ORGANOMETALLICS

Heavy Group 15 Element Compounds of a Sterically Demanding Bis(iminophosphorane)methanide and -methanediide

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Supporting Information

ABSTRACT: Complexes of the heavy pnictogen elements Sb and Bi of monoanionic (*C*,*N*-chelated: Sb, Bi) and dianionic (*N*,*C*,*N*-pincer type: Bi) bulky substituted bis(diphenyl-(arylimino)phosphorano)methane $H_2C(Ph_2PNR)_2$ (R = 2,6-diisopropylphenyl (dipp)) have been prepared via metathetical reactions, and tautomerism within the monoanionic ligand backbone has been observed. The complexes have been characterized by means of X-ray analysis and NMR studies.



The dianionic complex was found to feature the rare structural motif of a formal carbon–bismuth(III) double bond. The molecular structure of the solvate-free potassium salt $K[HC(Ph_2PNdipp)_2]$ is reported.

INTRODUCTION

In recent years, the coordination chemistry of neutral, monoand dianionic, sterically hindered bis(iminophosphorane)methane ligands with main-group elements, transition metals, and f-block elements has been intensely studied.¹ A broad range of different coordination modes has been found, highlighting the flexibility of the ligand system going back to the great number of the systems' mesomeric descriptions and the delocalization of charge therein. The strong delocalization of charge in the case of the dianionic ligand demanded intensive discussions of adequate descriptions for the bonding situation, especially in the case of main-group complexes.^{1c,f,g} A variety of sterically demanding N-bond residues enables a fine tuning of the ligand systems' bulkiness, which has a direct influence on the oligomerization of the respective complexes.² The majority of the reported bis(iminophosphorane)methanide and -methanediide compounds apply trimethylsilyl and mesityl residues attached to the imino nitrogen atom, while the application of the sterically more demanding 2,6-diisopropylphenyl moiety is less common.^{1a,b,h,2d}

Most importantly, through an internally stabilized dianionic carbon moiety the dideprotonated bis(iminophosphorane)methane ligand class provides a formal precursor for carbon– element double bonds, which are interesting structural motifs in organometallic chemistry. Especially in the case of bismuth only a few structurally characterized examples of $R_2C=Bi^{III}(X/R)$ are known in the literature.³ Along with numerous examples of alkali-metal and alkali-earth-metal compounds there are several reported examples of group 13 and 14 complexes.^{2a,c,4} In the course of the preparation of this paper, complexes of the monoanionic *N*-trimethylsilyl system with $[EI_2]^+$ (E = As, Sb, Bi) have been reported.⁵ Bi and Sb compounds of the related dianionic bissulfido system bis(diphenylsulfidophosphorane)methane, $[ECl{C(Ph_2PS)_2}]$ (E = Sb, Bi), have also been forthcoming, as well as complexes of the structurally related mono- and dianionic N-dipp-substituted diketiminates (nacnac) with bismuth chloride.^{3,6}

We have investigated the coordination chemistry of bis-(diphenyl(arylimino)phosphorane)methane systems toward the heavy group 15 elements bismuth and antimony, applying the bulky N-bonded dipp residue $H_2C(Ph_2PNdipp)_2$ (1). Our work has resulted in the synthesis of $[EX_2\{C(Ph_2PNdipp)-(Ph_2PNHdipp)\}]$ (2, $EX_2 = BiCl_2$; 3, $EX_2 = SbI_2$) and $[BiCl\{C(Ph_2PNdipp)_2\}]$ (4), which we now report.

Scheme 1 summarizes the ligand and its alkali-metal salts that were used as precursors for this study. For the dilithio salt the



depicted description with alternating positive and negative charges was previously found to represent an important canonical description for bis(iminophosphorane)methanediides by means of computational methods.^{2a}

RESULTS AND DISCUSSION

The known potassium salt **1c** was shown to be a convenient synthetic precursor for the formation of various bis-(iminophosphorane)methanide complexes via salt metathesis reactions.^{4b} In the course of our studies we obtained an X-ray

Received: October 31, 2013 Published: December 9, 2013 structure from colorless crystals of the so far unknown solventfree potassium salt 1c from a hexane solution. X-ray analysis revealed a polymeric structure in which the potassium cation is coordinated by the ligand in a *C*,*N*-chelate type, further supported by η^6 coordination of the aromatic moiety of the dipp group attached to the noncoordinating nitrogen. An additional η^2 interaction is given with the aromatic phenyl moiety of an adjacent molecule. Figure 1 depicts the polymeric



Figure 1. ORTEP plot of the molecular structure of **1c**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): K(1)-N(1) 2.737(3), K(1)-C(1) 3.146(3), $K(1)-C_{dipp}$ range 3.173(3)–3.244(4), K(1)-C(17) 3.304(5), K(1)-C(18) 3.111(4), P(1)-N(1) 1.584(3), P(1)-C(1) 1.708(3), P(2)-C(1) 1.722(3), P(2)-N(2) 1.580(3).

structure found for the solvent-free potassium salt 1c. In comparison to the structural findings for the THF adduct, no significant changes for the bond length of the NPCPN moiety are observed. Nevertheless, polymeric 1c reveals shorter K1–C1 (3.146(3)/3.501(6) Å) as well as K1–N1 bonds (2.668(5)/2.737(3) Å). In the case of polymeric 1c, K1 is coordinated more symmetrically to the dipp group, indicated by a smaller $K(1)-C_{dipp}$ range (3.173(3)–3.244(4)/3.106(6)–3.450(8) Å).

