

Rearrangement of phosphinohydrazide ligand $-\text{NPh-N}(\text{PPh}_2)_2$ in transition metal coordination sphere: Synthesis and characterization of nickel and cobalt spirocyclic complexes $\text{M}(\text{NPh-PPh}_2=\text{N-PPh}_2)_2$ and their properties

Vyacheslav V. Sushev, Alexander N. Kornev*, Yuriy A. Min'ko, Natalia V. Belina, Yuriy A. Kurskiy, Olga V. Kuznetsova, Georgy K. Fukin, Evgenii V. Baranov, Vladimir K. Cherkasov, Gleb A. Abakumov

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 Tropinin Street, 603950 Nizhny Novgorod, Russia Federation

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Abstract

The reaction of diphosphinohydrazine $\text{PhNH-N}(\text{PPh}_2)_2$ (**1**) with cobalt(II) silylamide, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, proceeds via formation of unstable phosphinohydrazide complex $\text{Co}[\text{NPh-N}(\text{PPh}_2)_2]_2$ followed by rearrangement to a new chelating compound $\text{Co}(\text{NPh-PPh}_2=\text{N-PPh}_2)_2$ (**2**). Disproportionation of nickel(I) silylamide, $(\text{Ph}_3\text{P})_2\text{Ni-N}(\text{SiMe}_3)_2$, in the presence of **1**, yields Ni(0) and Ni(II) phosphinoamide complexes: $\text{Ni}[(\text{Ph}_2\text{P})_2\text{N-NPhH}]_2$ (**3**), $\text{Ni}(\text{NPh-PPh}_2=\text{N-PPh}_2)_2$ (**4**). X-ray analysis reveals tetrahedral environment of the cobalt atom in **2** and square-planar environment of the nickel atom in *cis*-**4**. In contrast to the crystalline patterns, the solutions of **2** in THF or toluene have EPR signal which is typical to square-planar low-spin d^7 cobalt complex. The reactions of **2** with dioxygen, elemental sulfur and diphenyldiazomethane led to the spirocyclic insertion products $\text{Co}(\text{NPh-PPh}_2=\text{N-PPh}_2=\text{X})_2$ ($\text{X} = \text{O}, \text{S}, \text{NNCPh}_2$) while the absorption of carbon monoxide is reversible.

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1. Introduction

Compounds bearing a phosphorus–nitrogen bond have attracted considerable attention both in heteroatom chemistry and as ligands for transition metals as well [1]. Phosphorus groups have been shown to form bonds with nitrogen groups with relative ease, which is important for ligand design and development of this branch of chemistry. Another important circumstance is a wide gradation in phosphorus–nitrogen bond energies inherent to different class of compounds [1,2]. This makes possible template-like

reactions involving thermal rearrangements and transformations of phosphazane ligands in transition metal coordination sphere.

Recently we have shown [3] that stability of the metal complexes containing σ -bonded phosphinohydrazide ligand $\{-\text{NPh-NPh-PPh}_2\}$ is strongly dependent on the nature of the metal, its oxidation state and ligand environment. Early and middle transition metals or non-transition metals form stable phosphinohydrazides $\text{M}[\text{N}(\text{Ar})\text{N}(\text{Ar})\text{PPh}_2]_2$, $\{\text{M} = \text{Li}, \text{Zn}, \text{Ge}(\text{II}), \text{Mn}(\text{II}), \text{Cr}(\text{III}), \text{Fe}(\text{II}); \text{Ar} = \text{Ph}, -\text{C}_6\text{H}_4\text{Bu}^t\}$ while the late transition metals (Co, Ni, Cu) and metals with enhanced oxidation state (Fe^{3+} in contrast to Fe^{2+}) cause transformation of phosphinohydrazide ligand. The rearrangement of $-\text{NPh-NPh-PPh}_2$ into

* Corresponding author.

E-mail address: akornev@iomc.ras.ru (A.N. Kornev).

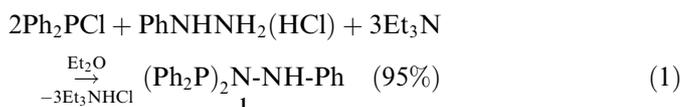
aminoiminophosphorane moiety, $-\text{NPh}-\text{PPh}_2=\text{NPh}$, is observed on Fe^{3+} , Co^{2+} , Ni^{2+} centers. The compound of Ni(I), $(\text{Ph}_3\text{P})_2\text{NiN}(\text{SiMe}_3)_2$, reacts with $\text{HNPh}-\text{NPh}-\text{PPh}_2$ to form azobenzene complex, $(\text{Ph}_3\text{P})_2\text{Ni}(\text{PhN}=\text{NPh})$, while copper(I) silylamide affords diphenylphosphide $\{\text{Ph}_2\text{PCu}\}_n$ and azobenzene [3].

In present paper we report another interesting findings involving rearrangement of diphosphinohydrazide ligand $-\text{NPh}-\text{N}(\text{PPh}_2)_2$ in coordination sphere of divalent cobalt and nickel. The chemical properties of novel complexes will be also considered.

2. Results and discussion

2.1. Synthesis of 1,1-bis(diphenylphosphino)-2-phenylhydrazine, $(\text{Ph}_2\text{P})_2\text{N}-\text{NH}-\text{Ph}$ (**1**)

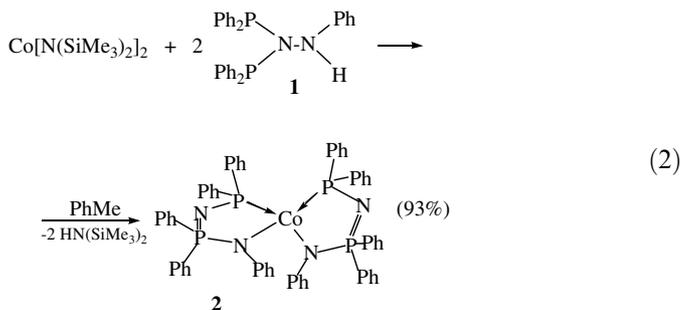
Diphosphinohydrazine **1** was easily prepared by interaction of phenylhydrazine hydrochloride with two equivalents of chlorodiphenylphosphine in the presence of triethylamine.



Diphosphinohydrazine **1** is relatively air-stable and water-resistant compound. It shows single resonance in ^{31}P NMR spectrum at δ 70.5 ppm. Interestingly, ^1H NMR shows NH singlet at 5.84 ppm while NH group reveals very weak absorption (3330 cm^{-1}) in IR spectrum.

2.2. Reactions of **1** with cobalt(II) bis(trimethylsilyl)amide, and bis(triphenylphosphine)nickel(I)-bis(trimethylsilylamide)

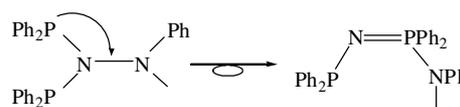
Cobalt silylamide, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ reacts with two equivalents of diphosphinohydrazine (**1**) in toluene solution under mild conditions for 24 h. Originally formed dark violet color of the mixture turned green-brown during the reaction time. We succeed to separate a single product of this reaction in high yield, which is proved to be the complex of phosphazene type (**2**) according to X-ray analysis.



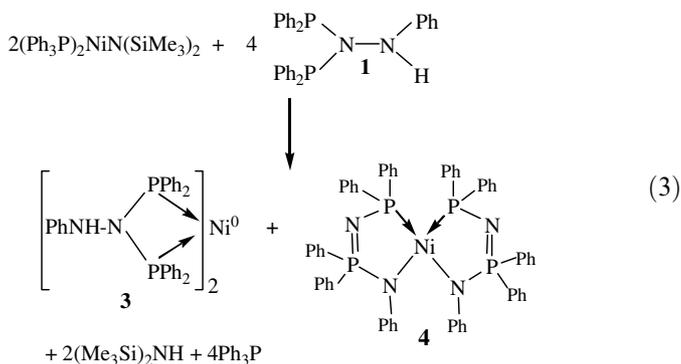
The IR spectrum of the crystals differs significantly from the spectrum of **1** and contains strong absorption at 1238 cm^{-1} assigned to $\nu(\text{P}^{\text{V}}=\text{N})$ bonds in phosphazenes [4].

Comparing the acidity of **1** and hexamethyldisilazane it may be assumed that both of them should not differ significantly from each other. Apparently, the driving force of the reaction is initial coordination of the ligand to cobalt atom which relieves the following substitution of $(\text{Me}_3\text{Si})_2\text{N}-$ group.

