The Deprotonated Iminophosphorane o-$C_6H_4PPh_2P{=}NSiMe_3$ as a Novel Chelating Ligand in Organocopper(I) and -zinc(II) Chemistry

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Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

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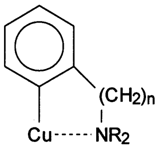
Lithiation of triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$ with MeLi gives the *ortho*-metallated species $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2 \cdot Et_2O$ (**1**), which exhibits all the requirements of an organometallic ligand capable of side-arm donation. The deprotonated *ortho*-phenyl carbon atom gives access to metal–carbon σ bonds in transmetallation reactions, while the $Ph_2P{=}NSiMe_3$ moiety can donate to the same metal center through the imine nitrogen atom. In transmetallation reactions with CuBr, the dimeric organocopper complex $[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (**2**) is obtained, while application of $ZnCl_2$ yields the monomeric zinc complex $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**). Reaction with $CuCl_2$ gives access to the new diiminophosphorane $(o\text{-}C_6H_4PPh_2NSiMe_3)_2$ (**4**) through oxidative coupling at the *ortho* positions. In all the metal complexes, the $Ph_2P{=}NSiMe_3$ residue acts as a side-arm donating group through the nitrogen atom. The intermolecular N→Cu donor bond in **2** is as short as copper–amide bonds, while the N→Zn bond lengths in **3** are in the region normally found for donor bonds. Compound **4** is a molecule, possessing two $Ph_2P{=}NSiMe_3$ moieties bridged by a biphenylene group.

Introduction

Since the landmark synthesis of $LiCuMe_2$ in 1952,[1] the application of organocopper reagents in organic synthesis has continued to increase exponentially.[2] Among the d-block metals, Cu^I species play the most prominent role in regio- and stereoselective synthesis.[3] The growing number of cuprates and organocopper compounds characterized by X-ray structure analysis is clearly evident.[4] Organocopper(I) compounds CuR are generally encountered as polynuclear species, which exist either as discrete aggregates or as polymers. Transformation of these aggregates and polymers into units of lower nuclearity can either be achieved by employing very bulky groups R, or by the action of suitable Lewis bases.[5] N, P, O, or S donor centers, as well as alkynes, have been reported to stabilize copper(I) species in low aggregation states.[6] The combination of both approaches leads to the side-arm donation concept pioneered by van Koten.[7] α-Metallated aryl ligands are substituted with $R_2N(CH_2)_n$ amido groups, permitting intramolecular complexation (Scheme 1).

In the compounds discussed in this paper, the $R_2N[CH_2]_n$ amido group is formally replaced by an $Me_3SiN{=}PPh_2$ imido group within the deprotonated triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$.



Scheme 1

The lithiation and reactivity of the trimethyl(trimethylsilylimino)phosphorane $Me_3P{=}NSiMe_3$ has been studied previously by Schmidbaur et al.[8] and the structure of the $[LiCH_2(Me_2)P{=}NSiMe_3]_4$ tetramer was recently determined by Dehnicke et al.[9] In analogy to this lithiation, the reaction of triphenyl(trimethylsilylimino)phosphorane $Ph_3P{=}NSiMe_3$ with MeLi gives $[Li(o\text{-}C_6H_4PPh_2\text{-}NSiMe_3)]_2 \cdot Et_2O$ (**1**) according to Equation 1.[10] The C_2-symmetric dimer contains a tetrahedrally coordinated and a trigonal-planarly coordinated lithium atom. The tripyridyl(trimethylsilylimino)phosphorane $Py_3P{=}NSiMe_3$ reacts completely differently. In a reductive coupling reaction of the substituents, the phosphorus(V) center is reduced to phosphorus(III), substituted by one pyridyl, one methyl, and an Me_3SiN group. The P−N double bond in the starting material is thus converted into a single bond (Equation 2).[10]

We embarked on the synthesis of organometallic compounds using lithiated triphenyl(trimethylsilylimino)phosphorane, $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2 \cdot Et_2O$ (**1**), as a starting material, as this species exhibits all the requirements of a ligand capable of side-arm donation. The deprotonated *ortho*-phenyl carbon atom should give access to metal−carbon σ bonds in transmetallation reactions, while the $Ph_2P{=}NSiMe_3$ moiety should be capable of donation to the same metal center through the imine nitrogen atom.

