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Phosphinohydrazines and phosphinohydrazides M(–N(R)–N(R)–PPh$_2$)$_n$ of some transition and main group metals: synthesis and characterization Rearrangement of Ph$_2$P–NR–NR– ligands into aminoiminophosphorane, RN=PPh$_2$–NR–, and related chemistry

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Abstract

The reactions of phosphinohydrazines ArNH–N(Ar)–PPh$_2$ {Ar = Ph (**2a**), *p*-Bu^t–C$_6$H$_4$– (**2b**)} with metal silylamides M[N(SiMe$_3$)$_2$]$_n$, {M = Fe(II), Fe(III), Co(II), Ni(I), Cu(I)} or the reactions of lithium salts ArN(Li)–N(Ar)–PPh$_2$ with metal halides (GeCl$_2$, ZnCl$_2$, FeBr$_2$, CoCl$_2$, NiBr$_2$, CrCl$_3$, MnCl$_2$) are strongly dependent on nature of a metal and its ligand environment. Early transition metals or non-transition metals form stable phosphinohydrazides M[N(Ar)N(Ar)PPh$_2$]$_n$ {M = Li, Zn, Ge(II), Mn(II), Cr(III), Fe(II)}. Starting ligand **2a** and germylene Ge(NPhNPhPPh$_2$)$_2$ (**7**) were characterized by X-ray analysis. Germanium is coordinated additionally with a phosphorus atom of one of the diphenylphosphine groups. The distance Ge···P was found to be 2.563(1) Å. This coordination leads to an appreciable increase in a pyramidal geometry of nitrogen atoms relatively to a non-coordinated fragment. Late transition metals (Co, Ni, Cu) and metals with enhanced oxidation state (Fe^{3+}) cause transformation of a phosphinohydrazide ligand. For Co(II), Ni(II), Fe(III) this leads quantitatively to aminoiminophosphoranates M(NAr–PPh$_2$=NAr)$_n$. Complex Co[N(C$_6$H$_4$Bu^t)–PPh$_2$=N–C$_6$H$_4$Bu^t]$_2$ (**11**) was characterized by X-ray analysis. Nickel(I) silylamide, (Ph$_3$P)$_2$NiN(SiMe$_3$)$_2$, being reacted with **2a** yields azobenzene complex, (Ph$_3$P)$_2$Ni(PhN=NPh), while copper(I) silylamide originally forms (PhNH–NPh–PPh$_2$)$_2$CuN(SiMe$_3$)$_2$ (**18**). Heating of the latter in toluene solution yields insoluble copper(I) diphenylphosphide, azobenzene, **2a** and hexamethyldisilazane. The reaction of hydrazobenzene with Ph$_2$PCl (1:1) in methylene chloride for three days gives aminoiminophosphorane dihydrochloride [PhNH–PPh$_2$=NPh] · 2HCl (**3**) inquantitative yield.

Keywords: Transition metal complexes; Phosphazanes; Phosphinoamides; Phosphinohydrazines; Amidoimidophosphoranes; Germylenes; X-ray diffraction

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1. Introduction

In spite of great variety of known neutral ambidentate (P, N)-ligands, our knowledge on the ligands of type **I**, containing σ-bonded nitrogen and terminal

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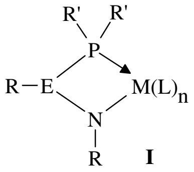
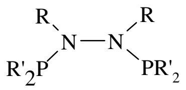
phosphorus(III) atoms are rather poor. In part this is due to low availability of starting compounds. Meanwhile, the coordination chemistry of such ligands is an area of increasing interest owing to their versatile behavior depending on metal nature. Here phosphorus, which has a predisposition for combination with soft metals (i.e. late transition metals or metals in low oxidation states), is juxtaposed with a hard nitrogen center (which is predisposed to combination with early transition metals or metals in high oxidation states).

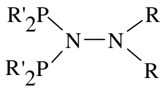


M-transition or non-transitionmetal;
E- nonmetal
L- concomitant ligand

Phosphinohydrazines of types II–IV, being considered as ligands in organometallic and coordination chemistry, possess unusual properties dependent on (1) partial double bonding between phosphorus and nitrogen; (2) relative weakness of P–N and N–N bonds. The stability and reactivity of the complexes containing phosphinohydrazine ligands are often determined by nature of a metal atom and its environment. The known transition metal complexes with ligands of the types **II** (R = Me, Et; R′ = Cl, Ph, OPh, CH_2Ph) [1–3]; **III** and **IV** (R = Me, R′ = Ph, R″ = Me, H) [4] include mono-P or bidentate P,P′-coordination to a metal. There are no sufficient evidences for a P,N-chelation in the complexes with ligands of type **II**–**IV** [4]. Apparently this is due to a strong interaction between phosphorus and nitrogen making the phosphorus centers more basic. The metal complexes containing single-charged ligands of type **V** are still unknown.



