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New Silylated Iminophosphorano(amino)phosphines $Me_3SiN{=}PPh_2N(R)PPh_2$ (R = Et, ^{n}Pr, ^{n}Bu). Crystal and Molecular Structure of Trimethylsilyliminophosphorano(propylamino)diphenylphosphine $Me_3SiN{=}PPh_2N(^nPr)PPh_2$. Further Oxidative Derivatization with S, Se, and Azides, Titanium(IV) Transmetalation of the Imine, and Syntheses of Rhodium(I), Palladium(II), and Platinum(II) Complexes of These Iminophosphorano(amino)phosphines

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Bis(phosphino)amines $Ph_2PN(R)PPh_2$ (R = Et, ^{n}Pr, ^{n}Bu) react with stoichiometric amounts of trimethylsilyl azide to give the trimethylsilyliminophosphorano(amino)phosphines $Me_3SiN{=}PPh_2N(R)PPh_2$ (**1**, R = Et; **2**, R = ^{n}Pr; **3**, R = ^{n}Bu) as crystalline compounds. The structure of **2** has been determined by single-crystal X-ray analysis. (Crystal data for **2**: monoclinic, $P2_1/c$, $a = 10.235(1)$ Å, $b = 16.802(2)$ Å, $c = 17.075(2)$ Å, $\beta = 101.05(1)°$, $V = 2882.9(5)$ Å^3, $Z = 4$.) The structure of **2**, which is the first example of an iminophosphoranophosphine with the $P^{III}{-}N{-}P^{V}{=}N$ skeleton, was solved by direct methods and refined to $R = 0.044$. Compound **2** readily reacts with elemental sulfur, selenium, or phosphoryl azide to give fully oxidized phosphinimines $Ph_2P(E)N(^nPr)Ph_2P{=}NSiMe_3$ (**4**, E = S; **5**, E = Se; **6**, E = NP(O)(OPh)$_2$). Compounds **4**−**6** are very sensitive to moisture and readily undergo desilylation to give the parent phosphinimines $Ph_2P(E)N(^nPr)Ph_2P{=}NH$, which can be isolated as moderately stable crystalline solids. The phosphiniminophosphine **2** and the oxidized phosphinimines (**4** and **5**) react with $CpTiCl_3$ to give new nitrogen-bound Ti(IV) derivatives $Ph_2P(E)N(^nPr)Ph_2P{=}NTi(Cp)Cl_2$ (**10**, E = lone pair; **11**, E = S; **12**, E = Se). Compounds **1**−**3** readily react with rhodium(I), palladium(II), and platinum(II) complexes to give five-membered metallacycles via phosphorus(III) and imine nitrogen coordination.

Introduction

We have described previously the synthesis of a series of phosphorus-based heterodifunctional ligands that can be obtained from the partial oxidation of one phosphorus in bis(phosphines) with azides[2−11] or chalcogens.[12,13] Of special interest are the silylated iminophosphoranophosphines, which are obtained from trimethylsilyl azide oxidation, because the silyl group can be subsequently replaced,[8,10] migrated,[14] or eliminated[15,16] to form a variety of products. These migration and elimination reactions provide ready routes to the formation of both early and late transition metal derivatives wherein element−nitrogen σ-bonds are developed. We now report the syntheses of the novel nitrogen-bridged iminophosphoranophosphines $Me_3SiN{=}PPh_2N(R)PPh_2$ (**1**, R = Et; **2**, R = ^{n}Pr; **3**, R = ^{n}Bu), spectroscopic characterization of all, and the X-ray structural analysis of **2**. Derivatization of **2** (R = ^{n}Pr) with sulfur, selenium, and phosphoryl azide provides dissymmetric ligands of the type $Me_3SiN{=}PPh_2N(R)P(E)Ph_2$ (wherein, in the present case, E is S (**4**), Se (**5**), or NP(O)(OPh)$_2$ (**6**)), which have incurred some recent interest.[17] We have also been able to form the moderately stable imines $HN{=}PPh_2N(R)P(E)Ph_2$ (**7**−**9**) by hydrolytic desilylation of the parent silylated compounds. The reactions of **2**, **4**, or **5** with $CpTiCl_3$ gave nitrogen-bound titanium(IV) derivatives (**10**−**12**) through the elimination of Me_3SiCl. Finally we demonstrate that rhodium(I), palladium(II), and platinum(II) chelate complexes (**13**−**23**) can be readily prepared with this suite of ligands. Some related oxidation and coordination chemistry of the heterofunctional mono(chalcogeno)bis(phosphine)amines, obtained from a similar limited oxidation of $(Ph_2P)_2NH$, was briefly described in recent reviews;[18,19] however, most of the developed coordination chemistry of this ligand

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Table 1. ^{31}P NMR[a] Spectroscopic Data for Iminophosphorano(amino)phosphines and Their Derivatives

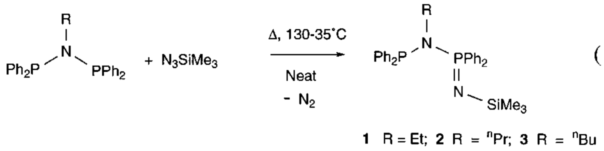
compound	no.	δ P^{III}/P(E)^{V}, ppm	δ P^{V}, ppm	$^{1}J_{PP}$, Hz	$J_{PSi(Se)}$, Hz
$Ph_2PN(Et)Ph_2P{=}NSiMe_3$	**1**	46.2 (d)	9.2 (d)	94.7	27.8[b]
$Ph_2PN(Pr)Ph_2P{=}NSiMe_3$	**2**	46.2 (d)	9.3 (d)	94.3	28.1[b]
$Ph_2PN(Bu)Ph_2P{=}NSiMe_3$	**3**	46.2 (d)	9.3 (d)	94.4	28.1[b]
$Ph_2(S)PN(Pr)Ph_2P{=}NSiMe_3$	**4**	67.5 (d)	9.6 (d)	2.4	
$Ph_2(Se)PN(Pr)Ph_2P{=}NSiMe_3$	**5**	64.8 (d)	10.7 (d)	7.6	761[c]
$(PhO)_2(O)P_cN{=}PbPh_2N(Pr)Ph_2P_a{=}NSiMe_3$	**6**	21.4(dd) (P_b), −10.8(d)(P_c)	9.6 (d)(P_a)	46.5 ($J_{P_bP_c}$), 9.9 ($J_{P_aP_b}$)	
$Ph_2(S)PN(Pr)Ph2P{=}NH$	**7**	41.3 (d)	21.5 (d)		
$Ph_2(Se)PN(Pr)Ph_2P{=}NH$	**8**	30.7 (d)	23.4 (d)	1.1	687[c]
$(PhO)_2(O)P_cN{=}P_bPh_2N(Pr)Ph_2P_a{=}NH$	**9**	1.5 (dd) (P_b), −10.8 (d) (P_c)	20.3 (d)(P_a)	31.4 ($J_{P_bP_c}$), 1.3 ($J_{P_aP_b}$)	
$Ph_2PN(Pr)Ph_2P{=}NTi(Cp)C_{l2}$	**10**	48.9 (d)	55.4 (d)	102.4	
$Ph_2(S)PN(Pr)Ph_2P{=}NTi(Cp)C_{l2}$	**11**	68.5 (d)	47.3 (d)	7.9	
$Ph_2(Se)PN(Pr)Ph_2P{=}NTi(Cp)Cl_2$	**12**	66.2 (d)	47.4 (d)	5.7	792[c]

[a] All spectra in CD_2Cl_2, ppm vs 85% H_3PO_4; d = doublet; dd = doublet of doublets; Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl. [b] $^{2}J_{PSi}$. [c] $^{1}J_{PSe}$.

system is derived from the deprotonated form of the symmetric bis(chalcogenophosphine)amine or bis(iminophosphoran)amine $(Ph_2P(E))_2NH$ (E = O, S, Se, NR) ligands.[19,20]