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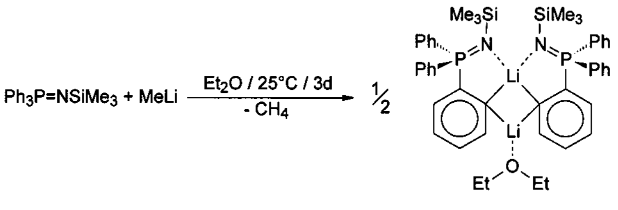

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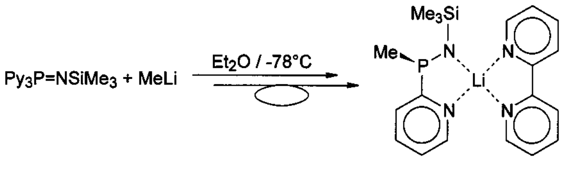


2

(2)

Results and Discussion

Preparation of 2−4

As synthetically important metals, we decided to employ monovalent Cu^I and divalent Zn^{II} and Cu^{II}. In a transmetallation reaction of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) with CuBr, the dimeric organocopper complex $[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (**2**) was obtained (Equation 3). Transmetallation using $ZnCl_2$ yielded the monomeric zinc complex $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) (Equation 4), while reaction with $CuCl_2$ led to the new diiminophosphorane $(o\text{-}C_6H_4PPh_2NSiMe_3)_2$ (**4**) as a result of oxidative coupling at the *ortho* positions (Equation 5).

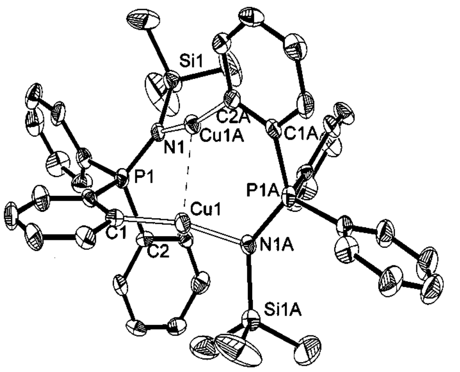
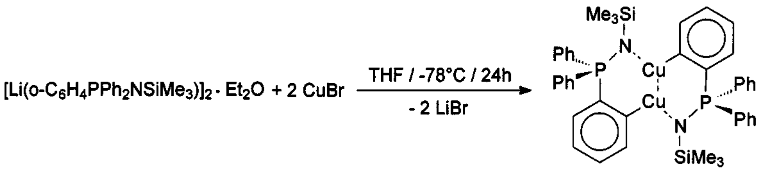


Figure 1. Solid-state structure of $[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (**2**); anisotropic displacement parameters are depicted at the 50% probability level

Crystal Structure of $[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (2)

In the organocopper complex $[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (**2**), both lithium atoms of the C_2-symmetric starting material are replaced by copper atoms to give a C_i-symmetric dimer (Figure 1).

Each copper atom is coordinated to an *ortho*-carbon atom and the nitrogen atom of the $Ph_2P{=}NSiMe_3$ side-arm of a second ligand. Hence, this moiety acts as an intermolecular rather than as an intramolecular donor function. The Cu−C distance in **2** is 190.5(5) pm (Table 1), which is comparable with the Cu−C(aryl) bond length determined in monomeric $Me_2SCuC_6H_3$-2,6-bis(2,4,6-triisopropylphenyl) [Cu−C: 189.4(6) pm].[11] Both distances fall at the short end of the range observed in organocopper com-