It was impossible to isolate the originally formed phosphazane complex $\text{Co}[\text{NPh}-\text{N}(\text{PPh}_2)_2]_2$. The attempts to stop the reaction at the initial period of time gave only intractable waxy solid, while maintaining the reaction mixture for 24 h affords excellent yield of **2** as dark-green crystals. Thus the rearrangement of the ligand in cobalt(II) coordination sphere is occurred. The process includes insertion of $\text{Ph}_2\text{P}-$ group into nitrogen–nitrogen bond, which is accompanied with the cycle extension.



Bis(triphenylphosphine)nickel(I) bis(trimethylsilyl)amide reacts with **1** in similar way, although this reaction is rather more complicated (Eqs. (3), (4a)–(4d)).



Mixing of the starting compounds in toluene at room temperature gave dark red-brown solution. Replacement of toluene by diethyl ether affords air sensitive dark cerise crystalline precipitate, which showed single resonance at 113.9 ppm in the ^{31}P NMR spectrum. According to element analysis, chemical behavior and NMR data we assign this compound to the complex of zero valent nickel $\text{Ni}[(\text{Ph}_2\text{P})_2\text{N}-\text{NPhH}]_2$ (**3**). Note, that ^{31}P NMR monitoring of the reaction mixture containing $\text{Ni}(\text{Ph}_3\text{P})_4$ and ligand **1** in molar ratio 1:2 gave the same signal at 113.9 ppm (together with -4.0 ppm of Ph_3P) which is additional evidence of the complex **3** formation (Eq. 4b). The ^{31}P NMR spectrum of remained reaction mixture showed two complicated multiplets at 71.5 and 49.6 ppm. Heating of the reaction mixture for 10 h at 40°C followed by removing of the solvent yields orange crystals of **4**. The compound **4** shows two triplets in ^{31}P NMR spectrum with splitting constant 17 Hz and chemical shifts at 72.1 and 50.6 ppm, which were assigned to P^{III} and P^{V} accordingly. The IR spectrum of the crystals contains two strong absorptions

at ν 1270, 1250 cm^{-1} assigned to ($\text{P}^{\text{V}}=\text{N}$) bonds stretching vibrations [4].

We tried to obtain **2** and **4** in another way, by interaction of metal halides with lithium salt of **1**. This method however affords **2** and **4** in worse yields apparently because of easy oxidation of diphosphinohydrazide ion $[(\text{Ph}_2\text{P})_2\text{N}-\text{NPh}]^-$ with metal salt. We noticed the appearance of bright scarlet coloration of the reaction mixtures at the beginning of the reagents mixing. The same bright scarlet coloration we observed in the course of oxidation of $(\text{Ph}_2\text{P})_2\text{N}-\text{N}(\text{Li})\text{Ph}$ in THF solution with molecular oxygen. An EPR spectrum reveals formation of a stable radical whose odd electron localized on two phosphorus and two nitrogen atoms. $A_i(\text{P}) = 6.50 \text{ G}$ (2P), $A_i(\text{N}) = 6.50 \text{ G}$ (1N), $A_i(\text{H}) = 3.25 \text{ G}$ (2H), $A_i(\text{H}) = 1.00 \text{ G}$ (2H), $A_i(\text{N}) = 3.45 \text{ G}$ (1N); $g_i = 2.0049$ (Fig. 1). The nature of spectra, however, doesn't allow to assign the last one to a certain structure. Tentatively we propose formation of nitrogen centered radical like $[(\text{Ph}_2\text{P})_2\text{N}-\text{N}^{\cdot}-\text{C}_6\text{H}_4-\text{X}]$ where X is unknown group.

2.3. Structural description of $M(\text{NPh}-\text{PPh}_2=\text{N}-\text{PPh}_2)_2$

$M = \text{Co}$ (**2**), Ni (**4**) and mechanistic aspects of their formation

The X-ray diffraction study (Fig. 2) has shown that molecule **2** in the solid state represents the spirocyclic complex

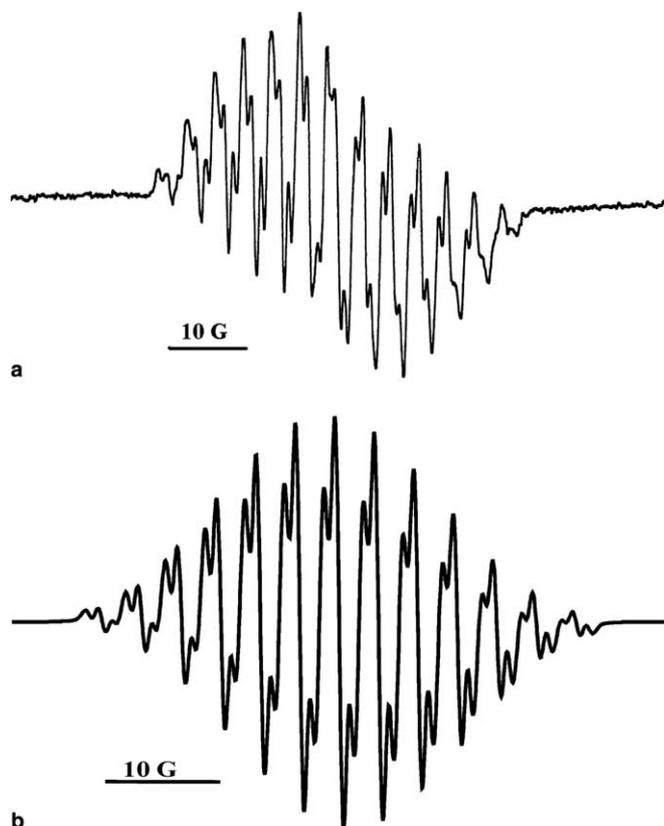


Fig. 1. EPR signal arising by oxidation of $[(\text{Ph}_2\text{P})_2\text{N}-\text{NPh}]^-$ with O_2 . (a) in THF at 290 K and simulation of $[(\text{Ph}_2\text{P})_2\text{N}-\text{N}^{\cdot}-\text{C}_6\text{H}_4-\text{X}]$ EPR spectrum (b).

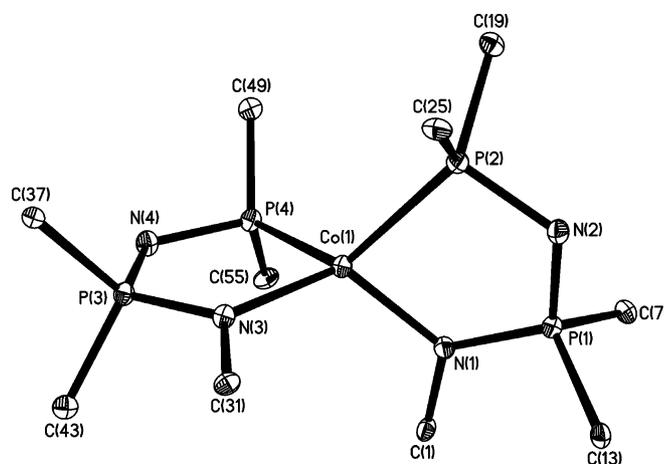
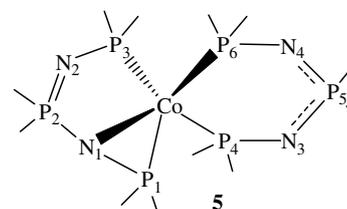


Fig. 2. Molecular structure of $\text{Co}(\text{NPh}-\text{PPh}_2=\text{N}-\text{PPh}_2)_2$ (**2**). Phenyl rings are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

containing two plane five-membered cycles CoNPNP unfolded relatively to each other to 84.6° . The cobalt atom has a distorted tetrahedral coordination. The bond angles $\text{N}(1)\text{Co}(1)\text{P}(2)$ and $\text{N}(3)\text{Co}(1)\text{P}(4)$ are close to 90° ($89.33(5)^\circ$ and $90.64(5)^\circ$), respectively (Table 2).

The P–N bond lengths all lie between the values of P–N single (1.77 \AA) and P=N double bonds (1.56 \AA) [5], as they occur in phosphazenes. The bonds $\text{P}(1)-\text{N}(2)$ $1.584(2) \text{ \AA}$ and $\text{P}(3)-\text{N}(4)$ $1.588(2) \text{ \AA}$ are mainly of double bond character, whereas the distances $\text{P}(1)-\text{N}(1)$, $\text{P}(2)-\text{N}(2)$, $\text{P}(3)-\text{N}(3)$ and $\text{P}(4)-\text{N}(4)$ ($1.632(2)-1.640(2) \text{ \AA}$) correspond rather to bond lengths between single and double bonds.

