Angewandte
Zuschriften

Main-Group Elements

DOI: 10.1002/ange.201310613

Coordination Complexes of Ph_3Sb^{2+} and Ph_3Bi^{2+}: Beyond Pnictonium Cations**

Alasdair P. M. Robertson, Neil Burford, Robert McDonald, and Michael J. Ferguson*

Abstract: *The syntheses of salts containing ligand-stabilized Ph_3Sb^{2+} and Ph_3Bi^{2+} dications have been realized by in situ formation of $Ph_3Pn(OTf)_2$ (Pn = Sb or Bi) and subsequent reaction with $OPPh_3$, dmap and bipy. The solid-state structures demonstrate diversity imposed by the steric demands and nature of the ligands. The synthetic method has the potential for broad application enabling widespread development of the coordination chemistry for Pn^V acceptors.*

The 1809 report of the amine-borane adduct $H_3N{\cdot}BF_3$[1] defines the origin of coordination chemistry. Nevertheless, coordination complexes of p-block acceptors are rare beyond the elements of Group 13, and are insignificant in comparison to the extensive coordination chemistry of transition metals, in which p-block elements are often the Lewis basic centers of the ligands. Cationic frameworks exhibit an enhanced Lewis acidity compared with neutral analogues and recent reports of cationic complexes of p-block acceptors represent a new direction for coordination chemistry.[2,3] For example, complexes of mono-,[4] di-,[5] and tricationic[6] Sb^{III} centers have been reported with the generic formula $[X_{3-n}PnL_n]^{n+}$, where X represents a notional anionic substituent and L is a neutral $2e^-$ donor. With this precedent, we envisage the formation of a more extensive series of coordination complexes involving Pn^V acceptors with the generic formulae $[X_{4-n}PnL]^{n+}$, $[X_{4-n}PnL_2]^{n+}$, $[X_{4-n}PnL_3]^{n+}$, etc., representing derivatives of pnictonium cations, $[PnX_4]^+$, through sequential replacement of an anionic substituent (X) by neutral ligand(s) (L). Indeed, a number of cationic complexes containing tetrahedral P^V acceptor centers have been structurally characterized,[7–11] although in all but a single case[7] ligand coordination is facilitated by a low coordination number at a phosphorus center involved in multiple bonding.

Here we report the synthesis and comprehensive characterization of complexes with the generic formula $[Ph_3PnL_2]^{2+}$ for Pn = Sb or Bi, and L = $OPPh_3$ or 4-(dimethylamino)pyridine (dmap), which demonstrate a preference for axial coordination of the L donors. In addition, we report analogous complexes of Ph_3Pn^{2+} for Pn = Sb or Bi, with the chelating donor 2,2′-bipyridine (bipy). The results confirm the cations of general formula $[R_3PnL_2]^{2+}$ (Pn = Sb or Bi) that were postulated on the basis of spectroscopic and conductivity measurements.[12,13]

Treatment of a solution of Ph_3SbCl_2 or Ph_3BiCl_2 in CH_2Cl_2 with two equivalents of AgOTf yielded $Ph_3Sb(OTf)_2$ (**1a**) and $Ph_3Bi(OTf)_2$ (**1b**), respectively, which were spectroscopically and crystallographically characterized (Figure 1). Addition of two equivalents of PMe_3 to **1a** or **1b**, generated in situ in CH_2Cl_2 at ambient temperature resulted in the immediate precipitation of a colorless solid characterized by multinuclear NMR spectroscopy as $[Me_3P{-}PMe_3][OTf]_2$.[14,15] The filtrate was shown by ^1H NMR spectroscopy to contain almost exclusively Ph_3Pn (Pn = Sb or Bi), suggesting that oxidation of PMe_3 is associated with consequential reduction of **1a/b** (Scheme 1). Formation of $[Me_3P{-}PMe_3][OTf]_2$ is independent of reaction stoichiometry such that the presence of limited PMe_3 effects incomplete consumption of **1a/b**. Also, formation of the diphosphonium dication has been previously observed through reductive elimination from $[Sb(PMe_3)_3]^{3+}$.[15] The direction of the observed redox couple, however, is counter to that reported previously for reactions

