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Deprotonated Iminophosphorane *o*-$C_6H_4Ph_2P{=}NSiMe_3$ as a Novel Ligand To Stabilize a Diarylstannylene and -plumbylene via Side Arm Donation[†]

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Lithiation of triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$ with MeLi gives the *ortho*-metalated species $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**1**). It has all the requirements of an organometallic ligand capable of side arm donation: the deprotonated *ortho* phenyl carbon atom leads to metal−carbon σ bonds in reactions with metal halides, and the $Ph_2P{=}NSiMe_3$ moiety donates an electron pair to that metal via the imine nitrogen atom. In reactions with $SnCl_2$ the Sn(II) organometallic complex $[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**2**) was obtained, while with $PbCl_2$ a new example of the rare lead(II) organometallic complexes was obtained. In $[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) the lead(II) center is bonded to the two *ortho*-carbon atoms and additionally stabilized by two Pb←N donor bonds. In all metal complexes the $Ph_2P{=}NSiMe_3$ unit acts as a side arm donating group via nitrogen.

Introduction

Since the synthesis of the first dialkylstannylene $[Sn\{CH(SiMe_3)_2\}_2]_2$,[1] a heavy carbene analogue that dimerizes in the solid state and exhibits a Sn−Sn distance of 2.764(2) Å,[2] by Lappert et al., stannylenes and plumbylenes have attracted continued interest.[3] After the synthesis of the first dialkylplumbylene, $[Pb\{CH(SiMe_3)_2\}_2]_2$,[2] another 15 years went by until the first diarylplumbylene was synthesized and structurally characterized.[4] In the monomeric $[Pb\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]$ molecule four short Pb···F contacts supported the low-coordinate lead(II) center. Apart from the steric bulk of the 2,4,6-tris(trifluoromethyl)phenyl ligand it was this feature that stabilized the monomeric stannylene $[Sn\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]$[5] as well as the dimeric species $[Sn\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]_2$[6] with a long-range Sn···Sn interaction (3.639(1) Å). Short metal−fluorine distances have already been observed in the starting material $[Et_2O{\cdot}Li\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]_2$.[7] Potential additional donor contacts of methyl groups to the low-valent metal center were not observed in $[Sn\{2,4,6\text{-}(Me_3C)_3C_6H_2\}_2]_2$.[8] However, the 2,4,6-tris(trifluoromethyl)phenyl ligand was recently successfully employed in the synthesis of the first plumbylene dimer $[Pb\{2,4,6\text{-}(F_3C)_3C_6H_2\}\{Si(SiMe_3)_3\}]_2$[9] with a Pb···Pb distance of 3.537(1) Å (synthesis and structure of $[Pb\{Si(SiMe_3)_3\}_2]$ see ref 10).

The side arm donation concept has been applied to stabilize Sn(II) centers by formation of Sn←N donor bonds. α-Metalated aryl ligands substituted with $R_2N(CH_2)_n$ amino groups make intramolecular complexation possible (**a** in Chart 1).

Compounds such as $[Sn\{C_6H_4CH_2NMe_2\text{-}o\}_2]$,[11] $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$[12] $[Sn\{C_{10}H_6NMe_2\}_2]$,[13] and $[Sn\{2,6\text{-}(NMe_2)_2C_6H_3\}_2]$[14] exhibit two Sn−C σ bonds and two Sn←N donor bonds, leaving the tin(II) center four-coordinated. In general, side arm donation encourages organotin compounds to be monomeric species.[15] In the

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[†] Dedicated to Professor Max Schmidt on the occasion of his 75th birthday.

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[⊥] University of Aveiro.

(1) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317.

(2) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(3) Recent review: Driess, M.; Grützmacher, H. *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 827.

(4) Brooker, S. A.; Buijink, J.-K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25.

(5) Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23.

(6) Lay, U.; Pritzkow, H.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1992**, 260.

(7) Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1990**, 833.

(8) Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem.* **1994**, *106*, 1938; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846.

(9) Klinkhammer, K. W.; Fässler, T. F.; Grützmacher, H. *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem., Int. Ed.* **1998**, *37*, 124.

(10) Klinkhammer, K. W.; Schwarz, W. *Angew. Chem.* **1995**, *107*, 1448; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1334.

(11) Angermund, K.; Jonas, K.; Krüger, C.; Latten, J. L.; Tsay, Y.-H. *J. Organomet. Chem.* **1988**, *353*, 17.

