

Migratory Insertion of the R₂P Group into a Nitrogen–Nitrogen Bond — A Novel Type of Rearrangement in Phosphorus–Nitrogen Ligand Chemistry. 3. The Rearrangement of Triphosphinohydrazide Ligand —N(PPh₂)—N(PPh₂)₂ to Triphosphazene Anion {[(Ph₂P—N)₂PPh₂][−] in the Coordination Sphere of Divalent Cobalt and Nickel

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Hydrazine dihydrochloride reacts with 3 equiv of Ph₂PCl in tetrahydrofuran in the presence of triethylamine to give tris(diphenylphosphino)hydrazine (**1**) in 70% yield. Each nitrogen atom in **1** has a trigonal-planar environment according to X-ray analysis. Thermolysis of **1** at 130 °C results in the formation of two products: bis(diphenylphosphino)amine and octaphenylcyclotetraphosphazene. The interaction of free ligand **1** with NiBr₂ affords a simple adduct [(Ph₂P)₂N—NH—PPh₂][NiBr₂], while its anionic (hydrazide) form undergoes rearrangement in a coordination sphere of divalent cobalt and nickel involving migratory insertion of the Ph₂P group into a nitrogen–nitrogen bond. The reaction of **1** with cobalt bis(trimethylsilyl)amide, [(Me₃Si)₂N]₂Co, yields the complex of phosphazene-type (Me₃Si)₂N—Co[(Ph₂PN)₂PPh₂] (**2**) in 86% yield. A similar reaction of **1** with nickelocene proceeds with substitution of one Cp ring to form durable 18-electron complex CpNi[(Ph₂PN)₂PPh₂] (**3**).

Introduction

The importance of rearrangements in phosphorus chemistry is difficult to overestimate. The Mikhaelis–Arbuzov rearrangement and its numerous modifications^{1–5} gave a powerful impetus to the development of synthetic phosphorus chemistry. In this paper, we report a novel type of rearrangement in phosphorus–nitrogen ligand chemistry, which is accompanied by the migratory insertion of an R₂P group into the nitrogen–nitrogen bond of a phosphinohydrazide ligand: R₂P—NR—NR— → RN=PR₂—NR—. Formally, the rearrangement is a redox process: three-valent, three-coordinate phosphorus becomes four-coordinate P(V), while a nitrogen atom reduces its coordination number to 2.

When we turned our attention to a novel amidophosphine η²[P,σ-N]—ligand system, namely, phosphinohydrazide ligands,

R₂P—NR′—NR*—M (M = metal atom; R, R′, R* = substituents of various natures), it was apparent that the stability of the metal complexes containing a σ-bonded phosphinohydrazide ligand {—N(Ar)—N(Ar)—PPh₂} (Ar = aryl) is strongly dependent on the nature of the metal, its oxidation state, and the ligand environment.^{6,7} Early and middle transition metals or nontransition metals form stable phosphinohydrazides M[N(Ar)N(Ar)PPh₂]_n {M = Li, Zn, Ge(II), Mn(II), Cr(III), and Fe(II)}, while late transition metals (Co, Ni, and Cu) and metals with an enhanced oxidation state (Fe³⁺ in contrast to Fe²⁺) cause a transformation of the phosphinohydrazide ligand.

We could then describe rearrangements of two kinds of ligands—monophosphinohydrazides⁶ and diphosphinohydrazides.⁷ This rearrangement is interesting not only in itself;