On reaction of the monolithiated ligand Li[HC- $(Ph_2PNdipp)_2$]^{4c} (1a) with 1 equiv of BiCl₃ in a THF/toluene mixture at -78 °C and workup, we obtained 2 as a bright yellow compound (Scheme 2). Single-crystal diffraction of





crystals from diethyl ether revealed **2** to be monomeric in the solid state. The $[BiCl_2]^+$ fragment turns out not to be incorporated into a six-membered ring by the ligand applying a *N*,*N*-chelate coordination mode but rather a four-membered BiCPN heterocycle is formed in which $[BiCl_2]^+$ is coordinated in an unsymmetrical *C*,*N*-chelate mode. The PCP carbon atom was unexpectedly found to be fully deprotonated. Most likely coordination of the Lewis acidic Bi³⁺ causes a sufficient change in acidity of the C–H to undergo an intramolecular 1,3-proton shift to the alkaline noncoordinating second *P*-imino nitrogen. Such a proton shift can be seen as a P analogue of the known imine—enamine tautomerism and has been described by most recent works published in the course of the preparation of this

paper.⁵ On consideration of the Lewis acidity of a coordinated element halide fragment to cause a proton shift, it is interesting that for smaller elements with potentially more Lewis acidic fragments such as [AlCl₂]⁺, [AlBr₂]⁺, and [GaCl₂]⁺, a N,Nchelating coordination mode forming a six-membered ring is adopted and no proton shift occurs.^{4d,7} A somehow comparable shift has already been described for neutral bis-(iminophosphorane) methane ligands coordinating to transition metals (Rh, Ir, Pt).8 On protonation of bis-(iminophosphorane)methanes $H_2C(Ph_2P=NR'')_2$ (R" = i-Pr,Ph) a similar shift has been observed, forming a cation with the constitution $[HC(Ph_2P=N(H)R'')_2]^{+,9}$ Additionally a substantial increase of the acidity of a methanide proton in metal complexes was described by Le Floch for the case of neodymium methanide complexes, in which a further deprotonation can be achieved by amine bases to yield a methanediide complex.¹ⁱ

Figure 2 shows the crystal structure of complex 2. Bright yellow crystals grew from hexane extracts of the crude reaction



Figure 2. ORTEP plot of the molecular structure of $2 \cdot 0.5(n$ -hexane). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (except H55) and the solvent molecule as well as a potential H55–Cl1 interaction have been omitted for clarity. Hydrogen atom H55 was located in the Fourier map. Selected bond lengths (Å) and angles (deg): C(1)–P(2) 1.708(3), C(1)–P(1) 1.727(3), P(1)–N(2) 1.630(3), P(2)–N(1) 1.672(3), C(1)–Bi(1) 2.217(3), N(2)–Bi(1) 2.354(2), P(1)–Bi(1) 2.9961(8), Bi(1)–Cl(2) 2.6121(10), Bi(1)–Cl(1) 2.7040(8), Cl(1)–H(55) 2.621(30); P(1)–C(1)–P(2) 132.1(2), C(1)–Bi(1)–N(2) 67.5(1), C(1)–Bi(1)–Cl(2) 105.2(1), C(1)–Bi(1)–Cl(1) 90.2(1), N(2)–Bi(1)–Cl(1) 157.2(1), Cl(1)–Bi(1)–Cl(2) 92.9(1), N(2)–Bi(1)–Cl(2) 88.9(1).

product or from saturated ethereal solutions. The crystal system was found to be monoclinic in the space group $P2_1/c$. In comparison to the free neutral ligand, C–P bond lengths are contracted and P–N bond lengths are elongated, indicating mesomeric delocalization of charge. C(1) is shown to be almost planar three-coordinate with a sum of bond angles of 358.4°.

