Coordination Chemistry

DOI: 10.1002/ange.201200854

σ-Accepting Properties of a Chlorobismuthine Ligand**

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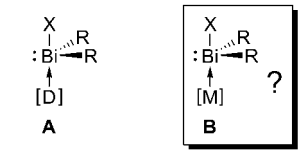
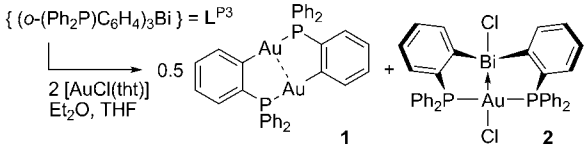
The coordination chemistry of bismuthine ligands is receiving a renewed interest that is fueled by applications in the domain of material science,[1] catalysis,[2] arylation reactions,[3] and C–H bond-activation chemistry.[4] Despite these recent advances, the use of these ligands remains much less developed than that of the lighter pnictogen analogues and is in fact limited to a few complexes in which the bismuthine behaves as a σ donor or L ligand.[5] Synthesis and isolation of such complexes is often complicated by: 1) the poor donicity of the bismuth 6s lone pair, which experiences relativistic effects; and 2) the lability of the Bi–C bond[6] which is prone to facile cleavage in the presence of metal salts, leading to unwanted side reactions. These factors have been held responsible for the fact that bismuthine–gold(I) complexes cannot be isolated.[7]

Stimulated by these challenges, we decided to investigate a new approach to such unknown linkages. In particular, inspired by the Lewis acidic behavior of organobismuth(III) compounds in adducts of type **A**,[8] we questioned whether structurally related architectures could be employed to stabilize M→Bi bonds as in **B**.[9]



D = NR_3, OR_2, SR_2; M = transition metal
X = halide, Ar; R = organic substituent

With this idea in mind, we decided to investigate the synthesis and ligating properties of the trisphosphanylbismuthine ligand (o-$(Ph_2P)C_6H_4)_3Bi$; referred to as $\mathbf{L}^{P3}$). This ligand, which could be conveniently obtained by reaction of $BiCl_3$ with o-$(Ph_2P)C_6H_4Li$ in Et_2O/THF (Scheme 1), can be stored in air for extended period of times. It features a ^{31}P NMR resonance at −8.1 pm indicating equivalence of the three phosphanyl arms. Interestingly, reaction of $\mathbf{L}^{P3}$ with [AuCl(tht)] (tht = tetrahydrothiophene) results in the appearance of two phosphorus-containing species characterized by resonances at 35.8 ppm and 25.1 ppm in a 1:2 intensity ratio (Supporting Information). The former can be confidently assigned to the dinuclear complex [{o-$(Ph_2P)C_6H_4Au\}_2$] (**1**), which has been previously fully characterized.[10] Formation of this compound indicates that $\mathbf{L}^{P3}$ acts as an organometallic reagent and is able to transfer at least one of its o-phenylenephosphino group to gold, presumably through exchange with a chloride anion.[7]



Scheme 1. Synthesis of **1** and **2**.

Fractional crystallization afforded a moderate yield of the second species (**2**) as yellow crystals, which were subjected to an X-ray analysis. The crystal structure of **2** confirmed the exchange of one of the three o-phenylenephosphino groups of $\mathbf{L}^{P3}$ for a chloride ligand, leading to the generation of the chlorobismuthine (o-$(Ph_2P)C_6H_4)_2BiCl$ ligand ($\mathbf{L}^{P2Cl}$) directly in the coordination sphere of the AuCl fragment (Figure 1).[11] The two phosphine arms of the complex are coordinated to the gold center in a *trans* arrangement, placing the bismuth atom only at 2.9738(17) Å from the gold atom. This separation is much shorter than the value of 3.7284(5) Å reported for $[Au(C_6F_5)_2][Bi(2\text{-}NMe_2CH_2C_6H_4)_2]$, a ion pair in which the heavy elements are held by weak Coulombic and