The nitrogen atoms $\text{N}(1)$ and $\text{N}(3)$ have near planar geometry with the sum of the angles (358.58° and 359.42°). The $\text{Co}(1)-\text{P}(2,4)$ and $\text{Co}(1)-\text{N}(1,3)$ distances in **2** are $2.3376(6)$, $2.3164(6) \text{ \AA}$ and $1.944(2)$, $1.987(2) \text{ \AA}$, respectively. It is worth to cite an instance of related spirocyclic cobalt(II) phosphazene complex $\text{Co}[\text{Ph}_2\text{PNPPH}_2-\text{NPPH}_2]_2$ (**5**) [6,7], which can be considered as a $\text{N}(1)$ -capped CoP_4 tetrahedron or as a distorted tetragonal pyramid with an apical $\text{P}(3)$ and a $\text{N}(1)-\text{P}(1)-\text{P}(4)-\text{P}(6)$ base. The complex is in low-spin electronic state showing $\mu_{\text{eff}} = 2.39 \mu_{\text{B}}$. It should be noted that two Co–P distances in **5** (2.319 , 2.342 \AA) are close to the analogues bond lengths in **2** whereas two other Co–P(1) 2.217 \AA , and Co–P(4) 2.206 \AA are significantly shorter.



Interestingly, while the crystalline sample of **2** has no EPR signal (on account of high spin d^7 state of cobalt), dissolution of **2** in THF or toluene is accompanied with

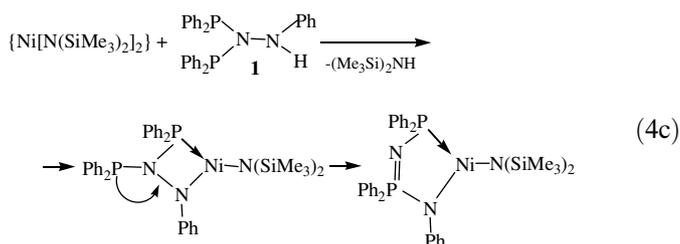
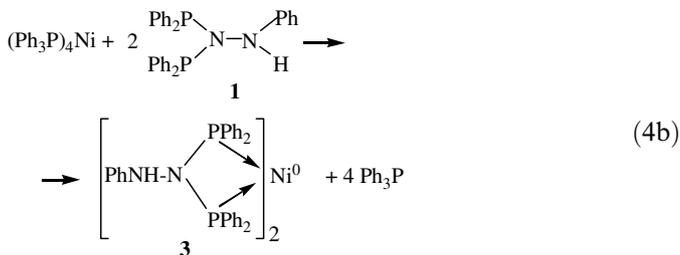
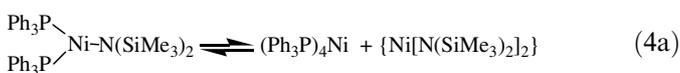
appearance of EPR signal ($g_i = 2.256$) indicating the localization of odd electron on the metal. At low temperature (145 K) the complex exhibits anisotropic EPR spectrum with g -tensor close to axial ($g_1 = 2.0091$, $g_2 = 2.313$, $g_3 = 2.407$) (Fig. 3). Such spectrum is typical to the square-planar low-spin d^7 cobalt complexes [8].

Analogous nickel phosphazene complex **4** is diamagnetic. Nickel atom has square-planar environment. The crystal structure (Fig. 4) reveals formation of *cis*-**4** which is much more sterically hindered than the possible *trans*-isomer. The crystal structure consists of discrete molecules of **4** and a toluene molecule which has no shortened contacts with **4** and may be considered as a solvation molecule. Heterocycles Ni(1)–P(1)–N(1)–P(2)–N(2) and Ni(1)–N(3)–P(3)–N(4)–P(4), are non-planar contrary to **2**, so the spirocyclic molecule adopt chair-like conforma-

tion. Selected bond distances and angles for **4** are given in Table 2. The Ni–P bond length of 2.1604(4) and 2.1618(4) Å are within the normal range observed for Ni(II) chelate complexes [3,9]. Meanwhile these distances are substantially shorter than Co–P ones {2.3164(6) and 2.3376(6) Å} in **2**. Apparently this fact together with tense conformation of *cis*-isomer may cause NiNPNP-ring strain and its puckered conformation. In addition note that valent angles at phosphazene nitrogen atoms in **4** {P(3)–N(4)–P(4), P(2)–N(1)–P(1) both approx. 112°} are far less than those ones found for related cobalt complex **2** {P(3)–N(4)–P(4), P(1)–N(2)–P(2) both approx. 120°}. The N–P bond distances in **4** are in the range 1.60–1.63 Å that is more justified as compared to analogous cobalt complex **2**.

The angles N(2)–Ni(1)–P(1) and N(3)–Ni(1)–P(4) are both 82.72°. Nitrogen atoms N(2) and N(3) have a trigonal-planar environment. Phenyl groups at these nitrogen atoms lie on each side of the plane N(2)N(3)Ni(1)P(4)P(1) apparently due to significant steric hindrances.

Formation of *cis*-**4** takes about 3 days at 20 °C or heating for 10 h at 40–50 °C. We did not find any traces of *trans*-**4** in the reaction mixture. Considering mechanistic aspects of the reaction we exclude formation of intermediate monovalent nickel species since (a) there are no EPR signal were registered in the course of the reaction; (b) it is known that small chelate angle at nickel atom is unfavorable for existence and formation of Ni(I) complexes [10]. On the other hand, as we realized earlier [9], nickel(I) silylamide is prone to disproportionation in the presence of phosphines.



It is well documented that phosphino groups show stronger *trans* influence in contrast with amino-substituents [11]. Since the addition of diphosphinohydrazine proceeds consecutively, coordination of Ph_2P -group of the second molecule is directed to more favorable *cis*-position.

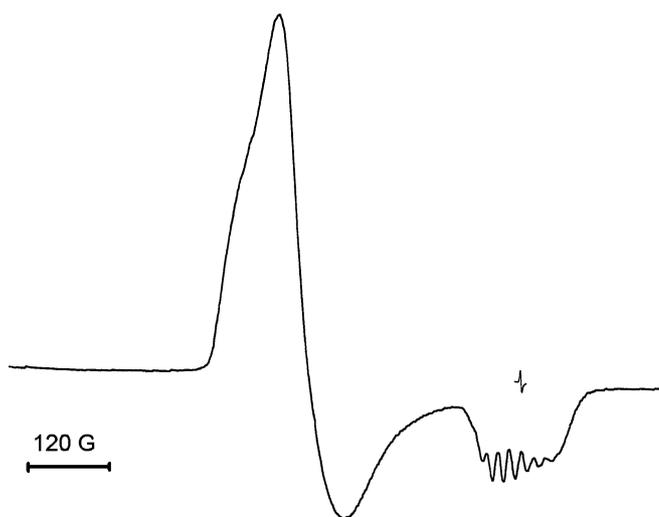


Fig. 3. EPR spectrum of $\text{Co}(\text{NPh-PPh}_2=\text{N-PPh}_2)_2$ (**2**) at 145 K.

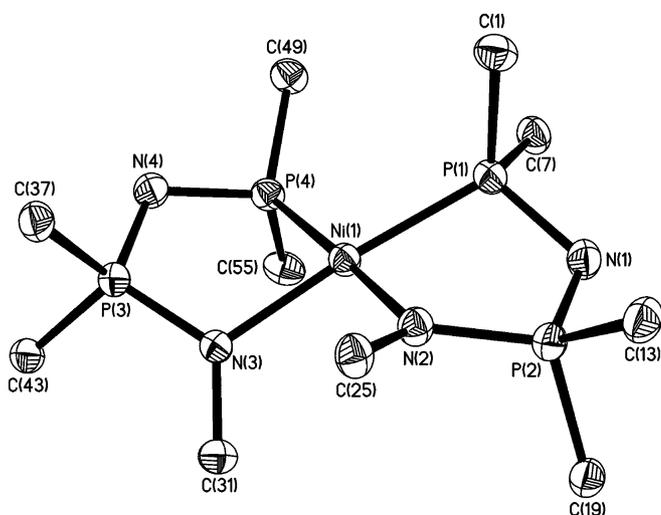
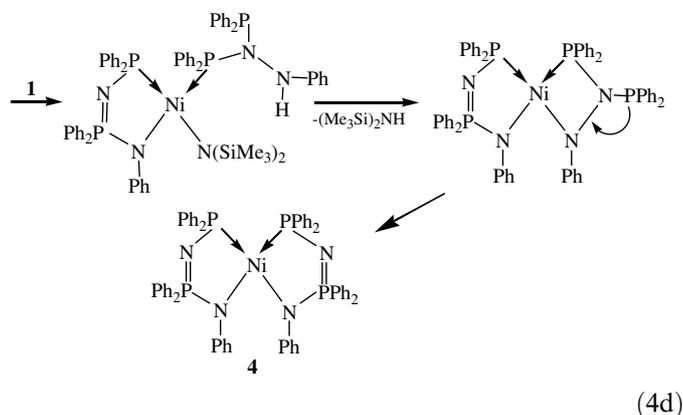


Fig. 4. Molecular structure of $\text{Ni}(\text{NPh-PPh}_2=\text{N-PPh}_2)_2$ (**4**). Phenyl rings are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.