II



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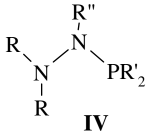
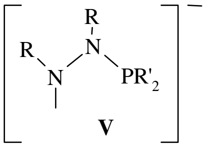


IV



V

The goals of our investigation include the preparation and study of η^2[P, σ-N]-bonded phosphinohydrazides of various metals as well as the investigation of phosphinohydrazines **2a**, **2b** as ligand precursors.

2. Results and discussion

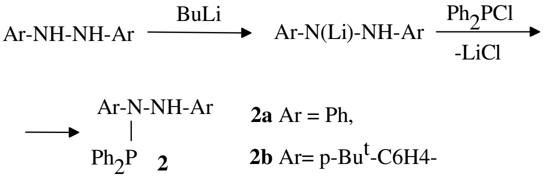
2.1. Phosphinohydrazines $ArNH{-}NAr{-}PPh_2$ {Ar = Ph (**2a**), p-$Bu^t{-}C_6H_4{-}$ (**2b**)}

Diphenylphosphino-1,2-diarylhydrazines (aryl = Ph (**2a**), *p*-Bu^t–C_6H_4– (**2b**)) were synthesized from corresponding nitrobenzenes in three steps (Eqs. (1) and (2)). Hydrazobenzene **1a** is a well-known compound [5], while 1,2-di(p-*tert*-butylphenyl)hydrazine **1b** has been synthesized for the first time. The reduction of p-*tert*-butylnitrobenzene with the zinc powder gave white crystalline **1b** in a good yield. The substance, however, is significantly more sensitive to oxygen than hydrazobenzene.

$$\mathrm{Ar{-}NO_2} \xrightarrow[\mathrm{H_2O/C_3H_7OH}]{\mathrm{Zn/NaOH}} \underset{\mathbf{1}}{\mathrm{Ar{-}NH{-}NH{-}Ar}} \qquad (1)$$

$$\mathrm{Ar} = \mathrm{Ph}\ (\mathbf{1a}),\ p\text{-}\mathrm{Bu}^t\text{–}\mathrm{C_6H_4}\text{–}\ (\mathbf{1b})$$

Monolithium derivatives of hydrazoarenes were prepared in situ by the reaction of butyllithium with an equivalent of the corresponding diaryhydrazine. Subsequent treatment with chlorodiphenylphosphine affords desirable hydrazophosphines **2a**, **2b**:



$$\text{Ar-NH-NH-Ar} \xrightarrow{\text{BuLi}} \text{Ar-N(Li)-NH-Ar} \xrightarrow[\text{-LiCl}]{\mathrm{Ph_2PCl}} \underset{\mathrm{Ph_2P}\quad \mathbf{2}}{\text{Ar-N-NH-Ar}} \quad \mathbf{2a}\ \text{Ar = Ph,}\ \ \mathbf{2b}\ \text{Ar= p-Bu}^t\text{-C6H4-} \qquad (2)$$

Large colorless crystals of **2a** and **2b** were obtained by crystallization from abs. ethanol. The compounds do not prone to alcoholysis at room temperature. ^{31}P NMR chemical shifts of compounds **2a** and **2b** at room temperature were found to be +63.62 and +62.9 ppm, respectively. Crystals of **2a** are fairly stable to oxygen; solution of **2a** in CCl_4 remains unchangeable for three days judging by ^{31}P NMR spectrum.

2.2. Structural investigations of **2a**

Crystal data and some details of the data collection and refinement for **2a** are given in Table 1. Selected bond distances and angles for **2a** are given in Table 2. The molecular structure of **2a** with the atom numbering scheme is shown in Fig. 1. Each nitrogen atom in diphenylphosphino-1,2-diphenylhydrazine (**2a**) has a slightly distorted planar-trigonal environment. The sums of the angles are 356.16° and 358.13° at the N(1) and N(2) atoms, respectively. The P–N and N–N distances are 1.7280(13) and 1.4008(18) Å, respectively, as expected.

