The Iminophosphorane $Ph_3P{=}NSiMe_3$ as a Synthon for $M-C_{aryl}$ σ Bonds (M = In, Fe, Ge) Implementing Imino Sidearm Donation

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Lithiation of triphenyl((trimethylsilyl)imino)phosphorane, $Ph_3P{=}NSiMe_3$ (**1**), with MeLi gives the ortho-metalated species $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**). It has all the requirements of an organometallic ligand capable of sidearm 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 $InCl_3$ the In(III) organometallic complex $[In(o\text{-}C_6H_4PPh_2NSiMe_3)_3]$ (**3**) was obtained, while with $FeCl_2$ a new example of the rare iron(II) 14-VE complexes $[Fe(o\text{-}C_6H_4PPh_2NSiMe_3)_2]$ (**4**) was obtained. Reaction of **2** with Ph_3GeCl gave $[Ph_3Ge(o\text{-}C_6H_4PPh_2NSiMe_3)]$ (**5**). While in **4** both imino sidearms coordinate to the metal, because of steric crowding only two of the three present coordinate in **3**. Because of the low Lewis acidity of the tetraorganogermanium moiety the imino sidearm does not donate to the central germanium atom in **5**.

Introduction

The concept of *sidearm* donation has been very effectively pioneered and utilized by van Koten and co-workers,[1−3] with the recent consummation of this concept being the design of *cartwheel* types of ligands, $C_6[3,5\text{-}(CH_2Y)_2C_6H_3]_6$ (Y = NMe_2, $P(O)Ph_2$, PPh_2, SPh), for supporting multimetallic assemblies.[3] The approach of sidearm donation[4] involves α-metalated aryl ligands substituted with CH_2Y, where the heteroatom in the group Y provides intramolecular coordination to the metal, thereby providing extra stabilization (Chart 1).

In the design of most of these ligands the group Y is linked to the aromatic moiety by the means of an alkyl bridge. Schmidbaur and co-workers have shown that the iminophosphorane $Ph_3P{=}NSiMe_3$ in its reactions with triphenylaluminum or -gallium first affords a complex where the group 13 metal is coordinated through the imino nitrogen atom.[5,6] More recently we have shown that ortho lithiation of the iminophosphorane $Ph_3P{=}NSiMe_3$ (**1**) affords a new type of sidearm donating ligand, $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**).[7] The lithiation and reactivity of the trimethyl((trimethylsilyl)-imino)phosphorane[8] $Me_3P{=}NSiMe_3$ and the structure of the tetrameric complex $[(LiCH_2)Me_2P{=}NSiMe_3]_4$ have been studied by Dehnicke et al.[9] The coordinating nitrogen atom of the sidearm is an imino nitrogen ($NSiMe_3$) that is connected to the aromatic group through the intervening phosphorus atom. In previous studies we have shown the utility of this ligand in stabilizing diarylstannylenes and plumbylenes in their monomeric forms,[10] besides demonstrating their effectiveness as a chelating ligand for Zn(II) and organocopper(I) compounds.[11] While with Sn(II), Pb(II), and Zn(II) two ligands per metal ion are coordinated, with Cu(I) only one ligand is involved. In all known com-

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

a b

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pounds the imino nitrogen atom is occupied by coordination to the metal ion. To explore the general scope of this ligand system with a view to understanding its coordination behavior toward diverse types of metals and metalloids, we have carried out the reactions of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**) with indium, germanium, and iron halides. In the choice of these reactions we had the following questions in mind:

(i) How is the formal P−N double bond affected by ortho phenyl ring metalation and metal coordination?

(ii) Can a metal ion accommodate more than two of these bulky ligands?

(iii) Under what conditions would the imino nitrogen not participate in sidearm donation?

(iv) What would be the mode of linkage to a typical transition-metal ion such as Fe(II)?

The results of these investigations are discussed in the following account.