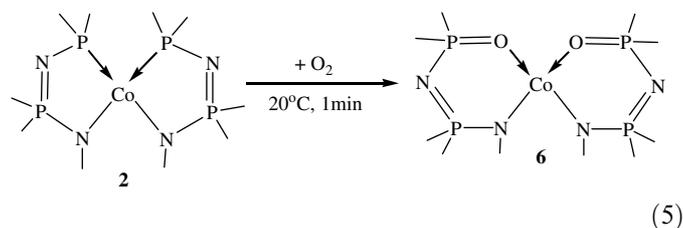
Note that most of known relative square-planar nickel(II) complexes with N,P-chelate ligands, e.g., $\{\text{Ni}[\text{Ph}_2\text{PCH}_2\text{-PPh}_2\text{=NH}]_2\}^{2+}$ [12], $[\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{NH}_2)_2]\text{Cl}_2$ [13] have also *cis*-conformation.

2.4. Chemical properties

One of the remarkable properties of the amidophosphine complexes **2** and **4** is their high resistance to hydrolysis in neutral and alkaline medium. This is rather exception in the chemistry of metal amides, but may be explained with strong chelation and charge redistribution along the conjugated N–P bonds. Strong acids (e.g., aqueous HCl) destroy the compounds. Phosphazene nickel complex **4** turned out to be quite inert also to atmospheric oxygen and carbon monoxide. Interaction of **4** with carbon monoxide in toluene solution at ambient temperature and pressure proceed slowly, for several days and gave no isolable products. On the other hand, cobalt complex **2** showed an interesting chemistry.

2.4.1. Interaction of **2** with dioxygen

Being quite stable to hydrolysis, **2** is oxidized easily with dioxygen to form insertion product **6** in quantitative yield.



Dark green solution of **2** in THF or toluene turned light blue after short contact with dry oxygen.

Replacement of THF for diethyl ether gave moisture sensitive blue crystals of **6**. The complex **6** shows strong absorption in the IR spectrum at 1270, 1235, 1210 and 1178 cm^{-1} which evidences on the presence of P=N and P=O bonds in the molecule.

Maintaining of ether solution of **6** for 3–5 h in air affords abundant colorless crystalline precipitate **7**. The same precipitate is formed immediately after addition of small quantities of water. The substance showed two wide

singlets in ^{31}P NMR spectrum at 16.3 and 11.7 ppm. There are several strong absorption bands in the IR spectrum of **7** is observed in the region 1300–1180, 1165 cm^{-1} which are indicative of the presence of P=N and P=O bonds in the molecule. The X-ray investigation shows formation of free amido-phosphinoyl ligand $\text{PhNH-PPh}_2\text{=N-PPh}_2\text{=O}$ (**7**), which is dimer in the solid state located on the inversion center. (Fig. 5). The crystal structure consists also a molecule of diethyl ether which has no shortened contacts with **7** and may be considered as a solvation molecule. The H(1A)...O(1B) (1.93(4) Å) distance is significantly shorter of the geometrical criterion for the formation of hydrogen bonds (2.15 Å [14]) and the N(1A)...O(1B) (2.754(5) Å) distance is close to the value of typical van-der-waals contact between O and N atoms (2.78 Å [14]). The bond N(1A)H(1A)O(1B) angle is 169.2°. The distribution of the bond lengths in the P(1)N(2)P(2)N(1) framework indicates one formally double P(2)–N(2) bond (1.557(4) Å) and two single bonds N(1)–P(2) (1.641(4) Å), N(2)–P(1) 1.597(4) Å. The last one is contracted significantly apparently due to strong positive charge on P(1) atom ($-\text{Ph}_2\text{P}^+-\text{O}^-$). It should be noted that the P(1)–O(1) (1.489(3) Å) distance is a typical for the P=O (1.489 Å [15]) bonds.

We cleared up the composition of **6** by the back synthesis. Addition of **7** to cobalt silylamide, $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, in stoichiometric amount immediately gave blue complex **6** as can be judged on visible and IR spectra (see Section 3).

2.4.2. Interaction of **2** with elemental sulfur

Complex **2** being sensitive to electrophilic oxidation, easily reacts with elemental sulfur. Heating of toluene solution of **2** with two equivalents of sulfur at 40 °C for 30 min yields dark blue solution. Concentration and maintaining of the solution at 20 °C overnight gave blue-violet crystals of the complex **8**, which is formed by insertion of sulfur into both Co–P bonds.

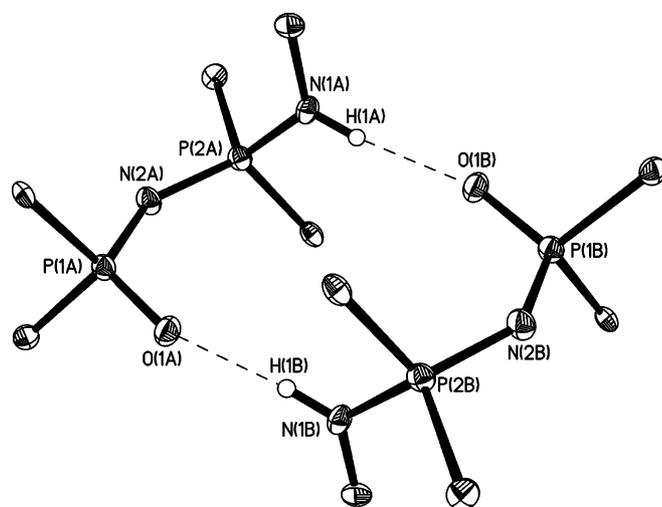
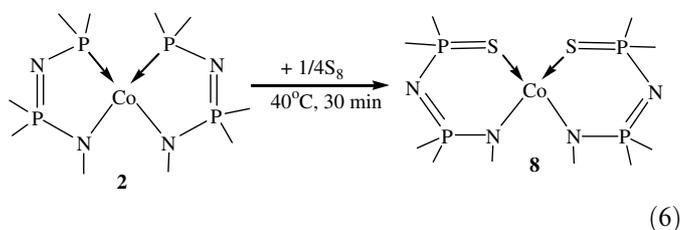


Fig. 5. Molecular structure of $\text{PhNH-PPh}_2\text{=N-PPh}_2\text{=O}$ (**7**). Phenyl rings are omitted for clarity. Thermal ellipsoids are drawn at 30 % probability.



IR spectrum of **8** contains very strong absorptions at 1191, 1175 and 578 cm^{-1} referred to stretching vibrations of P=N and P=S fragments, respectively. The X-ray investigation reveals the formation of spirocyclic complex with central cobalt atom in tetrahedral environment. The six-member cycles are non-planar.

The P–N distances in **8** are greatly justified. So formally double bonds (P(2)–N(1), P(4)–N(3)) and single bonds (P(1)–N(1), P(3)–N(3)) are 1.592(2), 1.590(1) Å and 1.599(1), 1.590(2) Å, respectively. The P(2)–N(2) and P(4)–N(4) bonds at σ -bonded nitrogen atoms, bearing negative charge, are significantly longer (1.631(2) and 1.637(1) Å, respectively). The Co–N bond distances in **8** (1.985(1) and 2.002(1) Å) are also longer than in a relative complex **2** (1.944(2) and 1.987(7) Å). That may be explain rather weaker chelating effect of the ligand $\text{–NPh–PPh}_2\text{=N–PPh}_2\text{=S}$ in **8** as compared to $\text{–NPh–PPh}_2\text{=N–PPh}_2$ ligand in **2**. The Co(1)–S(1) (2.3676(5) Å) and Co(1)–S(2) (2.3525(5) Å) distances vary in the typical range of the coordination P=S \rightarrow Co bonds [16] (Fig. 6).