It was found that crystals of **2a** (as well as **2b**) obtained from different solvents have various positions of the NH band in IR-spectra. Product **2a**, prepared by slow crystallization from abs. ethanol, shows a single

Table 1
Summary of crystal and refinement data for complexes

	Ph_2P–NPh–N(Ph)H (**2a**)	{Ge(NPh–NPh–$PPh_2)_2$}($C_4H_8O_2$) (**7**)	[$Bu^tC_6H_4N{=}Ph_2P$–$NC_6H_4Bu^t]_2Co \cdot$ (C7H8) (**11**)	$(Ph_3P)_2$Ni(PhN=NPh) (**13**)
Empirical formula	$C_{24}H_{21}N_2P$	$C_{52}H_{48}N_4P_2GeO_2$	$C_{71}H_{80}CoN_4P_2$	$C_{48}H_{40}N_2NiP_2$
Formula weight	368.40	895.45	1110.26	765.47
Temperature (K)	223(2)	243(2)	293	100(2) K
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$
Unit cell dimensions				
a (Å)	9.9509(14)	9.5505(10)	30.906(5)	14.6589(9)
b (Å)	10.1626(16)	25.345(3)	21.514(3)	13.6712(8)
c (Å)	11.3099(17)	18.926(2)	21.509(3)	18.8730(11)
α (°)	95.902(3)	90	90	90
β (°)	95.893(3)	96.959(2)	111.094(3)	94.401(1)
γ (°)	118.851(2)	90	90	90
V Å^{-3}	981.1(3)	4547.4(8)	13343(3)	3771.1(4)
Z	2	4	8	4
D_{calc} (Mg/m^3)	1.247	1.308	1.105	1.348
Absorption coefficient (mm^{-1})	0.151	0.789	0.346	0.637
Crystal size (mm^3)	0.30 × 0.20 × 0.10	0.30 × 0.30 × 0.10	0.25 × 0.25 × 0.10	0.15 × 0.15 × 0.15
Reflections collected	5162	26815	31167	11835
Independent reflections [R_{int}]	2807 [0.0200]	8921 [0.0374]	8733 [0.0600]	4423 [=0.0253]
Reflection with $I > 2\sigma(I)$	2501		6071	3918
Absorption correction	Semi-empirical from equivalents, SADABS	Semi-empirical from equivalents, SADABS	Semi-empirical from equivalents, SADABS	Semi-empirical from equivalents, SADABS
Maximum/minimum transmission	1.000/0.945	0.925/0.798	1.000/0.707	1.000/0.872
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2807/0/328	8921/12/604	8733/0/640	4423/0/320
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0310$, $wR_2 = 0.0879$	$R_1 = 0.0522$, $wR_2 = 0.1320$	$R_1 = 0.0939$, $wR_2 = 0.2474$	$R_1 = 0.0367$, $wR_2 = 0.0901$
R indices (all data)	$R_1 = 0.0352$, $wR_2 = 0.0925$	$R_1 = 0.0781$, $wR_2 = 0.1414$	$R_1 = 0.1203$, $wR_2 = 0.2660$	$R_1 = 0.0422$, $wR_2 = 0.0932$
Largest difference peak and hole (e Å^{-3})	0.203 and −0.180	0.794 and −0.267	1.746 and −0.509	0.533 and −0.231

Table 2
Selected bond lengths (Å) and angles (°) for **2a**

P(1)–N(2)	1.7280(13)
P(1)–C(13)	1.8266(16)
P(1)–C(19)	1.8318(17)
N(1)–C(1)	1.395(2)
N(1)–N(2)	1.4008(18)
N(1)–H(1)	0.83(2)
N(2)–C(7)	1.419(2)
N(2)–P(1)–C(13)	100.50(7)
N(2)–P(1)–C(19)	102.05(7)
C(13)–P(1)–C(19)	102.00(7)
C(1)–N(1)–N(2)	120.46(13)
C(1)–N(1)–H(1)	119(1)
N(2)–N(1)–H(1)	117(1)
N(1)–N(2)–C(7)	114.81(12)
N(1)–N(2)–P(1)	120.58(10)
C(7)–N(2)–P(1)	122.74(10)

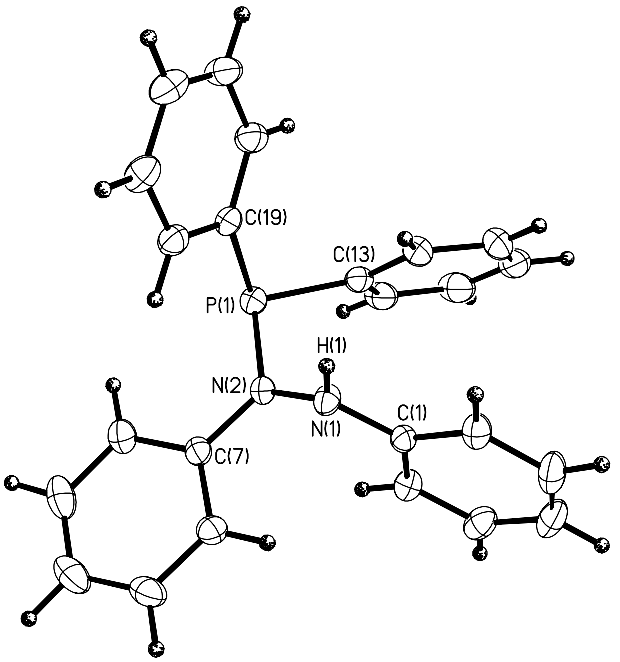
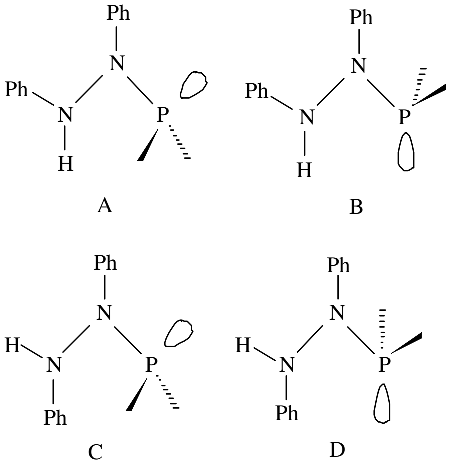