The *C*,*N*-chelating coordination of a monoanionic CPN moiety toward bismuth, forming a CPNBi four-membered heterocycle, represents a rare structural motif. The absence of significant pyramidalization at C(1) contradicts the assumption of a carbon-localized, stereochemically active lone pair and a formal residual negative charge (Scheme 3, C). Moreover, a bonding situation as depicted in **A** and **B** with delocalized double-bond character within the PCP system seems to be an appropriate description. The N(2)– C_{ipso} (dipp) bond is only



slightly twisted out of the Bi(1)N(2)P(1)C(1) least-squares plane by 15.3° (0° expected for pure sp² hybridization at N(2), 54.7° for sp³), indicating that sp²-type hybridization is considerably predominant (Scheme 3, **B**). The Bi1–N2 (2.354(2) Å) distance is essentially equal to those reported for four-membered NCNBi cycles in amidinate complexes of [BiCl₂]⁺ (2.333(5), 2.359(4) Å)¹⁰ but much shorter than in a comparable CCNBi four-membered cycle found in a dianionic nacnac complex coordinating two [BiCl₂]⁺ fragments (2.500(13), 2.539(11) Å).⁶

Solution ¹H NMR experiments for 2 revealed three sets of isopropyl moieties. For the iPr methine protons two overlapping septets in the range 3.70-3.85 ppm are observed. For the methyl protons two broad resonances at 1.34 and 0.56 ppm and one sharp doublet at 1.21 ppm with a relative integration of 1:1:2 are observed. The broad methyl resonances are assigned to the dipp group attached to N2, and their different chemical shifts are deduced from their orientation toward the CPNBi plane. The sharp doublet is assigned to the free dipp group attached to N1. By means of an ^IH-¹⁵N HSQC experiment a proton resonance at 7.65 ppm was clearly identified as the N1bonded amine proton. The chemical shift of the N-bonded proton is in accordance with iminophosphorane hydrochlorides known in the literature.¹¹ The ${}^{31}P{}^{\hat{1}}H{}$ NMR spectrum shows a very broad resonance at 45.3 ppm and a sharp doublet at 26.8 ppm with a ${}^{2}J_{PP}$ coupling constant of 48.3 Hz. ${}^{1}H-{}^{31}P$ experiments reveal cross-coupling between proton H55 and P2 and enable the assignment of the sharp doublet to P2. The reason for the significant broadening of the phosphorus incorporated in the CPNBi four-membered ring could not be fully determined, though it results most likely from dynamic effects. Coupling with the considerably strong quadrupole nucleus of Bi with $I = \frac{9}{2}$ and 100% natural abundance seemed likely, but no comparable broadening was observed for $[BiCl{C(Ph_2PNdipp)_2}]$ (4) (vide infra). When a sample in benzene- d_6 was heated to 50 °C, the half-width decreased significantly, but due to the thermolability of the compound decomposition was observed, indicated by increasing signals of the free ligand. However, this decomposition with formation of 1 was not accompanied by an observable formation of 4 (vide infra).

Taking into account that there is a considerably short H(55)-Cl(1) distance (2.62 Å) and a fitting spatial alignment indicating a concrete interaction, compound 2 can be described as a zwitterionic intramolecularly generated HCl adduct of the twice deprotonated [BiCl{C(Ph₂PNdipp)₂}] (4) (Scheme 3).

Analogously, the related antimony complex $[SbI_2\{C-(Ph_2PNdipp)(Ph_2PNHdipp)\}]$ (3) was obtained by treatment of antimony(III) iodide with 1c in a mixture of THF and toluene at -50 °C as a yellow solid that is highly sensitive toward water and oxygen. From various experiments with carefully dried solvents hydrolysis products such as 1.2HI or [1-H]I₃ crystallized. Plate-shaped crystals of 3 in the monoclinic space group $P2_1/c$ obtained by various approaches were repeatedly of low quality but reveal the same molecular structure as observed for the bismuth chloride analogue 2 (see the Supporting Information). Moreover, NMR spectroscopic data are found to be essentially identical. The thermolability above ambient temperature of 3 toward decomposition into the free ligand was found to be even more distinctive than for 2.

In both cases no further coordination contacts with halides of adjacent molecules were found. The coordination geometry around bismuth in 2 as well as around antimony in 3 represents a distorted seesaw analogous to the reported "cis"-type complexes found for the trimethylsilyl-substituted derivatives, in which the $[EX_2]^+$ fragment features a bent alignment.⁵ On the basis of a sole X-ray structure Chivers and Vargas-Baca et al. found a symmetrically N,C,N-chelating coordination type for an almost linear [BiI₂]⁺ fragment and applied quantum mechanical calculations to provide an explanation for the absence of the intramolecular 1,3-proton shift in the case of bismuth. In their findings the generally energetically favored CH tautomer of the ligand is overcompensated by a stabilizing interaction energy between the ligand anion and the metal fragment (for which only a linear arrangement was considered). The amount of the stabilizing interaction decreases descending from As to Bi, which is why $[AsI_2]^+$ and $[SbI_2]^+$ favor a coordination by the NH tautomer over the CH tautomer found for $[BiI_2]^{+,5}$ The fact that we found the NH tautomer [BiCl₂]⁺ complex as the sole product is interesting and may go back to differences in the nature of the halides (iodide vs chloride), the arrangement of the metal halide fragment (linear vs bent), and the basicity of the imino nitrogens depending on the residues attached (trimethylsilyl vs dipp). Nevertheless, it may be a good indication that the energetic differences between the two opponent coordination modes are small.