Results and Discussion

Raman and Infrared Spectroscopic Investigations and Theoretical Calculations of $Ph_3P{=}NSiMe_3$ (1) and $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (2). Ortho metalation of $Ph_3P{=}NSiMe_3$ (**1**) and imido group metal sidearm coordination is in all known cases accompanied by P−N bond lengthening. This effect should be detectable in vibrational spectroscopic experiments, as not all organometallic species can be obtained as single crystals. The Raman and infrared spectra of $Ph_3P{=}NSiMe_3$ (**1**) and $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**) were recorded and the vibrational modes assigned by DFT calculations. The geometrical parameters of $Ph_3P{=}NSiMe_3$ (**1**) and the model compound $[Li(o\text{-}C_6H_4PH_2NSiH_3)]_2{\cdot}H_2O$ (**2***) were calculated at the BPW91/6-31G* and BPW91/6-31+G* levels of theory. The geometry was computed without any symmetry restriction. Analytical harmonic vibrational modes have also been calculated for both structures to confirm that a local minimum on the potential energy surface was found. The computed geometry of both $Ph_3P{=}NSiMe_3$ (**1**) and the model compound $[Li(o\text{-}C_6H_4PH_2NSiH_3)]_2{\cdot}H_2O$ (**2***) match the experimental solid-state structures, especially at the BPW91/6-31+G* level of theory. The P=N bond length in the lithium complex (1.562(2) Å, calculated 1.573(4) Å) is 0.02 Å longer than that of the iminophosphorane **1**. The P−C bond lengths do not differ significantly for the lithium compound **2** comparing to the starting material **1** (1.802(2)−1.812(3) Å, calculated 1.818(3)−1.821(4) Å).

FT-Raman and infrared spectroscopy was employed to elucidate the coordination behavior of the lithiated triphenyl((trimethylsilyl)imino)phosphorane compound **2** in relation to the parent starting material **1**. The assignment of the vibrational modes was performed with the help of DFT calculations. The infrared and Raman spectra of $Ph_3P{=}NSiMe_3$ (**1**) and $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**), in the range from 400 to 1800 cm^{-1}, are presented in Figure 1.

One of the most relevant features of the vibrational spectra of organometallic compounds are the metal−carbon stretching vibrations, since they are directly related to the most substantial property of the molecule, that is the M−C bond strength.[12] However, the assignment of the ν(M−C) vibrational modes is often quite

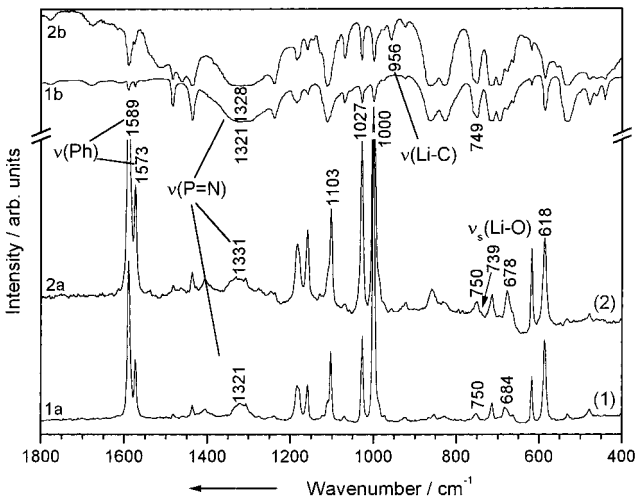

Figure 1. FT-Raman (1a, 2a) and FT-infrared (1b, 2b) spectra of $Ph_3P{=}NSiMe_3$ (**1**) and $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**). Complete assignment is given in Table 2 of the Supporting Information.