Fig. 1. Molecular structure of $\mathrm{Ph_2P{-}N(Ph){-}N(Ph)H}$ (**2a**).

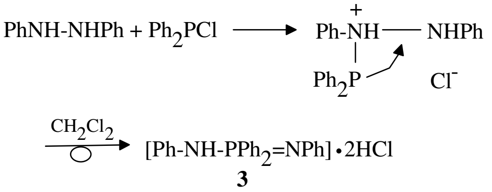
NH band at 3300 cm^{-1}. The same product prepared by fast crystallization from *i*-propanol shows two bands: at 3300 and 3320 cm^{-1}. The solutions of these products in dichloromethane show a sharp absorption peak at 3380 cm^{-1}. Such behavior of **2a** is in a good agreement with the properties of previously studied diphosphinohydrazine $\mathrm{F_2P{-}NMe{-}NMe{-}PF_2}$ [6], showing a temperature dependent ^{19}F NMR spectrum, suggesting large torsional barriers about the P–N and N–N bonds. On this basis, diphenylphosphino-1,2-diarylhydrazines with essentially planar nitrogen environments may adopt several conformations (A–D); the found structure of **2a** corresponds to conformation A.



Our attempts to prepare **2a** in another way, using $\mathrm{Et_3N}$ as dehydrochlorinating agent, were unsuccessful. Unexpectedly, hydrazobenzene in ether, toluene or methylene chloride solutions does not react with $\mathrm{Ph_2PCl}$ in the presence of $\mathrm{Et_3N}$.

$$\mathrm{PhNH{-}NHPh + Ph_2PCl + Et_3N \xrightarrow{\ /\!/\ } Ph_2P{-}NPh{-}NPhH + [Et_3NH]Cl} \qquad (3)$$

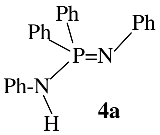
Starting reagents were separated from the reaction mixture after 3 h of contact. We found, however, another interaction between hydrazobenzene and $\mathrm{Ph_2PCl}$ in methylene chloride without $\mathrm{Et_3N}$. When an equimolar mixture of the reactants was allowed to stand for three days at 20 °C, the color of solution steadily turned orange then the solution becames colorless. Finally, an abundant white crystalline precipitate was formed. According to the element analysis, IR and NMR spectra we characterized this substance as amidoimidophosphorane dihydrochloride $\mathrm{[PhNH{-}PPh_2{=}NPh]\cdot 2HCl}$ (**3**). The yield of **3** was found to be ~100%. No other products were observed. We had no purposes in mechanistic investigation of such an interesting interaction; note, however, that methylene chloride acts not only as a solvent, but as a reactant, since product **3** contains two chlorine atoms per mole while the yield of **3** is quantitative. So, we have found conditions for the PNN→NPN rearrangement. Eq. (4) does not explain however the exact mechanism of this reaction.



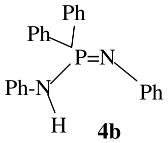
$$\mathrm{PhNH{-}NHPh + Ph_2PCl \longrightarrow Ph{-}\overset{+}{\underset{\displaystyle Ph_2P}{N}}H{-}NHPh \quad Cl^-} \qquad (4)$$
$$\mathrm{\xrightarrow[\circlearrowleft]{CH_2Cl_2} \underset{\mathbf{3}}{[Ph{-}NH{-}PPh_2{=}NPh]\cdot 2HCl}}$$

Dihydrochloride **3** forms pure free base $\mathrm{PhNH{-}PPh_2{=}NPh}$ (**4**) after washing with aqueous $\mathrm{NH_3}$ or NaOH. Compound **4** shows very strong absorption at

1300 cm^{-1} assigned to stretching vibrations of P=N double bond [7]. Interestingly, **4** shows a single resonance at −4.12 ppm in the ^{31}P NMR spectrum at 20 °C while the HPLC analysis shows two peaks of equal intensity, probably attributed to two isomers **4a** and **4b.**



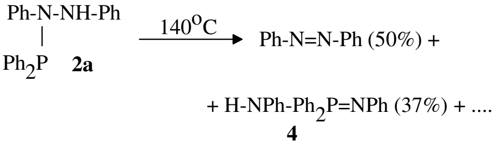
4a



4b

Therefore, reaction (4) can be considered as a novel approach to aromatic aminoiminophosphoranes [8,9].