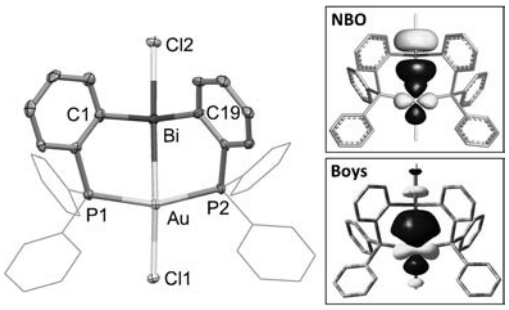


Figure 1. Left: Solid-state structure of **2**. Ellipsoids are set at 50% probability; phenyl groups are drawn in wireframe; hydrogen atoms and non-coordinated solvent molecules are omitted for clarity. Pertinent metrical parameters can be found in the text. Right: NBO plot showing the donor–acceptor interaction of a filled d(Au) orbital with a vacant p(Bi) orbital (top, isovalue = 0.05) and Au–Bi Boys orbital (bottom, isovalue = 0.02). Hydrogen atoms are omitted for clarity.

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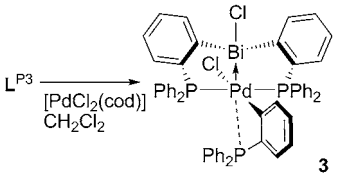
[**] Financial support from the Welch Foundation (A-1423), the National Science Foundation (CHE-0952912), Texas A&M University (Davidson Professorship), and the Laboratory for Molecular Simulation at Texas A&M University (software and computation resources) is gratefully acknowledged. We thank Lisa Pérez and Clark Landis for their help with the implementation of NBO.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200854.

dispersion forces.[12] In fact, the Bi–Au distance of **2** only exceeds the sum of the covalent radii of the two elements (2.75–2.84 Å)[13] by 4.7–8.1 %, thus suggesting the presence of a bond between these two centers. Although it is tempting to propose that this bond has the anticipated Bi→Au donor–acceptor character, a closer inspection of the coordination sphere of the metals suggests otherwise. Indeed, the values of the Bi-Au-Cl1 (162.36(5)°) and P1-Au-P2 (156.77(8)°) angles indicate that the gold atom adopts a distorted square-planar geometry characteristic of the trivalent state. Another anomaly can be observed in the coordination geometry of the bismuth atom which adopts a disphenoid rather than tetrahedral geometry, with the gold atom *trans* from the chlorine atom (Au-Bi-Cl2 = 172.84(6)°). Altogether, these structural peculiarities strongly suggest the presence of a Au→Bi interaction. In line with this conclusion, the Bi–Cl2 bond distance (2.640(3) Å) in **2** exceeds that observed for $(2,6\text{-}Mes_2C_6H_3)_2BiCl$ (2.483(3) Å)[14] and approaches that in $[Ph_2BiCl_2]^-$ (2.733 Å).[15] Altogether, this geometry is reminiscent of that of hypervalent bismuth compounds with intramolecular N→Bi dative bonds.[16] The picture that emerges from this structural assay is one in which the bismuth center acts a σ-acceptor or Z ligand toward the gold atom. Complex **2** is related to a series of complexes with gold→Lewis acid interactions pioneered by Bourissou and co-workers.[17] It is also reminiscent of Au→Sb complexes that we have recently reported.[18] Unlike in these complexes, however, the Group 15 element remains trivalent rather than pentavalent.

To establish whether the σ-acceptor character of bismuthines or at least halobismuthines may also be expressed in other complexes, we decided to investigate the interaction of $\mathbf{L}^{P3}$ with Group 10 metals. With this in mind, $\mathbf{L}^{P3}$ was allowed to react with $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene; Scheme 2). This reaction proceeded cleanly to afford **3** as an



Scheme 2. Synthesis of **3**.

air-stable complex. Formation of **3** was supported by the detection of two coupled resonances with ^{31}P NMR spectroscopy (15.8 ppm, d; −22.4 ppm, t; $J_{P\text{-}P} = 25.4$ Hz) in a 2:1 intensity ratio. The multiplicity of these signals as well as their chemical shift suggested that at least two of the phosphine arms are coordinated to the palladium center, as confirmed by the solid-state structure of this complex (Figure 2). An examination of the structure reveals that the third phosphine arms underwent an exchange with a chloride ligand, leading to arylation of the palladium center with an *o*-phenylenephosphino group and formation of a $\mathbf{L}^{P2Cl}$ ligand in the coordination sphere of the transition metal.[11] The *trans* arrangement of two of the phosphino arms in this complex