The complex **8** like **6** is also easily hydrolysable in ether solution to form free ligand $\text{HNPh–PPh}_2\text{=N–PPh}_2\text{=S}$ (**9**) in quantitative yield as stable colorless crystals. The ^{31}P NMR spectrum of **9** contains two wide singlets at 44.2 and 17.2 ppm while IR spectrum reveals strong absorptions at 1253, 1226, 1175 and 600 cm^{-1} characterizing P=N and P=S stretching vibrations accordingly.

2.4.3. Interaction of **2** with CO

A solution of **2** in toluene absorbs carbon monoxide at atmospheric pressure and ambient temperature with

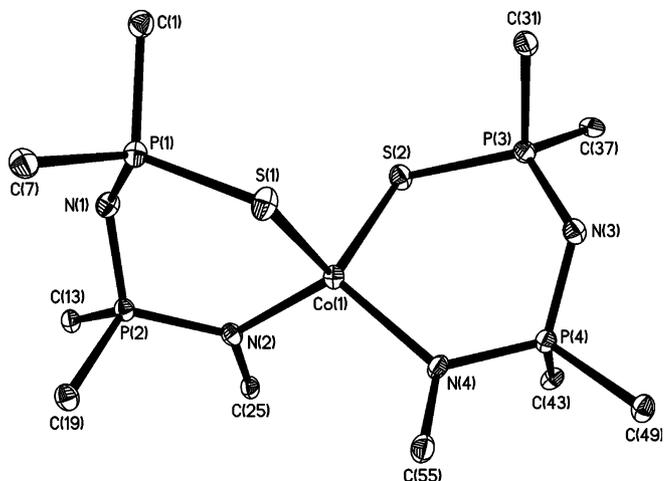
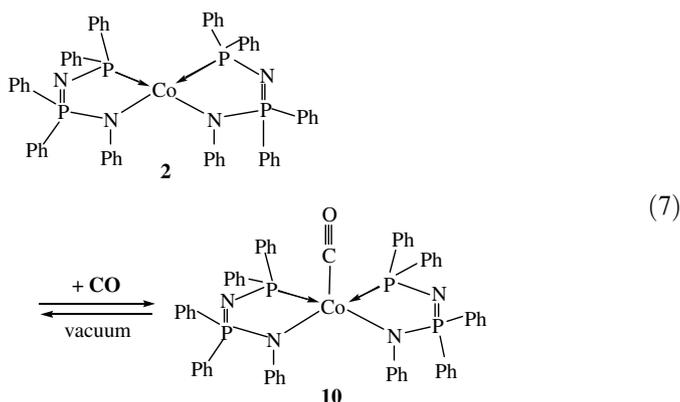


Fig. 6. Molecular structure of $\text{Co}(\text{NPh–PPh}_2\text{=N–PPh}_2\text{=S})_2$ (**8**). Thermal ellipsoids are drawn at 30% probability.

the rate of gas diffusion into a solution. The green color of the solution assumed yellow tint. The electronic spectrum showed fast disappearance of absorption bands of the initial complex (λ , nm: 503, 603, 686) while new broad absorption at 735 nm arose. IR spectrum revealed strong band at 1975 cm^{-1} (a special experiment in CHCl_3), indicating formation of carbonyl cobalt complex.

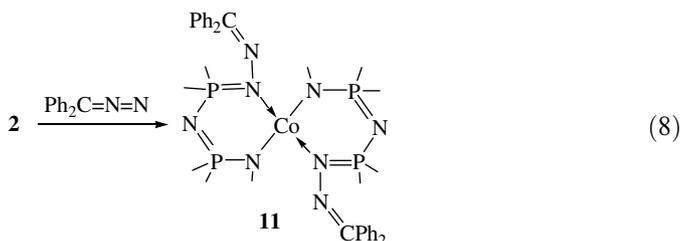
The hyperfine coupling constant with phosphorus nucleus (^{31}P) is known is sensitive to the coordination geometry. EPR spectrum of the reaction mixture (Fig. 7) showed appearance of novel doublet $A_p = 140$ G and additional hyperfine coupling $A = 27$ G ($g_i = 2.088$). Apparently, coordination of carbon monoxide to cobalt atom changes the geometry of the complex to tetragonal pyramid (**10**):



The coordination of carbon monoxide to cobalt atom in **2** is reversible. Solvent removal in vacuum led to the starting compound **2** as we can judge on EPR, electronic and IR spectra.

2.4.4. Interaction of **2** with diphenyldiazomethane

In a related reaction we tested the ability of **2** to intercept a diphenylcarbene unit from Ph_2CN_2 . Rather than undergoing carbene transfer and concomitant expulsion of N_2 we found that the reaction of **2** with two equivalents of Ph_2CN_2 proceeds by insertion of the last one into phosphorus–cobalt coordination bond.



We failed to separate **11** in crystalline form. Nonetheless, in the course of several attempts of crystallizations we obtained blue-violet crystals of related complex **12**, which turn out to be a product of partial hydrolysis of **11**.

Table 1
The details of crystallographic, collection and refinement data for **2**, **4**, **7**, **8** and **12**

	2	4	7	8	12
Empirical formula	C ₆₀ H ₅₀ CoN ₄ P ₄	C ₆₇ H ₅₈ N ₄ NiP ₄	C ₃₄ H ₃₆ N ₂ O ₂ P ₂	C ₆₀ H ₅₀ CoN ₄ P ₄ S ₂	C ₁₁₄ H ₁₀₄ Co ₂ N ₈ O ₂ P ₄
Formula weight	1009.85	1101.76	566.59	1073.97	1859.79
Temperature (K)	100	293	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.092(1)	45.393(2)	12.628(4)	12.7950(6)	13.5167(8)
<i>b</i> (Å)	13.037(1)	13.8295(6)	21.195(7)	13.5669(6)	13.8168(8)
<i>c</i> (Å)	18.216(2)	18.7768(8)	12.479(4)	16.2243(7)	15.8448(9)
α (°)	92.575(2)			88.993(1)	91.233(1)
β (°)	105.855(2)	106.024(1)	117.647(8)	80.666(1)	111.859(1)
γ (°)	100.540(2)			71.040(10)	115.862(1)
Volume (Å ³)	2478.6(4)	11329.3(8)	2959(2)	2626.4(2)	2410.6(2)
<i>Z</i>	2	8	4	2	1
Density (calculated) (g/cm ³)	1.353	1.292	1.272	1.358	1.281
Absorption coefficient (mm ⁻¹)	0.520	0.501	0.181	0.572	0.467
<i>F</i> (000)	1050	4608	1200	1114	974
Crystal size (mm)	0.40 × 0.20 × 0.15	0.3 × 0.20 × 0.10	0.05 × 0.05 × 0.01	0.61 × 0.17 × 0.14	0.30 × 0.16 × 0.12
θ_{\max} range for data collection (°)	25.00	29.03	23.32	24.00	25.00
Index ranges	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -21 ≤ <i>l</i> ≤ 21	-61 ≤ <i>h</i> ≤ 61 -18 ≤ <i>k</i> ≤ 18 -25 ≤ <i>l</i> ≤ 25	-14 ≤ <i>h</i> ≤ 14 -23 ≤ <i>k</i> ≤ 16 -13 ≤ <i>l</i> ≤ 12	-14 ≤ <i>h</i> ≤ 13 -11 ≤ <i>k</i> ≤ 15 -18 ≤ <i>l</i> ≤ 17	-16 ≤ <i>h</i> ≤ 16 -12 ≤ <i>k</i> ≤ 16 -14 ≤ <i>l</i> ≤ 18
Reflections collected	19591	59065	13727	13373	13352
Independent reflections	8691 [<i>R</i> _{int} = 0.0241]	15048 [<i>R</i> _{int} = 0.0333]	4277 [<i>R</i> _{int} = 0.1024]	8224 [<i>R</i> _{int} = 0.0164]	8456 [<i>R</i> _{int} = 0.0227]
Absorption correction	SADABS				
Max/min transmission	0.9260/0.8189	0.9516/0.8642	0.9982/0.9910	0.9242/0.7216	0.9461/0.8726
Refinement method	Full-matrix least-squares on <i>F</i> ²				
Data/restraints/parameters	8691/0/822	15048/20/919	4277/0/465	8224/0/840	8456/31/826
Goodness-of-fit on <i>F</i> ²	1.057	1.021	0.989	1.043	0.997
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0339 <i>wR</i> ₂ = 0.0820	<i>R</i> ₁ = 0.0440 <i>wR</i> ₂ = 0.1060	<i>R</i> ₁ = 0.0638 <i>wR</i> ₂ = 0.1418	<i>R</i> ₁ = 0.0325 <i>wR</i> ₂ = 0.0819	<i>R</i> ₁ = 0.0398 <i>wR</i> ₂ = 0.0933
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0427 <i>wR</i> ₂ = 0.0847	<i>R</i> ₁ = 0.0710 <i>wR</i> ₂ = 0.1208	<i>R</i> ₁ = 0.1250 <i>wR</i> ₂ = 0.1708	<i>R</i> ₁ = 0.0407 <i>wR</i> ₂ = 0.0849	<i>R</i> ₁ = 0.0569 <i>wR</i> ₂ = 0.0993
Largest diff. peak and hole (e Å ⁻³)	0.458/-0.235	0.538/-0.254	0.709/-0.384	0.449/-0.192	0.492/-0.234