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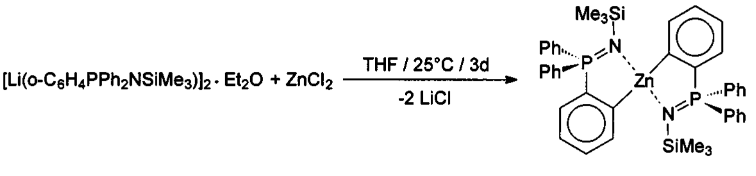

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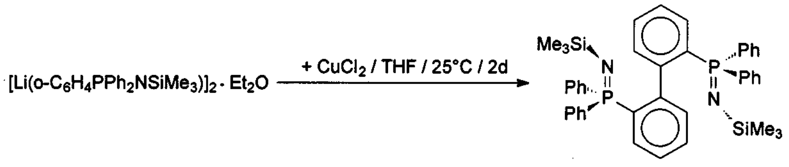


4

(5)

pounds (mean Cu−C: 205.5 pm).[12] On average, the Cu−C(alkyl) distances appear to be slightly longer, because an sp^2 carbon atom is about 4 pm smaller than an sp^3 carbon atom.[13] The dinuclear organylcopper complex $[CuC(SiMe_3)_2C_5H_4N]_2$ shows almost the same structural motif as complex **2**. However, the Cu−C(alkyl) bond length in the former complex is 195.0(4) and 195.4(2) pm[14] in $[CuLi\{CH(Me)P(Et)_2NSiMe_3\}_2]$.[15] The Cu−N distances in both complexes are very similar; 191.1(4) pm in **2** and 191.0(3) pm in $[CuC(SiMe_3)_2C_5H_4N]_2$. Both values correspond very closely to the value of Cu−N distances in secondary copper amides $[CuNR_2]_4$, which is generally close to 191 pm.[12][16] Hence, the Cu−imide donor bond in **2** is as short as a Cu−amide bond. The latter is probably extended by the higher coordination number at the copper centers (coordination number 4−6) compared to the coordination number 2 at the copper center in **2**. Although the P=N bond [159.1(4) pm] in **2** is 2.9 pm longer than that in the starting material **1** [156.2(3) pm][10] and 4.9 pm longer than that in the parent iminophosphorane $Ph_3P{=}NSiMe_3$ [154.2(2) pm],[17] the distance falls within the range normally observed in iminophosphoranes (147−162 pm).[18]

The Cu···Cu distance of 248.79(14) pm in complex **2** is rather short, both as a consequence of the bite of the bridging chelating ligand,[19] which forces the metal centers into close proximity, as well as metal d^{10}-d^{10} closed-shell attraction.[20] Although this distance is not remarkably short (in comparison with 240.3(2) pm in $[Li(thf)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$[21] and 236.9(1) pm in $[Cu_2\{Si(SiMe_3)_3\}_2BrLi(thf)_3]$[22]), the non-linear C···Cu−N angle of 167.8(2)° clearly indicates metal−metal interaction. This angle is caused by a close metal−metal contact. One would expect the metals to be pushed further out of the center (i.e. further away from the center of inversion located in the middle of the Cu···Cu vector) and a bend of the C−Cu−N unit in the opposite direction if there was no “sticky” interaction. This could easily be achieved by rotation of the metallated phenyl rings about the P−C(*ipso*) bonds. Steric requirements do not constrain the tilt of the two monomeric units and the observed lean would be maximized if the two metal cations were to favour separation.

Organozinc Compounds

The chemistry of organozinc compounds has a long history. They are used as intermediates in organic synthesis, specifically as mild alkylation or arylation agents in organometallic reactions. Organozinc reagents are generally less reactive than Grignard reagents, a property that is a distinct advantage when more gentle reaction conditions are required.[23] Furthermore, they do not tend to associate via μ_2-bridging alkyl or aryl groups like organocopper compounds. All known diarylzinc compounds are colourless solids made up of monomeric units, and are of good to moderate solubility in apolar organic solvents. Diorganozinc compounds bearing functional groups can be divided into two categories, i.e. compounds bearing substituents that do not interact directly with the central zinc atom, and compounds in which coordination of the heteroatoms of the substituents is observed.