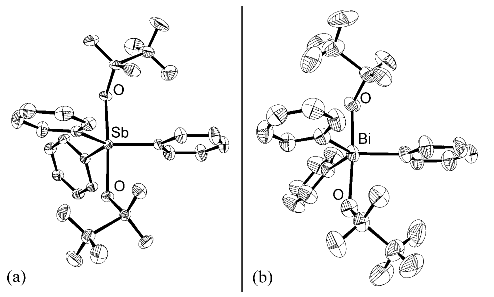
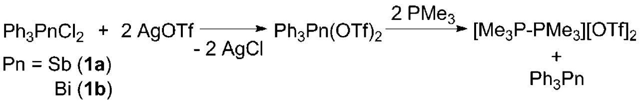


Figure 1. Solid-state structures of a) $Ph_3Sb(OTf)_2$ (**1a**) and b) $Ph_3Bi(OTf)_2$ (**1b**). All hydrogen atoms omitted for clarity.



$$\underset{\text{Pn = Sb (\textbf{1a}), Bi (\textbf{1b})}}{Ph_3PnCl_2} + 2\,AgOTf \xrightarrow[-\,2\,AgCl]{} Ph_3Pn(OTf)_2 \xrightarrow{2\,PMe_3} [Me_3P\text{-}PMe_3][OTf]_2 + Ph_3Pn$$

Scheme 1. Chloride/triflate exchange at Ph_3PnCl_2 to give $Ph_3Pn(OTf)_2$ [Pn = Sb (**1a**) or Bi(**1b**)], and subsequent redox reaction with two equivalents of PMe_3.

---

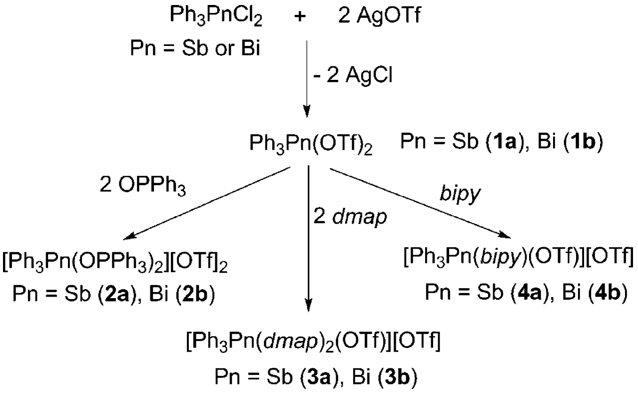
[*] Dr. A. P. M. Robertson, Prof. N. Burford
Department of Chemistry, University of Victoria
P.O Box 3065, Stn. CSC, Victoria, BC (Canada)
E-mail: nburford@uvic.ca
Dr. R. McDonald, Dr. M. J. Ferguson
X-Ray Crystallography Laboratory, Department of Chemistry
University of Alberta
11227 Saskatchewan Drive NW, Edmonton, AB (Canada)

[**] We thank the Natural Sciences and Engineering Council of Canada for funding.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310613.

of Ph_3Sb with dihalophosphines in the presence of a halide abstracting agent, which leads to oxidation of Ph_3Sb and reductive coupling of two phosphine centers.[16]

In contrast, reactions of **1a** and **1b** with the oxidation-resistant ligands $OPPh_3$, dmap or bipy led to the corresponding derivatives of $Ph_3PnL_2(OTf)_2$ ($L = OPPh_3$ or dmap) or $Ph_3Pn(bipy)(OTf)_2$, respectively (Scheme 2).[17] Reaction mixtures of **1a/b** with $OPPh_3$ show a single resonance [$\delta_P =$ 48.7 (Sb) and 43.1 ppm (Bi)] in the ^{31}P NMR spectra. Spectroscopic, analytical, and crystallographic data show the compounds to be salts of the form $[Ph_3Pn(OPPh_3)_2][OTf]_2$, containing Ph_3Pn^{2+} dications bearing two $OPPh_3$ ligands in an axial configuration (Figure 2). Analogous reactions of **1a/b** with two equivalents of dmap or an equivalent of bipy at ambient temperatures quantitatively furnish salts of the form $[Ph_3Pn(dmap)_2(OTf)][OTf]$ and $[Ph_3Pn(bipy)(OTf)][OTf]$ the cations of which are shown in Figure 3 and 4, respectively.