(12) (a) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336. (b) Jolly, B. S.; Lappert, M. F.; Engelhardt, L. M.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2653.

(13) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Heijdenrijk, D.; Goubitz, K.; de Ridder, D. J. A. *J. Organomet. Chem.* **1989**, *367*, 55.

(14) Drost, C.; Hitchcock, R. B.; Lappert, M. F.; Pierssens, L., J.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 1141.

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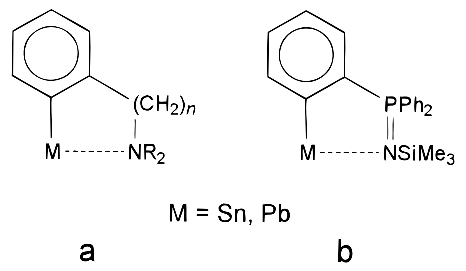
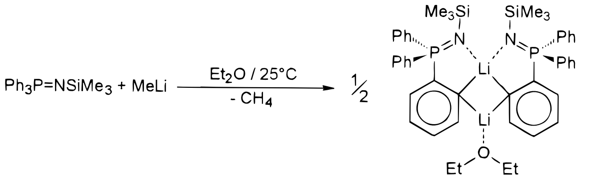
Chart 1. Amino Side Arm Donation (a) versus Imino Side Arm Donation (b)



compounds discussed in this paper the $R_2N(CH_2)_n$ amino group is formally replaced by a $Me_3SiN{=}PPh_2$ imino group within the deprotonated triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$ (**b** in Chart 1). Lithiation and reactivity of the trimethyl(trimethylsilylimino)phosphorane $Me_3P{=}NSiMe_3$ have been studied earlier by Schmidbaur et al.,[16] and the structure of the $[(LiCH_2)Me_2P{=}NSiMe_3]_4$ tetramer was determined recently by Dehnicke et al.[17]

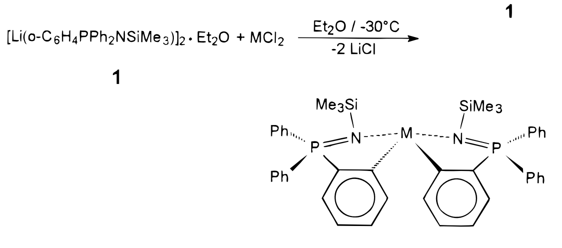
Results and Discussion

Preparation of 1−3. Lithiation of triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$ with MeLi gives $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**1**) according to eq 1.[18] The C_2 symmetric dimer contains a tetrahedrally coordinated and a trigonal planar coordinated lithium atom. We embarked on the synthesis of organometallic compounds using the lithiated triphenyl(trimethylsilylimino)phosphorane as a starting material, because $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**1**) meets all the requirements of a ligand capable of side arm donation: the deprotonated *ortho* phenyl carbon atom should lead to metal−carbon σ bonds in transmetalation reactions, and the $Ph_2P{=}NSiMe_3$ moiety should donate an electron pair to that metal via the imine nitrogen atom. In a reaction of $Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**1**) with $SnCl_2$ the diorgano tin complex $[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**2**) was obtained, while the reaction with $PbCl_2$ gave the diarylplumbylene $[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) (eq 2).



(1)

1



(2)

M = Sn(II) **2** , Pb(II) **3**

Crystal Structure of $[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (2). Pale yellow crystals of **2** suitable for X-ray crystallography were obtained within 3 days of storage of its ether solution at room temperature. The blocks turned colorless when exposed to traces of air. Data were collected at −90 °C, because at slightly lower temperatures they cracked due to a destructive solid/solid phase transition.

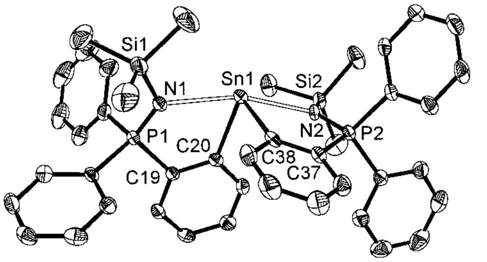


Figure 1. Solid state structure of $[Sn(o\text{-}C_6H_4PPh_2\text{-}NSiMe_3)_2]$ (**2**); anisotropic displacement parameters are depicted at the 50% probability level.