Crystal Structure of $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (3)

The complex $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**) belongs to the second group, because the two nitrogen atoms of the two $Ph_2P{=}NSiMe_3$ side-arms coordinate to the zinc atom. Hence, the o-$C_6H_4PPh_2NSiMe_3$ substituent in **3** is closely related to other bidentate monoanionic C,N-chelating ligands.[24]

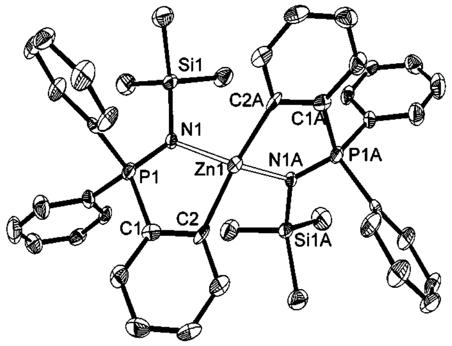


Figure 2. Solid-state structure of $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**3**); anisotropic displacement parameters are depicted at the 50% probability level

The zinc atom in **3** is tetrahedrally coordinated by both carbon and nitrogen atoms of the two ligands. The metal atom resides at a center of inversion. The Zn−C distance in **3** [200.8(5) pm, Table 1] is comparable with the Zn−C distances in other diarylzinc species (194.9−201.2 pm).[25] Zn−N distances span a wide range from 182 to 232 pm.[13][26] The Zn−N dative bond in **3** measures 215.8(4) pm and is thus considerably longer than Zn−N bonds in zinc amides (182 pm for $[Zn\{N(SiMe_3)_2\}_2]$ in the gas phase[27]). In the structure of $[HZnN(Me)C_2H_4NMe_2]_2$,[28] the two zinc−amide bonds within the central Zn_2N_2 four-membered ring are 206.1 pm in length, while the two $Zn{\leftarrow}N(Me_2)R$ donor bonds measure 218.6 pm. The P=N bond in **3** [157.4(4) pm] is 1.7 pm shorter than that in **2** [159.1(4) pm].

The Coupling Product $[(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (4)

The application of oxidative coupling to generate C−C bonds via organocopper compounds has a venerable history.[7] A large number of CuR and $CuLiR_2$ species bearing alkyl or functionalized alkyl, alkenyl, alkynyl, aryl or heteroaryl groups have been oxidatively dimerized to the symmetrical coupling products RR.[29] These oxidations have been accomplished by using $CuCl_2$, O_2 or nitrobenzene. In general, the best yields have been obtained employing $CuCl_2$ as the oxidizing reagent. Numerous reactions have been reported in which copper(II) salts have been treated with organometallic compounds [MR] to give organocopper(I) compounds [CuR] and reductive coupling products

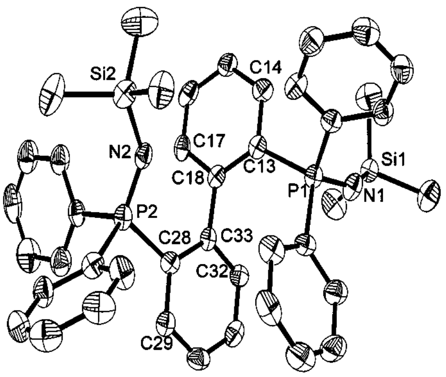


Figure 3. Solid-state structure of $(o\text{-}C_6H_4PPh_2NSiMe_3)_2$ (**4**); anisotropic displacement parameters are depicted at the 50% probability level

RR (reactions in which the CuX_2:MR molar ratio is 1:2). Reactions of species containing several M−C bonds in close proximity, such as $[Li_nR_n]$ or MgR_2 with CuX_2 afford exclusively the reductive elimination product RR. Thus, it was not surprising that we obtained the coupling product $(o\text{-}C_6H_4PPh_2NSiMe_3)_2$ (**4**) from the reaction of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) with $CuCl_2$.