Reacting BiCl₃ with the dilithium salt of the ligand $Li_2[C(Ph_2PNdipp)_2]$ (1b) in a mixture of THF and toluene at -35 °C or by treatment of 2 with 1 equiv of a non-nucleophilic base such as lithium 2,2,5,5-tetramethylpiperidide in THF resulted in the formation of another yellow compound with a singlet resonance in the ³¹P{¹H} NMR spectrum at 3.5 ppm (Scheme 4). Any attempts to generate the corresponding





homologous dianionic complex of Sb by an analogously performed deprotonation of 3 did not lead to any successful isolation but to a mixture of several products according to ${}^{31}P{}^{1}H{}$ NMR. For the reaction of the dilithiated *N*-trimethylsilyl bis(iminophosphorane)methane derivative with bismuth iodides an inseparable mixture of products was found previously.⁵ While some examples for monoanionic *N*,*C*,*N* pincer complexes of bismuth have been reported in the literature, ^{5,12} 4 represents the first dianionic compound featuring this structural motif.

Since the preparation of pure dilithium compound **1b** can be low-yielding, the two-step reaction with another 1 equiv of base represents an easier, more reliable access to **4**. Crystals of the symmetrically coordinated compound 4 can be obtained by gas-phase diffusion of n-pentane into solutions of 4 in benzene. X-ray analysis (Figure 3) revealed the monomeric methanediide



Figure 3. ORTEP plot of the molecular structure of 4 from a frontal perspective (top) and upon the CPNBi planes (bottom). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi1(1)-C(19) 2.1822(18), Bi1(1)-N(1) 2.3987(15), Bi(1)-N(2) 2.4496(15), Bi(1)-Cl(1) 2.5430(5), P(1)-C(19) 1.7098(18), P(2)-C(19) 1.7056(18), P(1)-N(1) 1.6310(17), P(2)-N(2) 1.6214(16); P(1)-C(19)-P(2) 150.9(1), N(1)-Bi(1)-N(2) 132.2(1), C(19)-Bi(1)-Cl(1) 105.6(1), N(1)-Bi(1)-Cl(1) 92.5(1), N(2)-Bi(1)-Cl(1) 90.1(1).

complex of the [BiCl]²⁺ fragment to be almost symmetric with a short Bi-C bond length of 2.182(2) Å, comparable to the bond length reported for the $[(S=PPh_2)_2C]^{2-}$ complex (2.160(7) Å).³ The bond lengths in the monoanionic complex $[BiI_2{HC(Ph_2PN(TMS))_2}]$ recently reported are 2.392(6) Å (Bi-C) and 2.412(5)/2.462(5) Å (Bi-N).⁵ Interestingly, further deprotonation almost solely results in shortening of the Bi-C bond by approximately 0.2 Å, while the Bi-N bonds are only shortened by approxinately 0.02 Å. The P-C and P-N bond lengths for $[BiI_2{HC(Ph_2PN(TMS))_2}]$ are 1.756(6)/ 1.763(6) and 1.581(5)/1.596(5) Å, respectively.⁵ In comparison to the findings for the dianionic complex 4, shortening of the P–C bonds by approximately 0.05 to 1.71 Å and a very small elongation of the P-N bonds are observed. These comparisons are potentially influenced by electronic differences caused by the N-bonded residue.

Unlike the pentacoordinated bismuth center in the dimerized sulfido complex, 4 features a tetracoordinated Bi(III) ion.³ The "open book"-type structure strongly resembles findings for the N-trimethylsilyl-substituted bis(iminophosphorane)-methanediide complexes of Ti and Zr halides.¹³ The two least-squares planes CPNBi intersect along the Bi–C bond at a small angle of approximately 12.6°, and the sum of angles

around C19 amounts to 351° with a large PCP angle of $150.93(12)^{\circ}$ (143.0(4)° for the sulfido system).³ Unlike what was stated in the respective literature in the NMR spectra, a ^{13}C resonance for the doubly deprotonated PCP carbon of the methanediide complex of Bi can be observed as a triplet at δ 64.1 ppm (${}^{1}J_{PC}$ = 134.49 Hz), demonstrating a stronger downfield shift and an increased coupling constant in comparison to those for a reported structurally related sulfido-Sb compound (δ 32.7 ppm, ${}^{1}J_{PC} = 42.2$ Hz).³ Nevertheless, the PCP ${}^{13}C$ resonances for the stated $[{(Me_3SiN=PPh_2)_2C}(MCl_2)]$ (M = Ti, Zr) emerge at lower field (191.7, 101.0 ppm), indicating an increased carbene character therein with consequences for the M=C double bond.^{13b} Recently the PCP ¹³C resonance for [{(Me₃SiN= PPh_2_2C (Ce(Odipp)₂)] has been reported at δ 324.6 ppm as an example of a methanediide complex featuring the typical strong downfield shift known for carbene complexes.1f Taking this into consideration and including the expectably weak orbital overlap between carbon and bismuth, a significant carbon-bismuth π interaction (and therefore a Bi=C bond) can be neglected. Altogether, the bonding situation is potentially best described by a partially ionic model with a polar Bi-C single bond and two dative N-Bi bonds. Within the NPCPN backbone an anionic charge is delocalized, balancing a residual positive charge on the bismuth halide fragment.

