Irvine, G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whitell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685–2722; c) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559; d) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1–51; e) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882–1898; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786–1801.
[15] The crystal data of **2** were collected at a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the SHELX software package (G. Sheldrick, University of Göttingen, **1997**) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned

idealized positions and were included in structure factor calculations. Crystal data for **2**: $C_{51}H_{81}AlCl_3P_2Pt$, $M_r = 1084.52$, colorless plates, $0.35 \times 0.25 \times 0.08\ mm^3$, triclinic space group $P\bar{1}$, $a = 11.0306(5)$, $b = 19.0585(9)$, $c = 24.4351(12)$ Å, $\alpha = 86.181(2)$, $\beta = 84.304(2)$, $\gamma = 87.857(2)°$, $V = 5097.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.413\ g\,cm^{-3}$, $\mu = 3.023\ mm^{-1}$, $F(000) = 2236$, $T = 100(2)$ K, $R_1 = 0.0365$, $wR^2 = 0.0755$, 29252 independent reflections ($2\theta = 64.06°$) and 1195 parameters. CCDC-651210 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] J. M. Ritchey, D. C. Moody, R. R. Ryan, *Inorg. Chem.* **1983**, *22*, 2276 – 2280.

[17] H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 5796 – 5799; *Angew. Chem. Int. Ed.* **2005**, *44*, 5651 – 5654.

[18] D. Weiss, T. Steinke, M. Winter, R. A. Fischer, *Organometallics* **2000**, *19*, 4583 – 4588.

[19] A. Y. Timoshkin, A. V. Suvorov, H. F. Bettinger, H. F. Schaefer III, *J. Am. Chem. Soc.* **1999**, *121*, 5687 – 5699.

[20] S. Tragl, K. Gibson, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 470 – 472.

[21] F. Thomas, T. Bauer, S. Schulz, M. Nieger, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2018 – 2027.

[22] For $^{31}P\{^1H\}$ NMR of *trans*-$[(Cy_3P)_2Pt(H)X]$ (X = Br, I) see: a) N. A. Jasmin, R. N. Perutz, *J. Am. Chem. Soc.* **2000**, *122*, 8685 – 8693; for $^{31}P\{^1H\}$ NMR of *trans*-$[(Cy_3P)_2PtX_2]$ (X = Br, I), see b) T. S. Cameron, H. C. Clark, A. Linden, A. M. Nicholas, *Polyhedron* **1990**, *9*, 1683 – 1688; c) I. M. Al-Najjar, *Inorg. Chim. Acta* **1987**, *128*, 93 – 104.

[23] $N = |{}^1J_{PC} + {}^3J_{PC}|$; for details on the virtual coupling constant N see J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, M. Weeks, *J. Am. Chem. Soc.* **1969**, *91*, 1941 – 1947.