Results and Discussion

The stoichiometric reaction of the bis(diphenylphosphino)amines $Ph_2PN(R)PPh_2$ (R = Et, ^nPr, or ^nBu) with trimethylsilyl azide in the absence of solvents at 130−135 °C gave the respective trimethylsilyliminophosphoranaminophosphines $Me_3SiN{=}PPh_2N(R)PPh_2$ (**1**, R = Et; **2**, R = ^nPr; **3**, R = ^nBu) as crystalline products with yields up to 70−85% (eq 1). The



(1)

N-ethyl derivative was particularly slow to crystallize and gave the poorest yield; only 60−70% of the starting material was converted to **1**. The desired product in this case can be separated from starting material by slow recrystallization from acetonitrile at room temperature. Reaction of $Ph_2PN(Et)PPh_2$ with an excess of trimethylsilyl azide results in more complex reaction pathways to give a mixture of products that could not be characterized. In contrast, the *N*-propyl and *N*-butyl derivatives reacted smoothly with the azide to give pure products **2** and **3** in good yield. A previous study of this kind of system suggested that structures of type (**1**−**3**) were very unstable toward polymerization;[21] however, that does not appear to be the case in our present system. The new iminophosphoranophosphines **1**−**3** are moderately air-stable crystalline solids that are soluble in dichloromethane, toluene, tetrahydrofuran, and warm acetonitrile.

Table 2. Crystal Data for $Me_3SiN{=}PPh_2N(^nPr)PPh_2$ (**2**)

formula	$C_{30}H_{36}N_2P_2Si$	mol wt	514.67
a, Å	10.235(1)	space group	$P2_1/c$ (No. 14)
b, Å	16.802(2)	temp, °C	−52
c, Å	17.075(2)	λ (Mo Kα),[a] Å	0.710 73
β, deg	101.05(1)	ρ_{calcd}, g cm^{-3}	1.19
V, Å^3	2882.9(5)	μ (Mo Kα), cm^{-1}	2.1
Z	4	R^b	0.044
		$R_w{}^c$	0.054

[a] Graphite monochromator. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

It is interesting that the analogous *N*-methyl and *N*-phenylaminobis(phosphines) did not react with trimethylsilyl azide even at their melting point temperatures. Reaction occurs at more elevated temperatures, but the result under these conditions was a complex mixture of several products that could not be characterized. This reluctant reactivity contrasts with the earlier suggestion[21] that facile polymerization was to be expected for these P−N−P=N systems, but we see that the reactivity of this system is very greatly influenced by the substituent on the amine N center. Presumably also the substituents on P and the imine nitrogen will exert similar differentiation, but we have not systematically explored this latter aspect of the chemistry. Clearly, the relative reactivity of the bis(diphenylphosphino)amines toward trimethylsilyl azide increases with the apparent basicity at the bridging amine nitrogen, increasing along the series N(aryl) < N(Me) < N(Et) < N(Pr) < N(Bu). These substituents control the basicity at the phosphorus center, the point of attack of the azide. The N−^nPr derivative is therefore ideally suited for preparation of a monooxidized phosphine imine−phosphophine amine with trimethylsilyl azide through an ideal combination of reactivity and melting temperature of the parent bis(phosphino)amine.

We note that all of these *N*-aryl and *N*-alkyl bis(phosphino)amines reacted cleanly with other azides such as $(PhO)_2P(O)N_3$, p-$CN{-}C_6F_4N_3$, and p-$CH_3{-}C_6H_4N_3$ to give monooxidized products.[2,13]

The new iminophosphoranophosphines (**1**−**3**) were characterized by mass spectrometry, elemental analyses, NMR spectroscopic data, and, in the case of **2**, a single-crystal X-ray structural determination. The spectroscopic data are given in Table 1 and in the Experimental Section. The ^{31}P NMR spectra of compounds **1**−**3** show the expected doublet of doublets with $^{2}J_{PP}$ values of 94.7 (**1**), 94.3 (**2**), and 94.4 (**3**) Hz. The P^{III} signals are found at 46.2 ppm (**1**−**3**), and the P^{V} signals are at considerably higher field, 9.2 (**1**) and 9.3 (**2** and **3**) ppm. The P^{V} signals of these silylated compounds also show satellites due to $^{2}J_{PSi}$ couplings. The ^{29}Si (INEPT)[22] NMR spectra of **1**−**3** show doublets at −14.1 (**1**) and −14.0 (**2** and **3**) ppm due to coupling with the P^{V} center across two bonds. The $^{2}J_{PSi}$ values are 27.8 (**1**) and 28.1 (**2** and **3**) Hz.

The structure of $Ph_2PN(^nPr)Ph_2P{=}NSiMe_3$, **2** (Table 2), is shown with the atom numbering scheme in Figure 1.[23] Selected bond lengths and bond angles are listed in Table 3.

Compound **2** is only the second example[13] of a structurally characterized nitrogen-bridged iminophosphoranophosphine. The structure consists of a chain of alternating phosphorus and

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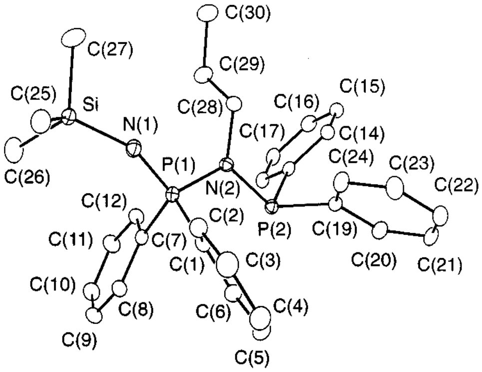


Figure 1. Perspective ORTEP[23] view of **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity, and the remaining atoms are shown as 20% ellipsoids.

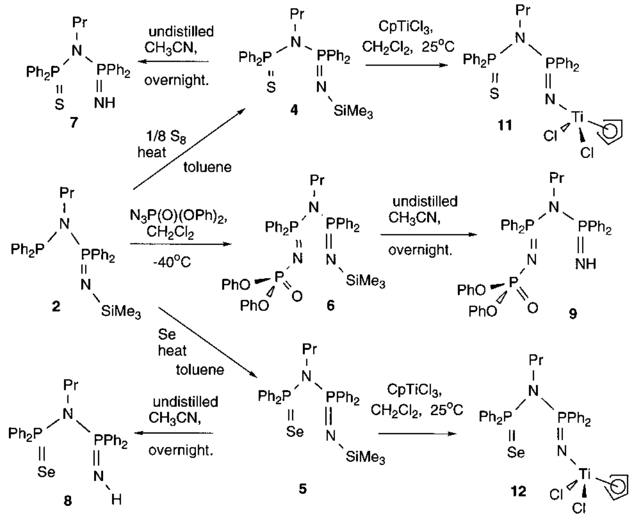
Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Me_3SiN{=}PPh_2N(^nPr)PPh_2$ (**2**)[a]

	Bond Distances (Å)		
P(1)−N(1)	1.521(3)	P(2)−C(19)	1.838(3)
P(1)−N(2)	1.694(2)	Si−N(1)	1.669(3)
P(1)−C(1)	1.821(3)	Si−C(25)	1.870(3)
P(1)−C(7)	1.815(3)	Si−C(26)	1.862(3)
P(2)−N(2)	1.713(2)	Si−C(27)	1.854(4)
P(2)−C(13)	1.835(3)	N(2)−C(28)	1.481(4)
	Bond Angles (deg)		
N(1)−P(1)−N(2)	110.7(1)	P(1)−N(2)−C(28)	118.0(2)
N(1)−P(1)−C(1)	111.7(1)	P(2)−N(2)−C(28)	123.4(2)
N(1)−P(1)−C(7)	116.1(1)	P(1)−C(1)−C(2)	117.3(2)
N(2)−P(1)−C(1)	106.4(1)	P(1)−C(1)−C(6)	123.6(2)
N(2)−P(1)−C(7)	104.6(1)	P(1)−C(7)−C(8)	121.6(2)
C(1)−P(1)−C(7)	106.6(1)	P(2)−C(7)−C(12)	119.4(2)
N(2)−P(2)−C(13)	103.1(1)	P(2)−C(13)−C(14)	124.8(2)
N(2)−P(2)−C(19)	105.0(1)	P(2)−C(13)−C(18)	116.7(2)
P(1)−N(2)−P(2)	118.2(1)	P(2)−C(19)−C(20)	117.2(2)
P(1)−N(1)−Si	154.3(2)	P(2)−C(19)-C(24)	124.0(2)
C(13)−P(2)−C(19)	101.8(1)		