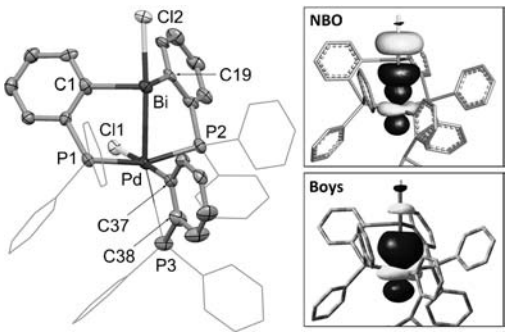


Figure 2. Left: Solid-state structure of **3**. Ellipsoids are set at 50% probability; phenyl groups are drawn in wireframe; hydrogen atoms and non-coordinated solvent molecules are omitted for clarity. Pertinent metrical parameters can be found in the text. Right: NBO plot showing the donor–acceptor interaction of a filled d(Pd) orbital with a vacant p(Bi) orbital (top, isovalue = 0.05) and Pd–Bi Boys orbital (bottom, isovalue = 0.02). Hydrogen atoms are omitted for clarity.

positions the bismuth atom directly above the palladium center, leading to a Pd–Bi separation of 2.9233(9) Å and a Pd-Bi-Cl2 angle of 175.09(6)°. Furthermore, the Bi–Cl2 bond in **3** (2.620(3) Å) shows a similar elongation to that observed in **2** (2.640(3) Å), in agreement with the presence of a Pd→Bi interaction. The Pd–Bi separation, which is in the upper range for Pd–Bi distances observed in heterometallic Pd/Bi complexes,[19] only exceeds the sum of the covalent radii (2.71–2.87 Å)[13] by 1.8–7.9 %. A further inspection of the structure shows that the palladium-bound *o*-phenylenephosphino group is interacting with the palladium center. This statement is supported by the Pd-C37-C38 (112.8(8)°) and P3-C38-C37 angles (117.1(8)°), which are both smaller that the ideal 120° value, leading to a Pd–P3 contact of 3.040(3) Å. The angles of Cl1-Pd-C37 (174.8(3)°), P1-Pd-P2 (161.91(11)°), and Bi-Pd-P3 (155.42(6)°) indicate that the coordination environment around palladium is best described as a distorted octahedron reminiscent of the tetravalent state.

To shed light on the electronic structure of these complexes, their structures were optimized by DFT methods using the Gaussian program[20] (BP86[21] with 6-31g for H, C; Stuttgart relativistic small core (RSC) 1997 ECP for Pd, Au; Stuttgart relativistic large core (RLC) ECP for P, Cl, Bi).[22] These optimized structures, which are in good agreement with the X-ray diffraction results (d_{calc}(Au–Bi) = 3.021 Å, d_{calc}(Pd–Bi) = 2.989 Å) were subjected to a NBO analysis. For both **2** and **3**, the NBO analysis treats the bismuth-bound chloride as an independent unit that interacts with the bismuth atom by a strong lp(Cl)→p(Bi) interaction. This interaction may be viewed as a dative bond resulting from the donation of a chloride lone pair into a vacant bismuth p orbital (Supporting Information). Interestingly, the same p orbital is involved in a d(M)→p(Bi) (M = Au or Pd) interaction, indicating that the late transition metal donates to the bismuth center by one of its filled d orbitals. Both molecules are thus described on the basis of classical three-center/four-electron hypervalent bonding. Deletion energies (E_{del}) calculated for the d(M)→p(Bi) interactions ($E_{del} = 16.4$ kcal mol^{-1} for **2** and 19.2 kcal mol^{-1} for **3**) indicate that they are substantial contributors to the stability of the complexes, although notably weaker than

the lp(Cl)→p(Bi) interactions (E_{del} = 90.8 kcal mol^{-1} for **2** and 101.3 kcal mol^{-1} for **3**).[23] The presence of a d(M)→p(Bi) interaction in these two complexes is supported by a Boys localization analysis, which treats the M–Bi bonds of **2** and **3** as σ bonds with elevated contribution from the late transition metal atomic orbitals (Au 85.5%, Bi 4.4% for **2**; Pd 91.2%, Bi 3.6% for **3**). Finally, both the NBO and Boys analyses treat the bismuth 6s lone pair as essentially non-bonding, indicating that the bismuth atom does not behave as a donor toward the late transition metal atom (Supporting Information).