The ${}^{31}P{}^{1}H{}$ NMR spectrum confirms the symmetry within the molecule in solution at room temperature. The symmetric coordination mode is preserved in potentially coordinating donor solvents such as THF- d_8 . At room temperature the ¹H NMR reveals one broad resonance for the *i*Pr methine protons (δ 3.92 ppm) and two *i*Pr methyl resonances (one broad at δ 1.17 ppm, one sharp at δ 1.03 ppm). When the sample is cooled in toluene- d_{8} , a splitting of this pattern is observed with a coalescence near -20 °C. Upon further cooling down to -80 °C the methine resonances split into two resonances at δ 4.73 and 3.17 ppm. The methyl protons split into a set of four broad singlet signals at δ 1.83, 0.98, 0.91, and 0.41 ppm. The ³¹P{¹H} NMR remains unchanged by variation of the temperature. The spectra correspond to the structure determined by X-ray diffraction. In the case of lower temperatures the two methine signals represent an orientation of the *i*Pr moiety above or below the NBiCP planes, while the four methyl signals discriminate between the orientation above or below the respective plane and their orientation toward the front of the molecule or the PPh₂ groups within the backbone. A putative mechanism to explain the changes on cooling includes the assumption of restricted rotation around the N-C_{ipso}(dipp) bond. The suppression of free rotation at lower temperatures is consistent with the changes observed in the spectra. Another explanation including a rapid change of the chloride orientation within the coordination sphere of bismuth in the room temperature case can be ruled out, since two multiplet resonances of higher order can be found in the ¹³C{¹H} spectra for C_{ipso} of the phenyl groups attached to phosphorus representing orientations "cis" and "trans" to the bismuthbonded chloride.

Preliminary insights into the formation processes of some discussed species were drawn from a simple NMR-scale experiment in which an excess of approximately 1.5 equiv of the monolithiated ligand **1a** was added to BiCl₃. After a few minutes the ${}^{31}P{}^{1}H{}$ NMR spectrum of the reaction mixture revealed four singlet signals for the lithium salt **1a**, the free

Article



ligand 1, the methanediide complex 4, and another yet unassigned singlet at 25.1 ppm (Figure 4). After a few hours a sample drawn from the same reaction revealed only the signals for 2, 4, and 1. The monolithiated compound 1a has completely reacted, and the unassigned resonance at 25.1 ppm is no longer observed. We conclude that the singlet at 25.1 ppm represents a transiently formed symmetrical monoanionic complex (2a) of the $[BiCl_2]^+$ fragment that undergoes quick subsequent deprotonation by excess 1a to form 1 and 4. Further tautomerism to the structurally characterized 2 is potentially slower. A possible ligand disproportion reaction of 2 equiv of pure 2 into 1 and 4 has never been observed. Moreover, NMR sample solutions in benzene- d_6 or THF- d_8 of pure 2 and 3 stored at room temperature were stable even for several weeks. In the synthesis of 2, attempts to isolate 2a by quenching the reaction through solvent removal at an early stage followed by extraction of the residue remained unsuccessful and only 2 was obtained. It should be mentioned that the formation of methanediide complexes by metathetical reactions applying an excess of monolithiated bis-(iminophosphorane)methane as additional base has been described earlier in the case of the synthesis of group 14 vinylidene analogues.^{4e} The N,C,N-pincer structure for 2a depicted in Figure 4 is putative but is supported by Chivers' findings and does not exclude the possibility of a N,N-chelate type coordination as found for some nacnac systems.^{5,6} Nevertheless, the first coordination type may represent a more reasonable intermediate, considering the obvious subsequent tautomerism.

CONCLUSION

In summary, we have prepared bulky bis(iminophosphorane)methanide and -methanediide complexes of heavy group 15 elements. Tautomerism within the methanide complex was observed, adding a further example of a recently reported new coordination type of this flexible ligand system. Moreover, an unprecedented dianionic Bi N,C,N-pincer-type complex with interesting structural features and a formal C=Bi double bond has been prepared and characterized, augmenting the still small number of structurally determined examples for such carbon–bismuth interactions.^{3,14}

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or an MBraun glovebox. THF, diethyl ether, and benzene were distilled from sodium/benzophenone, toluene was distilled from sodium, and hexane was distilled from potassium. Pentane was obtained from an MBraun solvent purification system. Benzene- d_6 was distilled from sodium and stored over potassium; THF- d_8 was distilled from LiAlD₄ and stored under exclusion of light.