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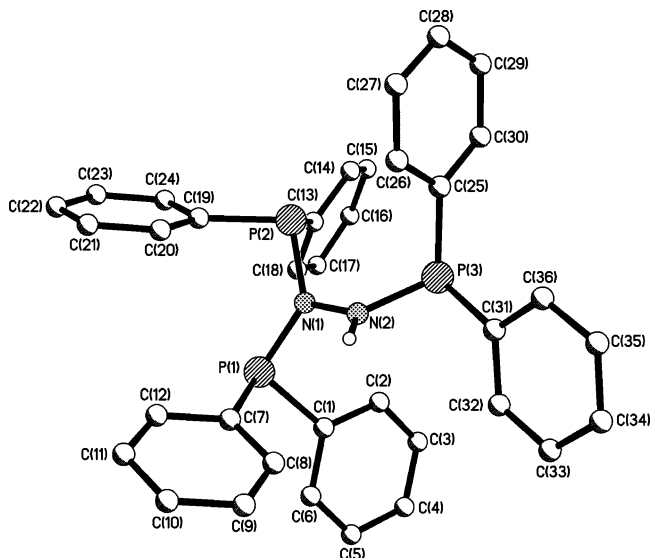
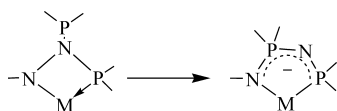
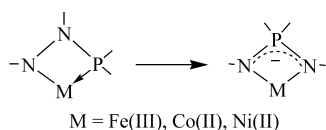
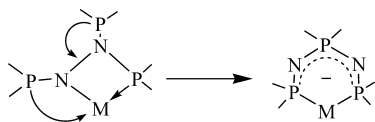


Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity.

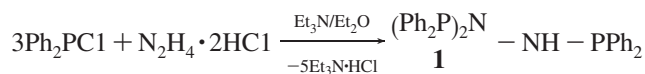


it also represents a key to the synthesis of various useful transition metal complexes of phosphazene and amidophosphine types. Another interesting finding involving the rearrangement of the triphosphinohydrazide ligand $\text{--N(PPh}_2\text{)--N(PPh}_2\text{)}_2$ in the coordination sphere of divalent cobalt and nickel is



Results and Discussion

The starting tris(diphenylphosphino)hydrazine **1** (precursor for the corresponding hydrazide ligand) is easily prepared by the interaction of hydrazine dihydrochloride with 3 equiv of chlorodiphenylphosphine in the presence of triethylamine.



Triphosphinohydrazine **1** forms relatively air-stable colorless crystals. The ³¹P NMR spectrum of **1** in CDCl₃ contains a doublet (77.7 ppm) and a triplet (47.0 ppm) with splitting constant $J_{\text{P,P}} = 8.6$ Hz. The ¹H NMR spectrum of **1** exhibits a doublet at 4.23 ppm ($J_{\text{H,P}} = 8.5$ Hz) assigned to the NH group. Note that the NH group shows sharp and very weak absorption (3270 cm^{−1}) in the IR spectrum.

The molecular structure of **1**, recorded at 100 K, shows discrete molecular units (Figure 1). Each nitrogen atom in **1** has a trigonal-planar environment. The change of the nitrogen atoms' geometry from pyramidal (at free hydrazine) to

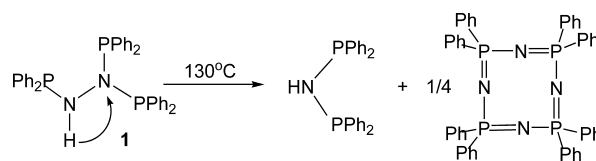
Table 1. Crystal Data and Structure Analysis Results for **1–3**