[a] Numbers in parentheses are the standard deviations in the least significant figure.

nitrogen atoms with notably a trigonal planar geometry around the bridging nitrogen. The sum of the bond angles at this bridging nitrogen is 359.6°. The P(1)−N(2)−P(2) bond angle is 118.2(1)°, within the range of typical P−N−P bond angles (110−123°) observed in symmetric bis(phosphino)amines[24−26] (wherein the trigonal planar geometry around the bridging nitrogen is retained), and is also comparable with that in the iminophosphoranophosphine, p-CN−$C_6F_4N{=}Ph_2PN(Me)PPh_2$ (119.44(8)°).[13] The bond angle at the imine nitrogen P(1)−N(1)−Si of 154.3(2)° is slightly larger than that observed in the analogous P−CH_2−P backbone derivative[27] $Ph_2PCH_2Ph_2P{=}NSiMe_3$ (150.2(2)°). The P(1)−N(2) bond (1.694(2) Å), which is formally a bond from an amine nitrogen to a pentavalent phosphorus, is shorter than the P(2)−N(2) bond (1.713(2) Å), formally a bond to trivalent phosphorus. This difference is expected because of the multiple bond character contributed to the P^V−N bond from the greater delocalization of the bridging nitrogen lone pair toward the pentavalent phosphorus compared to the trivalent phosphorus center. Similar trends are generally observed in P^V−N−P^{III} systems.[13,28] The P(1)−N(1) bond length of 1.521(3) Å is slightly shorter than the typical phospinimide but is comparable to that observed in $Ph_2PCH_2Ph_2P{=}NSiMe_3$ (1.529(3) Å).[27]

Scheme 1



Derivatives of 2. Oxidation with S, Se, or Azide. Reaction of $Ph_2PN(^nPr)Ph_2P{=}NSiMe_3$ (**2**) with elemental sulfur or selenium in toluene under refluxing conditions afforded the thioyl- (or selenoyl-) phosphino(amino)iminophosphoranes (**4** and **5**), respectively, in good yield (Scheme 1). Reaction of **2** with phosphoryl azide, $N_3P(O)(OPh)_2$, in CH_2Cl_2 at −40 °C gave the bis(iminophosphorano)amine, $Me_3SiN{=}PPh_2N(^nPr)$-$Ph_2P{=}NP(O)(OPh)_2$ (**6**), wherein two different imine functionalities are developed, in 78% yield. Compounds **4**−**6** are monomeric crystalline solids, and relevant data are given in Table 1.

The ^{31}P NMR spectra of the thioyl- (**4**) and selenoyl- (**5**) derivatives show the expected doublet of doublets with small $^2J_{PP}$ coupling constants because both phosphorus centers are pentavalent. Derivatives **4** and **5** show very small coupling constants of 2.4 (**4**) and 7.6 (**5**) Hz. The chalcogenyl P^V signals are found at 67.5 (**4**) and 64.8 (**5**) ppm, and the iminophosphorane P(V) signals appear essentially unchanged, 9.6 (**4**) and 10.7 (**5**) ppm, relative to the starting material, 9.3 ppm (**2**). The selenoyl derivative (**5**) also show $^1J_{PSe}$ satellite coupling of 761 Hz, which clearly identifies the P(V) signal arising from the P=Se center. The mixed bis(iminophosphorane) (**6**) shows three sets of signals in the ^{31}P NMR spectrum due to the presence of three different phosphorus(V) centers. The trimethylsilylimine P(V) center shows a sharp doublet at 9.6 ppm, which is coupled to the central P(V) center across two bonds ($^2J_{P^VP^V} = 9.9$ Hz). The ^{31}P signal due to the latter imino phosphoryl P(V) center is also a sharp doublet at −10.8 ppm with a r $^2J_{P^VP^V}$ value (46.5 Hz) much larger than those shown in the chalcogen derivatives. The central P(V) signal is therefore a doublet of doublets as the result of coupling to both of the other phosphorus centers ($^2J_{P^V_NP^V_N}$) (9.9 Hz) and $^2J_{P^V_NP^V_O}$ (46.5 Hz)) in the molecule.

Conversion of Oxidized Silyl Imides (4−6) to Imides (7−9). In contrast to the heterodifunctional phosphoraniminophosphines (**1**−**3**), the mixed derivatives (**4**−**6**) were found to be very moisture-sensitive. Desilylation occurred readily via hydrolysis with (wet) undistilled acetonitrile or toluene solvents to give the corresponding phosphinimines $Ph_2P(E)N(^nPr)Ph_2P{=}$

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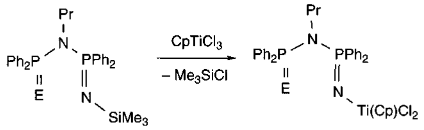
NH (**7**, E = S; **8**, E = Se; **9**, E = NP(O)(OPh)$_2$). These imines can be isolated as moderately air-stable crystalline solids that are readily soluble in dichloromethane, acetonitrile, and toluene. The ^{1}H NMR spectra of **7**−**9** clearly indicate that the trimethylsilyl groups have been removed. The mass spectrometric and C, H, and N elemental analysis data are also consistent with a silicon-free product. Further evidence for desilylation also comes from ^{31}P NMR spectroscopy. The ^{31}P NMR data are given in Table 1. The ^{31}P NMR spectrum of the desilylated thioyl derivative (**7**) exhibits two singlets at 41.3 and 21.5 ppm assigned to thioylphosphorus(V) and iminephosphorus(V) centers, respectively; however, no $^2J_{PP}$ coupling was observed. The phosphinimine center also shifted to higher field (21.5 ppm), a difference of ca. 12 ppm as a result of desilylation. Similarly, desilylation shifts the thioyl phosphorus(V) center to ca. 42 ppm, a difference of −26.2 ppm compared to silyl derivative **4**. A similar difference is observed in the analogous desilylated selenoyl derivative **8** relative to **5**. The $^1J_{PSe}$ coupling in **8** (687 Hz) is also decreased by 74 Hz relative to **5**, and the $^2J_{PP}$ coupling in **8** is a small but observable value of 1.13 Hz. The ^{31}P NMR spectrum of the desilylated bis(imine) **9** exhibits three sets of signals that are, as expected, similar to the parent compound **6** with a considerable decrease in the magnitude of $^2J_{P-N-P}$ (from 9.9 to 1.3 Hz) and $^2J_{P=N-P(O)}$ (from 46.5 to 31.4 Hz) as a result of desilylation. In addition two of the P(V) centers are shifted substantially to higher field; the phosphoryl phosphorus resonance is unchanged in keeping with its remote location from the desilylation site.