Compounds **2a**, **2b** are thermally stable up till to 140 °C. Above this temperature the crystals of **2a** decompose to form azobenzene and the mixture of phosphorus-containing products. The main product, aminoiminophosphorane, H–N(Ph)–PPh_2=NPh (**4**), which is the structural isomer of **2a**, was identified by ^{31}P NMR and HPLC.

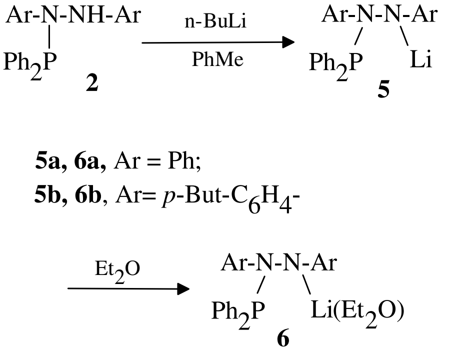


$$\underset{Ph_2P\quad \mathbf{2a}}{\text{Ph-N-NH-Ph}} \xrightarrow{140^{o}C} \text{Ph-N=N-Ph (50\%)} + \text{H-NPh-}Ph_2P\text{=NPh (37\%)} + \ldots \quad (\mathbf{4}) \tag{5}$$

The crystals of **2b** decompose similarly giving presumably substituted azobenzene and H–N(Ar)–PPh_2=NAr (Ar = *t*-BuC_6H_3–) (tentative suggestion).

2.3. Lithium phosphinohydrazides

The treatment of **2a** and **2b** with butyllithium yields pale yellow solutions which after concentrating gave viscous oil. The study of NMR spectra of **5a** in C_6D_6 shows a ^7Li resonance at $\delta = -2.88$ (s) ppm, and a ^{31}P resonance at 55.00 (s) ppm. Absence of the ^7Li–^{31}P coupling suggests that there is no strong Li–P interaction in benzene solution. The NMR spectrum of **5a** in C_6D_6 does not change for two months. An addition of small amounts of ether to toluene solutions of **2a** and **2b** affords colorless fine crystalline solids of their lithium salts **6a** and **6b**, respectively.



$$\underset{Ph_2P\quad \mathbf{2}}{\text{Ar-N-NH-Ar}} \xrightarrow[\text{PhMe}]{\text{n-BuLi}} \underset{Ph_2P\quad Li\ \ \mathbf{5}}{\text{Ar-N-N-Ar}} \tag{6}$$

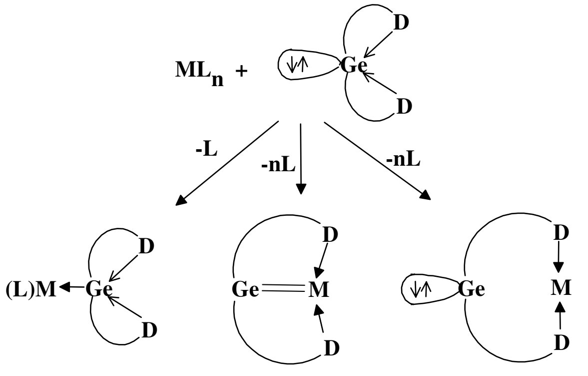
5a, 6a, Ar = Ph;
5b, 6b, Ar= *p*-But-C_6H_4-

$$\xrightarrow{Et_2O} \underset{Ph_2P\quad Li(Et_2O)\ \ \mathbf{6}}{\text{Ar-N-N-Ar}}$$

We explored another method synthesizing of **5a**, by the reaction of dilithium-1,2-diphenylhydrazide with one equivalent of chlorodiphenylphosphine, however this way lead to essential quantities of byproducts. By this reason the direct synthesis of bis(diphenylphospino)-1,2-diphenylhydrazine also was unsuccessful.

2.4. Germanium (II) phosphinohydrazide, {Ge(NPh–NPh–PPh_2)$_2$}(dioxane) (7)

Lappert type germylenes Ge(NR_2)$_2$ (R = Me_3Si, alkyl, aryl) are quite stable compounds [10–12] widely used as monodentate ligands in coordination and organometallic chemistry [13]. At the same time, the carbenoids GeR_2, whose substituent R contains additional chelating functions, are few in number but attract considerable interest [14]. In particular, such compounds can be used as convenient ligands in coordination and organometallic chemistry due to their versatile co-ordination properties depending on the σ-donor and π-acceptor activity of the Ge(II), M and D centers.