| | 1 | 2 | 3 · (THF) |
|--|---|---|--|
| formula | C ₃₆ H ₃₁ N ₂ P ₃ | C ₄₂ H ₄₈ CoN ₃ P ₃ Si ₂ | C ₄₅ H ₄₃ N ₂ NiOP ₃ |
| <i>M</i> _r | 584.54 | 802.85 | 779.43 |
| space group | monoclinic, <i>P</i> 2(1)/ <i>c</i> | monoclinic <i>P</i> 2(1)/ <i>c</i> | triclinic <i>P</i> $\bar{1}$ |
| <i>a</i> , Å | 14.9713(10) | 9.7803(6) | 9.8206(5) |
| <i>b</i> , Å | 9.5166(6) | 31.657(2) | 10.1212(5) |
| <i>c</i> , Å | 21.922(2) | 13.6636(8) | 20.944(1) |
| α | 90 | 90 | 100.428(1) |
| β (deg) | 103.129(1)° | 103.676(1) | 96.917(1) |
| γ | 90 | 90 | 107.854(1) |
| <i>V</i> , Å ³ | 3041.7(3) | 4110.5(4) | 1914.02(16) |
| <i>Z</i> | 4 | 4 | 2 |
| ρ _{calcd} , g cm ^{−3} | 1.276 | 1.297 | 1.352 |
| <i>T</i> (K) | 100(2) | 100(2) | 100(2) |
| <i>F</i> (000) | 1224 | 1684 | 816 |
| μ (mm ^{−1}) | 0.224 | 0.626 | 0.670 |
| color | colorless | brown | red-brown |
| size (mm ³) | 0.16 × 0.10 × 0.08 | 0.43 × 0.18 × 0.12 | 0.50 × 0.40 × 0.30 |
| θ (deg) | 1.91–25.06 | 1.66–24.25 | 1.01–26.00 |
| collected reflns | 16355 | 21096 | 11438 |
| independent reflns | 5375 | 6638 | 7464 |
| <i>R</i> _{int} | 0.0377 | 0.0461 | 0.0140 |
| GOF(<i>F</i> ²) | 1.029 | 0.983 | 1.042 |
| <i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) | 0.0490 | 0.0389 | 0.0332 |
| <i>wR</i> ₂ (all data) | 0.1319 | 0.0919 | 0.0845 |
| largest diff. peak and hole eÅ ^{−3} | 0.736/−0.477 | 0.548 −0.220 | 0.646/−0.250 |

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

| | |
|----------------|----------|
| P(1)–N(1) | 1.712(2) |
| N(1)–N(2) | 1.437(3) |
| N(1)–P(2) | 1.728(2) |
| N(2)–P(3) | 1.700(2) |
| N(1)–N(2)–P(3) | 116.8(2) |
| N(2)–N(1)–P(1) | 117.8(2) |
| N(2)–N(1)–P(2) | 117.3(2) |
| P(1)–N(1)–P(2) | 124.8(1) |
| N(1)–P(1)–C(1) | 103.5(1) |
| N(1)–P(1)–C(7) | 104.2(1) |
| C(1)–P(1)–C(7) | 102.1(1) |

trigonal-planar points to the significant reduction of basicity in the nitrogen atoms. Table 1 displays the crystal data for **1**; Table 2 depicts selected bond distances and angles. The dihedral angle between the P(1)N(1)P(2) and HN(2)P(3) planes is 49.6°. P–N and N–N bond lengths in the molecule are typical for phosphazenes and phosphinohydrazines.^{7,8} Note, however, that the N(1)–N(2) bond distance, 1.437(3), is somewhat longer than that found in monophosphinohydrazine analog PhNH–NPh–PPh₂ (1.401(2)).⁶ The tris(diphenylphosphino)hydrazine is stable up to 130 °C, at which temperature it decomposes to form two well-known products: bis(diphenylphosphino)amine and octaphenylcyclotetraphosphazene. These products were separated and characterized by IR, ³¹P NMR data, and melting points:



