Transformations of phosphazane ligands in the coordination sphere of transition metals. Reactions of phosphinotriazene $Ph_2P—N(Ph)—N=NPh$ with Ni^0 and Ni^I complexes

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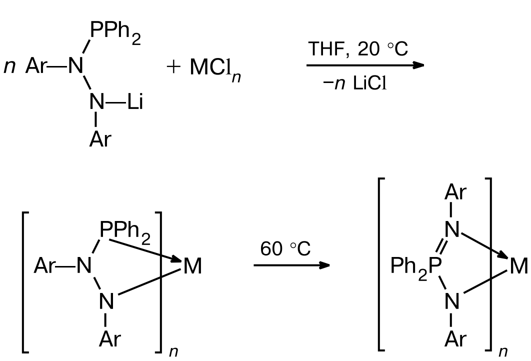
3-(Diphenylphosphino)-1,3-diphenyltriazene $Ph_2P—NPh—N=NPh$ was synthesized. The reactions of this compound with bis(cycloocta-1,5-diene)nickel, $(cod)_2Ni$, and nickel(I) bis(triphenylphosphino)bis(trimethylsilyl)amide, $(Ph_3P)_2Ni—N(SiMe_3)_2$, afforded the anionic nickel complex $[Ph_4P]^+[Ni(PhNNNPh)_3]^-$ in 15 and 78% yields, respectively.

Key words: transition metals, nickel complexes, phosphazanes, triazene, X-ray diffraction analysis.

The N—N and N—P chemical bonds in phosphazanes are rather weak.[1,2] Since the nitrogen and phosphorus atoms are prone to coordinate to metals, various molecular rearrangements and transformations of the phosphazane ligands can occur in the coordination sphere of transition metals. Earlier,[3] we have studied thermal transformations of the phosphinohydrazine ligands $\{—NAr—NAr—PPh_2$ (Ar = Ph, $4\text{-Bu}^tC_6H_4)\}$ in the coordination sphere of transition metals. In particular, it has been demonstrated that reactions of the phosphinohydrazine ligand with Co^{2+}, Ni^{2+}, or Fe^{3+} complexes result in isomerization of the former to the aminoiminophosphorane ligand $\{—NPh—PPh_2=NPh\}$ giving rise to the corresponding metal complexes $M[NPh—PPh_2=NPh]_n$ in quantitative yields (Scheme 1).

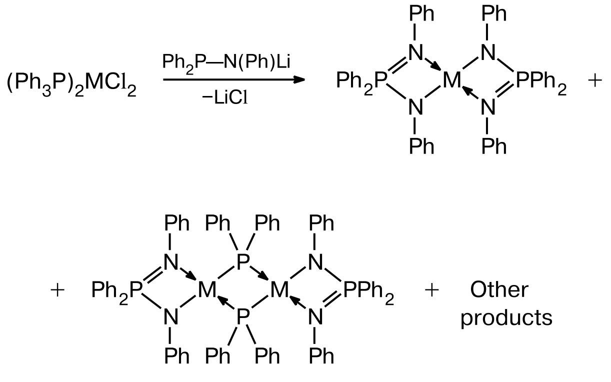
Scheme 1



n = 2, M = Co, Ar = Ph, $4\text{-Bu}^tC_6H_4$; M = Ni, Ar = Ph
n = 3, M = Fe, Ar = Ph

It is of importance that the character of the process occurring in the metal coordination sphere depends both on the nature of the metal and its oxidation state. Monovalent nickel behaves differently: the reaction of nickel(I) silylamide, $(Ph_3P)_2Ni—N(SiMe_3)_2$, with diphenylphosphino-1,2-diphenylhydrazine $(HNPh—NPh—PPh_2)$ is accompanied by the nitrogen—phosphorus bond cleavage to form the nickel azobenzene complex, $(Ph_3P)_2Ni(PhN=NPh)$. Other examples of the N—P bond cleavage in phosphazanes, in particular, in the reactions of lithium diphenylphosphinophenylamide with cobalt and nickel halides,[4] were also documented (Scheme 2).