the cycles as depicted in graphic formula of **12**. Instead, two terminal bonds P(1)–N(1) and P(2)–N(3) (1.6205(14) and 1.6390(15) Å, respectively) are elongated relatively of two middle bonds P(1)–N(2) and P(2)–N2 (1.5954(11) and 1.5889(13) Å, respectively). This suggests more negative charge location on N(1) and N(3) atoms coordinated to cobalt. The Co–N bond distances in **12** (2.029(1) and 2.037(1) Å) are slightly longer than in a relative complexes **2** and **8** that may be explain rather weaker chelating effect of the ligand –NPh–PPh₂=N–PPh₂=N–N=CPh₂.

Discussing the mechanistic aspects of Ph₂CN₂ insertion into Co–P coordination bond, we suggest initial coordination of terminal nitrogen to cobalt atom to form η₁-bonded complex. It is known an example of such complexation in the reaction of diphenyldiazomethane with Co(I) complex PhB(CH₂PPh₂)₃Co(PMe₃) [17]. The resulting compound {PhB(CH₂PPh₂)₃CoNNCPh₂} exhibits high thermal and photo stability.

2.4.5. Interaction of **2** with H₂S

Using the reaction of **2** with H₂S we attempted to separate free ligand HNPh–PPh₂=N–PPh₂ from the metal. The interaction of **2** and H₂S in THF proceed fast to form dark-brown solution. Single strong absorption band at λ_{max} = 430 nm is observed in electron spectrum. According

to elemental analysis only one molecule of H₂S was absorbed per cobalt atom of **2**. IR spectrum shows no SH bonds in the region 2400–2500 cm⁻¹, instead absorption of NH bond is appeared at 3210 cm⁻¹. General view of the spectrum reveals similarity to IR spectra of the ligand PhNH–PPh₂=N–PPh₂=S. However no ³¹P NMR spectrum was registered probably due to paramagnetism of the complex. The H₂S-adduct was found to be sufficiently less oxygen sensitive as compared to starting complex **2**. However, keeping of the THF solution of (**2** · H₂S) overnight in contact with air affords colorless crystals of PhNH–PPh₂=N–PPh₂=O (**7**) according to IR and ³¹P NMR spectra. It means that hydrogen disulfide does not destroy the phosphazene ligand when interact with **2**. Unfortunately, we failed to obtain (**2** · H₂S) in crystalline form, suitable for X-ray analysis. Tentatively the complex was formulated as phosphino-sulfide [(HNPh–PPh₂=N–PPh₂)₂CoS]_{*n*}.

3. Experimental

3.1. General considerations

Solvents were purified following standard methods [18]. Toluene and methylene chloride were thoroughly dried and

Table 2
The selected distances (Å) and angles (°) for **2**, **4**, **7**, **8** and **12**

Co(NPh-PPh ₂ =N-PPh ₂) ₂ (2)	Ni(NPh-PPh ₂ =N-PPh ₂) ₂ (4)	PhNH-PPh ₂ =N-PPh ₂ =O (7)	Co(NPh-PPh ₂ =N-PPh ₂ =S) ₂ (8)	[Co(NPh-PPh ₂ =N-PPh ₂ =N-N=CPh ₂) ₂](μ-OH) ₂ (12)					
<i>Bond distance (Å)</i>									
Co(1)–N(1)	1.944(2)	Ni(1)–N(2)	1.986(1)	P(1)–O(1)	1.489(3)	Co(1)–N(2)	1.985(1)	Co(1)–O(1)	1.949(1)
Co(1)–N(3)	1.987(2)	Ni(1)–N(3)	1.987(1)	P(1)–N(2)	1.597(4)	Co(1)–N(4)	2.002(1)	Co(1)–O(1)#1	1.959(1)
Co(1)–P(4)	2.316(1)	Ni(1)–P(1)	2.160(1)	N(2)–P(2)	1.557(4)	Co(1)–S(2)	2.353(1)	Co(1)–N(1)	2.029(1)
Co(1)–P(2)	2.338(1)	Ni(1)–P(4)	2.162(1)	P(2)–N(1)	1.641(4)	Co(1)–S(1)	2.368(1)	Co(1)–N(3)	2.037(1)
P(1)–N(2)	1.584(2)	P(1)–N(1)	1.633(1)	H(1)...O(1)#1	1.93(4)	S(1)–P(1)	2.010(1)	Co(1)–Co(1)#1	2.968(1)
P(1)–N(1)	1.632(2)	N(1)–P(2)	1.598(1)	N(1)...O(1)#1	2.754(5)	S(2)–P(3)	2.015(1)	P(1)–N(2)	1.595(1)
P(2)–N(2)	1.638(2)	P(2)–N(2)	1.620(1)			P(1)–N(1)	1.599(1)	P(1)–N(1)	1.621(1)
P(3)–N(4)	1.588(2)	P(3)–N(4)	1.599(1)			P(2)–N(1)	1.592(1)	P(2)–N(2)	1.589(1)
P(3)–N(3)	1.640(2)	P(3)–N(3)	1.628(1)			P(2)–N(2)	1.631(1)	P(2)–N(3)	1.639(1)
P(4)–N(4)	1.635(2)	P(4)–N(4)	1.628(1)			P(3)–N(3)	1.590(2)	N(1)–C(1)	1.410(2)
						P(4)–N(3)	1.590(1)	N(3)–N(4)	1.398(2)
						P(4)–N(4)	1.637(1)		
<i>Bond angles (°)</i>									
N(1)–Co(1)–N(3)	122.53(7)	N(2)–Ni(1)–N(3)	94.46(5)	O(1)–P(1)–N(2)	119.3(2)	N(2)–Co(1)–N(4)	116.16(6)	O(1)–Co(1)–O(1)#1	81.18(5)
N(1)–Co(1)–P(4)	114.30(5)	N(2)–Ni(1)–P(1)	82.72(4)	P(2)–N(2)–P(1)	139.8(3)	N(2)–Co(1)–S(2)	107.02(4)	O(1)–Co(1)–N(1)	119.35(5)
N(3)–Co(1)–P(4)	90.64(5)	N(3)–Ni(1)–P(1)	175.69(4)	N(2)–P(2)–N(1)	119.5(2)	N(4)–Co(1)–S(2)	107.16(4)	O(1)#1–Co(1)–N(1)	117.65(5)
N(1)–Co(1)–P(2)	89.33(5)	N(2)–Ni(1)–P(4)	175.42(4)	N(1)–H(1)–O(1)	169.2(4)	N(2)–Co(1)–S(1)	106.86(4)	O(1)–Co(1)–N(3)	113.89(4)
N(3)–Co(1)–P(2)	119.41(5)	N(3)–Ni(1)–P(4)	82.72(3)			N(4)–Co(1)–S(1)	104.24(4)	O(1)#1–Co(1)–N(3)	119.93(5)
P(4)–Co(1)–P(2)	123.84(2)	P(1)–Ni(1)–P(4)	100.29(2)			S(2)–Co(1)–S(1)	115.77(2)	N(1)–Co(1)–N(3)	104.48(5)
N(2)–P(1)–N(1)	112.21(9)	N(1)–P(1)–Ni(1)	105.39(5)			P(1)–S(1)–Co(1)	101.06(2)	N(2)–P(1)–N(1)	109.36(7)
N(2)–P(2)–Co(1)	100.99(6)	N(1)–P(2)–Co(1)	33.60(5)			P(3)–S(2)–Co(1)	101.19(2)	N(2)–P(2)–N(3)	108.32(7)
N(4)–P(3)–N(3)	113.58(9)	P(2)–N(1)–P(1)	111.95(8)			N(1)–P(1)–S(1)	117.39(6)	Co(1)O(1)Co(1)#1	98.82(5)
N(4)–P(4)–Co(1)	101.76(6)	N(1)–P(2)–N(2)	108.74(6)			N(1)–P(2)–N(2)	113.50(7)	C(1)–N(1)–P(1)	123.2(1)
C(1)–N(1)–P(1)	120.5(1)	P(2)–N(2)–Ni(1)	114.58(6)			N(3)–P(3)–S(2)	117.14(5)	C(1)–N(1)–Co(1)	127.0(1)
C(1)–N(1)–Co(1)	122.1(1)	N(4)–P(3)–N(3)	108.87(6)			P(3)–P(4)–N(4)	115.04(8)	P(1)–N(1)–Co(1)	109.1(1)
P(1)–N(1)–Co(1)	116.0(1)	P(3)–N(3)–Ni(1)	112.44(6)			P(2)–N(1)–P(1)	126.14(9)	P(2)–N(2)–P(1)	129.0(1)
P(1)–N(2)–P(2)	119.9(1)	N(4)–P(4)–Ni(1)	105.43(5)			P(2)–N(2)–Co(1)	119.63(8)	N(4)–N(3)–P(2)	109.7(1)
C(31)–N(3)–P(3)	123.3(1)	P(3)–N(4)–P(4)	112.29(8)			P(3)–N(3)–P(4)	127.21(9)	N(4)–N(3)–Co(1)	135.7(1)
C(31)–N(3)–Co(1)	122.5(1)					P(4)–N(4)–Co(1)	117.39(8)	P(2)–N(3)–Co(1)	107.5(1)
P(3)–N(3)–Co(1)	113.7(1)							C(37)–N(4)–N(1)	119.9(1)
P(3)–N(4)–P(4)	120.2(1)							N(4)–C(37)–C(38)	126.1(2)