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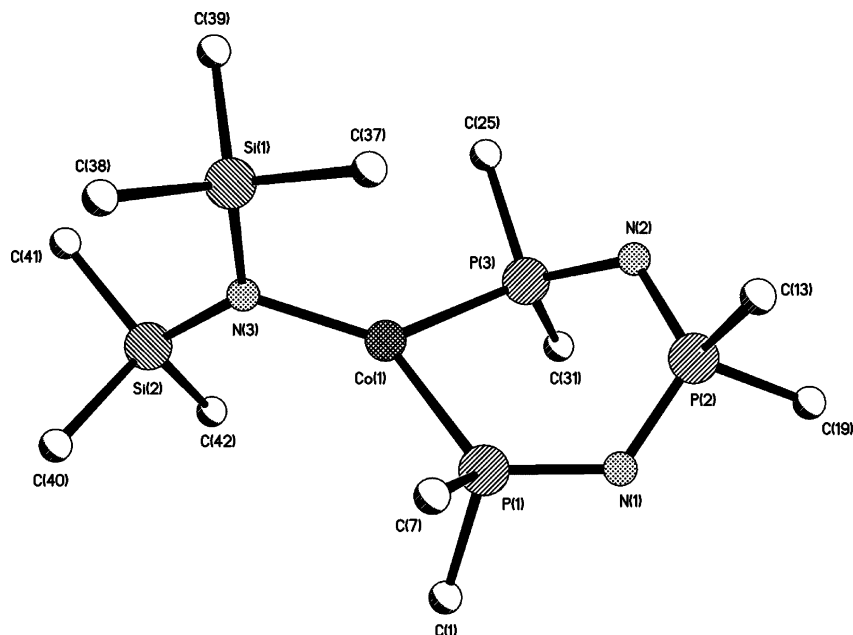
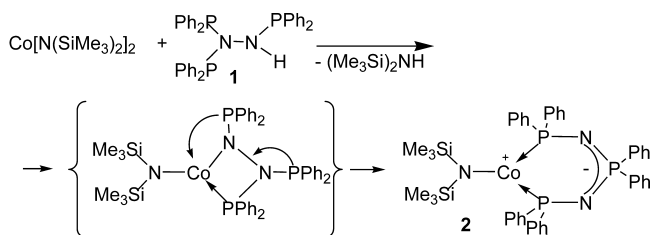


Figure 2. Molecular structure of **2**. Hydrogen atoms and Ph rings are omitted for clarity.

The transformation of **1** may be described formally as a hydrogen migration from one nitrogen atom to another and the tetramerization of the remaining phosphanitrene {Ph₂PN}.

Tris(diphenylphosphino)hydrazine as a free ligand forms a stable complex with metal halides. Consequently, the interaction of **1** with nickel dibromide gives a red adduct **1**·NiBr₂. The IR spectrum of this compound is very similar to the spectrum of free ligand **1** except for the shift of the absorption band $\nu(\text{NH})$ from 3270 to 3205 cm⁻¹. Unlike the free ligand, its anionic form, namely, tris(diphenylphosphino)hydrazide-anion, undergoes rearrangement in the coordination sphere of cobalt(II) and nickel(II).

Cobalt silylamide Co[N(SiMe₃)₂]₂ reacts with 1 equiv of tris(diphenylphosphino)-hydrazine (**1**) in toluene under mild conditions over 24 h. We succeeded in separating a single product of this reaction in 86% preparative yield, which was proved to be the complex of phosphazene type (**2**).



It was not possible to isolate the originally formed phosphinohydrazide complex (Me₃Si)₂N–Co[N(PPh₂)–N–(PPh₂)₂]. Attempts to stop the reaction at the initial period of time gave only an intractable waxy solid.

The IR spectrum of **2** contains strong absorptions at 1245, 840, and 1155 cm⁻¹ assigned to stretching vibrations of Me₃Si and P=N fragments, respectively. The X-ray investigation reveals the formation of a mixed-ligand complex (Figure 2) with a central cobalt(II) atom in a rare trigonal-planar environment (the sum of the angles at Co 359.41°). Table 1 displays crystal data for **2**; Table 3 shows selected