Scheme 2. Synthesis of $[Ph_3Pn(OPPh_3)_2][OTf]_2$, $[Ph_3Pn(dmap)_2(OTf)]$-$[OTf]$ and $[Ph_3Pn(bipy)(OTf)][OTf]$.

In the solid-state, $[Ph_3Sb(OPPh_3)_2][OTf]_2$ (**2a**) and $[Ph_3Bi(OPPh_3)_2][OTf]_2$ (**2b**) each contain a dication (Figure 2) and two distinct anions in the asymmetric unit, the pnictogen center adopts a trigonal bipyramidal geometry. The two statistically identical $Ph_3PO{-}Sb$ bonds in **2a** [average 2.102(2) Å] are similar in magnitude to the sum of the covalent radii [Σ_{CR} 2.05 Å][18] and those in other cationic and neutral adducts of phosphine oxides and antimony [2.15–2.23 Å].[19,20] The shortest cation–anion Sb−O distance [4.998(3) Å] is well in excess of the sum of the van der Waals radii [3.61 Å].[21] The $Ph_3PO{-}Bi$ bonds in **2b** [average 2.265(2) Å] are slightly greater than the sum of the covalent radii [Σ_{CR} 2.14 Å][22] but shorter than other examples of O−Bi coordinate bonds,[23,24] possibly due to the greater Lewis acidity of the dicationic acceptor in this case.[23,24] As for the antimony analogue, the shortest cation–anion Bi−O contact [4.922(3) Å] is significantly greater than the sum of the van der Waals radii [3.61 Å].[21]

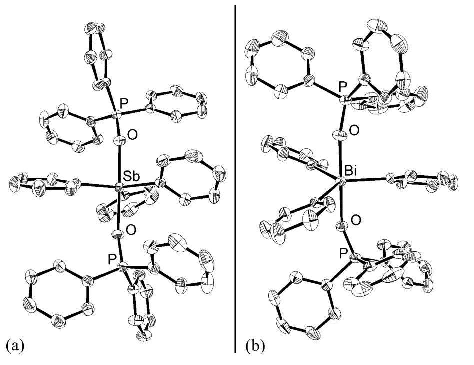


Figure 2. Solid-state structures of the dications in a) $[Ph_3Sb(OPPh_3)_2]$-$[OTf]_2$ (**2a**) and b) $[Ph_3Bi(OPPh_3)_2][OTf]_2$ (**2b**). All hydrogen atoms omitted for clarity.

In contrast to derivatives of $[Ph_3Pn(OPPh_3)_2][OTf]_2$, the pnictogen centers in the solid-state structures of $[Ph_3Pn(dmap)_2(OTf)][OTf]$ [Pn = Sb (**3a**), Bi (**3b**)] involve a close Pn−O contact with one triflate anion (Figure 3) [Sb−OTf 2.714(2) Å, cf. **1a** 2.172(2) Å and Σ_{CR} Sb−O 2.05 Å][22] [Bi−OTf 2.888(2) Å, cf. **1b** 2.325(2) Å and Σ_{CR} Bi−O 2.14 Å][22] These Pn−O contacts impose a distorted octahedral geometry at the pnictogen center, with the two dmap ligands in a *trans* configuration. In each case, the second triflate anion is > 5 Å from the pnictogen center. The N−Pn coordinate bonds [N−Sb 2.222(2) Å; N−Bi 2.373(2) Å] in both cases are greater in magnitude than the sum of the covalent radii of the two elements [Σ_{CR} N−Sb 2.10 Å; Σ_{CR} N−Bi 2.19 Å], but shorter than other examples of $N{-}Sb^+$ [2.23–2.81 Å].[6,20,25–27] and $N{-}Bi^+$ bonds [2.50–2.84 Å],[20,27–30] respectively. We interpret the cations in **3a/b** as ligand-stabilized pseudo-dications, with a short contact to a triflate anion.

