Coordination Chemistry

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Redox and Anion Exchange Chemistry of a Stibine–Nickel Complex: Writing the L, X, Z Ligand Alphabet with a Single Element[**]

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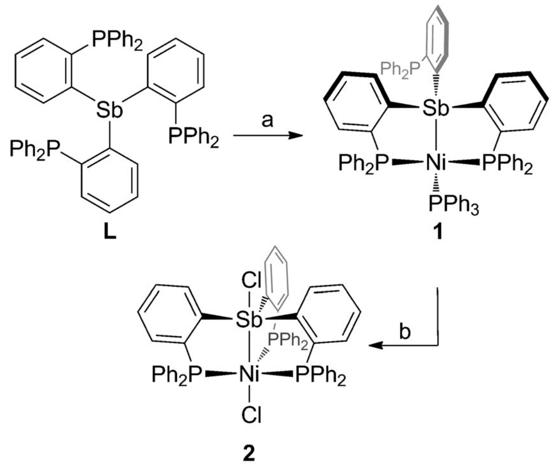
Dedicated to Professor Alan H. Cowley on the occasion of his 80th birthday

Abstract: *According to the covalent bond classification (CBC) method, two-electron donors are defined as L-type ligands, one-electron donors as X-type ligands, and two-electron acceptors as Z-type ligands. These three ligand functions are usually associated to the nature of the ligating atom, with phosphine, alkyl, and borane groups being prototypical examples of L-, X- and Z-ligands, respectively. A new SbNi platform is reported in which the ligating Sb atom can assume all three CBC ligand functions. Using both experimental and computational data, it is shown that* $PhICl_2$ *oxidation of* $(o\text{-}(Ph_2P)C_6H_4)_3SbNi(PPh_3)$ *(**1**) into* $[(o\text{-}(Ph_2P)C_6H_4)_3ClSb]NiCl$ *(**2**) is accompanied by a conversion of the stibine L-type ligand of **1** into a stiboranyl X-type ligand in **2**. Furthermore, the reaction of **2** with the catecholate dianion in the presence of cyclohexyl isocyanide results in the formation of* $[(o\text{-}(Ph_2P)C_6H_4)_3(o\text{-}O_2C_6H_4Sb)]Ni(CNCy)$ *(**4**), a complex featuring a nickel atom coordinated by a Lewis acidic, Z-type, stiborane ligand.*

In 1995, Green[1] introduced the Covalent Bond Classification as a new method for the description of ligands and the way by which they bind to metal centers (M). This method, which is predicated on the nature of the bond connecting M to the ligating atom of the ligand, identifies three distinct situations. In the first situation, a Lewis basic or L-type ligand acts as a two-electron donor to form a L→M dative interaction. In the second situation, which is the charge reverse analog of the first one, a Lewis acidic or Z-type ligand interacts with the metal through a M→L interaction.[2] A third, intermediate situation arises when a one electron donor or X-type ligand combines with an electron from the metal center to form a covalent bond. Prototypical examples of such ligands include PR_3 or CO for L-type ligands, H or CH_3 for X-type ligands, and BR_3 for Z-type ligands. As part of our ongoing interest in the coordination chemistry of redox active ligands, we have now questioned whether the L-, X-, and Z-ligand function could be sustained by a single ligating element. In this communication, we describe a Ni/Sb platform in which the antimony ligand can be switched from L to X to Z by successive formal one-electron redox processes.

Reaction of $(o\text{-}(Ph_2P)C_6H_4)_3Sb$ (L)[3] with $Ni(PPh_3)_4$ in THF afforded $LNi(PPh_3)$ (**1**) as an orange powder (Scheme 1). Solutions of compound **1** slowly decompose at ambient temperature, but are stable indefinitely at −20 °C. The ^{31}P NMR spectrum of **1** in C_6D_6 consists of a doublet at 52.54 ppm, a triplet at 39.73 ppm ($^2J_{P\text{-}P} = 46.89$ Hz), and a singlet at −8.62 ppm in a 2:1:1 ratio, suggesting a κ-P-P-Sb coordination mode of L to a $[(Ph_3P)Ni]$ fragment. This assignment was corroborated by a single-crystal diffraction study (Figure 1).[4] In the solid-state structure of **1**, the nickel center adopts a distorted tetrahedral geometry with large P-Ni-P angles, the sum of which is equal to 348.75(15)°. As a result of the constraints enforced by the ligand backbone, the four coordinate antimony center also displays an unusual geometry characterized by a large Ni-Sb-C angle of 159.77(11)°. The Ni-Sb distance of 2.4574(10) Å in **1** is comparable to the average Ni-Sb distance of 2.449(2) Å in $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)_2$, one of the few structurally characterized arylstibine complexes of zerovalent nickel.[5]