In **4**, the distances are almost identical to the corresponding distances in the iminophosphorane $Ph_3P{=}NSiMe_3$.[9] It is worthy of note that the two symmetry-independent P−N−Si angles in the iminodiphosphorane **4** are significantly different [P1−N1−Si1: 145.1(3)° and P2−N2−Si2: 138.7(3)°, see Figure 3, Table 1], as a result of the steric demand of the bulky groups.

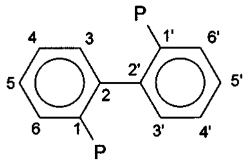


Figure 4

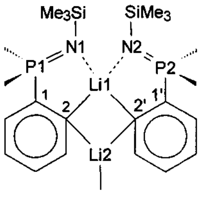
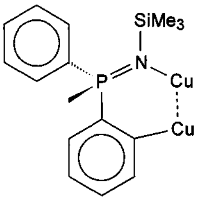
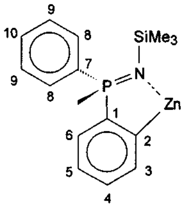
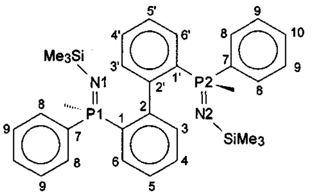
In 1,1′-phosphorus-substituted biphenylenes, the central C2−C2′ distances range from 146.8 to 153.3 pm.[12] The $P{-}C_{biphenylene}$ distances are found between 182.0 and 187.5 pm, the angles P−C1−C2 vary from 114.5 to 124.2°, and the P−C1−C6 angles from 115.7 to 125.1°. The corresponding distances in **4** are 149.3(7) pm for the C2−C2′ distance of the biphenylene (C18−C33 in Figure 3), and 181.9(6) and 184.6(5) pm for the $P{-}C_{biphenylene}$ distances (P2−C28 and P1−C13), while the angles amount to 122.9(4) and 127.5(4)° (P−C1−C2) (P2−C28−C33 and P1−C13−C18), and 117.9(4) and 112.2(4)° (P−C1−C6) (P2−C28−C29 and P1−C13−C14). It seems worthy of note that the extreme values for the bond angle of 127.5(4)° and the angle of 112.2(4)° do not fall within the range previously observed in 1,1′-P-substituted biphenylenes. The best planes of the two phenyl rings of the biphenylene unit intersect at an angle of 64.7°.

In conclusion, the transmetallation of the *ortho*-lithiated triphenyl(trimethylimino)phosphorane $[Li(o\text{-}C_6H_4PPh_2\text{-}NSiMe_3)]_2\cdot Et_2O$ gives access to side-arm *N*-donating chelating ligands in organometallic chemistry. The nitrogen donor bond can be as short as a metal−amide bond, as observed in the dimeric copper(I) complex.

Experimental Section

All experiments were performed under nitrogen, either by using modified Schlenk techniques or in a drybox. Solvents were freshly

Table 1. Selected bond lengths [pm] and angles [°] of **2**−**4** compared to those in the starting material **1**