The results presented herein indicate that chlorobismuthine ligands may behave as Z rather than L ligands. The emergence of this ligative behavior is correlated to the presence of an electronegative chloro substituent, which enhances the acidity of the bismuth center. A parallel to this phenomenon may be found in the chemistry of electron-deficient phosphines, such as PF_3, which behave as σ-donor/π-acceptor ligands.[24] In the case of the chlorobismuthine described herein, the 6s bismuth lone pair is too inert to be involved in bonding, thus unveiling an essentially pure electron-accepting behavior. We are currently exploring the generality of this phenomenon by investigating whether this σ-acceptor character may also be observed for other trivalent Group 15 fragments.

Experimental Section

[AuCl(tht)][25] and [$PdCl_2$(cod)][26] were prepared according to the reported procedures. Solvents were dried by passing through an alumina column (*n*-pentane and CH_2Cl_2) or refluxing under N_2 over Na/K (Et_2O and THF). All other solvents were used as received. $BiCl_3$ was purchased from Aldrich. Ambient-temperature NMR spectra were recorded on a Varian Unity Inova 400 FT NMR spectrometer (399.59 MHz for ^{1}H, 161.74 MHz for ^{31}P, 100.45 MHz for ^{13}C). Chemical shifts (δ) are given in ppm and are referenced against residual solvent signals (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Elemental analyses were performed at Atlantic Microlab (Norcross, GA). Electrospray mass spectra were obtained with a SciexQstarr Pulsar and a Protana Nanospray ion source.

$\mathbf{L}^{P3}$: An *n*-hexane solution of *n*BuLi (2.87 M, 1.12 mL, 3.22 mmol) was added to an Et_2O solution (10 mL) of *o*-(Ph_2P)C_6H_4Br (1.0 g, 2.93 mmol) at ambient temperature. The mixture was stirred for 20 min, resulting in the formation of a white precipitate of *o*-(Ph_2P)C_6H_4Li. The lithium salt was washed with Et_2O (3 × 5 mL) and suspended in an Et_2O solution (5 mL). A THF solution (5 mL) of $BiCl_3$ (314 mg, 0.997 mmol) was added dropwise to this suspension at ambient temperature. After stirring for 12 h, the solvent was removed under reduced pressure to afford a light brown solid. The product was re-dissolved in CH_2Cl_2 (20 mL) and filtered through celite. Removal of CH_2Cl_2 gave a white solid which was washed with a mixture of Et_2O/MeOH (1/20, 3 × 5 mL) and dried under vacuum to afford $\mathbf{L}^{P3}$ as a white power (0.78 g, 79% yield). ^{1}H NMR (399.59 MHz; $CDCl_3$): δ = 7.08 (pseudo t, 3H, *meta*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.25 Hz), 7.15–7.24 (m, 36H), 7.63 ppm (d, 3H, *ortho*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.69 Hz). ^{13}C{^{1}H} NMR (100.45 MHz; $CDCl_3$): δ = 127.6 (s), 128.1 (s), 128.2 (s), 131.6 (s), 133.6 (d, $J_{C\text{-}P}$ = 18.9 Hz), 134.6 (s), 137.3 (d, $J_{C\text{-}P}$ = 11.7 Hz), 139.9 (d, $J_{C\text{-}P}$ = 16.1 Hz), 145.3 (s), 171.9 ppm (dt, $J_{C\text{-}P}$ = 59.4 Hz, $J_{C\text{-}P}$ = 15.05 Hz). ^{31}P{^{1}H} NMR (161.74 MHz; $CDCl_3$): δ = −8.10 ppm (s). Elemental analysis calcd (%) for $C_{54}H_{42}BiP_3$: C 65.33, H 4.26; found: C 64.87, H 4.43.