Scheme 1. Synthesis of **1**, and oxidation of **1** into **2**. a) $Ni(PPh_3)_4$, THF and b) 2 $PhICl_2$, toluene.

With compound **1** in hand, we sought to determine whether the Sb-Ni heterobimetallic core could sustain

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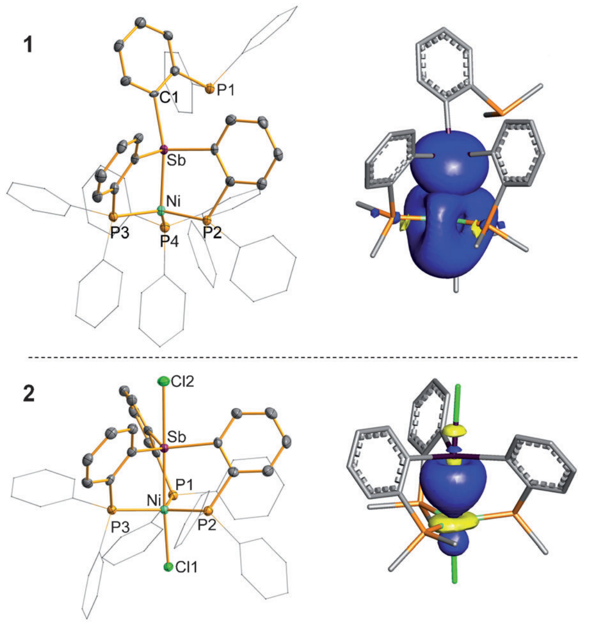
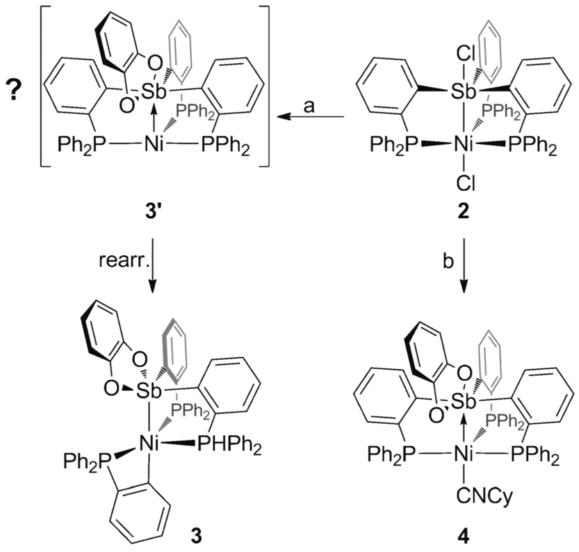


Figure 1. Left side: Crystal structures of and **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in [Å] and angles in [°]. **1**: Sb–Ni 2.4574(10); Ni-Sb-C1 159.76(11), P2-Ni-P3 114.38(5), P2-Ni-P4 113.88(5), P3-Ni-P4 120.49(5). **2**: Sb–Ni 2.4853(5), Sb–Cl2 2.6834(9), Ni–Cl1 2.2813; P1-Ni-P2 119.47(4), P1-Ni-P3 121.09(4), P2-Ni-P3 117.41. Right side: NBO plots of the major Sb-Ni bonding interactions in compounds **1** and **2** (isodensity value = 0.05). Hydrogen atoms are omitted, and selected phenyl groups are truncated for clarity.