Compounds **2**, **4**, and **5** readily react with CpTiCl$_3$ in dichloromethane at room temperature with the elimination of Me$_3$SiCl to provide the Ti(IV)-metalated phosphinimines (**10**−**12**) (eq 2). The oxidized compounds **4** and **5** react more quickly than the phosphine Ph$_2$PN(^{n}Pr)Ph$_2$P=NSiMe$_3$, **2**, indicating that the oxidation of the free phosphine reduces the delocalization of the lone pair into the backbone structure and weakens the N−Si bond and/or increases the basicity at the silylimine center. This is consistent with the observation that the oxidized compounds **4** and **5** are more sensitive to moisture than **2**. These compounds, **10**−**12**, are thus very good synthons for formation of bimetallic complexes with a variety of transition metal derivatives. In the present cases we do not expect the Ti^{IV} center, being a very hard center with little affinity for soft donors, to chelate with the phosphine or the chalcogens, and all indications are that this is so.

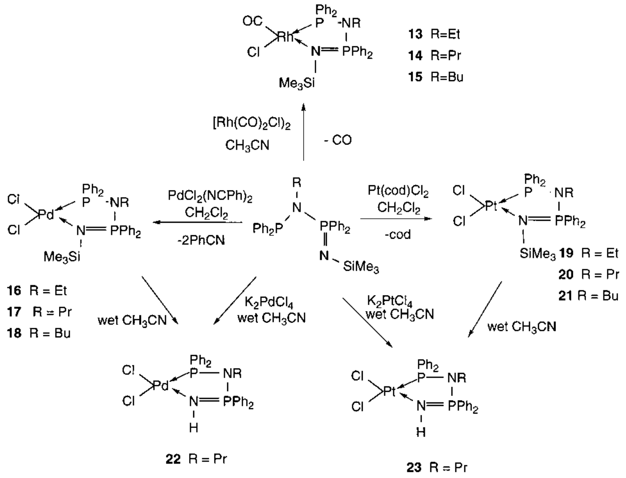


(2)

10 E = lone pair
11 E = S
12 E = Se

The ^{31}P NMR spectrum of **10** exhibits two doublets at 48.9 and 55.4 ppm, which are assigned to the phosphorus(III) and phosphorus(V) centers, respectively, with a $^2J_{PP}$ value of 102.4 Hz. In this and the other titanated derivatives the phosphorus(V) center signal shows considerable deshielding upon metalation of the imine with titanium, whereas the chemical shift arising from the phosphorus(III) or the P^V chalcogen centers is essentially unaffected by this metalation. Thus, for **10** the chemical shift difference of the P^{III} center is only 2.7 ppm vs the free ligand. The ^{31}P NMR spectra of **11** and **12** are quite similar to that of **10**, showing again a large low-field (deshielding) shift at the imine phosphorus, about 37 ppm relative to the values of the parent silylated compounds. The signals are found at 47.3 (**11**) and 47.4 (**12**) ppm with the expected doublet of doublets having $^2J_{PP}$ values of 7.9 (**11**) and 5.7 (**12**) Hz. The chalcogenyl phosphorus(V) signals, however, are found at 68.5 (**11**) and 66.2 (**12**) ppm, a low field shift of only about 1.0 ppm relative to the free ligand. Although the electronic perturbation arising from the conversion of the imine from a silyl imine to a titanated imine is substantial, as indicated by the change in the NMR chemical shift of the P^V center, these effects are not effectively transmitted to the more remote phosphorus center, which is consistent with there being little interaction between the Ti and the remote phosphorus center. This also signifies that electronic effects are not being transmitted through the backbone.

Scheme 2



Rh(I), Pd(II), and Pt(II) Complexes. The heterodifunctional (trimethylsilyl)(iminophosphoran)aminophosphines, Me$_3$SiN=PPh$_2$N(R)−PPh$_2$ (**1**, R = Et; **2**, R = ^{n}Pr; **3**, R = ^{n}Bu) react smoothly with [Rh(CO)$_2$Cl]$_2$ in acetonitrile at 25 °C to give the five-membered metallacycles **13**−**15** in good yield as crystalline solids (Scheme 2). NMR data are given in Table 4, and other data are included in the Experimental Section. The infrared spectra of complexes **13**−**15** show ν_{CO} absorptions close to 1977 cm^{-1}, in all cases indicating the mutual cis disposition of CO and phosphorus(III) centers.[2,12] The ^{31}P{^{1}H} NMR spectra of complexes **13**−**15** show doublet of doublets for the P^{III} centers with a $^1J_{RhP}$ value of about 169 Hz. Thus, the P^{III} signal is clearly identified. The P^V centers also appear as a doublet of doublets in the case of **13** (because of a small $^2J_{RhP}$ = 1.5 Hz) and simple doublets in the case of **14** and **15** where Rh−P^V coupling is not observed.

Reactions of **1**−**3** with Cl$_2$M(cod) (M = Pd or Pt) in CH$_2$Cl$_2$ at 25 °C similarly gives the expected five-membered chelates **16**−**21** as shown in Scheme 2. The ^{31}P{^{1}H} NMR spectra of complexes **16**−**21** again exhibit two doublets due to the P^{III} and P^V centers, respectively. The $^2J_{PP}$ couplings are in the range 34.8−37.5 Hz. The platinum complexes **19**, **20**, and **21** exhibit very large $^1J_{PtP}$ couplings of 3900, 3895.4, and 3894 Hz, respectively, clearly indicative of P^{III} coordination to Pt and identifying the P^{III} center. The corresponding $^2J_{PtP}$ couplings are 114.7, 92, and 114 Hz, respectively.

Reactions of **2** with K$_2$PdCl$_4$ or K$_2$PtCl$_4$ in a mixture of water and acetonitrile under reflux conditions give the desilylated imine complexes **22** and **23** in good yield. Alternatively, the **22** or **23** can be obtained by refluxing **17** or **20** in undistilled acetonitrile for 6 h. In both cases hydrolysis (forming (Me$_3$Si)$_2$O) occurs with the formation of stable imine complexes of

Table 4. ^{31}P NMR^a Spectroscopic Data for Complexes **13**−**23**^{a}

compound	no.	δ P^{III}, ppm	δ P^V, ppm	$^2J_{PP}$, Hz	$^1J_{MP}$, Hz	$^2J_{MP}$, Hz
[(CO)Rh(Cl){PPh$_2$N(Et)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**13**	91.7 (dd)	37.1 (dd)	47.0	169	1.5
[(CO)Rh(Cl){PPh$_2$N(Pr)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**14**	92.2 (dd)	36.4 (d)	47.0	169	
[(CO)Rh(Cl){PPh$_2$N(Bu)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**15**	92.4 (dd)	36.6 (d)	47.1	169	
[Cl$_2$Pd{PPh$_2$N(Et)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**16**	69.7 (d)	44.1 (d)	37.5		
[Cl$_2$Pd{PPh$_2$N(Pr)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**17**	70.3 (d)	43.5 (d)	37.6		
[Cl$_2$Pd{PPh$_2$N(Bu)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**18**	70.0 (d)	44.5 (d)	36.9		
[Cl$_2$Pt{PPh$_2$N(Et)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**19**	41.8 (d)	45.8 (d)	34.8	3900	115
[Cl$_2$Pt{PPh$_2$N(Pr)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**20**	42.3 (d)	45.1 (d)	34.7	3895	114
[Cl$_2$Pt{PPh$_2$N(Bu)Ph$_2$P═NSiMe$_3$}-κP,κN$_{imine}$]	**21**	42.5 (d)	45.2 (d)	34.8	3894	114
[Cl$_2$Pd{PPh$_2$N(Pr)Ph$_2$P═NH}-κP,κN$_{imine}$]	**22**	90.2 (d)	67.3 (d)	47.1		
[Cl$_2$Pt{PPh$_2$N(Et)Ph$_2$P═NH}-κP,κN$_{imine}$]	**23**	61.1 (d)	66.1 (d)	38.0	4092	92

^{a} All spectra in CDCl$_2$ or CD$_2$Cl$_2$; ppm vs 85% H$_3$PO$_4$; d = doublet; dd = doublet of doublets.

the metals. This behavior parallels that observed for the reaction of Ph$_2$PCH$_2$PPh$_2$═NSiMe$_3$ with these same metal salts under similar conditions.[3] The major difference is that the methylene-bridged system seems to be more reactive. The presence of N−H bonds in complexes **22** and **23** is clearly indicated by infrared absorptions for ν_{NH} at 3336 and 3340 cm^{-1}, respectively. Further evidence is provided by the substantive changes in the ^{31}P{^{1}H} NMR spectra of the complexes: the palladium complex **22** appears as a doublet of doublets arising from P^{III} (90.2 ppm) and P^V (67.3 ppm) centers. Both centers are considerably deshielded relative to the (trimethylsilyl)imine analogue **23**. The low-field shifts of 44 and 58 ppm for P^{III} and P^V centers, respectively, are parallel to similar large shifts in the free ligands as the result of desilylation.