2: A THF solution (3 mL) of [AuCl(tht)] (65 mg, 0.20 mmol) was added dropwise to a THF solution (2 mL) of $\mathbf{L}^{P3}$ (100 mg, 0.10 mmol) at ambient temperature. The resulting mixture was allowed to stir for 12 hours. The solvent was then removed under reduced pressure to give a light yellow solid, which was washed with Et_2O (3 × 5 mL) to afford a mixture of **1** (white solid) and **2** (yellow solid) (113 mg, 77% yield) in exact 1:2 ratio determined by ^{1}H and ^{31}P NMR. Both complexes are air stable and are only sparsely soluble in CH_2Cl_2 and $CHCl_3$. Fractional crystallization from CH_2Cl_2/Et_2O afforded yellow crystals of **2**·CH_2Cl_2. ^{1}H NMR of **2** (399.59 MHz; $CDCl_3$): δ = 6.96 (d, 2H, *ortho*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.07 Hz), 7.42–7.51 (m, 18H), 7.77 (t, 4H, *para*-PPh, $^3J_{H\text{-}H}$ = 7.26 Hz), 7.88 (d of pseudo t, 2H, *meta*-P(Bi)C_6H_4, $^4J_{P\text{-}H}$ = 1.16 Hz, $^3J_{H\text{-}H}$ = 7.62 Hz), 9.10 ppm (d, 2H, *ortho*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.48 Hz). ^{13}C{^{1}H} NMR of **1** + **2** (100.45 MHz; $CDCl_3$): δ = 125.7 (t, $J_{C\text{-}P}$ = 3.57 Hz), 127.4 (t, $J_{C\text{-}P}$ = 28.58 Hz), 128.3 (t, $J_{C\text{-}P}$ = 5.00 Hz), 128.6 (t, $J_{C\text{-}P}$ = 5.00 Hz), 129.2 (t, $J_{C\text{-}P}$ = 5.72 Hz), 129.4 (s), 129.8 (t, $J_{C\text{-}P}$ = 4.33 Hz), 130.2 (s), 132.1 (d, $J_{C\text{-}P}$ = 12.04 Hz), 133.2 (t, $J_{C\text{-}P}$ = 6.02 Hz), 134.0 (t, $J_{C\text{-}P}$ = 6.40 Hz), 134.2 (t, $J_{C\text{-}P}$ = 6.73 Hz), 134.4 (t, $J_{C\text{-}P}$ = 6.68 Hz), 135.5 (s), 137.7 (s), 137.9 (t, $J_{C\text{-}P}$ = 11.44 Hz), 140.2 (t, $J_{C\text{-}P}$ = 11.44 Hz), 142.3 (d, $J_{C\text{-}P}$ = 3.31 Hz), 143.3 (t, $J_{C\text{-}P}$ = 31.65 Hz), 176.8 ppm (t, $J_{C\text{-}P}$ = 22.70 Hz). ^{31}P{^{1}H} NMR of **2** (161.74 MHz; $CDCl_3$): δ = 25.1 ppm (s). HRMS (ESI$^+$) calcd for [M−Cl]$^+$ ($C_{36}H_{28}AuBiClP_2^+$): 963.0819, found: 963.0842.