oxidation without decomposition. Gratifyingly, **1** undergoes a clean, two-electron oxidation by $PhICl_2$ in toluene to afford the dark purple complex **2** characterized by a single ^{31}P NMR resonance at 35.42 ppm in $CDCl_3$ (Scheme 1). An X-ray diffraction study revealed that **2** is a Sb-Ni lantern complex with a Sb-Ni distance (2.4852(5) Å) almost identical to that in **1**.[4] In contrast to **1** however, the nickel atom adopts a trigonal bipyramidal geometry with the antimony atom and a chloride ligand at the axial positions. The three equatorial positions are occupied by the phosphine arms of the L ligand ($\Sigma\sphericalangle$(P-Ni-P) = 357.97(12)°; Figure 1). This coordination geometry of the nickel center is reminiscent of that observed in related complexes such as $(o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4)_3\mathrm{SiNiCl}$.[6] The most distinguishing feature of **2** is the presence of a chloride ligand bound to the antimony center, in a position trans from the nickel atom. With this chloride as an additional ligand, the antimony center adopts a trigonal bipyramidal geometry ($\Sigma\sphericalangle$(C-Sb-C) = 355.8(4)°) with a Sb-Cl distance (2.6835(9) Å) very close to that of 2.668(1) Å found in Ph_4SbCl.[7] Venanzi and Dawson had reported a complex of similar composition to that of **2**, but with the chloride dissociated from the antimony center.[8] We believe that this species was in fact complex **2** whose structure had been misassigned.

While **1** can be regarded as a classical stibine complex, the presence of an antimony-bound chloride ligand in **2** makes its classification somewhat more ambiguous. Indeed, with chloride as an extra ligand, the antimony moiety in **2** is tetrasubsituted and thus akin to a stiboranyl unit bound to the nickel atom.[9] On the basis of this analysis, it can be proposed that oxidation of **1** into **2** triggers a L- to X-type conversion of the antimony ligand. This view is supported by the natural bond orbital (NBO) analyses of the Sb-Ni bonding present in these complexes (Scheme 2). Implementation of this method at the DFT optimized geometries shows that while the Sb-Ni bond in **1** may be described as a lp(Sb)→Ni donor–acceptor interaction ($E^2 = 53.07\ \mathrm{kcal\,mol^{-1}}$),[10] the Sb-Ni bond in **2** is treated as a covalent bond with a distinct polarization toward the nickel atom (Sb 36.3%/Ni 57.7%). These results show that the Sb-Ni bonding in **1** is best described as a classical Sb→Ni dative bond, in which the stibine moiety of L acts as an L-type ligand.[10] In the case of **2**, the presence of a polar covalent bond shows that the antimony center acts as a strongly σ-donating, X-type stiboranyl fragment. With the observation of the L- and X-ligand functions on the same platform, the conversion of the antimony center into a Lewis acidic, Z-type stiborane ligand became a stimulating fundamental possibility.[11]



Scheme 2. Syntheses of **3** and **4**. a) Catechol, TEA, THF and b) CyNC, catechol, TEA, THF.

In our first approach to this idea, **2** was allowed to react with catechol in the presence of a base to yield red-orange **3** (Scheme 2). The ^{31}P NMR spectrum of **3** in [D$_8$]toluene consists of a doublet at 60.31 ppm and a triplet at −52.87 ppm ($^2J_{\text{P-P}} = 139.20$ Hz), the strong upfield shift of the latter resonance being diagnostic of an *ortho*-metallated phosphine in a four-membered chelate ring.[12] The solid-state structure of **3**[4] (see the Supporting Information) confirmed migration of an *ortho*-diphenylphosphinophenylene group from antimony to nickel, leading us to speculate the intermediacy of the nickel(0) complex (**3′**) that would evolve into **3** through insertion of the nickel center into a Sb−C bond. Repeating the reaction under an atmosphere of H_2 did not alter the course of this reaction, with **3** being the only product observed.[13]