complicated due to the presence of other bands in the same region or of their low intensities. In our case, the lithium−carbon stretching vibration appears only in the infrared spectrum of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**) as a weak band at 956 cm^{-1}. The assignment of the ν(Li−C) vibration was based on the results of theoretical calculations. Significant changes in the position and relative intensities of some bands could be observed in the Raman spectrum of **2**. Thus, the band at 684 cm^{-1} (calculated 687 cm^{-1}) assigned in the spectrum of **1** to the ν_a(Si−C) vibration is shifted to lower wavenumbers by 6 cm^{-1} and the intensity is increased due to convolution of the ν_s(Li−N) vibration in the same spectral range.[13] The band around 1100 cm^{-1} assigned to the ν(P−Ph) vibration[14] is more intense in the spectrum of lithium compound **2**. The new shoulder that appears in the spectrum of **2** at 739 cm^{-1} was attributed to the ν_s(Li−O) vibration.[12] In the Raman spectrum of $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2{\cdot}Et_2O$ (**2**) the broad band at about 1331 cm^{-1} (calculated 1332 cm^{-1}) was assigned to the ν(P=N) stretching mode.[15] In comparison to the corresponding vibration of $Ph_3P{=}NSiMe_3$ (**1**), this band is shifted to higher wavenumbers by 10 cm^{-1}, due to the N−Li coordination. The shift of the ν(P=N) vibration confirms our observation that the iminophosphorane units coordinate through the imino nitrogen atoms.

Synthesis of 3−5. The reactions of the lithiated iminophosphorane **2** with indium trichloride, ferrous dichloride, or triphenylgermanium chloride proceed quite smoothly by the complete replacement of chlorine atoms, with the elimination of lithium chloride and with the formation of three, two, or one M−C_{aryl} σ bonds to afford products **3**−**5** respectively (eqs 1−3).

X-ray Crystal Structure of $[In(o\text{-}C_6H_4PPh_2NSiMe_3)_3]$ (3). The molecular structure of the complex

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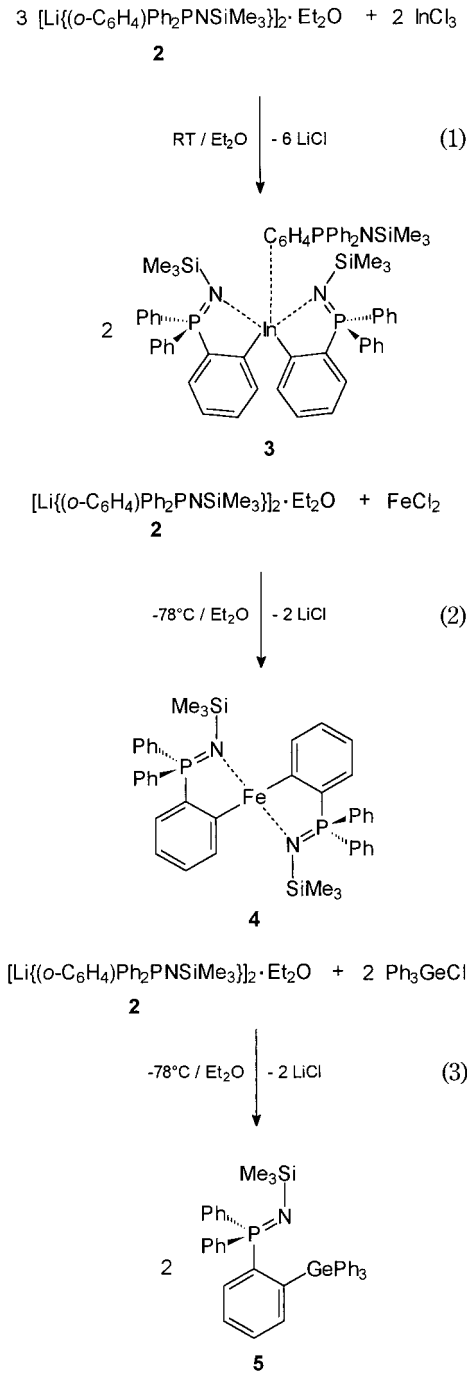

3 is shown in Figure 2. The asymmetric unit of this complex also contains two noncoordinating toluene molecules.

The complex **3** is monomeric, and the central indium atom is five-coordinated in a distorted-trigonal-bipyramidal geometry. The coordination environment around indium is composed of three equatorial aryl substituents and two apical imino nitogens which function as sidearm donors. The third imino nitrogen is not involved in coordination to the indium atom. The sum of the equatorial bond angles is 358.85°. However, there is considerable variation in the individual equatorial C−In−C angles besides their deviation from the ideal value of 120°. Thus, the largest angle is seen for C202−In−C302, 141.23(9)°, while the other two angles C102−In−C202 and C302−In−C102 are 110.31(9) and 107.31(9)°, respectively. Similar to the distortion in the equatorial bond angles, the axial bond angle N1−In−N3 also deviates from the ideal value of 180° to 168.82(6)°. A related indium compound, In(*o*-$C_6H_4CH_2NMe_2)_3$, [16] which contains the sidearm donating dimethylamino group, is isostructural with **3**, suggesting that the deviation from regular trigonal-bipyramidal geometry in **3** is probably a reflection of the short bite of the chelate spanning the equatorial−axial positions.