Scheme 2



M = Co, Ni

Based on the results of our earlier studies,[3] the reactions of phosphinotriazene with nickel complexes are

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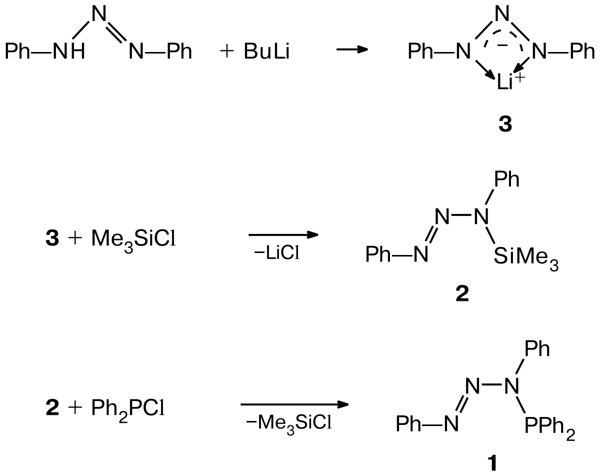
presumably accompanied by the rearrangement of the former giving rise to azaaminoiminophosphorane PhN=PPh$_2$—N=NPh.

In the present study, we performed the synthesis of phosphinotriazene Ph$_2$P—NPh—N=NPh (**1**) and carried out its reactions with bis(cycloocta-1,5-diene)nickel, (cod)$_2$Ni, and nickel(I) bis(triphenylphosphino)bis(trimethylsilyl)amide, (Ph$_3$P)$_2$Ni—N(SiMe$_3$)$_2$.

Results and Discussion

3-(Diphenylphosphino)-1,3-diphenyltriazene (**1**) was prepared in three steps through trimethylsilyl derivative **2**, which was, in turn, produced in 90% yield by the reaction of the lithium salt of aminoazobenzene **3** with trimethylchlorosilane (Scheme 3).

Scheme 3

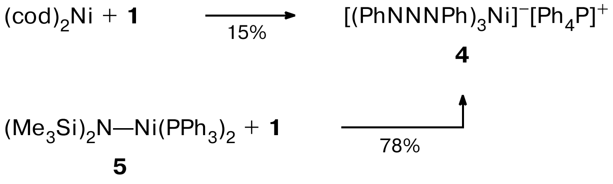


Compound **1** is a yellow-brown oil, which slowly eliminates nitrogen, with a half-life (NMR monitoring) of one month. The ^{31}P NMR spectrum of a freshly prepared sample shows a singlet at δ 55.0. Attempts to prepare ligand **1** in pure form by the direct reaction of the lithium salt of aminoazobenzene with diphenylchlorophosphine failed because of the formation of a very stable complex of **1** with lithium chloride. Lithium chloride can be removed only by treating the complex with water, but this process is accompanied by partial hydrolysis of the ligand. Hence, a mixture of the reaction products is technically difficult to separate.

Phosphinotriazene **1** reacts with bis(cycloocta-1,5-diene)nickel, (cod)$_2$Ni, in THF at 20 °C to form a dark-brown solution. The ^{31}P NMR spectrum of the reaction mixture has a complex set of signals, in which multiplets of the AA´XX´ and AA´X types at δ_P 60—130 can be distinguished. The spin-spin coupling constants for these multiplets are in the range of 10—55 Hz, which corresponds to $^2J_{P,P^*}$ for the nickel arylphosphine complexes (R$_3$P)$_2$Ni(R´$_3$P)$_2$ and (R$_3$P)$_2$Ni(R$_3$P).[5,6] This indicates that coordination and decomposition of the ligand in the coordination sphere of Ni^0 takes place. It should be noted that the intensity of the main signal (δ_P 55.0) in the ^{31}P NMR spectrum of free ligand **1** decreases with time (2 weeks) with a simultaneous increase in the intensities of the singlets. The transformation of the free ligand is accompanied by nitrogen elimination, whereas the reaction of **1** with (cod)$_2$Ni occurs without nitrogen elimination.