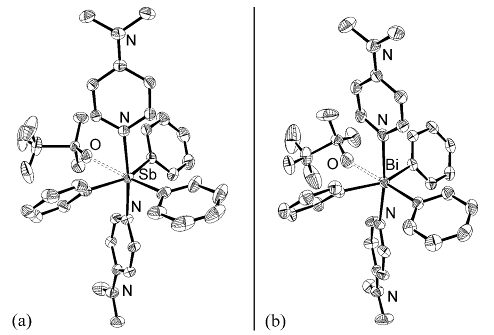


Figure 3. Solid-state structures of the dication and one anion in a) $[Ph_3Sb(dmap)_2(OTf)][OTf]$ (**3a**) and b) $[Ph_3Bi(dmap)_2(OTf)][OTf]$ (**3b**). All hydrogen atoms omitted for clarity.

The distinct structural differences between the $OPPh_3$ and dmap complexes reflect the different steric bulk of the ligands, with the planarity of dmap enabling interaction of the triflate anion. Interestingly, spectroscopic evidence for the formation of the dmap complexes **3a/b** was also apparent on the treatment of **2a/b** with two equivalents of dmap over 18 h in CH_2Cl_2, with quantitative release of Ph_3PO apparent by ^{31}P NMR spectroscopy ($\delta_P = 28.3$ ppm). This ligand-exchange process is in line with the interpretation of these compounds as coordination complexes of Ph_3Pn^{2+} acceptors.

Reaction of **1a** or **1b** with an equivalent of bipy in CH_2Cl_2 solution results in quantitative formation of $[Ph_3Pn(bipy)(OTf)][OTf]$ [Pn = Sb (**4a**), Bi (**4b**)] based on ^1H and

^{13}C NMR spectra and elemental microanalyses. X-ray crystallographic characterization of **4a** provided information about connectivity and configuration (Figure 4), but loss of solvent precluded determination of definitive structural parameters. A distorted octahedral environment at antimony is imposed by a triflate anion, three phenyl rings and a chelating bipy ligand. The inherent binding constraints of the bipy ligand preclude the axial configuration of the nitrogen donors that is observed for dmap complex **3a** and the *cis* configuration of triflate and bipy imposes a facial configuration of the phenyl substituents in contrast to the $OPPh_3$ and dmap complexes **2a** and **3a**. Given the structural consistency for the antimony and bismuth derivatives of **2** and **3**, it is reasonable to postulate that the spectroscopically characterized bismuth complex **4b** adopts a similar structure to its antimony analogue **4a** in the solid state.

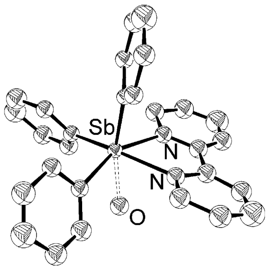


Figure 4. Preliminary structure of the cation in $[Ph_3Sb(bipy)(OTf)][OTf]$ (**4a**). All hydrogen atoms omitted for clarity, along with all but the bound oxygen atom of a disordered triflate anion.

In conclusion, the first structurally characterized examples of ligand-stabilized Ph_3Sb^{2+} and Ph_3Bi^{2+} acceptors have been prepared by displacement of triflate anions in $Ph_3Pn(OTf)_2$ [Pn = Sb (**1a**) or Bi (**1b**)] by the neutral donors, $OPPh_3$, dmap and bipy. The new complexes exhibit structural diversity dictated by the steric demands and the nature of the ligands. Future research will target complexes with alternative substituents and ligands with a view to increasing the observed structural diversity, and will assess complexes bearing 3+, 4+ and 5+ charges, with a view towards potential catalytic activity.