	1 (M = Li)	2 (M = Cu)	3 (M = Zn)	4
				
M–C:	Li1–C2: 233.1(5) Li2–C2: 213.8(6) Li1–C2': 226.3(5) Li2–C2': 212.0(6)	190.7(5)	200.8(5)	–
M–N:	Li1–N1: 203.7(5) Li2–N2: 202.7(4)	191.2(4)	215.8(4)	–
P–N:	P1–N1: 156.2(2) P2–N2: 156.2(3)	159.3(4)	157.4(4)	153.7(5) 153.3(5)
average P–C:	181.2(3)	180.5(6)	181.0(5)	182.9(6)
P–C1:	P1–C1: 180.2(2) P2–C1': 180.4(3)	180.6(6)	181.2(5)	P1–C1: 184.6(5) P1–C1': 181.9(6)
P–N–Si:	P1–N1–Si1: 135.18(13) P2–N2–Si2: 133.47(13)	131.7(3)	127.4(2)	P1–N1–Si1: 145.1(3) P2–N2–Si2: 138.7(3)
N–P–C:	N1–P1–C1: 109.81(11) N2–P2–C1': 110.98(11)	115.0(2)	107.8(2)	N1–P1–C1: 115.1(2) N2–P2–C1': 112.7(2)
M–N–P:	Li1–N1–P1: 107.5(2) Li1–N1–P1: 41.79(11) Li1–N2–P2: 107.9(2) Li1–N2–P2: 41.42(11)	120.4(2)	108.0(2)	–
M–N–Si:	Li1–N1–Si1: 117.3(2)	107.7(2)	120.0(2)	–

distilled from a sodium/potassium alloy prior to use. − ^{1}H-, ^{13}C-, ^{29}Si- and ^{31}P-NMR spectra were recorded in [D$_8$]THF or C_6D_6 solution using a Bruker AM 250, a Bruker MSL 400 or a Bruker AMX 400 spectrometer. − IR spectra were recorded as Nujol mulls with a Perkin-Elmer 283 spectrometer. − Melting (decomposition) points were determined by using a Laboratory Devices MEL TEMP II 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 Departments of Inorganic Chemistry at Göttingen and Würzburg.

$[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot OEt_2$ (1) was prepared by reaction of $Ph_3P{=}NSiMe_3$ with MeLi in diethyl ether.[10]

$[Cu(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (2): To $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot OEt_2$ (**1**) (1.86 g, 2.37 mmol) in THF (20 ml), a suspension of CuBr (0.34 g, 2.37 mmol) in THF (20 ml) was added dropwise at −78°C. The light-yellow solution was allowed to warm to room temp. and was then stirred overnight. The reaction mixture turned deep yellow. The THF was removed in vacuo until the product precipitated. After filtration, yellow crystals suitable for X-ray analysis were obtained from the mother liquor after storage for several weeks at room temp. Yield: 0.56 g (0.68 mmol, 28.7%); m.p. 148−175°C (decomp.). − IR (Nujol, KBr): $\tilde{\nu}$ = 2894 cm^{-1} (Si−CH$_3$), 1444 (P−Ph), 1363 (CH$_3$), 1243 (SiMe$_3$), 1092 (P=N), 965, 823, 711. − ^{1}H NMR (C_6D_6, room temp., TMS): δ = 0.34 (s, 18 H, SiMe$_3$), 6.98−7.73 (m, 28 H, Ph). − ^{13}C NMR (C_6D_6, room temp., TMS): δ = 4.4 (s, SiMe$_3$), 127.8−132.4 (m, Ph). − ^{31}P NMR (C_6D_6, room temp., 85% H_3PO_4): δ = −1.01. − MS (70 eV); *m/z* (%): 824 (2.0) [M^{+}], 681 (76) [M^{+} − 2Cu − Me], 424 (86) [$(C_6H_4PPhN)_2Si$], 334 (100) [$C_6H_4PPh_2NSiMe_2$]. − $C_{42}H_{46}Cu_2N_2P_2Si_2$ (824.00): calcd. C 61.22, H 5.63, N 3.40; found C 61.33, H 5.48, N 3.24.