In due course, a complex compound is formed and gradually crystallizes in the {**1**—(cod)$_2$Ni} reaction mixture (signal at δ_P 24.4). According to the results of X-ray diffraction study, this complex has the structure [Ph$_4$P]$^+$[Ni(PhNNNPh)$_3$]$^-$ (**4**) (Fig. 1). The presence of the tetraphenylphosphonium cation suggests that the ligand undergoes complex transphenylation. In addition, the facts that Ni^0 was transformed into Ni^{II}, while nickel metal was not detected in the reaction mixture, may indicate that a redox reaction involving reductive decomposition of ligand **1** occurs. Investigation of the reaction of **1** with (PPh$_3$)$_2$NiN(SiMe$_3$)$_2$ (**5**) demonstrated that this reaction also produced complex **4**, the yield of the latter being substantially higher than that in the above-considered process (Scheme 4).

Scheme 4



Monovalent nickel silylamide **5** is similar in chemical properties to homoleptic Ni^0 phosphine complexes. This is associated with the facts that the metal—amide bond in this compound is weak and the silylamide group is readily eliminated upon disproportionation.[5,7]

An increase in the yield of **4** in the latter reaction can be explained assuming that [Ph$_4$P]$^+$ is generated from triphenylphosphine, which is involved as the coordinated group in nickel silylamide **5**. The ^{31}P NMR spectrum of the reaction mixture contains a singlet at δ_P −5.2, which can be assigned to triphenylphosphine. However, the rearrangement of phosphinotriazene **1** into aminoiminophosphorane PhN=PPh$_2$—N=NPh, whose signal may appear in the same region of the ^{31}P NMR spectrum, cannot be ruled out.

It should be noted that the 1,3-diphenyltriazenide ion (DFTA) is a very stable species, which forms numerous complex compounds with transition and main-group elements.[8,9] X-ray diffraction study of **4** demonstrated that