The structure of $[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**2**) displays two Sn−C σ bonds and two Sn←N donor bonds in the monomer (Figure 1). The two Sn−C distances of 2.243(3) and 2.232(3) Å (Table 1), respectively, fall in the range covered by other Sn−C(aryl) bonds in diarylstannylenes (av 2.214(5) Å in $[Sn\{2,6\text{-}(NMe_2)_2\text{-}C_6H_3\}_2]$,[14] av 2.222(3) Å in $[Sn\{C_6H_4CH_2NMe_2\text{-}o\}_2]$,[11] 2.225(5) Å in $[Sn\{2,6\text{-}(Mes)_2C_6H_3\}_2]$,[19] 2.261(4) Å in $[Sn\{2,4,6\text{-}(Me_3C)_3C_6H_2\}_2]$,[8] and 2.281(5) Å in $[Sn\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]$[5]). The Sn←N bonds in **2** of 2.495(2) and 2.575(2) Å differ significantly, as in the structure of $[Sn\{C_6H_4CH_2NMe_2\text{-}o\}_2]$[11] (2.516(3) and 2.660(3) Å). In $[Sn\{2,6\text{-}(NMe_2)_2C_6H_3\}_2]$[14] the two shortest Sn···N distances are 2.607(5) and 2.669(5) Å. The C−Sn−C angle of 86.88(9)° in **2** is remarkably acute, and to our knowledge it is the smallest ever observed in a diorganostannylene. They range from 95.3° in $SnMe_2$[20], 98.3(1)° in $[Sn\{2,4,6\text{-}(F_3C)_3C_6H_2\}_2]$,[5] 100.5(1)° in $[Sn\{C_6H_4CH_2NMe_2\text{-}o\}_2]$,[11] 103.6(1)° in $[Sn\{2,4,6\text{-}(Me_3C)_3C_6H_2\}_2]$,[8] 112° in $[Sn\{CH(SiMe_3)_2\}_2]_2$,[2] to 114.7(2)° in $[Sn\{2,6\text{-}(Mes)_2C_6H_3\}_2]$.[19] This small value even below 90° is in accordance with the electronic configuration of a $^1\sigma^2$ singlet carbene homologue at Sn with the lone pair in a spherical s orbital and both bonding electrons in orthogonal p orbitals each.[3,15b] Normally the ideal 90° angle is expected to be widened by steric repulsion between the substituents. In **2**, however, it is squeezed below 90° due to parallel orientation of the bonded phenyl rings and $NSiMe_3$/phenyl repulsion of both substituents across the metal. Because of the limited bite of the ligand the N→Sn←N angle of 164.05(7)° is bent from linearity toward the bisection of the C−Sn−C angle.

Crystal Structure of $[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (3). $[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) (Figure 2) is isostructural to **2**, but the cell contains a single noncoordinating lattice solvent molecule of toluene. The two Pb−C distances in **3** of 2.319(5) and 2.331(6) Å (Table 1), respectively, match those found in other diarylplumbylenes (2.296(4) Å in $[Pb\{2,4,6\text{-}(^iPr)_3C_6H_2\}\{Si(SiMe_3)_3\}]_2$,[21]

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[15] For review see: (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) Jastrzebski, J. T. B. H.; van Koten, G. *Adv. Organomet. Chem.* **1993**, *35*, 241.

[16] Schmidbaur, H.; Jonas, G. *Chem. Ber.* **1967**, *100*, 1120.

[17] Müller, A.; Neumüller, B.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 253.

[18] Steiner, A.; Stalke, D. *Angew. Chem.* **1995**, *107*, 1908; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1752.