$[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (3): A mixture of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) (1.50 g, 1.91 mmol) and $ZnCl_2$ (0.26 g, 1.91 mmol) was dissolved in THF (15 ml), and the pale-yellow solution was stirred for 3 d at room temp. The solvent was then removed in vacuo. Toluene (30 ml) was added to the residue and the mixture was stirred overnight. The insoluble LiCl was removed by filtration and the colourless mother liquor was concentrated until the product precipitated. THF was then added dropwise to redissolve the precipitate. The resulting clear solution was cooled to 0°C for 14 d to afford $[Zn(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ (**3**) as colourless crystals. The mother liquor was filtered and the solvent was removed from the filtrate in vacuo. The white residue was washed with pentane (30 ml) and dried in vacuo. Spectroscopic data of the crystals and the precipitate were identical. Total yield: 0.70 g (0.92 mmol, 48%); m.p. 234°C (decomp.). − IR (Nujol, KBr): $\tilde{\nu}$ = 2930 cm^{-1} (Si−CH$_3$), 1440 (P−Ph), 1385 (CH$_3$), 1261 (SiMe$_3$), 1098 (P=N), 1020, 801, 534. − ^{1}H NMR (C_6D_6, room temp., TMS): δ = 0.43 (s, 18 H, SiMe$_3$), 7.08 (m$_c$, 14 H), 7.36 (m$_c$, 4 H), 7.91 (m$_c$ 8 H), 8.27 (d, $^{3}J_{3,4}$ = 7.0 Hz, 2 H, 3-H). − ^{13}C NMR (C_6D_6, room temp., TMS): δ = 4.7 (d, $^{3}J_{\text{C-P}}$ = 3.4 Hz, SiMe$_3$), 125.0−140.3 (m, Ph), 172.8 (dd, $^{2}J_{\text{C-P}}$ = 30.8 Hz, $^{3}J_{\text{C-P}}$ = 4.1 Hz, 2-P). − ^{29}Si NMR (C_6D_6, room temp., TMS): δ = −0.1 (d, $^{2}J_{\text{Si-P}}$ = 5.0 Hz). − ^{31}P NMR (C_6D_6, room temp., 85% H_3PO_4): δ = 21.8. − MS (70 eV); *m/z* (%): 763 (23) [M^{+}], 492 (47) [PPh_3NSiMe_3ZnPh], 488 (100) [$PPh_3NSiMe_3ZnNPSi$], 412 (60) [PPh_3NSiMe_3Zn], 334 (78) [PPh_3NSiMe_2], 318 (86) [PPh_3NSiMe]. − $C_{42}H_{46}N_2P_2Si_2Zn$ (762.30): calcd. C 66.18, H 6.08, N 3.67; found C 66.37, H 5.98, N 3.60.

$(o\text{-}C_6H_4PPh_2NSiMe_3)_2$ (4): A mixture of $CuCl_2$ (0.26 g, 1.93 mmol) and $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$ (**1**) (1.55 g, 1.97 mmol) was stirred in THF (30 ml) for 2 d at room temp. The solvents were then removed in vacuo, toluene (30 ml) was added to the residue, and the suspension was stirred for a further day. The precipitated material was removed from the mother liquor by filtration. The filtrate was concentrated in vacuo until the product precipitated, and then THF was added dropwise until the precipitate redissolved. After storage of the resulting solution at room temp. for 10 d, colourless crystals were obtained. These were filtered off and the

Table 2. Crystal data for **2**−**4**

	2	**3**	**4**
Formula	$C_{42}H_{46}Cu_2N_2P_2Si_2$	$C_{42}H_{46}N_2P_2Si_2Zn$	$C_{42}H_{46}N_2P_2Si_2$
Mol. mass	824.00	762.30	696.93
Cryst. size [mm]	0.2 × 0.2 × 0.1	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3
Space group	$P4_32_12$ (no. 96)	*Pbcn* (no. 60)	$P2_1/c$ (no. 14)
a [pm]	1742.31(14)	1441.0(3)	1726.6(4)
b [pm]	1742.31(14)	1663.5(3)	1014.3(2)
c [pm]	1343.4(3)	1699.9(3)	2225.3(5)
β [°]	90	90	92.24(3)
V [nm^3]	4.0748(9)	4.0748(14)	3.8942(14)
Z	4	4	4
T [K]	173(2)	153(2)	153(2)
$\rho_{\text{calcd.}}$ [Mgm^{-3}]	1.343	1.243	1.189
μ [mm^{-1}]	1.212	0.771	0.205
F(000)	1712	1600	1480
2Θ range [°]	6−47	8−45	8−45
No. of reflns. measd.	5981	2313	5208
No. of unique reflns.	3095	2313	5066
No. of restraints	24	−	−
Refined param.	226	225	439
$R1$[a] [$I > 2\sigma(I)$]	0.0490	0.0475	0.0667
$wR2$[b] (all data)	0.0795	0.1114	0.1618
$g1$; $g2$[c]	0.0240; 0.0	0.0359; 7.5914	0.0445; 7.6971
Flack x param.	−0.01(2)	−	−
Highest diff peak [10^{-6} e pm^{-3}]	0.262	0.314	0.309
Absorpt. corr.	semi-empirical	−	−
Transm. min; max	0.7935; 0.8884		