distilled over P₂O₅ prior to use. Ether and THF were dried and distilled over Na/benzophenone.

Metal silylamides Co[N(SiMe₃)₂]₂ [19,20], (Ph₃P)₂NiN(SiMe₃)₂ [21] were prepared according to known methods. All manipulations were performed with rigorous exclusion of oxygen and moisture, in vacuum or under an argon atmosphere using standard Schlenk techniques.

Hexamethyldisilazane liberated in the course of the metal silylamides reactions was detected by gas chromatography analyses with Tsvet-500 device, equipped with stainless steel columns 0.4 cm × 200 cm, packed with 5% SE-30 on Chromatone N-Super, with a thermoconductivity detector and with helium as carrier gas.

Spectrophotometric determination of the metals (Co and Ni) in the prepared compounds was provided by the methods described in [22].

Infrared spectra were recorded on a Perkin–Elmer 577 spectrometer from 4000 to 400 cm^{−1} in nujol.

NMR spectra were recorded in CDCl₃ or C₆D₆ solutions using “Bruker DPX-200” device. EPR spectra were recorded on a Bruker ER 200 D-SRC spectrometer with ER041 MR microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unite. The spectra were simulated using WinEPR SimFonia v1.25 (Bruker) by iteration of the (an)isotropic g values, hyperfine coupling constants, and line widths.

3.2. X-ray structure determinations

A summary of crystal data collection and refinement parameters for **2**, **4**, **7**, **8** and **12** are given in Table 1. The data were collected on a Bruker AXS “SMART APEX” diffractometer (graphite-monochromated, Mo K α -radiation, ϕ - ω -scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated in the SAINT program [23]. SADABS [24] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package [25]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in all complexes were found from Fourier synthesis and refined isotropically except for H atoms in solvate molecules in **4** (toluene), **7** (diethyl ether) and **12** (toluene), which were placed in calculated positions and refined in the “riding-model”. The details of crystallographic, collection and refinement data are shown in the Table 1. The selected distances and bond angles are listed in Table 2.

CCDC-282024 (**2**), 282025 (**4**), 282026 (**7**), 282027 (**8**) and 282028 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; deposit@ccdc.cam.ac.uk].

3.3. Synthesis

3.3.1. $(Ph_2P)_2N-NH-Ph$ (**1**)

An excess of triethylamine (5.05 g, 50 mmol) was added to a mixture of fine crystalline $PhNHNH_2(HCl)$ (1.44 g, 10 mmol) and chlorodiphenylphosphine (4.41 g, 20 mmol) in 60 mL of diethyl ether. The mixture was stirred for 12 h at 20 °C then washed two times with water. Ether solution was dried over anhydrous Na_2SO_4 , the major part of the solvent was removed in vacuum. A slow crystallization at 20 °C was completed in about 5 h to leave colorless crystals of **1**. Yield: 4.38 g (92%). Anal. calc. for $C_{30}H_{26}P_2N_2$, %: C, 75.62; I, 5.50; P, 13.00. Found, %: C, 75.90; I, 5.38; P, 13.11. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 70.5 ppm. 1H NMR δ (ppm): 7.70–7.15 (m, 20H, Ph_2P), 7.10–6.40 (m, 5H, PhN), 5.84 (s, 1H, NH); IR (Nujol), ν , cm^{-1} : 3330 (ww), (NH), 1600 (m), 1430 (m), 1330 (w), 1300 (m), 1240 (m), 1170 (w), 1150 (w), 1080 (s), 1020 (m), 890 (vs), 830 (m), 745 (vs), 700 (vs), 530 (w), 510 (ww), 480 (m). *T* decomp. 150 °C.

3.3.2. $Co(NPh-PPh_2=N-PPh_2)_2$ (**2**)

A mixture of toluene solutions of (**1**) (0.95 g, 2 mmol, 20 mL) and $Co[N(SiMe_3)_2]_2$ (0.38 g, 1 mmol, 10 mL) was maintained at 20 °C for 24 h. Toluene was pumped in vacuum and changed for ether (10 ml). Dichroic dark-green crystals of **2** formed overnight were filtered, washed with cold ether and dried in vacuum. Yield 0.94 g (93%). Anal. calc. for $C_{60}H_{50}P_4N_4Co$, %: C, 71.36; I, 4.99; Co, 5.84. Found, %: C, 71.23; I, 5.14; Co, 5.93. IR (nujol) ν (cm^{-1}): 1590 (m), 1238 (s), 1185 (m), 1140 (vs), 1117 (m), 1105 (w), 1026 (m), 997 (w), 950 (s), 918 (w), 800 (s), 748 (m), 742 (m), 720 (m), 695 (vs), 631(w), 616 (w), 539 (m), 546 (m), 530 (s), 522 (ww), 510 (m), 597 (w), 475 (w). Single crystals of **2** suitable for X-ray crystallography were obtained by slow cooling of the solution of **2** in the mixture of the solvents THF, Et_2O , PhMe (1:1:1). Dissolution of **2** in THF or toluene is accompanied with appearance of EPR signal with $g_i = 2.256$; temperature lowering (to 145 K) results in hyperfine splitting of the signal ($g_1 = 2.009$, $g_2 = 2.313$, $g_3 = 2.407$). Electronic (vis) spectrum in PhMe (λ , nm): 503 ($\epsilon = 80$), 603 ($\epsilon = 160$), 686 ($\epsilon = 70$).

3.3.3. Reaction of $(Ph_3P)_2Ni-N(SiMe_3)_2$ with **1**

A mixture of toluene solutions of $(Ph_3P)_2Ni-N(SiMe_3)_2$ (0.58 g, 1.5 mmol, 10 mL) and **1** (1.43 g, 3.0 mmol, 20 mL) was maintained at 20 °C for 1 h. The yellow mixture turned dark-red. Toluene was changed for diethyl ether. A dark-cherish crystalline precipitate of $[PhNH-N(PPh_2)_2]_2Ni$ (**3**) was formed overnight. It was filtered, washed with cold ether and dry in vacuum. Yield (0.65 g, 86%). Anal. calc. for $C_{60}H_{52}P_4N_4Ni$ (**3**), %: C, 71.23, H, 5.18, Ni, 5.80. Found, %: C, 71.18; H, 5.10, Ni, 5.70. IR (cm^{-1}): 1600 (m), 1310 (w), 1250 (w), 1160 (w), 1100 (m), 880 (m), 750 (m), 700 (s), 530 (m), 510 (m), 470 (w). 1H NMR (C_6D_6) δ 6.05 (s, 2H, NH); 6.6–8.2 (m, 50H, Ph). ^{31}P NMR (C_6D_6) δ 113.9 ppm.