With the goal of damping the reactivity of the low valent nickel center in **3′** and its tendency toward insertion reactions, we considered the use of a π-acidic ligand which would help stabilize the electron rich nickel atom. To this end, the same reaction was repeated in the presence of cyclohexyl isocyanide. This reaction afforded the stiborane–nickel complex **4** in good yield (Scheme 2). While orange-red solutions of **4** slowly decompose in air, solid samples appear to be indefinitely stable. The ^{31}P NMR spectrum of **4** in CDCl$_3$ shows a doublet at 68.91 ppm and a triplet at 39.68 ppm ($^2J_{\text{P-P}} = 83.89$ Hz), indicating the inequivalence of the phosphine arms of the ligand. The crystal structure of **4** confirmed coordination of the catecholate ligand to the antimony center, leading to the formation of a square pyramidal triarylcatecholatostiborane moiety whose open square base faces the neighbouring nickel atom (Figure 2).[4] Correspondingly, the isocyanide tris(phosphine) nickel moiety forms a trigonal pyramid ($\Sigma\sphericalangle$(P-Ni-P) = 357.8(1)°) with the antimony positioned directly above the NiP$_3$ trigonal base. Although the Sb-Ni distance in **4** (2.6253(4) Å) is 0.17 Å longer than that measured in **1**, the observed arrangement of the two moieties supports the presence of a direct Ni→Sb interaction.[10] In support of this view, the $\nu_{(\text{CN})}$ of **4** (2142 cm^{-1}), which is considerably higher than that found in (CyNC)Ni(PPh$_3$)$_3$ (2020 cm^{-1}),[14] shows that the transfer of electron density from nickel to antimony reduces the metallobasicity of the nickel atom and thus the strength of the Ni→isocyanide π-backbonding interaction. A similar effect has been observed by Figueroa upon coordination of a Lewis acidic thallium cation to isocyanide nickel(0) complexes.[15] A precedent also exists in carbonyl rhodium and iridium boratrane complexes,[16] which feature significantly higher CO stretching frequencies than their Lewis acid-free analogs. From these structural and spectroscopic features, we conclude that the stiborane moiety in **4** acts as a Z-type ligand.[11,17] The presence of a Ni→Lewis acid interaction in **4** is reminiscent of the situation encountered in nickel borane or alane complexes such as **A**,[18] **B**,[13a] and **C**[19] which have been obtained from (COD)$_2$Ni for **A** and **C** or by reduction of a nickel halide precursor for **B**. Although complex **4** is chemically related to these derivatives, it is unique in that the Z-type ligand function is the result of an anion-induced internal redox reaction. The nature of the Ni→Sb interaction present in **4** has also been probed using the NBO method, which defines a series of Ni→p(Sb)[20] and Ni→σ*(Sb-C) donor–acceptor interactions involving the Ni d$_{z^2}$ orbital (see Figure 2 and the Supporting Information). The sum of the second-order stabilization energies of these interaction (ΣE^2) is equal to 20.85 kcal mol^{-1}, a value significantly smaller than that of the lp(Sb)→Ni in **1** ($E^2 = 53.07$ kcal mol^{-1}). These results show that the umpolung of the Ni-Sb bond induced by conversion of **1** into **4** is accompanied by a relative weakening of the dative interaction present at the core of this complex. This bond umpolung bears an interesting parallel with the donor/acceptor role inversion described by Wagler for a family of SnPd complexes.[21]

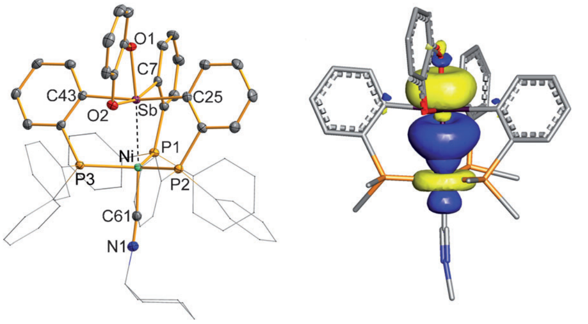
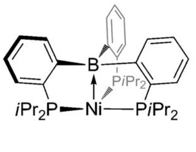


Figure 2. Left side: Crystal structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in [Å] and angles in [°]. Sb-Ni 2.6253(4), Sb-O1 2.0920(12), Sb-O2 2.1169(12), Ni-C61 1.8586(19), N1-C61 1.161(2), O1-Sb-Ni 173.06(3), O2-Sb-C7 166.99(6), C25-Sb-C43 170.65(6); P1-Ni-P2 120.43(2), P1-Ni-P3 113.919(19), P2-Ni-P3 123.49(2), C61-N1-C62 174.73(19). Right side: NBO plot of the major Sb-Ni bonding interaction in compound **4** (isodensity value = 0.05). Hydrogen atoms are omitted, and selected phenyl groups and the cyclohexyl group are truncated for clarity.