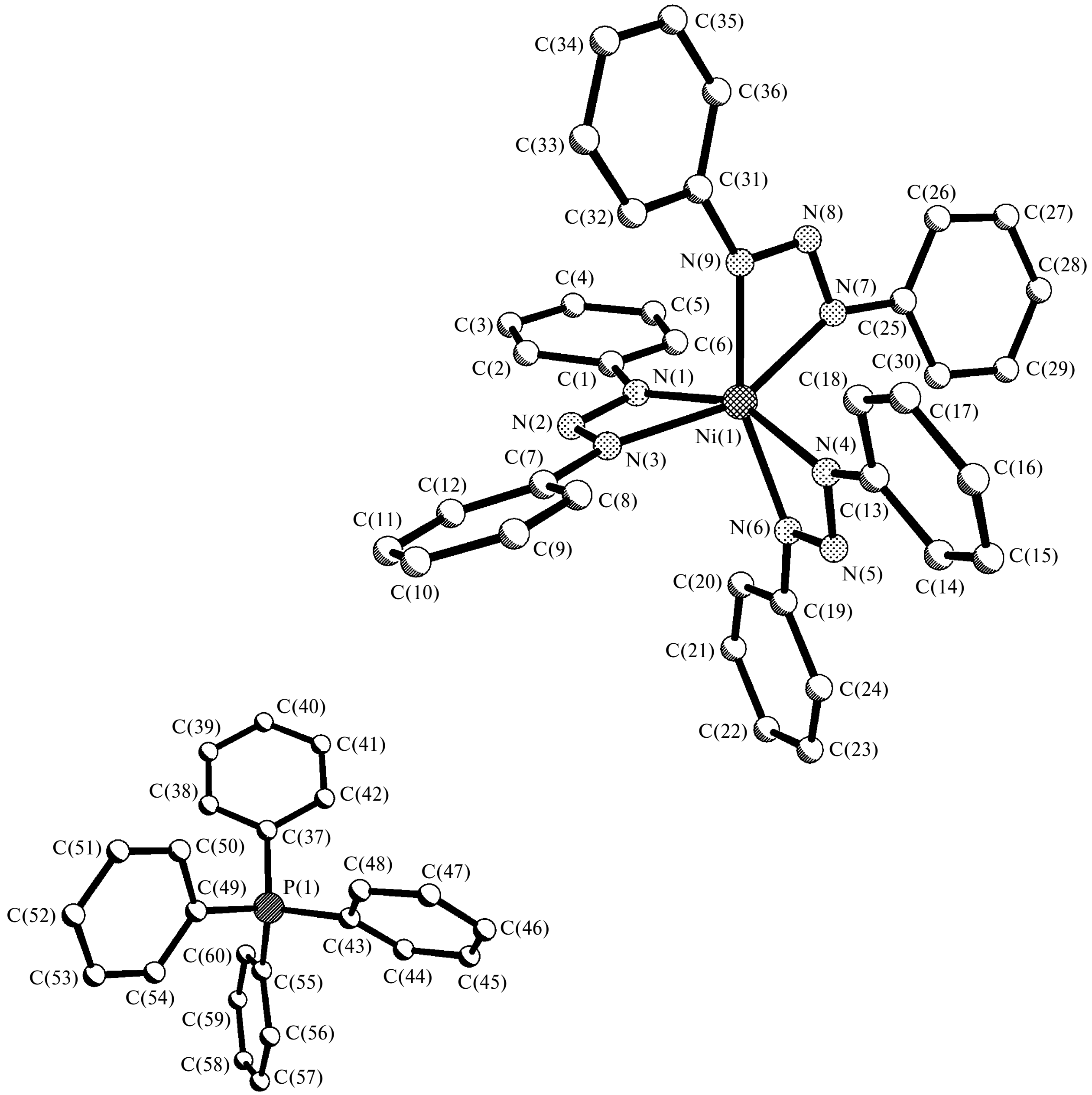


Fig. 1. Molecular structure of $[Ph_4P]^+[Ni(PhNNNPh)_3]^-$ (**4**). The hydrogen atoms and toluene solvate molecules are omitted.

the nickel atom is in a distorted octahedral coordination and forms an anionic complex with three DFTA ligands (see Fig. 1).

The central nitrogen atoms of the DFTA fragments (N(2), N(5), and N(8)) form a triangle with the nickel atom lying in this plane. The skeleton of the anionic moiety of the molecule, $Ni(NNN)_3$, can be described as a three-blade propeller with the planar NiNNN rings being inclined to the N(2)N(5)N(8) plane at angles of 57.6—60.2°. The dihedral angles between the planes of the DFTA ligands are in the range of 79.8—94.9°, which corresponds to the minimum steric repulsion between these rings.

The N—N distances in the DFTA ligands are in the range of 1.299(4)—1.321(5) Å and are virtually equal to those observed in the diphenyltriazene complexes of other metals (1.297—1.327 Å).[8,9] This equalization of the N—N distances in the DFTA ligands is indicative of a high degree of charge delocalization. Due to the p—π conjugation, the phenyl rings of all triazenide ligands tend to be located in the planes orthogonal to the NNN π-orbital.

In compound **4**, the Ni—N distances are in the range of 2.074(4)—2.112(3) Å, *i.e.*, they are slightly longer than the analogous distances (1.888—1.964 Å) in another known dinuclear divalent nickel homotriazene complex, $Ni_2(PhNNNPh)_4$,[10] in which the terminal nitrogen atoms of each ligand are coordinated to different nickel atoms.

Let us compare the structural parameters of the free ligand (PhNH—N=N—Ph),[11] the $[Ni(PhNNNPh)_3]^-$ anion, and the structurally similar $[Al(PhNNNPh)_3]^{\bullet -}$ radical anion,[12] in which two ligands are anions and the third ligand is a radical ion. The N—N—N bond angles in these compounds (ions) change in the following order: 114.97°,[11] 106.1(3)—107.2(3)°, and 99.4(8)°.[12] In the radical anion of DFTA, the N—N bond is substantially elongated (1.41(1) Å).[12]

In the crystal, the anions of $(DFTA)_3Ni$ form pseudodimers through weak intermolecular interactions between the central N(5) atom of the triazenide fragment and the H(28) atom of the phenyl ring. The N...H intermolecular distances are 2.568(7) Å, which is slightly smaller than the average length of the normal van der Waals contact for these atoms (2.64 Å).[13]

Yellow solutions of complex **4** in THF and acetone are stable both upon heating in air and addition of water. However, complex **4** is decomposed under the action of ammonia or acetic acid.

The mechanism of phenyl group transfer to the phosphorus atom and the formation of the phosphonium cation $[Ph_4P]^+$ will be addressed in future studies.