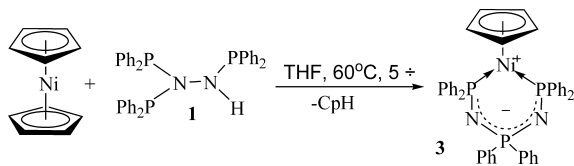
Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**

| | |
|-----------------|-----------|
| Co(1)–N(3) | 1.845(2) |
| Co(1)–P(3) | 2.1601(8) |
| Co(1)–P(1) | 2.1631(8) |
| P(1)–N(1) | 1.617(2) |
| P(2)–N(1) | 1.597(2) |
| P(2)–N(2) | 1.608(2) |
| P(3)–N(2) | 1.615(2) |
| N(3)–Co(1)–P(3) | 135.51(7) |
| N(3)–Co(1)–P(1) | 134.56(7) |
| P(3)–Co(1)–P(1) | 89.32(3) |
| N(1)–P(1)–Co(1) | 124.05(9) |
| N(1)–P(2)–N(2) | 117.6(1) |
| N(2)–P(3)–Co(1) | 117.47(9) |
| P(2)–N(1)–P(1) | 124.7(1) |
| P(2)–N(2)–P(3) | 120.0(1) |

bond distances and angles. The chelate P(3)–Co(1)–P(1) angle is 89.32(3)°. The N–P bond distances in **2** are justified and lie in the range 1.597(2)–1.617(2) Å, which is typical for other known metal complexes with this ligand.^{9,10} The Co–N bond distance (1.845(2) Å), in spite of the steric bulkiness of **2**, is the least among the other cobalt(II) bis(trimethylsilyl)amido derivatives (1.90–2.06 Å^{11–14}).

A similar rearrangement of the tris(diphenylphosphino)-hydrazide anion occurs in the Ni(II) coordination sphere. The reaction of **1** with dicyclopentadienylnickel proceeds by the substitution of one Cp ring with a triphosphinohydrazide ligand followed by rearrangement of the ligand. We succeeded in separating a single product (**3**) of this reaction in 88% preparative yield. The IR spectrum of the crystalline

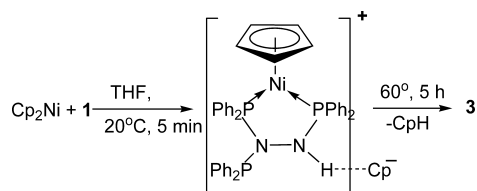
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product **3** differs significantly from the spectrum of **1** and contains wide and strong absorptions in the region 1230–1050 cm⁻¹ assigned to $\nu(\text{P}^{\text{V}}=\text{N})$ vibrations, as is typical for phosphazenes.¹⁵

The ³¹P NMR spectrum of **3** represents the spin system AA'X, showing a doublet at 65.0 ppm and a triplet at 30.5 ppm ($J_{\text{P,P}} = 34$ Hz), assigned to P^{III} and P^V, respectively. The proton NMR spectrum of the complex contains a multiplet in the aromatic region and a single resonance of Cp protons at 4.9 ppm (30H, 5H, respectively), which is indicative of the substitution of only one Cp ring. An X-ray investigation confirms the formation of a mixed-ligand complex (Figure 3). Table 1 displays the crystal data for **3**; Table 4 shows selected bond distances and angles. No essential differences in structures exist between cobalt and nickel metallocycles [M(PNPNP)]. The chelate P(3)–Ni(1)–P(1) angle, 91.34(2)°, is slightly broader than P(3)–Co(1)–P(1), 89.32(3)°, in **2**. The phosphorus and nitrogen atoms of the ligand lie in the same plane with an average deviation of about 0.11 Å. The dihedral angle between the plane of the ligand and the P(1)Ni(1)P(3) plane is 139.2°.

The mechanism of this last reaction invites mention of an important observation. After mixing the tetrahydrofuran (THF) solutions of the starting reagents (**1** and Cp₂Ni), a noncrystalline greenish-yellow precipitate forms. The IR spectrum of this substance showed intense absorption at 2490 and 2010 cm⁻¹, indicating the presence of charged nitrogen (NH)⁺ in the molecule. At the same time, the absorption band of the Cp ring (773 cm⁻¹ in Cp₂Ni) is shifted to 837 cm⁻¹ in an intermediate product, which suggests that elimination of the Cp group is accompanied by charge separation.