An insoluble impurity of BiOCl (up to 15%) was removed from $BiCl_3$ (Aldrich, >98%) by extraction of $BiCl_3$ with THF and removal of the solvent under reduced pressure (0.001 mbar) for 2 days. 1 was synthesized according to literature procedures.^{1e} All other compounds were purchased commercially (Aldrich) and used without further purification.

Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen, using a Vario MICRO EL analyzer.

[BiCl₂{C(Ph₂PNdipp)(Ph₂PNHdipp)}] (2). To a solution of BiCl₃ (0.223 g, 0.708 mmol, 1.05 equiv) in THF (5 mL) at -78 °C was slowly added a solution of 1a (0.500 g, 0.675 mmol, 1 equiv) dropwise, and the initially pale yellow solution was stirred overnight, during which time the mixture was warmed to room temperature. The solvents of the orange solution were completely removed under reduced pressure, and the yellow residue was washed with warm hexane (2 × 8 mL). The residue was then repeatedly extracted with warm ether (15, 10, 5 mL), and the combined ethereal extracts were reduced in volume to approximately 15–20 mL and stored at -28 °C for a few days to obtain bright yellow crystals of 2·Et₂O (0.200 g, 0.186 mmol, 28%, first crop). Further amounts of crystalline 2 could be obtained by further concentration of the supernatant solution and storage in the freezer. Crystals suitable for X-ray diffraction were

obtained from ethereal solutions as described above or (in very small quantities) from the hexane wash phases. The crystals discussed in the text 2.0.5(n-hexane) were obtained from the hexane solutions, though molecular parameters such as bond lengths and angles do not differ significantly from those of the Et₂O cosolvate structure. For 2·Et₂O, Et₂O does not show any coordinative interaction. Analytical data are as follows. ¹H (400.13 MHz, C₆D₆): δ 7.80–7.75 (m, 8H, o-C_{Ph}H), 7.65 (br s, 1H, PN(H)dipp), 7.18–7.16 (m, 2H, m-C_{dipp}H), 7.11–7.09 (m, 2H, m-C_{dipp}H), 7.03-6.98 (m, 4H, p-C_{dipp}H/p-C_{Ph}H), 6.92-6.88 (m, 10H, m-C_{ph}H/p-C_{ph}H), 3.79 (sept, 2H, CHMe₂, $^{3}J_{H-H} = 6.75$ Hz), 3.74 (sept, 2H, CHMe₂, $^{3}J_{H-H} = 6.75$ Hz), 3.38 (quart, 4H, $O(CH_2Me)_2$, ${}^{3}J_{H-H} = 7.00$ Hz), 1.34 (br s, 6H, CHMe₂), 1.23 (t, 6H, O(CH₂Me)₂, ${}^{3}J_{H-H} = 7.00$ Hz), 1.21 (d, 12H, CHMe₂, ${}^{3}J_{H-H} = 6.5$ Hz), 0.56 (br s, 6H, CHMe₂). ${}^{13}C{}^{1}H$ -UDEFT (100.62 MHz, C₆D₆): δ 148.2 (d, J_{P-C} = 3.0 Hz, quat- C_{dipp}), 147.9 (d, J_{P-C} = 5.5 Hz, quat- C_{dipp}), 137.6 (s, *i*- C_{Aryl}), 136.7 (s, *i*- C_{Aryl}), 135.9 (vtr, $J_{P-C} = 6.1$ Hz), 133.7 (d, $J_{P-C} = 10.8$ Hz, $o-C_{Ph}$), 132.7 (d, 10.2 Hz, $o-C_{Ph}$), 131.6 (d, $J_{\rm P-C} = 2.1$ Hz, m/p- $C_{\rm Ph}$), 130.8 (d, $J_{\rm P-C} = 2.6$ Hz, m/p- $C_{\rm Ph}$), 127.7 (s, overlaid by strong solvent signals, $p-C_{dipp} + m/p-C_{Ph}$, 125.3 (d, $J_{P-C} = 3.3 \text{ Hz}$, $p-C_{dipp}$), 123.5 (s, $m-C_{dipp}$), 123.3 (d, $J_{P-C} = 2.9 \text{ Hz}$, $m-C_{dipp}$), 69.1 (t, ${}^{1}J_{P-C} = 116.6 \text{ Hz}$, PCP), 65.7 (s, O(CH₂Me)₂), 29.9 (s, CHMe₂), 28.3 (s, CHMe₂), 28.0 (br, CHMe₂) 23.6 (s, CHMe₂), 22.7 (br, CHMe₂), 15.3 (s, O(CH₂Me)₂). ³¹P{¹H} (169.97 MHz, C₆D₆): δ 45.3 (br, CPNBi-ring), 26.8 (d, ${}^{2}J_{P-P}$ = 48.3 Hz, $P(Ph)_{2}(NHdipp)$). Anal. Calcd for $C_{53}H_{65}N_{2}P_{2}BiCl_{2}O$: C, 58.51; H, 6.02; N, 2.57. Found: C, 58.87; H, 6.23; N, 2.52.