[19] Simons, R. S., Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 2 and 3

	2, M = Sn		**3**, M = Pb	
M−C	2.243(3)	2.232(3)	2.331(6)	2.319(5)
M−N	2.575(2)	2.495(2)	2.633(4)	2.638(4)
P−N	1.572(2)	1.573(2)	1.572(5)	1.567(5)
P−C(C_6H_4M)	1.794(3)	1.801(3)	1.802(6)	1.813(5)
P−C(C_6H_5)	1.812(3)−1.813(3)	1.806(3)−1.812(3)	1.822(6)	1.809(6)−1.814(6)
av P−C	1.806(3)		1.814(6)	
C−M−C	86.88(9)		86.0(2)	
N−M−N	1.6405(7)		1.628(2)	
P−N−Si	130.1(2)	130.8(2)	130.2(3)	132.9(3)
N−P−C(C_6H_4)	109.3(2)	109.1(2)	110.3(2)	110.7(2)
M−N−P	108.6(2)	111.2(2)	109.1(2)	110.7(2)
M−N−Si	120.5(2)	118.0(2)	120.7(2)	116.1(2)
Cα−M−N	77.2(9)	78.4(9)	76.1(2)	76.2(2)
C−C−C angle at themetalated C	116.2(2)	115.7(3)	115.3(5)	116.5(5)
deviation of				
the metalated C from the C_5H_4-plane	0.01	0.006	0.012	0.017
the M from the C_5H_4-plane	0.034	0.098	0.089	0.073

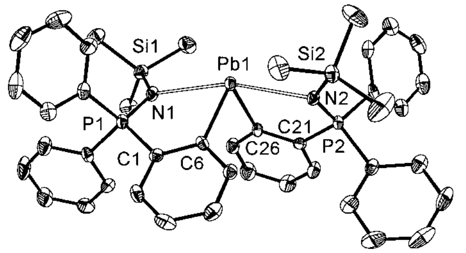

Figure 2. Solid state structure of [Pb(*o*-$C_6H_4PPh_2$-$NSiMe_3)_2$] (**3**); anisotropic displacement parameters are depicted at the 50% probability level. The single lattice solvent molecule of toluene has been omitted.

av 2.334(12) Å in [Pb{2,6-$(Mes)_2C_6H_3\}_2$],[19] 2.366(4) Å in [Pb{2,4,6-$(F_3C)_3C_6H_2\}_2$],[4] and 2.369(7) Å in [Pb{2,4,6-$(F_3C)_3C_6H_2$}{Si$(SiMe_3)_3\}]_2$[9]). The Pb←N bonds in **3** of 2.633(4) and 2.638(4) Å are identical within estimated standard deviations and are about 0.49 Å longer than those in [Pb{N$(SiMe_3)_2\}_2$].[22] As anticipated, proceeding toward the higher homologue, the C−Pb−C angle of 86.0(2)° in **3** is even more acute than that in **2**. Because of the bigger radius and longer M−C bonds of lead compared to tin and the same bite of the ligand the N→Pb←N angle in **3** is only 162.8(2)°.

Structural Comparison. The coordination geometry in **2** and **3** is orbital controlled due to the ns^2np^2 electron configuration of tin and lead. In contrast the coordination geometry of the central Zn^{2+} atom in the related complex [Zn(*o*-$C_6H_4PPh_2NSiMe_3)_2$][23] is governed by electrostatics. The closed shell d^{10} configuration can be considered as a point charge. The ligands arrange themselves around that charge so as to maximize the interatomic distances. The zinc atom is tetrahedrally coordinated by both carbon and nitrogen atoms of the two ligands (C−Zn−C, 129.3(3)°; N→Zn←N, 116.1(2)°). The P═N bonds of 1.57 Å on average in **2** and **3** are only marginally longer than in the starting material [Li-(*o*-$C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) (1.562(3) Å)[18] and are less than 0.03 Å longer than in the parent iminophosphorane $Ph_3P{=}NSiMe_3$ (1.542(2) Å).[24] The distances are covered by the range normally observed in iminophosphoranes (1.47−1.62 Å).[25]

The metalated phenyl ring atom in the *ortho* position is partially sp^3 rehybridized, as indicated by the acute C−C−C angle of 116°.[26] It is slightly displaced from the best C_5H_4 plane. This leads to an even more pronounced dislocation of the σ-bonded metal from the C_5H_4 plane (Table 1).

NMR Spectroscopic Investigations. Although in solution the two lithium sites in **1** at room temperature gave rise to only one signal at δ 3.0 (LiCl ext.), the signal broadened upon cooling and at −50 °C two signals could be resolved at δ 3.4 and 2.2. Therefore, we expected to resolve the two sites in the ^7Li MAS NMR experiment as well. This technique proved in the past to be a valuable tool to monitor rearrangement processes in the solid state either by ^7Li MAS NMR spectroscopy[27] or by ^7Li quadrupole nutation MAS NMR spectroscopy.[28] The ^7Li high-power proton-decoupled MAS NMR of **1** showed a broad structured signal, which could be deconvoluted by line shape analysis with Lorentzian/Gaussian curves. The isotropic shifts of the 1:1 signals are δ 0.4 and 0.9, respectively.