Experimental Section

The syntheses of all six compounds were carried out by analogous method, presented as a representative example for $[Ph_3Sb(OPPh_3)_2][OTf]_2$ (**2a**): To a solution of Ph_3SbCl_2 (0.25 g, 0.59 mmol) in CH_2Cl_2 (4 mL) was added AgOTf (0.30 g, 1.18 mmol) and the mixture was stirred for 1 h at 20 °C. The mixture was filtered and solid $OPPh_3$ (0.33 g, 1.18 mmol) then added to the filtrate. The resulting solution was stirred for 1 h before removing all volatiles under high vacuum to furnish a colorless solid, which was recrystallized from CH_2Cl_2/Et_2O at −30 °C. Yield: 0.51 g, 71 % (crystalline); ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta_H = 7.71–7.63$ (15 H, m, Ph), 7.55–7.46 (6 H, m, Ph), 7.45–7.36 (12 H, m, Ph), 7.08–6.98 (12 H, m, Ph); ^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ_P 48.40 ppm (s, $Ph_3Sb(OPPh_3)_2$; ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.75$ ppm (s, OTf); FT-IR (Nujol Mull, ranked intensities): 1262(1), 1150(3), 1115(4), 1030(2), 1009(6), 993(5), 687(7), 636(8), 534(9), 516(10), 456(11); elemental analysis: calcd: C 55.69, H 3.76; found: C 55.41, H 3.57; Mp. 196–198 °C.[31]

$[Ph_3Sb(dmap)_2(OTf)][OTf]$ (**3a**): Colorless solid; yield: 0.38 g, 71 % (powder); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta_H = 7.79–7.69$ (15 H, m, Ph), 7.59 (4 H, d, $J_{HH} = 7.6$ Hz, Ar-H [dmap]), 6.56 (4 H, d, $J_{HH} = 7.6$ Hz, (Ar-H [dmap]), 3.09 ppm (12 H, s, NMe_2); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_C = 156.8$ (s), 145.0 (s), 135.3 (s), 134.5 (s), 132.1 (s), 130.0 (s), 121.3 (q, $J_{CF} = 321.2$ Hz, CF_3), 108.7 (s), 40.2 ppm (s, $N(CH_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.80$ ppm; FT-IR (Nujol Mull, ranked intensities): 1621(7), 1258(1), 1228(4), 1150(5), 1028(2), 1008(6), 995(8), 739(10), 725(9), 635(3); elemental analysis: calcd: C 45.60, H 3.94, N 6.26; found: C 45.32, H 3.97, N 6.22; Mp. 200–202 °C.

$[Ph_3Sb(bipy)(OTf)][OTf]$ (**4a**): Colorless solid; yield: 0.29 g, 61 % (crystalline); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta_H = 9.12$ (2 H, d, $J_{HH} = 8.3$ Hz, bipy), 8.65 (2 H, d, $J_{HH} = 6.0$ Hz, Ar-H [bipy]), 8.62 (2 H, t, $J_{HH} = 8.0$ Hz, Ar-H [bipy]), 7.93 (2 H, t, $J_{HH} = 6.8$ Hz, Ar-H [bipy]), 7.71 (6 H, $J_{HH} = 7.6$ Hz, Ph), 7.66–7.61 (3 H, m, Ph), 7.61–7.56 ppm (6 H, m, Ph); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_C = 146.7$ (s), 144.1 (s), 141.8 (s), 136.3 (s), 135.1 (s), 133.4 (s), 131.4 (s), 130.1 (s), 126.5 (s), 120.5 ppm (q, $J_{CF} = 320.3$ Hz, CF_3); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.59$ ppm (s, OTf); FT-IR (Nujol Mull, ranked intensities): 1601(11), 1261(1), 1232(4), 1201(5), 1157(2), 1030(3), 987(7), 734(8), 723(9), 691(10), 631(6), 517(12); elemental analysis: calcd: C 44.63, H 2.87 N 3.47; found: C 44.60, H 2.87, N 3.47; Mp. 180–182 °C.

$[Ph_3Bi(OPPh_3)_2][OTf]_2$ (**2b**): Colorless solid; yield: 0.32 g, 63 % (crystalline); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 7.86–7.80$ (6 H, m, Ph), 7.68–7.59 (15 H, m, Ph), 7.45–7.39 (12 H, m, Ph), 7.30–7.20 ppm (12 H, m, Ph); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): 43.08 (br. s, $Ph_3Bi(OPPh_3)_2$); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_C = 158.9$ (s), 134.7 (s), 134.6 (br. s), 134.2 (s), 133.8 (s), 132.7 (d, $J_{PC} = 11.3$ Hz, PPh), 130.0 ppm (d, $J_{PC} = 13.2$ Hz, PPh); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.61$ ppm (s); FT-IR (Nujol Mull, ranked intensities): 1273(1), 1258(2), 1148(8), 1117(3), 1030(4), 1021(8), 995(9), 984(7), 636(6), 542(9), 536(5), 515(10); elemental analysis: calcd: C 51.93, H 3.50; found: C 52.40, H 3.61; Mp. 164–166 °C.