Experimental

The synthesis, isolation, and purification of compounds were carried out *in vacuo* or under argon using anhydrous (the "ketyl" method of purification) solvents. Monovalent nickel silylamide, $(PPh_3)_2NiN(SiMe_3)_2$ (**5**),[7] and 1,3-diphenyltriazene (aminoazobenzene, PhNH—N=NPh)[14] were prepared according to known procedures. Commercial Ph_2PCl, bis(cycloocta-1,5-diene)nickel, and *n*-butyllithium in hexane (Aldrich) were used. The nickel content was determined photometrically using dimethyl glyoxime.[15]

The ^{31}P NMR spectra were recorded on a Bruker DPX-200 instrument in THF and $CDCl_3$.

Crystals suitable for X-ray diffraction study were grown by recrystallization from a THF—toluene mixture. The X-ray diffraction data were collected on an automated Smart APEX diffractometer. The structure was solved by direct methods and refined by the least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms in complex **4** were placed in geometrically calculated positions and refined using a riding model. In the unit cell, toluene solvate molecules were localized in general positions. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[16] Principal crystallographic characteristics, details of X-ray diffraction study, and parameters of structure refinement for compound **4** are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1. Crystallographic data and characteristics of X-ray diffraction study for complex **4**

Parameter	Characteristics
Molecular formula	$C_{74}H_{66}N_9NiP$
Molecular weight	1171.04
Crystal system	Monoclinic
T/K	100(2)
Space group	$P2_1/n$
a/Å	12.7239(10)
b/Å	19.0643(15)
c/Å	25.0564(19)
β/deg	96.649(2)
V/Å^3	6037.1(8)
Z	4
ρ/g cm^{-3}	1.288
μ/mm^{-1}	0.401
F(000)	2464
Crystal dimensions/mm	0.13×0.12×0.06
$2\theta_{max}$/deg	46
Number of measured reflections	28088
Number of independent reflections with $I > 2\sigma$	8670
R_{int}	0.1162
Absorption correction	SADABS
Number of restrictions in refinement	25
Number of parameters in refinement	754
Goodness-of-fit (GOOF on F^2)	0.995
R_1	0.0651
wR_2 ($I > 2\sigma(I)$)	0.1339
R_1	0.1370
wR_2 (based on F^2 for all reflections)	0.1628
Residual electron density peaks (min/max), e/Å^{-3}	−0.546/0.582

3-(Diphenylphosphino)-1,3-diphenyltriazene, Ph_2P—NPh—N=NPh (1). Equivalent amounts of Me_3Si—NPh—N=NPh (2.69 g, 10 mmol) and diphenylchlorophosphine (2.21 g, 10 mmol) in toluene (10 mL) were mixed. The reaction mixture was kept at *ca.* 20 °C for 48 h and then separated from a fine suspension of a small amount of by-products by centrifugation. The solvent and Me_3SiCl were removed *in vacuo*. Compound **1** was obtained as a yellow-brown oil in a yield of 3.12 g (82%). Found (%): C, 75.63; H, 5.18; P, 8.06. $C_{24}H_{20}N_3P$. Calculated (%): C, 75.58; H, 5.29; P, 8.12. $^{31}P\{^1H\}$ NMR (toluene), δ: 55.0. Compound **1** slowly decomposed at *ca.* 20 °C (for two—three months), which was accompanied by nitrogen elimination.

1,2-Diphenyl-3-trimethylsilyltriazene, Me_3Si—NPh—N=NPh (2). A 0.8 *M* butyllithium solution in hexane (12.5 mL, 10 mmol) was added to a solution of 1,3-diphenyltriazene[14] (1.97 g, 10 mmol) in diethyl ether (20 mL). After 30 min, orange crystals of precipitated lithium salt of 1,3-diphenyltriazene were filtered off (in quantitative yield),