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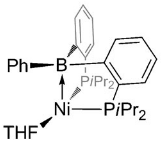

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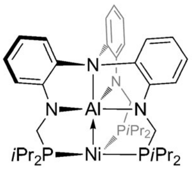

C

In summary, we provide the first example of a complex in which the ligating atom can adopt all three covalent bond classification ligand functions. Conversion among these three ligand functions is achieved by a combination of redox and anion exchange reactions which ultimately afford a zerovalent Ni-stiborane complex. The strategy defined herein, which exploits the non-innocence[22] of the antimony L ligand,[11a,23] is currently being used to tune the reactivity of transition-metal centers.

Experimental Section

Synthesis of **1**: A solution of Ni(PPh$_3$)$_4$ (174 mg, 157 μmol) in ca. 3 mL THF was added dropwise to a stirred suspension of L (142 mg, 157 μmol) in ca. 5 mL THF, immediately forming a dark red solution. The solution was stirred for 12 h. to give an orange suspension. The reaction mixture was filtered and washed with THF(2×2 mL) and dried in vacuo to yield 123 mg (64%) of **1** as a bright orange powder. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et$_2$O into a toluene solution of the compound at −20 °C. ^{1}H NMR (399.53 MHz; C$_6$D$_6$): $\delta = 6.61$–7.12 (m, 36H, *o*-P(Sb)C$_6$H$_4$ + Ph-C*H* + PPh$_3$ *meta*- and *ortho*-Ph-C*H*), 7.17–7.26 (m, 8H, *o*-P(Sb)C$_6$H$_4$ + Ph-C*H*), 7.27–7.58 (m, 10H, *o*-P(Sb)C$_6$H$_4$ + PPh$_3$ *ortho*-Ph-C*H*), 7.73 (d, 2H, *o*-P(Sb)C$_6$H$_4$ $^3J_{\text{H-H}} = 7.57$ Hz), 8.14 ppm (d, 1H, *o*-P(Sb)C$_6$H$_4$, $^3J_{\text{H-H}} = 6.10$ Hz). ^{31}P{^{1}H} NMR (161.73 MHz; C$_6$D$_6$): $\delta = -8.62$ (s, 1P, free arm), 39.73 (t, 1P, PPh$_3$, $^2J_{\text{P-P}} = 46.89$ Hz), 52.54 ppm (d, 2P, $^2J_{\text{P-P}} = 46.89$ Hz). Elemental analysis calculated (%) for C$_{72}$H$_{57}$NiP$_4$Sb: C 70.50, H 4.68; found C 69.23, H 4.95.

Synthesis of **2**: A solution of PhICl$_2$ (29 mg, 105 μmol) in 5 mL toluene was added dropwise to a stirred suspension of **1** (64 mg, 52 μmol) in 5 mL toluene at 0 °C. The red suspension quickly gave way to a deep blue solution, which was stirred for approximately

30 minutes. All volatiles were removed, and the resultant blue-purple solid was triturated with Et_2O, filtered, and dried in vacuum to yield 52 mg (93 %) of **2**. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of the compound at room temperature. ^1H NMR (399.59 MHz; $CDCl_3$): $\delta =$ 6.89 (t, 12 H, *ortho* Ph-C*H*, $^3J_{H-H} = 7.70$ Hz), 7.05 (m, 12 H, *meta* Ph-C*H*), 7.11–7.18 (m, 9 H, *o*-P(Sb)C_6H_4 + *para* Ph-C*H*), 7.45 (t, 3 H, *o*-P(Sb)C_6H_4, $^3J_{H-H} = 7.69$ Hz), 7.84 (t, 3 H, *o*-P(Sb)C_6H_4, $^3J_{H-H} =$ 7.69 Hz), 9.99 ppm (d, 3 H, *o*-P(Sb)C_6H_4, $^3J_{H-H} = 7.69$ Hz). See the Supporting Information for ^{13}C NMR data. Elemental analysis calculated (%) for $C_{54}H_{42}NiP_3Sb$: C 62.65, H 4.09; found C 62.38, H 4.21.