$[Ph_3Bi(dmap)_2(OTf)][OTf]$ (**3b**): Bright yellow solid; yield: 0.26 g, 41 % (crystalline); ^{1}H NMR (360 MHz, CD_2Cl_2): $\delta_H = 7.91$ (4 H, br. s, Ar-H [dmap]), 7.84–7.56 (15 H, m, Ph), 6.58 (4 H, d, $J_{HH} = 6.7$ Hz, Ar-H [dmap]), 3.09 ppm (12 H, s, NMe_2); ^{13}C NMR (91 MHz, CD_2Cl_2): $\delta_C = 154.6$ (s), 135.1 (s), 134.5 (s), 133.8 (s), 133.7 (s), 132.8 (s), 40.0 ppm (s, $N(CH_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.89$ ppm; FT-IR (Nujol Mull, ranked intensities): 1621(5), 1550(9), 1283(4), 1220(3), 1141(8), 1027(1), 1003(7), 978(6), 817(10), 634(2); elemental analysis: calcd: C 41.55, H 3.59, N 5.70; found: C 41.46, H 3.33, N 5.73; Mp. 134–136 °C.

$[Ph_3Bi(bipy)(OTf)][OTf]$ (**4b**): Colorless solid; yield: 0.31 g, 54 % (crystalline); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta_H = 8.63$ (2 H, d, $J_{HH} = 4.8$ Hz, Ar-H [bipy]), 8.56 (2 H, d, $J_{HH} = 7.6$ Hz, Ar-H [bipy]), 8.18 (2 H, br. s, Ar-H [bipy]), 7.95 (6 H, d, $J_{HH} = 7.6$ Hz, Ph), 7.81 (6 H, t, $J_{HH} = 8.0$ Hz, Ph), 7.67 (3 H, t, $J_{HH} = 7.6$ Hz, Ph), 7.57 ppm (2 H, br. s, Ar-H [bipy]; ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_C = 141.8$ (very broad singlet), 134.5 (s), 134.0 (s), 133.9 (s), 127.3 (very broad singlet), 124.7 ppm (very broad singlet); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_F = -78.31$ ppm; FT-IR (Nujol Mull, ranked intensities): 1594(14), 1554(12), 1256(1), 1235(2), 1205(3), 1160(4), 1030(5), 1008(6), 980(8), 770(10), 730(9), 647(11), 637(7), 514(13); elemental analysis: calcd: C 40.28, H 2.59 N 3.13; found: C 40.13, H 2.59, N 3.10; Mp. > 138 (decomposed).

Full experimental information and details of X-ray crystallographic studies can be found in the Supporting Information. CCDC 975311 (**2a**), 975312 (**2b**), 975313 (**3a**), 975314 (**3b**), 975315 (**1a**) and 975316 (**1b**) contain 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.

Received: December 6, 2013
Revised: January 23, 2014

Keywords: coordination chemistry · Lewis acids · main group elements · pnictogens · polycations

---

[1] J. L. M. Gay-Lussac, *Mémoires de la Société d'Arcueil* **1809**, *2*, 211.

[2] A. P. M. Robertson, P. Gray, N. Burford, *Angew. Chem.* **2014**, DOI: 10.1002/ange.201307658; *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201307658.

[3] J. L. Dutton, P. J. Ragogna, *Coord. Chem. Rev.* **2011**, *255*, 1414–1425.

[4] N. L. Kilah, S. Petrie, R. Stranger, J. W. Wielandt, A. C. Willis, S. B. Wild, *Organometallics* **2007**, *26*, 6106–6113.

[5] S. S. Chitnis, B. Peters, E. Conrad, N. Burford, R. McDonald, M. J. Ferguson, *Chem. Commun.* **2011**, *47*, 12331–12333.