[Sbl₂{C(Ph₂PNdipp)(Ph₂PNHdipp)}] (3). To a solution of SbI₃ (0.163 g, 0.324 mmol, 1 equiv) in THF (5 mL) at approximately -50 $^\circ C$ was added a solution of 1c~(0.250 g, 0.323 mmol, 1 equiv) in toluene/THF (5 mL/0.8 mL) dropwise. The resulting bright yellow solution was stirred overnight and slowly warmed to room temperature. Solvents were removed under reduced pressure, and the bright yellow residue was washed with warm hexane $(2 \times 8 \text{ mL})$ and extracted with toluene (3 \times 5 mL). The solvent of the combined toluene extracts was removed under reduced pressure to give 3 (0.240 g, 0.216 mmol, 67%) as a bright yellow solid. NMR spectral data and elemental analysis indicate the presence of some residual solvated toluene (approximately 0.3 molecules per 3). Plate-shaped crystals of 3-(toluene) of minor quality for X-ray diffraction were repeatedly obtained from overlaying solutions in toluene (3-4 mL) with hexane (20 mL). Analytical data are as follows. ¹H (250.13 MHz, C_6D_6): δ 7.64 (br, 9H, H, o-C_{Ph}H overlapping with PN(H)dipp), 7.22–6.80 (br m, 18H, CH_{Ar}), 3.85 (br, 2H, CHMe₂), 3.70 (br, 2H, CHMe₂), 1.38 (br d, 6H, CHMe₂, ${}^{3}J_{H-H}$ = 6.5 Hz), 1.23 (br, 12H, CHMe₂), 0.44 (br (b) (d) (d) (e) $(E_{2}, F_{H-H} = 6.6 \text{ Hz})$. $^{13}\text{C}\{^{1}\text{H}\}$ (62.90 MHz, $C_{6}D_{6}$): δ 148.3 (d) $J_{P-C} = 3.3 \text{ Hz}$, C_{ar}), 147.7 (d) $J_{P-C} = 5.2 \text{ Hz}$, C_{ar}), 137.6 (s, C_{ar}), 136.8 (vtr, $J_{P-C} = 5.8 \text{ Hz}$, C_{ar}), 133.6 (br d, $J_{P-C} = 7.1 \text{ Hz}$, C_{ar}), 132.9 (d) $J_{P-C} = 10.1 \text{ Hz}$, C_{ar}), 133.6 (br, C_{ar}), 130.9 (d) $J_{P-C} = 2.5 \text{ Hz}$, C_{ar}), 132.9 (d) $J_{P-C} = 2.8 \text{ Hz}$, C_{ar}), 133.8 (br, C_{ar}), 132.9 (d) $J_{P-C} = 2.5 \text{ Hz}$, C_{ar}), 129.8 (s, C_{ar}), 127.6 (s, C_{ar}), 125.4 (s, C_{ar}), 125.1 (d, J_{P-C} = 3.8 Hz, C_{ar}), 124.2 (d, J_{P-C} = 3.0 Hz, C_{ar}), 123.3 (d, J_{P-C} = 2.0 Hz, C_{ar}), 29.9 (s, CHMe₂), 28.4 (s, CHMe₂), 27.5 (s, CHMe₂), 23.2 (s, CHMe₂). $3^{1}P{^{1}H}$ (101.25 MHz, C₆D₆): δ 37.3 (br, CPNSb-ring), 28.9 (d, ${}^{2}J_{P-P}$ = 42.2 Hz, P(Ph)₂(NHdipp)). Anal. Calcd for 3.0.3C₇H₈, C51.1H57.4N2P2SbI2: C, 53.97; H, 5.09; N, 2.46. Found: C, 53.82; H, 5.29; N, 2.44. An X-ray structure of 3 is attached in the Supporting Information

[BiCl{C(Ph₂PNdipp)₂] (4). *Method A.* To a solution of BiCl₃ (0.106 g, 0.33 mmol, 1 equiv) in THF (3 mL) was added a solution of **1b** (0.250 g, 0.33 mmol, 1 equiv) in toluene/THF (5 mL/5 mL) dropwise at -35 °C. The orange solution was stirred overnight and slowly warmed to room temperature before the solvents were removed under reduced pressure. The orange-yellow residue was extracted with toluene (2 × 8 mL), and the toluene was removed from the combined extracts under reduced pressure. The yellow residue was repeatedly washed with Et₂O (3 × 2 mL) to remove impurities of **1** and **2** and dried under reduced pressure to obtain **4** (0.144 g, 0.147 mmol, 45%) as a pale yellow solid. Crystals suitable for X-ray analysis were grown from gas-phase diffusion of pentane into solutions of **4** in benzene. Analytical data are as follows. ¹H (500.13 MHz, C₆D₆): δ 8.00–7.96 (m, 4H, *o*-H(Ph₁)), 7.86–7.82 (m, 4H, *o*-H(Ph₂)), 7.20 (d, 4H, *m*-