The resonance for **2** in the ^{119}Sn NMR spectrum in toluene-d_8 solution shows a doublet of a doublet centered at δ 47.7 (Me_4Sn ext.) with a $^2J_{Sn-P}$ coupling of 57.8 Hz (confirmed in the ^{31}P NMR experiment). This chemical shift differs by more than a magnitude from that found in non-donor-stabilized stannylenes such as [Sn{2,4,6-$(Me_3C)_3C_6H_2\}_2$][8] (980 ppm), [Sn{2,4,6-$(F_3C)_3C_6H_2\}_2$][5] (723 ppm), or [Sn{2,6-$(Mes)_2C_6H_3\}_2$][19] (635 ppm), but it is closer to the area covered by stannylenes with two additional Sn←N donor bonds such as in [Sn{C(Si-$Me_3)_2C_5H_4N$-2}$_2$][12b] (141 ppm), [Sn{$C_6H_4CH_2NMe_2$-*o*}$_2$][11] (169 ppm), [Sn{$C_{10}H_6NMe_2\}_2$][13] (178 ppm), or [Sn{2,6-

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[20] Bleckmann, P.; Maley, H.; Minkwitz, R.; Neumann, W. P.; Watta, B.; Olbrich, G. *Tetrahedron Lett.* **1982**, *23*, 4655.

[21] Stürmann, M.; Saak, W.; Weidenbruch, M.; Klinkhammer, K. *Eur. J. Inorg. Chem.* **1999**, 579.

[22] Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639.

[23] Wingerter, S.; Gornitzka, H.; Bertrand, G.; Stalke, D. *Eur. J. Inorg. Chem.* **1999**, 173.

[24] Weller, F.; Kang, H.-C.; Massa, W.; Rübenstahl, T.; Kunkel, F.; Dehnicke, K. *Z. Naturforsch., B* **1995**, *50*, 1050.

[25] Niecke, E.; Gudat, D. *Angew. Chem.* **1991**, *103*, 251; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217.

[26] (a) Bohnen, F: M.; Herbst-Irmer, R.; Stalke, D. In *Crystallographic Computing G.*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; IUCr/Oxford Science Publications: New York, 1993. (b) Domenicano, A. In *Accurate Molecular Structures*; Domenicano, A., Hargittai, I., Eds.; IUCr/Oxford Science Publications: New York, 1992. (c) Jones, P. G. *J. Organomet. Chem.* **1988**, *345*, 405.

[27] (a) Freitag, S.; Kolodziejski, W.; Pauer, F.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 3479. (b) Gornitzka, H.; Stalke, D. *Angew. Chem.* **1994**, *106*, 695; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 693.

[28] Pauer, F.; Rocha, J.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1477.

$(NMe_2)_2C_6H_3\}_2]$[14] (380 ppm). The considerable upfield shift is certainly due to the presence of the phosphorus and silicon atom next to the imino nitrogen atom. They enhance the donor capacity of the new ligand compared to alkyl-substituted amino groups.

Conclusion

Transmetalation of the *ortho*-lithiated triphenyl(trimethylsilylimino)phosphorane $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) results in a side arm N-donating chelating organometallic ligand. In the diarylstannylene $[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**2**) and the diarylplumbylene $[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) the smallest observed C−M−C angles (<90°) indicate a $^1\sigma^2$ singlet carbene homologue electronic configuration at the heavy p-block metals with the lone pair in a spherical s orbital and both bonding electrons, each in orthogonal p orbitals.

Experimental Section

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a drybox. Solvents were freshly distilled from sodium−potassium alloy prior to use. ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded in THF-d_8 or toluene-d_8 solution by using a Bruker AM 250 or a Bruker MSL 400 spectrometer. The solid state ^7Li MAS NMR spectra were recorded on a Bruker MSL 400P (wide-bore) spectrometer employing a 4 mm CP/MAS probe. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 180, 325, or 735 B spectrometer. Melting (decomposition) points were determined by using a MEL TEMP II, laboratory devices, melting point apparatus. EI mass spectra were measured with Finnigan MAT 8230 or Varian MAT CH5 instruments. Elemental analyses were performed by the analytical laboratory of the Department of Inorganic Chemistry at Göttingen.