Since compound **3** is an 18-electron complex, it demonstrates high stability and may be kept in open air for a long time without change. Substitution of the second Cp ring for the (Ph₂P)₃N₂ ligand is not observed. Instead, cobalt complex **2** reacts with the second mole of the ligand to form a product of full substitution, Co(PPh₂–N=PPh₂–NPPH₂)₂. This product was characterized using elemental analysis and the IR spectrum, which was identical to the sample of Co(PPh₂–N=PPh₂–NPPH₂)₂ described earlier.¹⁶

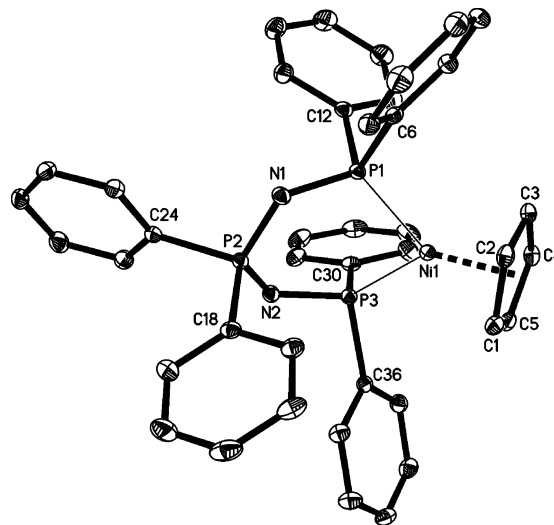


Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for **3**

| | |
|-----------------|----------------|
| Ni(1)–P(1) | 2.1557(5) |
| Ni(1)–P(3) | 2.1594(5) |
| P(2)–N(2) | 1.597(2) |
| P(2)–N(1) | 1.598(2) |
| P(1)–N(1) | 1.613(2) |
| P(3)–N(2) | 1.620(2) |
| Ni(1)–C(5) | 2.094(2) (min) |
| Ni(1)–C(4) | 2.151(2) (max) |
| P(1)–Ni(1)–P(3) | 91.34(2) |
| N(1)–P(1)–Ni(1) | 116.58(6) |
| N(2)–P(3)–Ni(1) | 118.89(6) |
| P(2)–N(1)–P(1) | 122.66(9) |
| N(2)–P(2)–N(1) | 118.91(8) |
| P(2)–N(2)–P(3) | 125.62(9) |

The tendency of the phosphino-hydrazide system toward rearrangement depends on several factors: (1) the energy of the M–N σ -bond, which is usually weakened on going from early to late transition metals, (2) the energy of the N–N bond, which strongly depends on the nature of the substituents on the nitrogen atoms, and (3) the energy of the metal–phosphorus bond, which is determined by a combination of electronic effects of direct and back-donation between metal and phosphorus atoms.

Our preliminary study showed that ligands containing phosphito groups (e.g., (ArO)₂P–NPh–NPh–) are prone to rearrangement at the coordination sphere of Co and Ni, while ligands bearing donor isopropyl- and *tert*-butyl substituents (*i*-Pr₂P–NPh–NPh– and *t*-Bu₂P–NPh–NPh–) give stable metal complexes. It is also worth noting that a negative charge at the nitrogen atom of the hydrazide moiety destabilizes the molecule. The lithium salt of tris(diphenylphosphino)hydrazine (Ph₂P)₂N–N(PPh₂)Li is unstable and decomposes during the synthetic procedure even at low temperatures. However, other lithium phosphino-hydrazides (e.g., Ph₂P–NPh–NPh–Li, (Ph₂P)₂N–NPhLi, *i*-Pr₂P–NPh–NPhLi, *t*-Bu₂P–NPh–NPh–Li, Ph₂P–N(CH₂Ph)–N(CH₂Ph)Li) may be handled without restrictions.

Our research shows that the chemistry of phosphino-hydrazide ligands is exceedingly varied and may serve as a

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key to the synthesis of various useful transition metal complexes of phosphazene and amidophosphine types.