D - donor atom (P, N, O)

The interaction of lithium phosphinohydrazide **6a** with $GeCl_2$(dioxane) in THF immediately gives an orange-red solution. The change of THF by toluene causes precipitation of LiCl. The latter was filtered off while the solution was concentrated and the final product was formed as a yellow powder (**7**) from diethyl ether.

$$GeCl_2(diox) + 2Ph_2P\text{–NPh–NPh–Li} \rightarrow \underset{\mathbf{7}}{Ge(NPh\text{–}NPh\text{–}PPh_2)_2} + 2LiCl + diox \tag{7}$$

The compound shows solvatochromic effect. While the color of **7** in THF is orange-red, the toluene or diethyl ether solutions have pale yellow coloring. Germylene **7** can be easily purified by re-crystallization from warm ether solution. However, the crystals suitable for X-ray analysis were obtained from the dioxane/toluene (1:1) mixture.

Table 3
Bond lengths (Å) and angles (°) for Ge(NPhNPh–PPh$_2$)$_2$ (**7**)

Ge(1)–N(3)	1.895(2)
Ge(1)–N(1)	1.997(2)
Ge(1)–P(1)	2.5630(7)
P(1)–N(2)	1.699(2)
P(2)–N(4)	1.753(2)
N(1)–N(2)	1.454(3)
N(3)–N(4)	1.380(3)
N(3)–C(25)	1.428(3)
N(2)–C(7)	1.436(3)
N(4)–C(31)	1.421(3)
N(3)–Ge(1)–N(1)	103.40(9)
N(3)–Ge(1)–P(1)	107.80(6)
N(1)–Ge(1)–P(1)	65.67(6)
N(2)–P(1)–C(19)	108.08(11)
N(2)–P(1)–C(13)	108.63(11)
C(19)–P(1)–C(13)	108.08(12)
N(2)–P(1)–Ge(1)	79.43(7)
N(4)–P(2)–C(43)	102.79(10)
N(4)–P(2)–C(37)	103.73(11)
C(43)–P(2)–C(37)	100.22(11)
C(1)–N(1)–N(2)	114.08(19)
C(1)–N(1)–Ge(1)	113.56(15)
N(2)–N(1)–Ge(1)	107.62(13)
C(7)–N(2)–N(1)	117.79(19)
C(7)–N(2)–P(1)	123.30(16)
N(1)–N(2)–P(1)	105.69(14)
N(4)–N(3)–C(25)	115.14(19)
N(4)–N(3)–Ge(1)	109.96(15)
C(25)–N(3)–Ge(1)	133.46(16)
N(3)–N(4)–C(31)	118.00(18)
N(3)–N(4)–P(2)	121.63(15)
C(31)–N(4)–P(2)	119.06(17)
C(6)–C(1)–C(2)	117.5(2)
C(6)–C(1)–N(1)	125.8(2)
C(2)–C(1)–N(1)	116.6(2)

2.5. Structural description of 7

The crystal data and some details of the data collection and refinement for **7** are given in Table 1. Selected bond distances and angles for **7** are in Table 3. Drawing of the molecular structure of **7** with the atom numbering scheme is shown in Fig. 2. The crystal structure consists of discrete molecules of **7** and a disordered dioxane molecule which has no shortened contacts with **7** and may be considered as a solvation molecule. The Ge(1) atom is coordinated to two N atoms and the P(1) atom of one of the diphenylphosphine groups. The distance Ge(1)···P(1) (2.563(1) Å) is significantly shorter than the sum of the van der Waals radii of these atoms (3.9 Å [15]). Owing to such coordination the germanium atom adopts pyramidal pseudo-sp^3 configuration. It is worth noting that the Ge(1)···P(1) distance (2.563(1) Å) in compound **7** is within the range of similar distances in germanium (II) phosphinometanid, Ge[(Me$_2$P)$_3$C]$_2$, (2.36–2.93 Å [16]). The coordination of one of the N(Ph)N(Ph)PPh$_2$ groups leads to significant changes in its geometry as compared with the non-coordinated fragment. The Ge(1)–N(1) and N(1)–N(2) distances (1.997(2) and 1.454(3) Å, respectively) are noticeably longer than the analogous Ge(1)–N(3) (1.895(2) Å) and N(3)–N(4) (1.380(3) Å) distances in the non-coordinated ligand. The N(1)–N(2) bond length in **1** is also longer than the nitrogen–nitrogen bond in phosphinohydrazine Ph$_2$P–N(Ph)–N(Ph)H (1.401(2) Å), while the N(2)–P(1) distance (1.699(2) Å) and the N(1)N(2)P(1) angle (105.69(14)°) are much less than the N(4)–P(2) bond length (1.753(2) Å) and the N(3)N(4)P(2) angle (121.63(15)°) in the non-coordinated fragment.