Summary

A stable multifunctional N═P^{V}N−P^{III} system can be readily obtained by oxidation of one phosphorus of a bis(phosphino)amine with azidotrimethylsilane. The propylamino derivative has been structurally characterized and shows a planar central nitrogen. In contrast to a previous literature suggestion that such P═N−P−N systems were unstable toward polymerization, we find these materials to be quite stable. A variety of chelate complexes of Rh, Pd, and Pt have been prepared from the iminophosphoranaminophosphine. The silylated imino (amino) phosphines readily yield metalated iminophosphoranaminophosphines as demonstrated by synthesis of the Ti^{IV} derivative, the first example of a metalated derivative of this particular system. The iminophosphoranaminophosphines readily undergo further oxidation with chalcogens and azides to give the doubly oxidized derivatives that have different functionalities on the phosphorus, thus creating asymmetric ligands of the form (R′)N═PPh$_2$N(R)P(E)Ph$_2$. In this way asymmetric bis(imines) as well as the hard−soft iminothio or iminoselenoyl ligands, all of which have great potential use as chelate ligands, can be prepared. On hydrolysis, those silylated imines in which the other phosphorus center was oxidized afforded the free imines as unexpectedly stable materials. In all cases the imine (N−H) ligand could be further stabilized by complexation, for example, to Pt or Pd centers.

Experimental Section

All experiments were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled prior to use. Ph$_2$PN(R)PPh$_2$ (R = Et, ^{n}Pr, or ^{n}Bu[29]), [Pd(cod)Cl$_2$],[30] [Pt(cod)Cl$_2$],[31] and [Rh(CO)$_2$Cl]$_2$ [32] were prepared according to published procedures or with small modifications thereof. N$_3$SiMe$_3$ and N$_3$P(O)(OPh)$_2$ were purchased from Aldrich.

^{1}H, ^{31}P, and ^{29}Si NMR spectra were obtained on a Bruker WH 400 instrument (operating at 400.13, 161.97, and 79.50 MHz, respectively) using SiMe$_4$, 85% H$_3$PO$_4$, and SiMe$_4$, respectively, as the external standards. An INEPT[22] sequence was employed to enhance signals in the ^{29}Si NMR spectra. CD$_2$Cl$_2$ was used both as solvent and as an internal lock. Positive shifts lie downfield of the standard in all cases. Infrared spectra were recorded on a Nicolet 20SX FTIR spectrometer in CH$_2$Cl$_2$ solution. Mass spectra were recorded on a Kratos MS9 instrument. Microanalysis were performed by the Microanalytical Laboratory in the Department of Chemistry at the University of Alberta. Melting points are uncorrected.

Synthesis of Ph$_2$PN(R)Ph$_2$P═NSiMe$_3$ (1, R = Et; 2, R = ^{n}Pr; 3, R = ^{n}Bu). A mixture of Ph$_2$PN(R)PPh$_2$ (10 mmol) and Me$_3$SiN$_3$ (11 mmol) placed in a 100 mL round-bottomed flask fitted with a condenser was heated with stirring in an oil bath maintained at 125−130 °C for 8 h. The resultant clear melt was subjected to vacuum to remove excess azide and any other volatile material, then cooled and dissolved in CH$_3$CN (25 mL). The solution was allowed to stand overnight at room temperature whereupon a colorless crystalline solid precipitated in good yield.

1. Yield: 73%. Mp: 118−119 °C. Anal. Calcd for C$_{29}$H$_{34}$N$_2$P$_2$Si: C, 69.60; H, 6.80; N, 5.60. Found: C, 69.67; H, 6.79; N, 5.28. MS EI (*m*/*z*): 500 (M$^+$). ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 7.90, 7.40 (m, 20H); δ CH$_2$, 3.58 (m, 2H); δ CH$_3$, 0.50 (t, 3H), δ Me$_3$Si, 0.0 (s, 9H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P^{III}, 46.2 (d); δ P^V, 9.2 (d), $^2J_{PP}$ = 94.7 Hz. ^{29}Si NMR (CD$_2$Cl$_2$): δ −14.1 (d, $^2J_{SiP}$ = 27.8 Hz).

2. Yield: 86%. Mp: 122−124 °C. Anal. Calcd for C$_{30}$H$_{36}$N$_2$P$_2$Si: C, 70.04; H, 7.00; N, 5.45. Found: C, 70.01; H, 7.07; N, 5.42. MS EI (*m*/*z*): 514 (M$^+$). ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 7.85, 7.45 (m, 20H); δ CH$_2$, 3.30 (m, 2H), 0.85 (m, 2H); δ CH$_3$, 0.40 (t, 3H); δ Me$_3$Si, 0.00 (s, 9H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P^{III}, 46.2 (d), δ P^V, 9.3 (d), $^2J_{PP}$ = 94.3 Hz. ^{29}Si NMR (CD$_2$Cl$_2$): δ −14.0 (d, $^2J_{SiP}$ = 28.1 Hz).

3. Yield: 79%. Mp: 104−106 °C. Anal. Calcd for C$_{31}$H$_{38}$N$_2$P$_2$Si: C, 70.45; H, 7.19; N, 5.30. Found: C, 70.43; H, 7.24; N, 5.26. MS EI (*m*/*z*): 528 (M$^+$). ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 7.82, 7.40 (m, 20H); δ (CH$_2$), 3.35 (m, 2H), 0.80 (m, 4H); δ (CH$_3$), 0.50 (t, 3H); δ Me$_3$Si, 0.0 (s, 9H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P^{III}, 46.2 (d); δ P^V, 9.3 (d), $^2J_{PP}$ = 94.4 Hz. ^{29}Si NMR (CD$_2$Cl$_2$): δ −14.0 (d, $^2J_{SiP}$ = 28.1 Hz).

Preparation of S═PPh$_2$N(^{n}Pr)Ph$_2$P═NSiMe$_3$ (4) and Se═PPh$_2$N(^{n}Pr)Ph$_2$P═NSiMe$_3$ (5). A mixture of Ph$_2$PN(^{n}Pr)Ph$_2$P═NSiMe$_3$ (0.5 g, 0.97 mmol) and sulfur (0.031 g, 0.97 mmol) in toluene (20 mL) was heated under reflux conditions for 12 h. The solution was then cooled to 25 °C and concentrated to 8 mL under vacuum, and 5 mL of *n*-hexane was added. Keeping this solution at 0 °C gave analytically pure crystalline product in 78% yield. The selenium analogue Se═PPh$_2$N(^{n}Pr)Ph$_2$P═NSiMe$_3$ (**5**) was prepared similarly and obtained as a pinkish-white crystalline product in 76% yield.

4. Mp: 109−111 °C. Anal. Calcd for C$_{30}$H$_{36}$N$_2$P$_2$SSi: C, 65.93; H, 6.59; N, 5.13. Found: C, 65.98; H, 6.73; N, 5.14. MS EI (*m*/*z*): 546

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(M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.95, 7.60, 7.37 (m, 20H); δ $\mathrm{CH_2}$, 3.40 (m, 2H); 1.10 (m, 2H); δ $\mathrm{CH_3}$, 0.30 (t, 3H); δ $\mathrm{Me_3Si}$, −0.35 (s, 9H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(S), 67.5 (d); δ P($\mathrm{NSiMe_3}$), 9.6 (d), $^2J_{\mathrm{PP}} = 2.4$ Hz.