Experimental Section

Solvents were purified following standard methods.¹⁷ Toluene was thoroughly dried and distilled over P_2O_5 prior to use. Ether and THF were dried and distilled over Na/benzophenone. Cobalt silylamide $Co[N(SiMe_3)_2]_2$ was prepared according to known methods.^{11,18} All manipulations were performed with rigorous exclusion of oxygen and moisture, in a vacuum or under an argon atmosphere using standard Schlenk techniques. Hexamethyldisilazane liberated in the course of the metal silylamides reactions was detected by gas chromatographic analyses with a Tsvet-500 device, equipped with stainless steel columns 0.4 cm \times 200 cm, packed with 5% SE-30 on Chromatone N-Super, with a thermoconductivity detector and using helium as the carrier gas. The spectrophotometric determination of cobalt and nickel in the prepared compounds was provided by the methods described in ref 19. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer from 400 to 4000 cm^{-1} in nujol. NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions using a Bruker DPX-200 device. X-ray data were collected on a Bruker AXS SMART APEX diffractometer (graphite monochromator, Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), φ - ω scan).

Preparation of Tris(Diphenylphosphino)Hydrazine (1). Et_3N (4.81 g, 47.6 mmol) in THF was added to a mixture of hydrazine dihydrochloride (1.06 g, 9.5 mmol) and Ph_2PCl (6.28 g, 28.5 mmol) in THF (15 mL). The mixture was stirred for 24 h at 20 °C and then filtered. Next, the THF was removed in a vacuum and exchanged with toluene. Then, the solution was concentrated to ~ 7 mL. Keeping the mixture overnight at 10 °C yielded large colorless crystals of **1**. Yield: 3.90 g (70%). Anal. Calcd for $C_{36}H_{31}N_2P_3$, %: C, 73.97; H, 5.31; P, 15.93. Found, %: C, 74.03; H, 5.12; P, 16.08. IR (nujol), ν/cm^{-1} : 3270ww, 1430m, 1300w, 1180w, 1150w, 1090m, 1070w, 1020w, 1000w, 910m, 820w, 740m, 720w, 700m, 630w, 550w, 520w, 490w. $^31P\{^1H\}$ NMR (C_6D_6 , 300K), δ (ppm): 77.8 (d), 47.1 (t) ($J_{P,P} = 9 \text{ Hz}$).

The thermolysis of **1** was carried out in a vacuum line (0.01 mm) with a heating rate of 3°/min. The sample (0.1 g) melted at 128–130 °C, and then spontaneous boiling (for 10–15 s) was observed. The sample was kept at 130 °C for 5 min, and then the mixture of toluene and diethyl ether (1:1) was added. Bis(diphenylphosphino)amine, $(Ph_2P)_2NH$, became a solution while poorly soluble octaphenylcyclotetraphosphazene $\{(-Ph_2P=N-)_4\}$ separated out as colorless crystals. Repeated crystallization gave pure crystals of both compounds.

$(Ph_2P)_2NH$. $^31P\{^1H\}$ NMR (C_6D_6 , 300K), δ : 44.0 ppm. IR (nujol), ν/cm^{-1} : 3230m, 3050m, 1430 c, 1250m, 1100c, 1020m, 1000w, 900vs, 730vs, 600vs, 520s.

$\{(-Ph_2P=N-)_4\}$. $^31P\{^1H\}$ NMR (C_6D_6 , 300K), δ : 14.0 ppm. mp: 317–319 °C (lit. data: 319–321 °C²⁰). IR (nujol): 1220vs, 1175w, 1117m, 1928w, 885m, 742w, 722m, 693s, 567m, 513s. Anal. Calcd for $C_{48}H_{40}P_4$, %: C, 72.36; H, 5.06; P, 15.55. Found, %: C, 72.44; H, 5.10; P, 15.34.