3: A solution of [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) (29 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $\mathbf{L}^{P3}$ (100 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) at ambient temperature, affording a red solution. After stirring for 12 hours, the solvent was removed under reduced pressure. The resulting residue was washed with Et_2O (3 × 5 mL) to afford **3** as a yellow crystalline solid (105 mg, 89% yield). Yellow crystals of **3**·2CH_2Cl_2·H_2O suitable for X-ray diffraction analysis were obtained from diffusing *n*-pentane into a CH_2Cl_2 solution of **3** over two days. ^{1}H NMR (399.59 MHz; $CDCl_3$): δ = 6.08 (d, 1H, *ortho*-P(Pd)C_6H_4, $^3J_{H\text{-}H}$ = 8.71 Hz), 6.37–6.42 (m, 1H, *meta*-P(Pd)C_6H_4), 6.45–6.49 (m, 3H), 6.75 (t, 4H, *para*-PPh, $^3J_{H\text{-}H}$ = 8.00 Hz), 6.78–6.81 (m, 2H), 6.88–6.94 (m, 8H), 7.03 (pseudo t, 2H, *meta*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.50 Hz), 7.16 (pseudo t, 2H, *meta*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.50 Hz), 7.25–7.29 (m, 5H), 7.33–7.37 (m, 2H), 7.83 (t, 2H, *para*-PPh, $^3J_{H\text{-}H}$ = 7.80 Hz), 8.02 (bs, 8H, *ortho*-PPh), 9.32 ppm (d, 2H, *ortho*-P(Bi)C_6H_4, $^3J_{H\text{-}H}$ = 7.59 Hz). ^{13}C{^{1}H} NMR (100.45 MHz; $CDCl_3$): δ = 124.3 (s), 127.8 (s), 127.9 (t, $J_{C\text{-}P}$ = 3.95 Hz), 128.0 (d, $J_{C\text{-}P}$ = 6.17 Hz), 128.7 (d, $J_{C\text{-}P}$ = 5.43 Hz), 129.7 (s), 131.5 (s), 132.4 (s), 132.7 (d, $J_{C\text{-}P}$ = 17.35 Hz), 132.9 (t, $J_{C\text{-}P}$ = 5.10 Hz), 133.3 (s), 134.4 (s), 135.9 (s), 136.4 (s), 136.6 (t, $J_{C\text{-}P}$ = 8.16 Hz), 137.2 (d, $J_{C\text{-}P}$ = 14.17 Hz), 140.0 (dt, $J_{C\text{-}P}$ = 29.12 Hz, $J_{C\text{-}P}$ = 4.72 Hz), 141.5 (d, $J_{C\text{-}P}$ = 16.53 Hz), 163.9 (d, $J_{C\text{-}P}$ = 34.04 Hz), 184.7 ppm (t, $J_{C\text{-}P}$ = 17.06 Hz). ^{31}P{^{1}H} NMR (161.74 MHz; $CDCl_3$): δ = −22.4 (t, 1P, $J_{P\text{-}P}$ = 25.4 Hz), 15.8 ppm (d, 2P, $J_{P\text{-}P}$ = 25.4 Hz). HRMS (ESI$^+$) calcd for [M−Cl]$^+$ ($C_{54}H_{42}BiClP_3Pd^+$): 1133.1042, found: 1133.1059. Elemental analysis calculated (%) for $C_{54}H_{42}BiCl_2P_3Pd$·H_2O: C 54.59, H 3.73; found: C 54.57, H 3.59 (2 equiv of CH_2Cl_2 was lost in drying).

Received: January 31, 2012
Published online: March 27, 2012

Keywords: bismuth · gold · hypervalence · Lewis acids · palladium

[1] a) R. D. Rogers, A. H. Bond, S. Aguinaga, A. Reyes, *J. Am. Chem. Soc.* **1992**, *114*, 2967–2977; b) R. D. Rogers, A. H. Bond, S. Aguinaga, *J. Am. Chem. Soc.* **1992**, *114*, 2960–2967; c) S. R. Breeze, S. Wang, L. K. Thompson, *Inorg. Chim. Acta* **1996**, *250*, 163–171; d) S. Wang, D. B. Mitzi, G. A. Landrum, H. Genin, R. Hoffmann, *J. Am. Chem. Soc.* **1997**, *119*, 724–732.

[2] a) C. Limberg, *Angew. Chem.* **2003**, *115*, 6112–6136; *Angew. Chem. Int. Ed.* **2003**, *42*, 5932–5954; b) T. A. Hanna, *Coord. Chem. Rev.* **2004**, *248*, 429–440.

[3] a) J.-P. Finet, *Chem. Rev.* **1989**, *89*, 1487–1501; b) C. Le Roux, J. Dubac, *Synlett* **2002**, 181–200.