5. Mp: 143 °C. Anal. Calcd for $\mathrm{C_{30}H_{36}N_2P_2SeSi}$: C, 60.70; H, 6.07; N, 4.72. Found: C, 60.82; H, 6.00; N, 4.67. MS EI (*m*/*z*): 593 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.90, 7.60, 7.50, 7.32 (m, 20H); δ $\mathrm{CH_2}$, 3.35 (m, 2H), 1.05 (m, 2H); δ $\mathrm{CH_3}$, 0.22 (t, 3H); δ $\mathrm{Me_3Si}$, −0.20 (s, 9H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(Se), 64.8 (d); δ P($\mathrm{NSiMe_3}$), 10.7 (d), $^2J_{\mathrm{PP}} = 7.6$ Hz, $^{21}J_{\mathrm{PSe}} = 761$ Hz.

Conversion of $\mathrm{E{=}PPh_2N(^nPr)Ph_2PNSiMe_3}$ to the Imines $\mathrm{E{=}PPh_2N(^nPr){-}Ph_2P{=}NH}$ (7, E = S; 8, E = Se). Recrystallization of **4** or **5** (0.18) in a mixture of undistilled (lab grade) toluene and hexane (1:1) or in acetonitrile at 0 °C led to the formation of pure **7** or **8**, respectively, as crystalline products in quantitative yield.

7. Mp: 134−136 °C. Anal. Calcd for $\mathrm{C_{27}H_{28}N_2P_2S}$: C, 68.35; H, 5.91; N, 5.91. Found: C, 68.10; H, 5.78; N, 5.97. MS EI (*m*/*z*): 474 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.00, 7.45 (m, 20H); δ $\mathrm{CH_2}$, 2.72 (m, 2H), 1.45 (m, 2H); δ $\mathrm{CH_3}$, 0.80 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(S), 41.3 (s); δ P(NH), 21.5 (s). No $^2J_{\mathrm{PP}}$ was observed.

8. Mp: 149−151 °C. Anal. Calcd for $\mathrm{C_{27}H_{28}N_2P_2Se}$: C, 62.18; H, 5.37; N, 5.37. Found: C, 62.09; H, 5.37; N, 5.40. MS EI (*m*/*z*): 521 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.05, 7.40 (m, 20H); δ $\mathrm{CH_2}$, 2.75 (m, 2H), 1.50 (m, 2H); δ $\mathrm{CH_3}$, 0.80 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(Se), 30.7 (d); δ P(NH), 23.4 (d), $^2J_{\mathrm{PP}} = 1.13$ Hz, $^1J_{\mathrm{PSe}} = 687$ Hz.

Preparation of $\mathrm{(PhO)_2P(O){=}NPPh_2N(^nPr)Ph_2P{=}NSiMe_3}$ (6) and the Imine (9). A solution of $\mathrm{N_3P(O)(OPh)_2}$ (0.27 g, 0.97 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a solution of **2** (0.5 g, 0.97 mmol), also dissolved in $\mathrm{CH_2Cl_2}$ (10 mL), at −40 °C. After the addition was complete the mixture was slowly warmed to room temperature and stirred for 3 h. The solution was then concentrated to 8 mL, 3−4 mL of *n*-hexane was added, and the solution was cooled to 0 °C whereupon **8** precipitated as a white crystalline solid. Recrystallization of **8** in LR grade (undistilled) $\mathrm{CH_3CN}$ and *n*-hexane (1:1) (manipulation under air) yielded the desilylated compound $\mathrm{(PhO)_2P(O)NPPh_2N(^nPr)\text{-}Ph_2P{=}NH}$ (**9**).

6. Yield: 78%. Mp: 114 °C. Anal. Calcd for $\mathrm{C_{42}H_{46}N_3O_3P_3Si}$: C, 66.23; H, 6.04; N, 5.51. Found: C, 66.3; H, 6.00; N, 5.33. MS EI (*m*/*z*): 761 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.20, 7.93, 7.70 (m, 30H); δ $\mathrm{CH_2}$, 3.70 (m, 2H), 1.25 (m, 2H); δ $\mathrm{CH_3}$, 0.50 (t, 3H); δ $\mathrm{Me_3Si}$, 0.0 (s, 9H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P{NP(O)($\mathrm{OPh)_2}$}, 21.4 (dd); δ P($\mathrm{NSiMe_3}$), 9.6 (d); δ P(O), −10.8 (d), $^2J_{\mathrm{P-N-P}} = 9.9$ Hz, $^2J_{\mathrm{P(O)-N{=}P}} = 46.5$ Hz.

9. Mp: 120−122 °C. Anal. Calcd for $\mathrm{C_{39}H_{38}N_3O_3P_3}$: C, 67.92; H, 5.51; N, 6.09. Found: C, 67.86; H, 5.53; N, 6.01. MS EI (*m*/*z*): 689 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.25, 7.90, 7.55, 7.40 (m, 30H); δ $\mathrm{CH_2}$, 2.0 (m, 2H), 1.38 (m, 2H); δ $\mathrm{CH_3}$, 0.30 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P{NP(O)($\mathrm{OPh)_2}$}, 1.5 (dd); δ P(NH), 20.3 (d); δ P(O), −10.5 (d), $^2J_{\mathrm{P-N-P}} = 1.3$ Hz, $^2J_{\mathrm{P(O)-N{=}P}} = 31.4$ Hz.

Preparation of $\mathrm{Ph_2PN(^nPr)Ph_2P{=}NTi(Cp)Cl_2}$ (10). A solution of **3** (0.2 g, 0.39 mmol) in $\mathrm{CH_2Cl_2}$ (8 mL) was added dropwise to a solution of $\mathrm{CpTiCl_3}$ (0.085 g, 0.39 mmol) in the same solvent (10 mL) at room temperature, and the mixture was stirred for 3 h. The clear-yellow solution was concentrated to 8 mL, 4 mL of *n*-hexane was added, and the solution was then cooled to 0 °C to give **10** as a yellow microcrystalline solid.

Yield: 81%. Mp: 108 °C (dec). Anal. Calcd for $\mathrm{C_{32}H_{32}Cl_2N_2P_2Ti}$: C, 61.45; H, 5.12; N, 4.48. Found: C, 61.20; H, 5.15; N, 4.38. MS FAB (*m*/*z*): 625 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.00, 7.60, 7.40 (m, 20H); δ ($\mathrm{C_5H_5}$), 6.22 (s, 5H); δ $\mathrm{CH_2}$, 3.50 (m, 2H), 0.90 (m, 2H); δ $\mathrm{CH_3}$ 0.40 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P$^{\mathrm{III}}$, 48.9 (d); δ P$^{\mathrm{V}}$, 55.4 (d), $^2J_{\mathrm{PP}} = 102.4$ Hz.

Preparation of $\mathrm{E{=}PPh_2N(^nPr)Ph_2P{=}NTi(Cp)Cl_2}$ (11, E = S; 12, E = Se). To a solution of **4** or **5** (ca. 30 mmol) (prepared in situ as described above) in toluene (20 mL) was added, dropwise, a solution of $\mathrm{CpTiCl_3}$ (ca. 30 mmol) also in toluene (10 mL) at room temperature. The mixture was stirred for 3 h before it was concentrated to 15 mL under vacuum. A total of 5 mL of diethyl ether was added, and a stream of argon was passed over the solution overnight whereupon yellow microcrystals of **11** or **12**, respectively, were obtained in 70−72% yield.