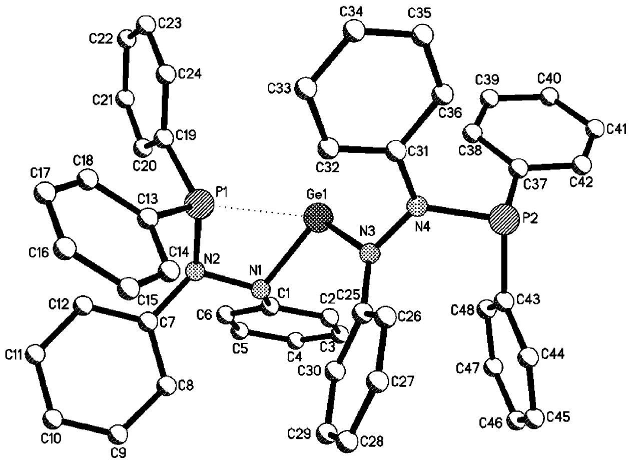
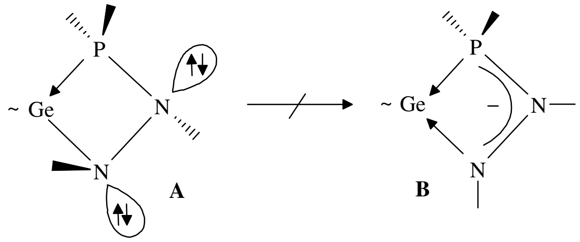


Fig. 2. Molecular structure of [Ge(NPhNPh–PPh$_2$)$_2$] · (C$_4$H$_8$O$_2$) (**7**). The H atoms and solvent molecule are omitted for clarity.

Four-membered cycle Ge-N(1)–N(2)–P(1) is flat, the atoms being on average 0.067 Å out of this plane. It is of interest that the N(1) and N(2) atoms of this cycle possess a pyramidal geometry in contrast to the N(3), N(4) atoms. The deviations of the N(1), N(2) atoms from the planes of the Ge(1)N(2)C(1) and N(1)P(1)C(7) fragments are 0.46 and 0.32 Å, respectively, while the analogous deviations of the N(3) and N(4) atoms from the Ge(1)N(4)C(25) and N(3)P(2)C(31) planes are 0.11 and 0.10 Å. The sums of angles at the N(1) and N(2) are 335° and 347°, respectively, while these sums for the N(3) and N(4) atoms were found to be 359°. The literature data indicate that the pyramidal geometry of N(1) and N(2) found in **7** is unusual, because the nitrogen atoms in phosphazanes [17] and phosphoranates [18] as well as germanium (II) amidinate Ge[CyNC(Me)NCy]$_2$ (Cy = cyclohexyl) [19] have a planar environment due to p_π–d_π and p_π–p_π conjugation. The consideration of the structure of **7** indicates that steric factors could not affect the geometry of the N(1) and N(2) atoms. The geometry change can be caused by specific charge localization in the co-ordinated fragment which makes impossible the conjugation according to the canonical formula “B”:



It is interesting that the ^{31}P NMR spectrum of **7** at ambient temperature shows only one resonance at 63.2 ppm, which can indicate the absence of coordination under these conditions or the existence of a fast equilibrium.

2.6. Zn[N(Ar)–N(Ar)–PPh$_2$]$_2$ (*8a, b*)

Anhydrous zinc chloride reacts with lithium phosphinohydrazides **2a** and **2b** in tetrahydrofurane to form yellow solutions. After work up we succeeded to separate a fine crystalline yellow precipitate of **8a** from ether solution.

$$\begin{aligned}&\mathrm{ZnCl_2 + 2Ph_2P{-}N(Ar){-}N(Ar)Li}\\&\quad\rightarrow \mathrm{Zn[N(Ar){-}N(Ar){-}PPh_2]_2 + 2LiCl}\qquad (8)\\&\quad \mathrm{Ar = Ph}\ (\mathbf{8a}),\ p\text{-}\mathrm{Bu}^t\text{–}\mathrm{C_6H_4}\text{–}\ (\mathbf{8b})\end{aligned}$$

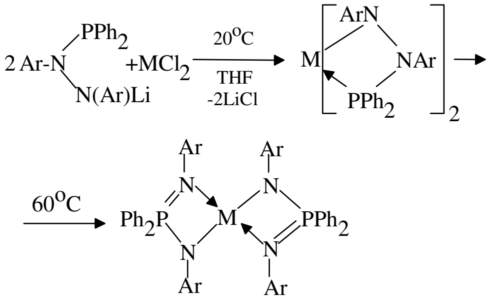
The appearance of two single resonances in the ^{31}P NMR spectrum of **8a** at $\delta = 63.10$ and 63.16 ppm is indicative of the existence of the P→Zn coordination in solution. In the case of a bidentate coordination of two NNP moieties, zinc should adopt a tetrahedral geometry and the phosphorus atoms will be equivalent. It may be proposed therefore that the coordination of only one NNP group to the zinc atom takes place in solution. Compound **8b** was prepared as viscous oil. ^{31}P NMR spectrum shows resonances at $\delta = 63.00$ and 62.91 ppm. Our attempts to crystallize the product from various solvents were unsuccessful. Compounds **8a**, **8b** are moisture sensitive and yield free ligands **2a** and **2b** after alkaline hydrolysis.