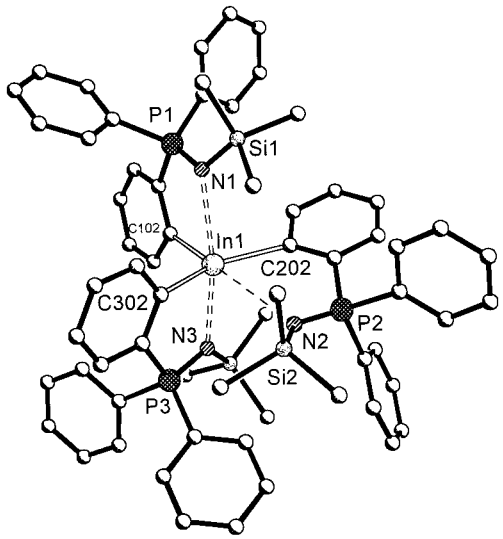

Figure 2. Solid-state structure of [In(*o*-$C_6H_4PPh_2NSiMe_3)_3$] (**3**). Selected bond lengths (Å) and angles (deg) are presented in Table 1.

The In−C bond distances in **3** (2.169(2)−2.228(3) Å) are similar to the In−C_{aryl} distances observed in other organoindium compounds such as (*t*-$Bu)_2$In(2,6-*i*-Pr_2-C_6H_3)$SiPh_3$ (2.222(6) and 2.223(6) Å)[17] and Me_2In(C_6H_4-NEt_2) (2.205(8) Å).[18] The In−N bond distances observed in **3** (N1, 2.696(3) Å; N3, 2.487(2) Å) are considerably longer than those observed in more covalent situations, as found, for example, in [In{$N(SiMe_3)_2$}$_3$] (2.049(1) Å).[19] However, these can be still considered as reasonably strong interactions, considering the sum of the covalence radii of In (1.5 Å) and N (0.7 Å).[20] Also, In−N_{coord} distances found in other compounds In(*o*-$C_6H_4CH_2$-$NMe_2)_3$ [16] (2.504, 2.565 Å) are consistent with trends observed in the present instance. In comparison, the distance between In1 and the third imino nitrogen N2 in **3** is 3.542(2) Å, clearly indicating the absence of any interaction between the two atoms.

The P−N bond distances of 1.570(2) Å (P1−N1), 1.582(2) Å (P3−N3), and 1.550(2) Å (P2−N2) are consistent with the structure of **3**. The shortest distance involves the imino nitrogen that does not participate in coordination.

X-ray Crystal Structure of [Fe(*o*-$C_6H_4PPh_2NSiMe_3)_2$] (4). Although a large number of organoiron compounds containing 18 valence electrons are known,[21] the corresponding compounds with 14 valence electrons

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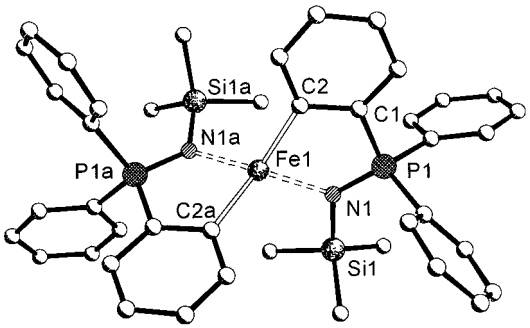

Figure 3. Solid-state structure of [Fe(*o*-$C_6H_4PPh_2NSiMe_3)_2$] (**4**). Selected bond lengths (Å) and angles (deg) are presented in Table 1.