11. Mp: 172 °C (dec). Anal. Calcd for $\mathrm{C_{32}H_{32}Cl_2N_2P_2STi}$: C, 58.45; H, 4.87; N, 4.26. Found: C, 58.02; H, 4.47; N, 4.13. MS EI (*m*/*z*): 567 (M$^+$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.05, 7.50 (m, 20H); δ ($\mathrm{C_5H_5}$), 6.20 (s, 5H); δ ($\mathrm{CH_2}$), 3.42 (m, 2H), 1.35 (m, 2H); δ ($\mathrm{CH_3}$), 0.20 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(S), 68.5 (d); δ P(N), 47.3 (d), $^2J_{\mathrm{PP}} = 7.9$ Hz.

12. Mp: 148 °C (melts with dec). Anal. Calcd for $\mathrm{C_{32}H_{32}Cl_2N_2P_2SeTi}$: C, 54.55; H, 4.54; N, 3.97. Found: C, 53.98; H, 4.46; N, 3.88. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.0, 7.50 (m, 20H); δ ($\mathrm{C_5H_5}$), 6.60 (s, 5H); δ ($\mathrm{CH_2}$), 3.40 (m, 2H), 1.35 (m, 2H); δ ($\mathrm{CH_3}$), 0.24 (t, 3H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(Se), 66.2 (d); δ P(N), 47.4 (d), $^2J_{\mathrm{PP}} = 5.7$ Hz, $^1J_{\mathrm{PSe}} = 792$ Hz.

Preparation of Complexes [(CO)Rh(Cl){$\mathrm{PPh_2N(R)Ph_2P{=}NSiMe_3}$}-$\kappa$P,$\kappa$N$_{\mathrm{imine}}$] (13−15). In general a solution of **1** (0.3 mmol) in dry $\mathrm{CH_3CN}$ (10 mL) was added to a solution of $\mathrm{[Rh(CO)_2Cl]_2}$ (0.15 mmol) also in $\mathrm{CH_3CN}$ (8 mL). The reaction mixture was stirred at room temperature for 2 h and cooled to 0 °C to give yellow crystalline products in good yield.

13. Yellow crystals, yield: 86%. Mp: 220 °C (dec). Anal. Calcd for $\mathrm{C_{30}H_{34}ClN_2OP_2RhSi}$: C, 54.00; H, 5.10; N, 4.20. Found: C, 53.84; H, 5.09; N, 4.16. IR ($\mathrm{CH_2Cl_2}$): ν_{CO} cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.95, 7.70, 7.50 (m, 20H); $\delta_{\mathrm{CH_2}}$, 2.95 (m, 2H); $\delta_{\mathrm{CH_3}}$, 0.90 (t, 3H); $\delta_{\mathrm{(CH_3)_3Si}}$, −0.10 (s, 9H). ^{29}Si NMR (INEPT, 79.5 MHz, in $\mathrm{CD_2Cl_2}$, ppm versus $\mathrm{Me_4Si}$): δ 7.24(d), $^2J_{\mathrm{PSi}} = 9.63$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 91.7 (dd); δ P(V), 37.1 (d), $^2J_{\mathrm{PP}} = 47$ Hz, $^1J_{\mathrm{RhP}} = 169$ Hz, $^2J_{\mathrm{PP}} = 1.5$ Hz.

14. Yellow crystals, yield: 89%. Mp: 206 °C (dec). Anal. Calcd for $\mathrm{C_{31}H_{36}ClN_2OP_2RhSi}$: C, 54.66; H, 5.29; N, 4.11. Found: C, 54.66; H, 5.15; N, 4.12. IR ($\mathrm{CH_2Cl_2}$): ν_{CO} cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.97, 7.70, 7.50 (m, 20H); $\delta_{\mathrm{(CH_2)_2}}$, 2.70 (m, 2H), 1.40 (m, 2H); $\delta_{\mathrm{CH_3}}$, 0.40 (t, 3H); $\delta_{\mathrm{CH_3)_3Si}}$, −0.15 (s, 9H). ^{29}Si NMR (INEPT, $\mathrm{CD_2Cl_2}$, 79.5 MHz, ppm versus $\mathrm{Me_4Si}$): δ 5.4 (d), $^2J_{\mathrm{PSi}} = 9.2$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 92.2 (dd); δ P(V), 36.4 (d), $^2J_{\mathrm{PP}} = 47$ Hz, $^1J_{\mathrm{RhP}} = 169$ Hz.

15. Bright yellow crystals, yield: 94%. Mp: 154 °C (dec). Anal. Calcd for $\mathrm{C_{32}H_{38}ClN_2OP_2RhSi}$: C, 55.29; H, 5.47; N, 4.02. Found: C, 55.18; H, 5.27; N, 4.10. IR ($\mathrm{CH_2Cl_2}$): ν_{CO} cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.90, 7.68, 7.56 (m, 20H); $\delta_{\mathrm{(CH_2)_3}}$, 2.78 (m, 2H), 1.35 (m, 2H), 0.75 (m, 2H); $\delta_{\mathrm{CH_3}}$, 0.50 (t, 3H); $\delta_{\mathrm{(CH_3)_3Si}}$, 0.22 (s, 9H). ^{29}Si NMR ($\mathrm{CD_2Cl_2}$, INEPT, 79.5 MHz, ppm versus $\mathrm{Me_4Si}$): δ 5.4 (d), $^2J_{\mathrm{PSi}} = 8.7$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 92.4 (dd); δ P(V), 36.6 (d), $^2J_{\mathrm{PP}} = 47.1$ Hz, $^1J_{\mathrm{RhP}} = 169$ Hz.

Preparation of Complexes [$\mathrm{Cl_2M}${$\mathrm{PPh_2N(R)Ph_2P{=}NSiMe_3}$}-$\kappa$P,$\kappa$N$_{\mathrm{imine}}$] (16, M = Pd, R = Et; 17, M = Pd, R = Pr; 18, M = Pd, R = Bu; 19, M = Pt, R = Et; 20, M = Pt, R = Pr; 21, M = Pt, R = Bu). A solution of **1**−**3** (0.3 mmol) in dry $\mathrm{CH_2Cl_2}$ (10 mL) was added dropwise to a solution of (cod)$\mathrm{MCl_2}$ (0.3 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The reaction mixture was stirred at room temperature for 3 h. The solution was then concentrated to 8 mL, and 3 mL of *n*-hexane was added. Cooling this solution to 0 °C gave analytically pure samples.

16. Yellow crystals, yield: 86%. Mp: 180 °C (dec). Anal. Calcd for $\mathrm{C_{29}H_{34}Cl_2N_2P_2PdSi}$: C, 51.36; H, 5.02; N, 4.13. Found: C, 51.28; H, 5.12; N, 3.96. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 8.05, 7.80, 7.65, 7.50 (m, 20H); $\delta_{\mathrm{CH_2}}$, 2.95 (m, 2H); $\delta_{\mathrm{CH_3}}$, 0.95 (t, 3H), −0.15 (s, 9H). ^{29}Si NMR ($\mathrm{CD_2Cl_2}$): δ 11.3 (d), $^2J_{\mathrm{PSi}} = 8.6$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 69.7(dd); δ P(V), 44.1 (d), $^2J_{\mathrm{PP}} = 37.5$ Hz.

17. Yellow crystals, yield: 91%. Mp: 164 °C (dec). Anal. Calcd for $\mathrm{C_{30}H_{36}Cl_2N_2P_2PdSi}$: C, 52.06; H, 5.20; N, 4.05. Found: C, 51.92; H, 5.16; N, 4.02. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.75 (m, 20H); $\delta_{\mathrm{(CH_2)_2}}$, 2.70 (m, 2H), 1.45 (m, 2H); $\delta_{\mathrm{CH_3}}$, 0.40 (t, 3H); $\delta_{\mathrm{(CH_3)_3Si}}$, 0.0 (s, 9H). ^{29}Si NMR ($\mathrm{CD_2Cl_2}$): δ 9.4 (d), $^2J_{\mathrm{PSi}} = 7.7$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 70.3(dd); δ P(V), 43.5 (d), $^2J_{\mathrm{PP}} = 37.6$ Hz.