$$\begin{split} H_{dipp} \, {}^{3}J_{\rm H-H} &= 7.56~{\rm Hz} \right), \, 7.12-7.04~(m, \, 8\rm H, \, overlapping \, signals \, of \, p-H_{dipp}~(2\rm H), \, m-H(\rm Ph_2)~(4\rm H), \, p-H(\rm Ph_2)~(2\rm H)), \, 7.00-6.97~(m, \, 2\rm H, \, p-H(\rm Ph_1)), \, 6.95-6.90~(m, \, 4\rm H, \, m-H(\rm Ph_1)), \, 3.92~(br, \, 4\rm H, \, CHMe_2), \, 1.17~(br, \, 12\rm H, \, CHMe_2(i\cdot\rm Pr_1)), \, 1.03~(d, \, 12\rm H, \, CHMe_2(i\cdot\rm Pr_2), \, ^{3}J_{\rm H-H} = 7.00~{\rm Hz}). \, ^{13}\rm C\{^1\rm H\}-UDEFT~(125.76~MHz, \, C_6\rm D_6): \, \delta~147.4~(s, \, o-C_{\rm dipp}), \, 140.0~(m, \, i-C(\rm Ph_1), \, ^{1}J_{\rm P-C} + \, ^{3}J_{\rm P-C} = 91.0~{\rm Hz}), \, 139.7~(s, \, i-C_{\rm dipp}), \, 136.6~(m, \, i-C(\rm Ph_2), \, ^{1}J_{\rm P-C} + \, ^{3}J_{\rm P-C} = 94.2~{\rm Hz}), \, 132.0~(vtr, \, o-C(\rm Ph_1), \, J_{\rm P-C} = 5.7~{\rm Hz}), \, 131.9~(vtr, \, o-C(\rm Ph_2), \, J_{\rm P-C} = 4.5~{\rm Hz}), \, 130.7~(s, \, p-C(\rm Ph_2)), \, 129.8~(s, \, p-C(\rm Ph_1)), \, 128.1-127.9~(overlapping \, with \, strong \, solvent \, resonances, \, m-C(\rm Ph_1), \, m-C(\rm Ph_2)), \, 124.3~(s, \, p-C_{\rm dipp}), \, 123.3~(s, \, m-C_{\rm dipp}), \, 63.4~(t, \, \rm PCP, \, ^{1}J_{\rm P-C} = 135.0~{\rm Hz}), \, 28.3~(s, \, \rm CHMe_2), \, 26.2~(s, \, \rm CHMe_2~(i-\rm Pr_2)), \, 24.1~(s, \, \rm CHMe_2~(i-\rm Pr_1)). \, \, ^{31}\rm P\{^1\rm H\}~(202.5~{\rm MHz}, \, C_6\rm D_6): \, \delta \, 3.5~(s). \, Anal. \, Calcd~for~C_{49}\rm H_{54}\rm N_2\rm P_2BiCl:~C, \, 60.22;~{\rm H}, \, 5.57; \, N, \, 2.87.~{\rm Found:} \, C, \, 60.25;~{\rm H}, \, 5.46;~{\rm N}, \, 3.08. \end{split}$$

Method B. To a solution of $2 \cdot \text{Et}_2 O$ (45 mg, 0.041 mmol, 1 equiv) in THF (0.5 mL) was added a solution of lithium 2,2,6,6-tetramethylpiperidide (LiTMP; 6 mg, 0.041 mmol, 1 equiv) in THF (0.8 mL) dropwise over a period of 5 min at room temperature. The bright yellow solution was stirred for 30 min before the solvents were removed under reduced pressure and the residue was redissolved in benzene (1.5 mL). Gas-phase diffusion of pentane into the benzene solution over 2 days afforded bright yellow crystals of 4 (32 mg, 0.033 mmol, 80%), which were isolated, washed with pentane (0.5 mL), and dried under reduced pressure. Spectral data were in accord with those reported for method A.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, a table, and CIF files giving specifications on NMR and X-ray instrumentation and data treatment, synthesis of the literature-known ligand precursor salts 1a,^{4c} 1b, and 1c,^{4b} X-ray structure of 3 along with selected bond lengths, tabulated crystallographic data for 1c, $2 \cdot 0.5C_6H_{14}$, $3 \cdot C_7H_8$, and 4, ¹H, $^{13}C{^{1}H}$, and $^{31}P{^{1}H}$ NMR spectra of 2–4 and the compiled low-temperature spectra for 4 and crystallgraphic data for all reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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