$[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (1) was prepared by reaction of $Ph_3P{=}NSiMe_3$ and MeLi in diethyl ether.[18] The ^7Li MAS NMR of **1** was recorded at 155.5 MHz in a 4 mm bottom layer ZrO_2 rotor. It was accumulated at a spinning speed of 14 kHz with proton high-power decoupling. The broad spectrum could be deconvoluted with the following features: signal 1 {δ 0.4; rel int 74.8; line width 471 Hz; ratio Lorentzian/Gaussian = 1; area 50.5%}; signal 2 {δ 0.9; rel int 25.0; line width 1800 Hz; ratio Lorentzian/Gaussian = 0.28; area 49.5%}.

$[Sn(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (2). A mixture of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) (1.30 g, 1.65 mmol) and $SnCl_2$ (0.31 g; 1.63 mmol) was dissolved in Et_2O (20 mL) at −30 °C. The pale yellow solution was stirred for 1 day at room temperature. The solvent was removed in a vacuum. Toluene (30 mL) was added to the solid residue, and the mixture was stirred overnight. The unsolvated LiCl was separated by filtration, and the volume of the yellow mother liquor was reduced until further product just started to precipitate. The solution was filtered again to remove traces of LiCl. After storage at room temperature for 3 days yellow crystals were obtained for the X-ray diffraction experiment. Further crystalline product was obtained from the supersaturated filtered solution (about 0.3 g). After isolating the crystals the solvent from the remaining solution was removed in a vacuum. The residue was washed with pentane (30 mL) and dried in a vacuum. Melting points and spectroscopic data of the crystals (first and second batch) and the yellow precipitate (third batch) were identical. Total yield: 0.90 g; 1.10 mmol; 65%. Mp: 218 °C. IR (Nujol, KBr): ν [cm^{-1}] 2900 (C−H aliphat.), 1440 (P−Ph), 1390 (CH_3), 1261 ($SiMe_3$), 1097 (P=N). ^1H NMR (toluene-d_8, room temperature, TMS): δ 0.39 (s, 18H, $SiMe_3$), 6.77 (m_c, 4H, 5-H), 6.86 (m_c, 4H, 4-H), 6.94 (m_c, 4H, 6-H), 7.01 (m_c, 4H, 9-H), 7.61 (m_c, 8H, 8-H), 8.27 (d, $^3J_{3,4}$ = 7.0 Hz, 4H, 3-H). ^{13}C NMR (toluene-d_8, room temperature, TMS): δ 5.0 (d, $^3J_{C-P}$ = 2.7 Hz, $SiMe_3$), 124.9−139.5 (m, Ph), 179.6 (dd, $^2J_{C-P}$ = 27.0 Hz, $^3J_{C-P}$ = 1.3 Hz, 2-C). ^{29}Si NMR (toluene-d_8, room temperature, TMS): δ −1.55 (d, $^2J_{Si-P}$ = 6.8 Hz). ^{31}P NMR (toluene-d_8, room temperature, 85% H_3PO_4): δ 28.0 (dd, $^2J_{P-Sn}$ = 56.7 Hz). ^{119}Sn (toluene-d_8, room temperature, Me_4Sn/C_6D_6): δ 47.7 (dd, $^2J_{Sn-P}$ = 57.8 Hz). MS (70 eV); m/z (%): 816 (47) [M$^+$], 468 (79) [$PPh_3NSiMe_3Sn^+$], 334 (100) [$PPh_3NSiMe_2^+$]. Anal. Calcd for $C_{42}H_{46}N_2P_2Si_2Sn$: C, 61.9; H, 5.68; N, 3.43. Found: C, 59.3; H, 5.28; N, 3.33.