18. Yellow crystals, yield: 89%. Mp: 196 °C (dec). Anal. Calcd for $\mathrm{C_{31}H_{38}Cl_2N_2P_2PdSi}$: C, 52.72; H, 5.39; N, 3.96. Found: C, 52.56; H, 5.38; N, 3.78. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ phenyl rings, 7.90, 7.75, 7.60, 7.45 (m, 20H); $\delta_{\mathrm{(CH_2)_3}}$, 2.75 (m, 2H), 1.40 (m, 2H), 0.90 (m, 2H); $\delta_{\mathrm{(CH_3)}}$, 0.50 (t, 3H); $\delta_{\mathrm{(CH_3)_3Si}}$, −0.15 (s, 9H). ^{29}Si NMR ($\mathrm{CD_2Cl_2}$): δ 9.7 (d), $^2J_{\mathrm{PSi}} = 7.8$ Hz. ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ P(III), 70.0 (dd); δ P(V), 44.5 (d), $^2J_{\mathrm{PP}} = 36.9$ Hz.

19. Yellow crystals, yield: 88%. Mp: 222 °C (dec). Anal. Calcd for $\mathrm{C_{29}H_{34}Cl_2N_2P_2PtSi}$: C, 45.43; H, 4.43; N, 3.65. Found: C, 45.278;

H, 4.43; N, 3.50. ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 8.00, 7.80, 7.65, 7.50 (m, 20H); δ CH$_2$, 3.05 (m, 2H); δ (CH$_3$), 1.00 (t, 3H); δ (CH$_3$)$_3$Si, 0.0 (s, 9H). ^{29}Si NMR (CD$_2$Cl$_2$): δ 12.6 (d), $^{2}J_{\mathrm{PSi}} = 9.7$ Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P(III), 41.8 (dd); δ P(V), 45.8 (d), $^{2}J_{\mathrm{PP}} = 34.8$ Hz, $^{1}J_{\mathrm{PtP}} = 3890$ Hz, $^{2}J_{\mathrm{PtP}} = 115$ Hz.

20. Yellow crystals, yield: 92%. Mp: 162 °C (dec). Anal. Calcd for $C_{30}H_{36}Cl_2N_2P_2PtSi$: C, 46.15; H, 4.61; N, 3.58. Found: C, 46.03; H, 4.79; N, 3.51. ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 7.75 (m, 20H); δ (CH$_2$)$_2$, 2.80 (m, 2H), 1.45 (m, 2H); δ (CH$_3$), 0.40 (t, 3H); δ (CH$_3$)$_3$Si, -0.05 (s, 9H). ^{29}Si NMR (CD$_2$Cl$_2$): δ 10.8 (d), $^{1}J_{\mathrm{PSi}} = 8.6$ Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P(III), 42.3 (dd); δ P(V), 45.1 (d), $^{2}J_{\mathrm{PP}} = 34.7$ Hz, $^{1}J_{\mathrm{PtP}} = 3895$ Hz, $^{2}J_{\mathrm{PtP}} = 114$ Hz.

21. Yellow crystals, yield: 86%. Mp: 256 °C (dec). Anal. Calcd for $C_{31}H_{38}Cl_2N_2P_2PtSi\cdot 0.5CH_2Cl_2$: C, 45.20; H, 4.66; N, 3.34. Found: C, 45.51; H, 4.67; N, 3.26. ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 8.00, 7.78, 7.63, 7.50 (m, 20H); δ (CH$_2$)$_3$, 2.88 (m, 2H), 1.43 (m, 2H); δ 0.85 (m, 2H); δ CH$_3$, -0.05 (s, 9H). ^{29}Si NMR (CD$_2$Cl$_2$): δ 10.7 (d), $^{2}J_{\mathrm{PSi}} = 8.5$ Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P(III), 42.5 (dd); δ P(V), 45.2 (d), $^{2}J_{\mathrm{PP}} = 34.8$ Hz, $^{1}J_{\mathrm{PtP}} = 3894$ Hz, $^{2}J_{\mathrm{PtP}} = 114$ Hz.

Preparation of Complexes [Cl$_2$M{PPh$_2$N(R)Ph$_2$P=NH}-κP,κN$_{\mathrm{imine}}$] (22, M = Pd; 23, M = Pt). A solution of **2** (3 mmol) in CH$_3$CN (10 mL) was added dropwise to a solution of K$_2$MCl$_4$ (M = Pd or Pt) (3 mmol) in distilled water (5 mL) at room temperature. After addition was complete, the mixture was refluxed for 3 h and then cooled to room temperature to give a yellow crystalline product. The product was further purified by crystallization from a mixture of CH$_2$Cl$_2$ and *n*-hexane (1:2) at 0 °C.

22. Orange yellow crystals, yield: 88%. Mp: 236 °C (dec). Anal. Calcd for $C_{27}H_{28}Cl_2N_2P_2Pd$: C, 52.30; H, 4.52; N, 4.52. Found: C, 52.26; H, 4.62; N, 4.34. ^{1}H NMR (CD$_2$Cl$_2$): δ (phenyl rings), 7.95, 7.75, 7.64, 7.55 (m, 20H); δ (CH$_2$)$_2$, 2.75 (m, 2H), 0.75 (m, 2H); δ CH$_3$, 0.30 (t, 3H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P(III), 90.2 (dd); δ P(V), 67.3 (d), $^{2}J_{\mathrm{PP}} = 47.1$ Hz.

23. Orange yellow crystals, yield: 84%. Mp: 259 °C (dec). Anal. Calcd for $C_{27}H_{28}Cl_2N_2P_2Pt$: C, 53.04; H, 4.74; N, 4.42. Found: C, 52.76; H, 4.59; N, 4.37. ^{1}H NMR (CD$_2$Cl$_2$): δ phenyl rings, 7.95, 7.40, 7.20 (m, 20H); δ (CH$_2$)$_3$, 2.85 (m, 2H), 1.40 (m, 2H), 0.95 (m, 2H); δ CH$_3$, 0.25 (t, 3H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ P(III), 61.1 (dd); δ P(V), 66.1 (d), $^{2}J_{\mathrm{PP}} = 38$ Hz, $^{1}J_{\mathrm{PtP}} = 4092$ Hz, $^{2}J_{\mathrm{PtP}} = 92$ Hz.

Crystal Structure Determination of Me$_3$SiN=PPh$_2$N(^{n}Pr)PPh$_2$, 2. A colorless crystal of **2** (0.36 mm × 0.17 mm × 0.25 mm), crystallized from CH$_3$CN, was mounted on a Pyrex filament with epoxy resin. Unit cell dimensions were determined from 25 well-centered reflections ($9° < \theta < 15°$). Intensity data (6193 total reflections measured, 5853 unique, 3531 reflections with $F_o^2 > 3.00\sigma(F_o)^2$ were collected with an Enraf-Nonius CAD4 diffractometer at the University of Toledo using graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation by the ($\omega - 2\theta$) scan technique ($2\theta_{\max} = 52.0°$). Parameters are given in Table 2. Direct methods were used for structure solution.[33] Hydrogen atoms were calculated on idealized positions and included in the refinement as riding atoms with fixed isotropic thermal parameters. The final cycle of refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ (weight w is defined as $4F_o^2/\sigma^2(F_o)^2$) led to the final agreement factors shown in Table 2. Scattering factors for neutral atoms and the corrections for anomalous dispersions were taken from International Tables for X-Ray Crystallography, 1974.[34] All computations were carried out using the Mo1EN program set.[35] The ORTEP[23] view of **2** is illustrated in Figure 1 showing the atom numbering scheme. Selected bond lengths and angles are given in Table 4. The full details are provided as Supporting Information.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of Me$_3$SiN=PPh$_2$N(^{n}Pr)PPh$_2$, **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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