are not very abundant. A few examples that are known include [$Fe(C_6Cl_5)_2(PEt_2Ph)_2$],[22] [$FeR_2(bpy)_2$] (R = Me, Et),[23] [$FeR_2(dippe)_2$],[24] [$Fe(CH_2Ph)_2$(TMEDA)],[25] [$Fe(Trip)_2(PyH)_2$],[26] etc. Furthermore, the number of homoleptic iron(II) compounds containing alkyl or aryl ligands are also quite rare, a few examples being the dimers [{FeR_2}$_2$] (R = Mes,[27] 2,4,6-*i*-$Pr_3C_6H_2$ [28]) and the monomer [Fe(2,4,6-*t*-$Bu_3C_6H_2)_2$].[29] Recently Leung et al. have reported homoleptic Fe(II) compounds containing intramolecular sidearm coordinating nitrogen atoms.[30] Compound **4** reported in this study belongs to this class of 14-VE type of molecules. The molecular structure of **4** is shown in Figure 3.

The structure of the complex is isostructural with the other 14-VE complex prepared with the *o*-$C_6H_4PPh_2$-$NSiMe_3$ ligand, viz., [Zn(*o*-$C_6H_4PPh_2NSiMe_3)_2$]. The coordination environment around Fe(II) is comprised of two carbon atoms and two nitrogen atoms arranged in a distorted-tetrahedral geometry. The bond angles around Fe vary from 88.70(10)° (N1−Fe1−C2) to 126.90(12)° (N1−Fe1−N1A). The Fe−C distance observed (2.071(3) Å) is one of the shortest Fe−C distances found for organoiron(II) compounds, which vary between 2.021 and 2.227 Å.[22−30] The Fe−N bond distances observed for **4** (2.111(2) Å) are similar to those observed for compounds containing sidearm donation.[30] The P−N bond distance in **4** is slightly longer (1.591(2) Å) in comparison with the ligand in **2** (1.562(2) Å)[6] and is in the range for observed trends in P=N distances.[31−34]

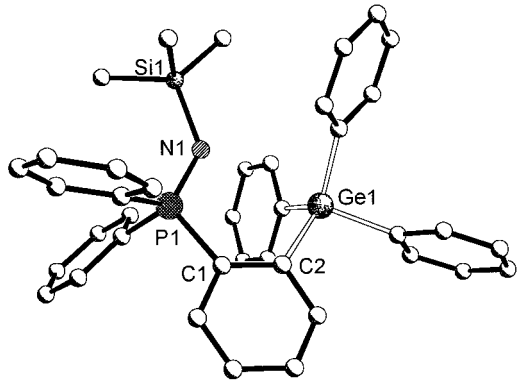

Figure 4. Solid-state structure of [Ph_3Ge(*o*-$C_6H_4PPh_2$-$NSiMe_3$)] (**5**). Selected bond lengths (Å) and angles (deg) are presented in Table 1.

X-ray Crystal Structure of [Ph_3Ge(*o*-$C_6H_4PPh_2$-$NSiMe_3$)] (5). The X-ray structure of **5** is shown in Figure 4. In the asymmetric unit of **5** a solvent diethyl ether molecule is also present which does not show any interaction with the organogermanium complex.

The germanium atom is surrounded by four covalently bound carbon atoms. The sidearm nitrogen N1 is at a distance of 3.111(4) Å from the central germanium atom, Ge1. Although the angle N1···Ge1−C34 is 173.8°, close enough to be an axial angle, we discount the possibility of the sidearm nitrogen interacting with germanium on the following grounds. (1) Ge1 is out of plane by a considerable 0.47 Å from an equatorial plane defined by Ge1, C2, C22, and C28. (2) The sum of the equatorial bond angles is 343.2°, in comparison to the ideal value of 360.0° (Figure 5). (3) The bond distances found in situations where the sidearm nitrogen is believed to participate in coordination to germanium are considerably smaller than those observed in the present instance. Thus, for example, in the compound MePhClGe(*o*-$C_6H_4CH_2NMe_2$) the Ge−N bond distance observed is between 2.479 and 2.508(11) Å.[35] This latter value corresponds to a value for a dative N→Ge bond. For covalent Ge−N bonds the distances are even smaller. For example, for [$Cl_3Ge{-}N{=}PMe_3]_n$ (n = 1, 2) the values observed are 1.837(7) and 1.972(1) Å.[36] Similarly for [Ge{$N(SiMe_3)_2$}$_2$] the Ge−N bond distances found are 1.877(8) and 1.873(5) Å.[37]