Table 2. Crystal Data for 2 and 3

	2	3
formula	$C_{42}H_{46}N_2P_2Si_2Sn$	$C_{42}H_{46}N_2P_2PbSi_2\cdot 0.5C_7H_8$
CCDC no.	143669	143670
mol. mass	815.62	950.19
cryst size [mm]	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.2
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.014(2)	11.079(2)
b [Å]	12.238(2)	14.968(3)
c [Å]	16.775(3)	15.756(3)
α [deg]	69.87(3)	105.55(3)
β [deg]	71.02(3)	108.69(3)
γ [deg]	82.35(3)	107.01(3)
V [nm^3]	2.0070(7)	2.1699(8)
Z	2	2
temp [K]	183(2)	153(2)
ρ_c [Mg/m^3]	1.350	1.454
μ [mm^{-1}]	0.807	4.049
F(000)	840	954
2θ-range [deg]	4−45	8−45
no. of refln measd	8964	5904
no. of unique reflns	5219	5638
no. of restraints	0	91
ref param	448	512
R1[a] [$I > 2\sigma(I)$]	0.0238	0.0321
wR2[b] (all data)	0.0555	0.0941
g1; g2[c]	0.0183; 1.6124	0.0523; 2.7435
resid electr density [e/Å^3]; min/max	−0.310; 0.285	−1.144; 1.336
abs corr	semiempirical	semiempirical
min/max transmsn	0.8828; 0.9307	0.6561; 1.0

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}$. [c] $P = (\max(F_o^2,0) + 2F_c^2)/3$.

$[Pb(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (3). Et_2O (30 mL) was added to a mixture of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) (1.45 g, 1.85 mmol) and $PbCl_2$ (0.51 g; 1.85 mmol) at −30 °C. The suspension was stirred for 3 days at room temperature. The solvent was removed in a vacuum. THF (50 mL) was added to the white residue and stirred overnight. The mixture was refluxed for 12 h. The solid dissolved and the solution turned pale yellow. The solvent was removed in a vacuum. Toluene (30 mL) was added to the solid residue, and the mixture was stirred over the weekend. The unsolvated LiCl was separated by filtration, and the volume of the mother liquor was reduced until the product just started to precipitate. The solution was filtered again to remove traces of LiCl. After storage at room temperature for 5 days colorless crystals were obtained for the X-ray diffraction experiment. After isolating the crystals the solvent from the remaining solution was removed in a vacuum. The residue was washed with pentane (30 mL) and dried in a vacuum. Melting points and spectroscopic data of the crystals (first batch) and the yellow precipitate (second batch) were identical. Total yield: 0.78 g; 0.86 mmol; 47%. Mp: 202 °C. IR (Nujol, KBr): ν [cm^{-1}] 2920 (C−H aliphat.), 1445 (P−Ph), 1395 (CH_3), 1256 ($SiMe_3$), 1098 (P=N). ^1H NMR (toluene-d_8, room temperature, TMS): δ 0.34 (s, 18H, $SiMe_3$), 7.05 (m_c, 18H, 4-,5-, 6-, 9-, 10-H), 7.63 (m_c 8H, 8-H), 8.49 (d, $^3J_{3,4}$ = 7.5 Hz, 2H, 3-H). ^{13}C NMR (THF-d_8, room temperature, TMS): δ 5.1 (d, $^3J_{C-P}$ = 3.0 Hz, $SiMe_3$), 124.0−146.7 (m, Ph), 224.5 (dd, $^2J_{C-P}$ = 26.8 Hz, $^3J_{C-P}$ = 1.0 Hz, 2-P). ^{29}Si NMR (THF-d_8, room temperature, TMS): δ −3.7 (d, $^2J_{Si-P}$ = 7.4 Hz). ^{31}P NMR (toluene-d_8, room temperature, 85% H_3PO_4): δ 31.7. MS (70 eV); *m/z* (%): 904 (3) [M^+], 556 (52) [$PPh_3NSiMe_3Pb^+$], 334 (100) [$PPh_3NSiMe_2{}^+$]. Anal. Calcd for $C_{42}H_{46}N_2P_2Si_2Pb$: C, 55.8; H, 5.13; N, 3.10. Found: C, 57.2; H, 5.34; N, 2.97. The analytical data almost fit the additionally present half-toluene molecule in the lattice.

Crystallographic Measurements. Crystal data for structures **2** and **3** are presented in Table 2. Data of all structures were collected at low temperatures using oil-coated shock-cooled crystals[29] on a Stoe-Siemens-AED diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Semiempirical absorption correction was applied. The structures were solved by Patterson or direct methods with SHELXS-90.[30] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[31] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Further details on structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) by quoting the supplementary publication no. (see Table 2).

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of the structures **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) (a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465. (c) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

(30) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

(31) Sheldrick, G. M. *SHELXL93, Program for Crystal Structure Refinement*; Universität Göttingen, Germany, 1996.