Synthesis of **4**: CyNC (20 µL, 160 µmol) was added via syringe to a stirred, purple suspension of **2** (163 mg, 160 µmol) in 5 mL THF to give a yellow-brown suspension, which was stirred for 15 min. A solution of triethylamine (48 µL, 346 µmol) and catechol (18 mg, 170 µmol) in 1 mL THF was added dropwise to the CyNC/**2** suspension, resulting in the rapid formation of a cloudy orange-red solution. After stirring for 2 h, the reaction mixture was filtered over a plug of Celite and concentrated to about 1 mL. The product was precipitated by addition of ca. 10 mL pentane, filtered, and dried in vacuum to yield **4** as an orange powder (168 mg, 90 %). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene solution of the compound at room temperature. ^1H NMR (399.59 MHz; $CDCl_3$): $\delta = 1.02$ (br, 4 H, Cy-CH_2), 1.31 (br, 6 H, Cy-CH_2), 3.09 (br, 1 H, Cy-C*H*), 5.28 (d, 1 H, catechol C*H*, $^3J_{H-H} = 7.69$ Hz), 6.10 (pseudo-t, 1 H, catechol C*H*), 6.26 (pseudo-t, 1 H, catechol C*H*), 6.60–6.68 (m, 6 H, *o*-P(Sb)C_6H_4 + Ph-C*H*), 6.70–6,84 (m, 18 H, *o*-P(Sb)C_6H_4 + Ph-C*H*), 6.84–6.93 (m, 5 H, *o*-P(Sb)C_6H_4 + Ph-C*H* + catechol C*H*), 6.96–7.10 (m, 10 H, *o*-P(Sb)C_6H_4 + Ph-C*H*), 7.48 (pseudo-t, 1 H, *o*-P(Sb)C_6H_4), 8.16 (d, 2 H, *o*-P(Sb)C_6H_4, $^3J_{H-H} = 7.32$ Hz), 9.18 ppm (d, 1 H, *o*-P(Sb)C_6H_4, $^3J_{H-H} = 7.32$ Hz). See the Supporting Information for ^{13}C NMR data. Elemental analysis calculated (%) for $C_{67}H_{57}NNiO_2P_3Sb{\cdot}2\,C_6H_6$: C 70.93, H 5.20; N 1.05; found C 70.96, H 5.30, N 1.10.

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[1] M. L. H. Green, *J. Organomet. Chem.* **1995**, *500*, 127 – 148.

[2] a) D. F. Shriver, *Acc. Chem. Res.* **1970**, *3*, 231 – 238; b) C. B. Dammann, J. L. Hughey, D. C. Jicha, T. J. Meyer, P. E. Rakita, T. R. Weaver, *Inorg. Chem.* **1973**, *12*, 2206 – 2209; c) D. M. T. Chan, T. B. Marder, *Angew. Chem.* **1988**, *100*, 436 – 437; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 442 – 443; d) G. Parkin, *Organometallics* **2006**, *25*, 4744 – 4747; e) A. F. Hill, *Organometallics* **2006**, *25*, 4741 – 4743; f) F.-G. Fontaine, J. Boudreau, M.-H. Thibault, *Eur. J. Inorg. Chem.* **2008**, 5439 – 5454; g) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924 – 3957; h) G. Bouhadir, A. Amgoune, D. Bourissou, *Adv. Organomet. Chem.* **2010**, *58*, 1 – 107; i) A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859 – 871; j) H. Braunschweig, R. D. Dewhurst, *Dalton Trans.* **2011**, *40*, 549 – 558; k) J. Bauer, H. Braunschweig, R. D. Dewhurst, *Chem. Rev.* **2012**, *112*, 4329 – 4346; l) G. R. Owen, *Chem. Soc. Rev.* **2012**, *41*, 3535 – 3546; m) H. Kameo, H. Nakazawa, *Chem. Asian J.* **2013**, *8*, 1720 – 1734; n) D. M. P. Mingos, *J. Organomet. Chem.* **2014**, *751*, 153 – 173.

[3] B. R. Higginson, C. A. McAuliffe, L. M. Venanzi, *Inorg. Chim. Acta* **1971**, *5*, 37 – 40.

[4] CCDC 995209 (**1**-Et_2O), 995210 (**2**), 995211 (**3**-0.5 C_6H_6) and 995212 (**4**-3.5 C_6H_6) 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.

[5] R. E. DesEnfants Ii, J. A. Gavney, Jr., R. K. Hayashi, A. D. Rae, L. F. Dahl, A. Bjarnason, *J. Organomet. Chem.* **1990**, *383*, 543 – 572.