[6] S. S. Chitnis, N. Burford, M. J. Ferguson, *Angew. Chem.* **2013**, *125*, 2096–2099; *Angew. Chem. Int. Ed.* **2013**, *52*, 2042–2045.

[7] J. J. Weigand, N. Burford, A. Decken, A. Schulz, *Eur. J. Inorg. Chem.* **2007**, 4868–4872.

[8] R. Boomishankar, J. Ledger, J.-B. Guilbaud, N. L. Campbell, J. Bacsa, R. Bonar-Law, Y. Z. Khimyak, A. Steiner, *Chem. Commun.* **2007**, 5152–5154.

[9] M. Blättner, M. Nieger, A. Ruban, W. W. Schoeller, E. Niecke, *Angew. Chem.* **2000**, *112*, 2876–2879; *Angew. Chem. Int. Ed.* **2000**, *39*, 2768–2771.

[10] M. Meisel, P. Lönnecke, A.-R. Grimmer, D. Wulff-Molder, *Angew. Chem.* **1997**, *109*, 1940–1942; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1869–1870.

[11] E. Rivard, K. Huynh, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 2286–2287.

[12] P. Raj, A. K. Aggarwal, *Synth. React. Inorg. Met.-Org. Chem.* **1992**, *22*, 543–557.

[13] R. G. Goel, H. S. Prasad, *J. Organomet. Chem.* **1973**, *59*, 253–257.

[14] J. J. Weigand, S. D. Riegel, N. Burford, A. Decken, *J. Am. Chem. Soc.* **2007**, *129*, 7969–7976.

[15] S. S. Chitnis, Y.-Y. Carpenter, N. Burford, R. McDonald, M. J. Ferguson, *Angew. Chem.* **2013**, *125*, 4963–4966; *Angew. Chem. Int. Ed.* **2013**, *52*, 4863–4866.

[16] E. Conrad, N. Burford, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2009**, *131*, 17000–17008.

[17] At the suggestion of a reviewer we also investigated the reactivity of the N-heterocyclic carbene (NHC) 1,3-di-*tert*-butyl-4,5-dihydroimidizol-2-ylidene (as an oxidation resistant ligand) with Ph$_3$Pn(OTf)$_2$, and observed a complicated mixture of products, which are now under investigation.

[18] Σ_{CR} values reported throughout are calculated from the values reported by Alvarez and co-workers: B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–3838.

[19] D. Cunningham, E. M. Landers, P. McArdle, N. Chonchubhair, *J. Organomet. Chem.* **2000**, *612*, 53–60.

[20] C. J. Carmalt, D. Walsh, A. H. Cowley, N. C. Norman, *Organometallics* **1997**, *16*, 3597–3600.

[21] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[22] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.

[23] W. Clegg, L. J. Farrugia, A. McCamley, N. C. Norman, A. G. Orpen, N. L. Pickett, S. E. Stratford, *J. Chem. Soc. Dalton Trans.* **1993**, 2579–2587.

[24] C. J. Carmalt, N. C. Norman, A. G. Orpen, S. E. Stratford, *J. Organomet. Chem.* **1993**, *460*, C22–C24.

[25] G. R. Willey, M. P. Spry, M. G. B. Drew, *Polyhedron* **1996**, *15*, 4497–4500.

[26] F. Huber, H. Preut, G. Alonzo, N. Bertazzi, *Inorg. Chim. Acta* **1985**, *102*, 181–186.

[27] R. Garbe, B. Vollmer, B. Neumüller, J. Pebler, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1993**, *619*, 271–276.

[28] C. J. Carmalt, L. J. Farrugia, N. C. Norman, *J. Chem. Soc. Dalton Trans.* **1996**, 443–454.

[29] M. Tershansy, A. Goforth, M. Smith, H.-C. Loye, *J. Chem. Crystallogr.* **2008**, *38*, 453–459.

[30] M. Schäfer, G. Frenzen, B. Neumüller, K. Dehnicke, *Angew. Chem.* **1992**, *104*, 354–356; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 334–335.

[31] The ^{13}C NMR spectrum of analytically pure **2a** indicates the formation of an additional solvation product, precluding spectral assignment. See Supporting Information for further details.