Preparation of $[(Ph_2P)_2NNHPh_2]NiBr_2$. A solution of **1** (0.32 g, 0.55 mmol) in 15 mL of THF was added to a powder of

$NiBr_2 \cdot 2THF$ (0.20 g, 0.55 mmol). The mixture was vigorously shaken at 20 °C for 3 h until all nickel bromide was dissolved and then was kept for 24 h. Adduct **1**· $NiBr_2$ formed as a poorly soluble, fine crystalline, red precipitate. Yield: 0.43 g (97.4%). Anal. Calcd for $C_{36}H_{31}N_2P_3NiBr_2$, %: C, 53.82; H, 3.86; Ni, 7.31. Found, %: C, 54.21; H, 4.15; Ni, 7.11. IR (nujol), ν/cm^{-1} : 3205w, 1585w, 1310w, 1190ww, 1155ww, 1095m, 920m, 850ww, 805w, 743m, 693s, 607w, 513m, 493m.

Preparation of $[Ph_2P(NPPh_2)_2]Co[N(SiMe_3)_2]_2$ (2). A mixture of toluene solutions of **1** (0.29 g, 0.5 mmol, 10 mL) and $Co[N(SiMe_3)_2]_2$ (0.19 g, 0.5 mmol, 5 mL) was kept at 20 °C for 24 h. Toluene was then removed under reduced pressure and changed for ether (10 mL). Yellow-brown crystals of the product, which formed overnight, were washed with cold ether and dried in a vacuum. Yield: 0.34 g (86%). Anal. Calcd for $C_{42}H_{48}Si_2P_3N_3Co$, %: C, 62.83; H, 6.03; Co, 7.44. Found, %: C, 62.75; H, 6.10; Co, 7.42. IR (nujol), ν/cm^{-1} : 1245m, 1155m, 1120m, 1065w, 1025w, 985w, 930w, 885m, 840s, 745m, 725m, 695 vs, 570w, 540m, 515s.

Preparation of $[Ph_2P(NPPh_2)_2]NiCp$ (3). A THF solution of **1** (0.58 g, 1.0 mmol, 10 mL) was added to a solution of Cp_2Ni (0.19 g, 1.0 mmol, 10 mL). A yellow-green precipitate formed in about 5 min. A sample of the precipitate was washed with THF, dried in a vacuum, and studied by IR spectroscopy (nujol), ν/cm^{-1} : 3100–3200 sw, 2490m, 2010m, 1765s, 1307w, 1273w, 1177s, 1107s, 1025w, 996w, 903m, 837m, 809w, 798w, 747s, 724s, 694vs, 520s, 497m. Following heating at 60 °C for 5 h, the precipitate was dissolved, and the solution turned red-brown. The main part of the solvent was removed under reduced pressure. Red crystals of **3** formed overnight at room temperature. The crystals were washed with cold THF and dried in a vacuum. Yield: 2.38 g (88%). Anal. Calcd for $C_{41}H_{35}P_3N_2Ni$, %: C, 69.62; H, 4.95; Ni, 8.31. Found, %: C, 69.44; H, 5.04; Ni, 8.22. IR (nujol), ν/cm^{-1} : 3050w, 1580w, 1430m, 1340w, 1300w, 1180s, 1160s, 1130s, 1090m, 1070m, 1020m, 1000w, 900w, 830w, 820m, 790m, 740m, 720m, 690m, 570m, 530s, 500m, 440w. $^31P\{^1H\}$ NMR (C_6D_6 , 300K) δ (ppm): 65.2 (d), 30.4 (t) ($^2J = 34 \text{ Hz}$). 1H NMR: 8.3–6.9 (m, 30H, $(C_6H_5)_3$), 4.9 (s, 5H, (Cp)).

All structures were solved by direct methods and refined against F^2 on all data by full-matrix least squares with SHELXTL.²¹ Absorption correction was applied using SADABS.²²

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Supporting Information Available: CIF files of the study compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 652102 (**1**), 652103 (**2**), and 652104 (**3**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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