The Ge−C bond distances found for **5**, 1.943(5)−1.974(5) Å are quite similar to those observed for other tetraarylgermanium compounds: tetra-*o*-tolylgermanium (average Ge−C = 1.966 Å),[38] $Ge(C_6F_5)_4$ (1.957(4) Å),[39] and $Ge(C_6H_5)_4$ (1.954 Å).[40] The P−N bond distance in **5** is 1.538(4) Å, and its similarity with that of Ph_3P=

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Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3−5

	3 (M = In)			**4** (M = Fe)	**5** (M = Ge)
		Bond Distances and Angles			
M−C	2.228(3)	2.192(2)	2.169(2)	2.071(3)	1.974(5)
M−N	2.696(3)	3.542(2)[a]	2.487(2)	2.111(2)	3.111(4)[a]
P−N	1.570(2)	1.550(2)	1.582(2)	1.591(2)	1.538(4)
P−C(C_6H_4M)	1.804(3)	1.819(3)	1.806(3)	1.802(3)	1.818(5)
P−C(C_6H_5)	1.821(3)−1.827(3)	1.828(3)−1.832(3)	1.818(2)−1.822(3)	1.811(3)−1.810(3)	1.824(5)
av(P−C)	1.820(3)			1.807(3)	1.822(5)
P−N−Si	126.0(2)	134.4(2)	125.4(2)	128.15(14)	128.8(2)
N−P−C(C_6H_4M)	110.8(2)	116.2(2)	109.9(2)	108.06(12)	112.7(2)
M−N−P	109.3		109.2(2)	110.54(11)	
M−N−Si	122.7		124.2(2)	118.28(12)	
C_α-M−N_α	76.5		81.8	88.70(10)	
C−C(M)−C	115.1(2)	115.9(2)	116.7(2)	120.8(2)	117.0(4)
		Deviations (Å)			
metalated C from C_5H_4 plane	0.031	0.010	0.006	0.003	0.0
M from C_6H_4 plane	0.038	0.151	0.314	0.055	0.181

[a] Nonbonding distances.

$NSiMe_3$ (1.542(2) Å)[41] also supports the notion of the noncoordinating imino nitrogen atom.

Structural Comparisons. Table 1 summarizes some of the important metric parameters for the compounds **3**−**5**.

In the lithium derivative **2** and the organometallic complexes **3** and **4** the participation of the sidearm imino nitrogen in coordination to the metal leads to the formation of five-membered metallacycle structures. In **5** formation of such a metallacycle is precluded because of the absence of coordination by the imino nitrogen. This is almost certainly due to the relatively weak Lewis acidic nature of a tetraaryl-substituted germanium center.

In examples of neutral or anionic pentacoordinate germanium compounds the central germanium is surrounded by at least one or more highly electronegative atoms such as halogens or oxygen atoms which increase the Lewis acidity and facilitate higher coordination around germanium.[35,42−44]

In the other cases (**2**−**4**) where the iminophosphorane functions as a chelating ligand, the maximum number of ligands accommodated around the central metal ion is 3, e.g., in the case of the indium complex **2**. However, even in the latter, the imino nitrogen coordination is restricted to only two ligands, with the third ligand bound to the indium only through a M−C_{aryl} σ-bond. Thus, in all the examples that we have studied so far with **2** as the starting material, the number of five-membered metallacycles formed does not exceed 2. It would be interesting if a similar situation would prevail with f-block metal ions.

An important indicator for the involvement of the imino nitrogen in coordination (apart from the M−N bond distance) is the extent of lengthening of the P═N bond. Thus, if one takes the distance found in Ph_3P═$NSiMe_3$ (**1**) as the reference (1.542(2) Å), the distance increases steadily in proceeding from **2** to **4**: **2** (1.562(2) Å), **3** (1.570(2), 1.582(2) Å), and **4** (1.591(2) Å). These trends have also been seen in the other metal complexes prepared from **2**. In **5**, where there is no coordination from the nitrogen, the P═N bond distance is the shortest one found (1.538(4) Å). The P−C distances do not vary significantly, however, and also are not diagnostic of the imino nitrogen coordination.