[4] a) S. Roggan, G. Schnakenburg, C. Limberg, S. Sandhöfner, H. Pritzkow, B. Ziemer, *Chem. Eur. J.* **2005**, *11*, 225 – 234; b) S. Roggan, C. Limberg, B. Ziemer, M. Brandt, *Angew. Chem.* **2004**, *116*, 2906 – 2910; *Angew. Chem. Int. Ed.* **2004**, *43*, 2846 – 2849; c) C. Knispel, C. Limberg, *Organometallics* **2011**, *30*, 3701 – 3703; d) I. J. Casely, J. W. Ziller, M. Fang, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2011**, *133*, 5244 – 5247.

[5] a) N. A. Compton, R. J. Errington, N. C. Norman in *Adv. Organomet. Chem.*, *Vol. 31* (Eds.: F. G. A. Stone, W. Robert), Academic Press, **1990**, pp. 91 – 182; b) C. Silvestru, H. J. Breunig, H. Althaus, *Chem. Rev.* **1999**, *99*, 3277 – 3328; c) M. Michael, *Coord. Chem. Rev.* **2007**, *251*, 974 – 1006.

[6] W. V. Steele, *J. Chem. Thermodyn.* **1979**, *11*, 187 – 192.

[7] O. Schuster, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4079 – 4083.

[8] a) K. Ohkata, S. Takemoto, M. Ohnishi, K.-y. Akiba, *Tetrahedron Lett.* **1989**, *30*, 4841 – 4844; b) Y. Yamamoto, X. Chen, K. Akiba, *J. Am. Chem. Soc.* **1992**, *114*, 7906 – 7907; c) H. Suzuki, T. Murafuji, N. Azuma, *J. Chem. Soc. Perkin Trans. 1* **1992**, 1593 – 1600; d) D. A. Atwood, A. H. Cowley, J. Ruiz, *Inorg. Chim. Acta* **1992**, *198 – 200*, 271 – 274; e) Y. Yamamoto, K. Ohdoi, X. Chen, M. Kitano, K. Akiba, *Organometallics* **1993**, *12*, 3297 – 3303; f) X. Chen, K. Ohdoi, Y. Yamamoto, K. Akiba, *Organometallics* **1993**, *12*, 1857 – 1864; g) T. Ogawa, T. Ikegami, T. Hikasa, N. Ono, H. Suzuki, *J. Chem. Soc. Perkin Trans. 1* **1994**, 3479 – 3483; h) K. H. Ebert, R. E. Schulz, H. J. Breunig, C. Silvestru, I. Haiduc, *J. Organomet. Chem.* **1994**, *470*, 93 – 98; i) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, K.-y. Akiba, *J. Am. Chem. Soc.* **1995**, *117*, 3922 – 3932; j) C. J. Carmalt, A. H. Cowley, A. Decken, N. C. Norman, *J. Organomet. Chem.* **1995**, *496*, 59 – 67; k) S. Kamepalli, C. J. Carmalt, R. D. Culp, A. H. Cowley, R. A. Jones, N. C. Norman, *Inorg. Chem.* **1996**, *35*, 6179 – 6183; l) H. J. Breunig, L. Konigsmann, E. Lork, M. Nema, N. Philipp, C. Silvestru, A. Soran, R. A. Varga, R. Wagner, *Dalton Trans.* **2008**, 1831 – 1842; m) H. J. Breunig, M. G. Nema, C. Silvestru, A. Soran, R. A. Varga, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2378 – 2386; n) S. L. Benjamin, L. Karagiannidis, W. Levason, G. Reid, M. C. Rogers, *Organometallics* **2011**, *30*, 895 – 904.

[9] a) Such species may be involved in the oxidative addition reaction of $BiCl_3$ to $[Pt(PCy_3)_2]$: b) H. Braunschweig, P. Brenner, P. Cogswell, K. Kraft, K. Schwab, *Chem. Commun.* **2010**, *46*, 7894 – 7896.

[10] M. A. Bennett, S. K. Bhargava, K. D. Griffiths, G. B. Robertson, W. A. Wickramasinghe, A. C. Willis, *Angew. Chem.* **1987**, *99*, 261 – 262; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 258 – 260.

[11] CCDC 864515 (**2**) and 864516 (**3**) 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.