The mother liquor was heated at 40 °C for 10 h then kept for 3 days at 20 °C. The second batch of crystals precipitated. The product was recrystallized from warm ether affords orange crystals. Yield of $Ni(NPh-PPh_2=N-PPh_2)_2$ (**4**) 0.62 g, (82%). Anal. calc. for $C_{60}H_{50}P_4N_4Ni$ (**4**), %: C, 71.37; H, 4.99; Ni, 5.81. Found, %: C, 71.42; H, 5.14; Ni, 5.90. IR (cm^{-1}): 1270 (m), 1250 (m), 1160 (w), 1100 (vs), 1080 (vs), 970 (s), 830 (m), 800 (m), 750 (m), 700 (s), 620 (m), 550 (w), 520 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 72.1 (P^{III} , t, AA'); 50.6 (P^V , t, XX'); $^2J_{AX} + ^3J_{AX'} = 17$ Hz.

3.3.4. $Co(NPh-PPh_2=N-PPh_2=O)_2$ (**6**)

(A). A dry air was allowed to contact with ether solution of **2**. Green color of the solution immediately turns blue. Cooling of the solution up to 0 °C results in formation of blue fine crystalline precipitate of **6** in quantitative yield. Anal. calc. for $C_{60}H_{50}P_4N_4O_2Co$, %: C, 69.17; H, 4.84; Co, 5.66. Found, %: C, 69.10; H, 4.89; Co, 5.73. Electronic (vis) spectrum (toluene) λ , nm (ϵ): 530 (80), 600 (200), 629 (40). IR (cm^{-1}): 1587 (m), 1285 (sh), 1270 (s), 1235 (vs), 1210 (vs), 1178 (m), 1121 (vs), 1077 (m), 1058 (vs), 1027 (m), 988 (w), 973 (s), 950 (w), 900 (m), 815 (m), 800 (sh), 750 (s), 725 (s), 695 (vs), 625 (w), 565 (s), 550 (s), 540 (sh), 525 (w), 510 (m).

(B). A solution of $HNPh-PPh_2=N-PPh_2=O$ (**7**) (0.21 g, 0.5 mmol) in 10 ml of ether was added to a solution of $Co[N(SiMe_3)_2]_2$ (0.095 g, 0.25 mmol) in the same solvent (5 mL). The mixture immediately turned blue. The mixture was maintained at 20 °C for 1 h. Solvent and hexamethyldisilazane were pumped in vacuum to leave blue crystals of **6** with analytical data described above. Yield 0.21 g (95%).

3.3.5. $HNPh-PPh_2=N-PPh_2=O$ (**7**)

An ether solution of **6** was allowed to contact with moist air overnight in closed vessel. Large poor soluble colorless crystals were separated in quantitative yield. Anal. calc. for $C_{30}H_{26}P_2N_2O$, %: C, 73.16; H, 5.32; P, 12.58. Found, %: C, 73.03; H, 5.40; P, 12.64. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ (ppm) 16.3, 11.3. 1H NMR δ 6.12 (d, 1H, NH); 6.6–8.2 (m, 25H, Ph). IR (cm^{-1}): 3150 (m, NH), 1600 (m), 1295 (sh), 1255 (vs, P=N), 1230 (sh), 1165 (vs, P=O), 1116 (s), 1070 (w), 1024 (w), 1000 (w), 950 (s), 820 (w), 753 (s), 720 (s), 690 (s), 596 (w), 550 (vs), 512 (s).

3.3.6. $Co(NPh-PPh_2=N-PPh_2=S)_2$ (**8**)

A mixture of toluene solutions of **2** (0.50 g, 0.5 mmol, 10 mL) and elemental sulfur (0.047 g, 1.5 mmol, 5 mL) was heated at 40 °C for 30 min. Toluene was changed for diethyl ether. A minor precipitate was filtered off. A blue solution was concentrated and cooled with ice water. Blue-violet crystals of **8** were separated by filtration. Yield 0.37 g (70%). Anal. calc. for $C_{60}H_{50}P_4N_4S_2Co$, %: C, 67.10; H, 4.69; Co, 5.49. Found, %: C, 66.80; H, 4.75; Co, 5.54. Electronic (vis) spectrum (toluene) λ , nm (ϵ): 540 (120), 640 (400), 735 (160). IR (cm^{-1}): 1585 (m), 1435 (s), 1305 (w), 1280(w), 1235 (m), 1190 (vs), 1175 (s); 1120 (m),

1110 (s), 1068 (w), 1028 (m), 1003 (m), 968 (vs), 806 (s), 747 (s), 725 (m), 692 (vs), 623 (m), 578 (vs), 531 (vs), 496 (m). Crystals of **8** suitable for X-ray analysis were grown by slow cooling of toluene solution.

3.3.7. *HNPh-PPh₂=N-PPh₂=S (9)*

An ether solution of **8** was allowed to contact with moist air overnight in closed vessel. Large poor soluble colorless crystals were separated in quantitative yield. Anal. calc. for C₃₀H₂₆P₂N₂S, %: C, 70.85; H, 5.15; S, 6.30. Found, %: C, 70.78; H, 5.15; S, 6.30. ¹H NMR δ 5.90 (d, 1H, NH); 6.5–8.3 (m, 25H, Ph). ³¹P{¹H} NMR (CDCl₃), δ (ppm) 44.2 (s), 17.2 (s). IR (cm⁻¹): 3208 (w, N-H), 1597 (s), 1498 (m), 1437 (m), 1400 (w), 1296 (w), 1253 (vs), 1226 (s), 1175 (m), 1120 (m), 1104 (m), 1026 (m), 1000 (w), 941 (s), 893 (w), 812 (m), 753 (s), 708 (m), 692 (vs), 602 (vs, P=S), 527 (s), 511(w), 500 (m).

3.3.8. *Interaction of 2 with CO*

An excess of CO was allowed to react with solution of **2** in toluene at ambient temperature and pressure. Approximately 1 mol of CO was absorbed per mole of **2**. The green color of the solution turned greenish-brown. The electronic spectrum showed fast disappearance of absorption bands of the initial complex (λ, nm: 503, 603, 686) while new broad absorption at 735 nm arose. IR spectrum revealed strong band at 1975 cm⁻¹ (a special experiment in CHCl₃), indicating formation of carbonyl cobalt complex. EPR spectrum of the reaction mixture showed appearance of novel doublet A_p = 140 G and additional hyperfine coupling A = 27 G (g_i = 2.088). Solvent removal gave starting compound **2** according EPR, IR and electronic spectroscopy.

3.3.9. *Interaction of 2 with diphenyldiazomethane*

A solution of **2** (0.50 g, 0.5 mmol) and diphenyldiazomethane (0.194 g, 1.0 mmol) in 30 mL of toluene was irradiated with UV lamp of low pressure for 2 h. The solution was concentrated to ~5 mL. Keeping the mixture overnight at 10 °C affords large blue-violet crystals of **12**. Yield 0.28 g (74%). Anal. calc. for C₈₈H₇₂P₄N₈O₂Co₂, %: C, 69.75; H, 4.79; Co, 7.78. Found, %: C, 69.52; H, 4.85; Co, 8.07. IR (nujol) (cm⁻¹): 3680 (m, sharp, OH), 1590 (m), 1265 (w), 1205 (s), 1115 (m), 1035 (m), 1020 (m), 975 (w), 890 (m), 800 (m), 765 (w), 745 (m), 725 (m), 690 (s), 642 (m), 625 (m), 550 (m), 530 (m). Mother liquor shows two signals in ³¹P NMR spectrum, δ (ppm): 20.8 (d, J = 4.7 Hz) and 4.3 (d, J = 4.7 Hz), been tentatively referred to a free ligand (HNPh-PPh₂=N-PPh₂=N-N=CPh₂), while the solution of pure **12** has no ³¹P NMR spectrum.

3.3.10. *Interaction of 2 with H₂S*

An excess of H₂S (33.6 mL, 1.5 mmol) was allowed to react with THF solution of **2** (0.50 g, 0.5 mmol) at ambient temperature and pressure for 1 h. Deep brown solution was evaporated to dryness in vacuum yields brown solid. No EPR or ³¹P NMR spectra were registered. Anal. calc. for

C₆₀H₅₂P₄N₄SCo, %: C, 69.03; H, 5.02; Co, 5.65; S, 3.07. Found, %: C, 69.53; H, 5.75; Co, 5.44; S, 3.16. Electronic (vis) spectrum (THF) λ, nm (ε): 430 (350). IR (cm⁻¹): 3190 (w, NH), 1600 (m), 1280 (s), 1220 (m), 1115 (m), 1025 (w), 1000 (w), 915 (m), 750 (s), 720 (s), 690 (s), 600 (w), 520 (s). The product was formulated tentatively as phosphino-sulfide [(HNPh-PPh₂=N-PPh₂)₂CoS]_x.

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