Conclusion

The questions risen in the Introduction can be answered as follows:

(i) All analytical tools employed in this paper indicate the lengthening of the P═N bond upon N→M dative bonding. Spectroscopic infrared and Raman investigations indicate for the ν(P═N) vibration a shift to higher wavenumbers (M = Li). Density functional theory calculations (M = Li) and X-ray structure determinations (M = Li, Fe, In) find longer P−N bonds in the intramolecular metal complexed compounds than in the starting material. If the imino sidearm is not employed in metal coordination (M = Ge), the P═N bond is as short as in the starting material. We will further elaborate this analytical combination to scale the shift of the ν(P═N) vibration to bond distance changes in the solid state, to deduce from the vibrational spectra the role of the metal imide coordination.

(ii) Not until now has a metal complex with more than two of these bulky ligands been observed. However, the large trivalent indium atom clearly can accommodate three ligands. The imino sidearm is flexible enough to fill vacant coordination sites or to act as a pendent spectator.

(iii) As in most coordination compounds, the presence of a dative bond is predominantly governed by steric conditions (i.e. the radius of the metal). In the indium complex there is not enough room for the third imino group to coordinate the metal, but in the germanium complex there would be plenty of space. Although the orientation of the three phenyl groups indicates the release of a vacant coordination site, the imino group would not coordinate, as the Lewis acidity of the central germanium atom is not high enough because electron-withdrawing substituents are missing.

(iv) The imino sidearm donation can be employed to stabilize a rare example of a 14-VE iron complex.

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Experimental Section

All manipulations were performed under an inert gas atmosphere of dry N_2 with Schlenk techniques or in an argon glovebox. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained in benzene-d_6 as solvent with $SiMe_4$ or H_3PO_4 as the external reference on a Bruker AM 250. Mass spectra were recorded on a Finnigan Mat 8230 or Varian Mat CH5 spectrometer. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Würzburg. The lithiated aminoiminophosphorane **2** was prepared according to literature procedures.[6]

[In(*o*-$C_6H_4PPh_2NSiMe_3$)$_3$] (3). The lithiated iminophosphorane **2** (1.10 g, 1.40 mmol) and indium trichloride (0.21 g, 0.93 mmol) were taken up in diethyl ether (20 mL) and stirred at room temperature for 24 h. Removal of solvent under vacuum afforded a white residue, which was taken up in toluene (20 mL); this mixture was stirred at room temperature for 3 days. The mixture was filtered, and the filtrate was concentrated and kept for crystallization at room temperature. After 3 days colorless crystals suitable for X-ray analysis were obtained. The mother liquor, after the removal of crystals, was evaporated to dryness under vacuum to afford a solid. It was washed with pentane (20 mL) and dried. The crystals and the white solid were found to be the same and correspond to the title compound. Yield: 0.51 g, 47%. Mp (DTA): 175 °C dec. ^{1}H NMR (C_6D_6): δ 0.50 (s, 27H, $SiMe_3$), 7.10−8.70 (m, 42H, Ph H). ^{13}C NMR (C_6D_6): δ 3.24 (d, $^3J_{C,P}$ = 3.2 Hz, $SiMe_3$), 124.3−135.3 (m, Ph C), 166.0 (s, In−C). ^{31}P NMR (C_6D_6): δ −20.3. MS (70 eV, EI): *m*/*z* (%) 334 (100) [$C_6H_4PPh_2NSiMe_2^+$], Anal. Calcd for $C_{63}H_{69}InN_3P_3Si_3$: C, 65.2; H, 5.99; N, 3.62. Found: C, 66.1; H, 6.13; N, 3.49.