[6] M. T. Whited, N. P. Mankad, Y. Lee, P. F. Oblad, J. C. Peters, *Inorg. Chem.* **2009**, *48*, 2507 – 2517.

[7] V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, T. P. Platonova, O. P. Zadachina, A. V. Gerasimenko, *Russ. J. Coord. Chem.* **2003**, *29*, 89 – 92.

[8] J. W. Dawson, L. M. Venanzi, *J. Am. Chem. Soc.* **1968**, *90*, 7229 – 7233.

[9] W. Malisch, P. Panster, *Angew. Chem.* **1974**, *86*, 708 – 709; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 670 – 672.

[10] This compound can also be described on the basis of two resonance structures (see Figure S4).

[11] a) I.-S. Ke, J. S. Jones, F. P. Gabbaï, *Angew. Chem.* **2014**, *126*, 2671 – 2675; *Angew. Chem. Int. Ed.* **2014**, *53*, 2633 – 2637; b) C. R. Wade, F. P. Gabbaï, *Angew. Chem.* **2011**, *123*, 7507 – 7510; *Angew. Chem. Int. Ed.* **2011**, *50*, 7369 – 7372.

[12] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229 – 266.

[13] a) W. H. Harman, J. C. Peters, *J. Am. Chem. Soc.* **2012**, *134*, 5080 – 5082; b) C. Tsay, J. C. Peters, *Chem. Sci.* **2012**, *3*, 1313 – 1318.

[14] E. Wenschuh, D. Wilhelm, H. Hartung, U. Baumeister, *Z. Anorg. Allg. Chem.* **1994**, *620*, 2048 – 2052.

[15] B. J. Fox, M. D. Millard, A. G. DiPasquale, A. L. Rheingold, J. S. Figueroa, *Angew. Chem.* **2009**, *121*, 3525 – 3529; *Angew. Chem. Int. Ed.* **2009**, *48*, 3473 – 3477.

[16] a) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu, D. Bourissou, *Chem. Eur. J.* **2008**, *14*, 731 – 740; b) H. Kameo, H. Nakazawa, *Organometallics* **2012**, *31*, 7476 – 7484.

[17] a) C. R. Wade, T.-P. Lin, R. C. Nelson, E. A. Mader, J. T. Miller, F. P. Gabbaï, *J. Am. Chem. Soc.* **2011**, *133*, 8948 – 8955; b) T.-P. Lin, R. C. Nelson, T. Wu, J. T. Miller, F. P. Gabbaï, *Chem. Sci.* **2012**, *3*, 1128 – 1136.

[18] M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729 – 16738.

[19] P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young, C. C. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 20724 – 20727.

[20] The NBO analysis separates **4** into four distinct units: (*o*-(Ph_2P)C_6H_4)$_3$Sb, Ni, *o*-$O_2C_6H_4$, and CyNC. The antimony-based accepting orbital for the major Ni→Sb interaction is therefore parsed as a vacant p orbital.

[21] E. Brendler, E. Wächtler, T. Heine, L. Zhechkov, T. Langer, R. Pöttgen, A. F. Hill, J. Wagler, *Angew. Chem.* **2011**, *123*, 4793 – 4797; *Angew. Chem. Int. Ed.* **2011**, *50*, 4696 – 4700.

[22] a) C. K. Jørgensen, *Coord. Chem. Rev.* **1966**, *1*, 164 – 178; b) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794 – 795; c) W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **2010**, *254*, 1580 – 1588; d) R. Eisenberg, H. B. Gray, *Inorg. Chem.* **2011**, *50*, 9741 – 9751; e) R. Eisenberg, *Coord. Chem. Rev.* **2011**, *255*, 825 – 836; f) P. J. Chirik, *Inorg. Chem.* **2011**, *50*, 9737 – 9740; g) S. Sproules, K. Wieghardt, *Coord. Chem. Rev.* **2011**, *255*, 837 – 860; h) O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440 – 1459; i) R. F. Munhá, R. A. Zarkesh, A. F. Heyduk, *Dalton Trans.* **2013**, *42*, 3751 – 3766.

[23] S. L. Benjamin, W. Levason, G. Reid, R. P. Warr, *Organometallics* **2012**, *31*, 1025 – 1034.