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$. − [c] $w = 1/[\sigma^2(F_o^2) + (g1\cdot\mathbf{P})^2 + g2\cdot\mathbf{P}]$; $P = (F_o^2 + 2F_c^2)/3$.

solvents were removed from the filtrate in vacuo. The pale-yellow residue was washed with pentane (30 ml) and dried in vacuo. Spectroscopic data of the crystals and the pale-yellow precipitate were identical. Total yield: 0.48 g (0.69 mmol, 35%); m.p. 179°C. − IR (Nujol, KBr): $\tilde{\nu}$ = 3051 cm^{-1} (Ar−CH), 2900 (Si−CH_3), 1442 (P−Ph), 1390 (CH_3), 1271 ($SiMe_3$), 1102 (P=N), 860, 826, 531, 516. − ^1H NMR ($[D_8]$THF, room temp., TMS): δ = −0.10 (d, $^4J_{H\text{-}P}$ = 0.45 Hz, 18 H, $SiMe_3$), 7.05 (m_c, 4 H), 7.27 (m_c, 10 H), 7.44 (m_c, 6 H), 7.72 (m_c, 8 H). − ^{13}C NMR ($[D_8]$THF, room temp., TMS): δ = 4.0 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, $SiMe_3$), 127.2−145.4 (m, Ph). − ^{29}Si NMR ($[D_8]$THF, room temp., TMS): δ = −12.7 (d, $^2J_{Si\text{-}P}$ = 21.0 Hz). − ^{31}P NMR ($[D_8]$THF, room temp., 85% H_3PO_4): δ = 1.9. − MS (70 eV); *m/z* (%): 696 (8) [M^+], 681 (76) [M^+ − CH_3], 536 (37) [M^+ − $NSiMe_3PPh_2$], 424 (100) [M^+ − $NSiMe_3PPh_2$], 333 (46) [$Ph_3PNSiMe_2$]. − $C_{42}H_{46}N_2P_2Si_2$ (696.93): calcd. C 72.38, H 6.65, N 4.02; found C 72.67, H 6.43, N 3.99.

Crystallographic Measurements: Crystal data for structures **2**−**4** are presented in Table 2. Data of **2** were collected using an Enraf-Nonius CAD4 diffractomer and data of **3** and **4** were collected with a Stoe AED 2 diffractometer fitted with a classical scintillation counter using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). All data were collected at low temperatures using oil-coated shock-cooled crystals.[30] A semiempirical absorption correction was applied for structure **2**.[31] The structures were solved by Patterson or direct methods using SHELXS-90.[32] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[33] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Although the anisotropic displacement parameters of the trimethylsilyl group in **2** indicate slight rotational disorder, refinement to split occupation sites of the methyl groups was not successful. The elongation of the anisotropic displacement parameter of the *ipso*-carbon atom C2 in **3** along the Zn−C bond is due to the lack of absorption correction. Unfortunatelly, the crystal of **3** decomposed right after data collection of the unique set. Further details of the structure investigation may be obtained from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., on quoting the supplementary publication nos. CCDC-102400, -102401, -102402.

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