[Fe(*o*-$C_6H_4PPh_2NSiMe_3$)$_2$] (4). A mixture of **2** (1.50 g, 1.91 mmol) and $FeCl_2$ (0.24 g, 1.91 mmol) was taken up in THF (25 mL). The resulting red-brown solution was stirred at room temperature for 24 h. To this solution was added toluene (25 mL), this mixture was filtered over Celite, and the clear red filtrate was kept at −40 °C. After a couple of weeks red crystals corresponding to the title compound were isolated. Total yield: 0.91 g, 63%. Mp (DTA): 97 °C dec. ^{1}H NMR (C_6D_6): δ 0.08 (broad signal, 18H, $SiMe_3$), 6.89 (broad signal, 28H, Ph H).^{31}P NMR (C_6D_6): δ 1.24 (broad signal). MS (70 eV, EI): *m*/*z* (%) 404.1 (2.63) [$Ph_3PNSiMe_3$·Fe], 334.1 (100) [$Ph_3PNSiMe_2$], 318.1 (6.1) [$Ph_3PNSiMe$], Anal. Calcd for $C_{42}H_{46}FeN_2P_2Si_2$: C, 67.0; H, 6.16; N, 3.72. Found: C, 67.4; H, 6.14; N, 3.90.

[Ph_3Ge(*o*-$C_6H_4PPh_2NSiMe_3$)] (5). A mixture of **2** (0.16 g; 0.20 mmol) and triphenylgermanium chloride (0.14 g; 0.41 mmol) were taken up in diethyl ether (15 mL) and stirred at room temperature. The reaction mixture at first turned yellow. After 1 day precipitation of a white solid was noticed. The reaction mixture was stirred for a further 2 days and the solvent stripped off in vacuo to afford a white solid. It was taken up in toluene (10 mL), and this mixture was stirred for 12 h and filtered over Celite to remove LiCl. The filtrate was stored at room temperature. After several days colorless crystals were obtained. Yield: 0.07 g, 27%. Mp (DTA): 123 °C dec. ^{1}H NMR (C_6D_6): δ 0.38 (s, 9 H, $SiMe_3$), 6.93−7.82 (m, 29 H, Ph H). ^{31}P NMR (C_6D_6): δ 8.4. MS (70 eV, EI): *m*/*z* (%) 334 (100) [$C_6H_4PPh_2NSiMe_2^+$]. Anal. Calcd for $C_{39}H_{38}GeNPSi$: C, 71.8; H, 5.87; N, 2.15. Found: C, 73.0; H, 5.71; N, 2.34.

Raman Spectroscopic Experiments. The FT-Raman spectra of the polycrystalline samples were recorded at room temperature using a Bruker IFS 120HR spectrometer equipped with a FRA 106 Raman module. The spectral resolution was 2 cm^{-1}. Radiation of 1064 nm from a Nd:YAG laser with an output power of 600 mW was employed for excitation. A Ge detector cooled with liquid nitrogen was used.

For infrared measurements the samples were mixed with KBr in order to obtain thin pellets with a thickness of about 0.3 mm. The infrared spectra were recorded in the range from 400 to 4000 cm^{-1} with a Bruker IFS 120HR spectrometer and an MCD detector. The spectra were obtained with a 2 cm^{-1} resolution.

Calculations. The DFT calculations were performed using GAUSSIAN98.[45] All calculations of harmonic wavenumbers were performed by using a fully optimized geometry as reference geometry. The DFT geometry optimization was carried out with a combination of exchange and correlation functionals which gave the best results in test calculations: Becke's 1988 exchange functional[46] in combination with the Perdew-Wang 91 gradient-corrected correlation functional[47] (BPW91). The 6-31G* and 6-31+G* basis sets for all atoms have been employed in the geometry optimization and the vibration calculations.

Crystallographic Measurements. Data for all structures were collected at low temperatures using oil-coated shock-cooled crystals[48] on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A semiempirical absorption correction was applied. The structures were solved by Patterson or direct methods with SHELXS-90.[49] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[50] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Further details on the structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk), by quoting the supplementary publication numbers 159642 (**3**), 159643 (**4**), and 159644 (**5**).

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Supporting Information Available: Tables of calculated geometric data, complete IR/Raman band assignments for **1** and **2**, and crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of the structures **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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