[12] E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Nema, M. E. Olmos, J. Pérez, C. Silvestru, *Chem. Commun.* **2007**, 571 – 573.

[13] a) P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186 – 197; b) B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832 – 2838.

[14] N. J. Hardman, B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 2884 – 2886; *Angew. Chem. Int. Ed.* **2000**, *39*, 2771 – 2773.

[15] J. P. H. Charmant, A. G. Orpen, S. C. James, N. C. Norman, J. Starbuck, *Acta Crystallogr. Sect. E* **2002**, *58*, m488 – m489.

[16] a) T. Murafuji, N. Azuma, H. Suzuki, *Organometallics* **1995**, *14*, 1542 – 1544; b) C. J. Carmalt, A. H. Cowley, R. D. Culp, R. A. Jones, S. Kamepalli, N. C. Norman, *Inorg. Chem.* **1997**, *36*, 2770 – 2776; c) X.-W. Zhang, J. Xia, H.-W. Yan, S.-L. Luo, S.-F. Yin, C.-T. Au, W.-Y. Wong, *J. Organomet. Chem.* **2009**, *694*, 3019 – 3026.

[17] a) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem.* **2007**, *119*, 8737 – 8740; *Angew. Chem. Int. Ed.* **2007**, *46*, 8583 – 8586; b) M. Sircoglou, M. Mercy, N. Saffon, Y. Coppel, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem.* **2009**, *121*, 3506 – 3509; *Angew. Chem. Int. Ed.* **2009**, *48*, 3454 – 3457; c) A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859 – 871; d) E. J. Derrah, S. Ladeira, G. Bouhadir, K. Miqueu, D. Bourissou, *Chem. Commun.* **2011**, *47*, 8611 – 8613.

[18] a) C. R. Wade, F. P. Gabbaï, *Angew. Chem.* **2011**, *123*, 7507 – 7510; *Angew. Chem. Int. Ed.* **2011**, *50*, 7369 – 7372; b) 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; c) C. R. Wade, I.-S. Ke, F. P. Gabbaï, *Angew. Chem.* **2012**, *124*, 493 – 496; *Angew. Chem. Int. Ed.* **2012**, *51*, 478 – 481.

[19] a) J. L. Stark, B. Harms, I. Guzman-Jimenez, K. H. Whitmire, R. Gautier, J.-F. Halet, J.-Y. Saillard, *J. Am. Chem. Soc.* **1999**, *121*, 4409 – 4418; b) B. Li, H. Zhang, L. Huynh, C. Diverchy, S. Hermans, M. Devillers, E. V. Dikarev, *Inorg. Chem.* **2009**, *48*, 6152 – 6158; c) F. Lips, R. Clérac, S. Dehnen, *J. Am. Chem. Soc.* **2011**, *133*, 14168 – 14171.

[20] Gaussian 03, version C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowswi, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Jonhson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Pittsburgh PA, **2006**.

[21] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 – 8824.

[22] a) G. Igel-Mann, H. Stoll, H. Preuss, *Mol. Phys.* **1988**, *65*, 1321 – 1328; b) A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuß, *Mol. Phys.* **1993**, *80*, 1431 – 1441; c) D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571 – 1586; d) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045 – 1052.

[23] a) Energy deletion calculations are carried out by zeroing the Kohn–Sham matrix elements corresponding to an interaction and by recalculating the total energy of a molecule. The total energies of the molecule with and without the interaction are then substracted from each other, affording $E_{del.}$ A positive E_{del} value indicates that the deleted interaction is stabilizing. Examples are given in a Review: b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926.

[24] a) G. Frenking, K. Wichmann, N. Fröhlich, J. Grobe, W. Golla, D. L. Van, B. Krebs, M. Läge, *Organometallics* **2002**, *21*, 2921 – 2930; b) H.-q. Yang, Q.-s. Li, Y. Xie, R. B. King, H. F. Schaefer, *J. Phys. Chem. A* **2010**, *114*, 8896 – 8901.

[25] R. Uson, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85 – 91.

[26] D. Drew, J. R. Doyle, *Inorg. Synth.* **1990**, *28*, 346 – 349.