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Bond	*d*/Å	Angle	ω/deg
Ni(1)—N(1)	2.084(3)	N(6)—Ni(1)—N(3)	95.0(1)
Ni(1)—N(3)	2.082(4)	N(6)—Ni(1)—N(1)	100.5(1)
Ni(1)—N(4)	2.112(3)	N(3)—Ni(1)—N(1)	60.3(1)
Ni(1)—N(6)	2.074(4)	N(6)—Ni(1)—N(7)	106.03(14)
Ni(1)—N(7)	2.087(4)	N(3)—Ni(1)—N(7)	154.79(13)
Ni(1)—N(9)	2.093(4)	N(1)—Ni(1)—N(7)	101.38(13)
N(1)—N(2)	1.321(5)	N(6)—Ni(1)—N(9)	159.49(14)
N(2)—N(3)	1.299(4)	N(3)—Ni(1)—N(9)	102.35(14)
N(4)—N(5)	1.313(5)	N(1)—Ni(1)—N(9)	97.60(13)
N(5)—N(6)	1.319(4)	N(7)—Ni(1)—N(9)	60.60(14)
N(7)—N(8)	1.307(5)	N(6)—Ni(1)—N(4)	60.64(14)
N(8)—N(9)	1.313(5)	N(3)—Ni(1)—N(4)	101.94(13)
		N(1)—Ni(1)—N(4)	154.50(14)
		N(7)—Ni(1)—N(4)	100.48(13)
		N(9)—Ni(1)—N(4)	104.49(14)
		N(2)—N(1)—C(1)	115.8(3)
		N(3)—N(2)—N(1)	106.1(3)
		N(4)—N(5)—N(6)	106.8(3)
		N(7)—N(8)—N(9)	107.2(3)

and then a new portion of the solvent (15 mL) and trimethylchlorosilane (1.08 g, 10 mmol) were added. The lithium salt of diphenyltriazene was rapidly dissolved followed by precipitation of LiCl (5 h, 20 °C). The solution was separated from the precipitate, the solvent was removed *in vacuo*, and a yellow oil was obtained. The major portion of the latter was transformed into yellow crystals within 16 h. The yield was 2.28 g (85%). Found (%): C, 66.58; H, 7.05; Si(remainder), 10.54. $C_{15}H_{19}N_3Si$. Calculated (%): C, 66.87; H, 7.11; Si, 10.43. ^{1}H NMR ($CDCl_3$), δ: 0.41 (s, 9 H, $SiMe_3$); 6.80—8.00 (m, 10 H, Ph).

Reaction of 1 with $(cod)_2$Ni. A solution of bis(cycloocta-1,5-diene)nickel (0.14 g, 0.05 mmol) in tetrahydrofuran (10 mL) was mixed with a solution of 3-(diphenylphosphino)-1,3-diphenyltriazene (**1**) (0.38 g, 1.0 mmol) in toluene (10 mL) at 20 °C. In the course of the reaction, the color of the solution gradually changed from yellow to brown. The ^{31}P NMR spectrum of the reaction mixture showed the following signals (δ): 41.6 (t, J = 52.4 Hz); 86.5 (t, J = 52.4 Hz); 118.8 (d, J = 10.9 Hz); 119.3 (d, J = 10.9 Hz); 24.4 (s); −5.2 (s). After 24 h, the formation of yellow crystals started. The pale-yellow crystals of complex **4** were separated from the reaction mixture, washed with toluene in the cold, and dried under argon (prolonged drying *in vacuo* led to destruction of the crystal structure). The yield was 0.06 g (15%). Found (%): C, 75.63; H, 5.76; Ni, 5.10. $C_{74}H_{66}N_9PNi$ $\{[Ph_4P]^+[Ni(PhNNNPh)_3]^- \cdot 2PhMe\}$. Calculated (%): C, 75.90; H, 5.68; Ni, 5.01. ^{31}P {^{1}H} NMR (THF), δ: 24.4.

Reaction of 1 with $(PPh_3)_2NiN(SiMe_3)_2$ (5). A solution of nickel bis(triphenylphosphino)bis(trimethylsilyl)amide (**5**) (0.74 g, 1.0 mmol) in toluene (10 mL) was mixed with a solution of phosphinotriazene **1** (0.76 g, 2.0 mmol) in toluene (10 mL) at 20 °C *in vacuo*. The reaction mixture was kept at 20 °C for 48 h. The pale-yellow crystals that precipitated were separated from the reaction mixture, washed with cold toluene, and dried under argon. The yield of **4** was 0.60 g (78%). The data from elemental analysis and NMR spectroscopy were completely identical to those for the sample prepared by the reaction of **1** with $(cod)_2$Ni.

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