2.7. The behavior of phosphinohydrazide ligands depending on transition metal nature and the environment

2.7.1. Co, Ni

The metal–nitrogen bond in amido complexes (L$_n$M–NR$_2$) of late transition metals is relatively weak in comparison with the other late-metal M–X bonds (halide, alkyl, hydrido, etc.). This is in part due to the contrast between the hard nitrogen-donor ligands and the soft electron rich metals, that is considered to be energetically destabilizing. This effect is exacerbated by the general lack of stabilizing π-donor interactions. Strategies for the synthesis of amido complexes of the low-valent late transition metals usually involve the incorporation of soft phosphine as supporting ligand or the utilization of sterically hindering ligands [20]. In our investigation we used the first approach. The behavior of phosphinohydrazide ligands bonded to late transition metal seems to be intriguing from this point of view.

Lithium diphenylphosphino-1,2-diphenylhydrazide (**3a**) easily reacts at room temperature with cobalt (II) and nickel (II) halides in THF forming dark colored solutions. The attempts to separate pure samples of Co (II) and Ni (II) phosphinohydrazides, M[NAr–NAr–PPh$_2$]$_2$ (Eq. (9)), were unsuccessful and lead to a mixture of small-sized crystals of different nature. The prolonged heating of the solutions yields, however, the individual product. Poor soluble Ni and Co complexes **9**, **10** (Eq. (8)) are formed quantitatively in both reactions. These compounds show high thermal stability, and have identical IR spectra with strong peaks at 1300 and 1270 cm^{-1}.

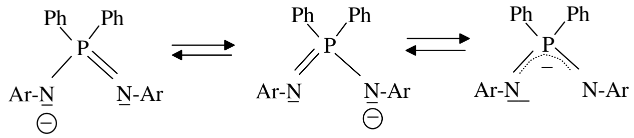


(9)

9 M= Co, Ar= Ph
10 M= Ni, Ar= Ph
11 M= Co, Ar= -C$_6$H$_4$-Bu^t

Lithium diphenylphosphino-1,2-di(*p*-*tert*-butylphenyl)hydrazide (**6b**) reacts with CoCl$_2$ in the same way. The final complex (**11**) is better soluble and can be recrystallized from various solvents.

The crystals suitable for an X-ray study were prepared from a toluene solution. The structure of cobalt complex **11** is depicted in the Fig. 3. Selected bond distances and angles for **11** are given in Table 4. Each aminoiminophosphorane ligand is bonded to the cobalt(II) center by a *N*,*N*′-chelating fashion, forming a {CoN$_4$P$_2$} moiety. Both CoN$_2$P-fragments are planar within 0.06 Å. The coordination of the Co atom is a significantly distorted tetrahedron with dihedral angles between two average CoN$_2$P planes of 82.7(2)°. The Co–N bond distances are similar with an average distance of 2.015(11) Å. The planar conformation of the PN$_2$Co fragments with the close values of the Co–N distances testify to the delocalized structure of Ph$_2$P(NAr)$_2$ ligands without a π-interaction with the metal atom:



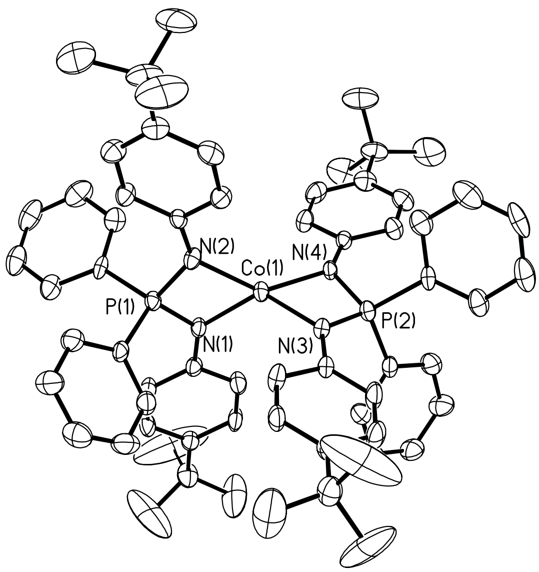
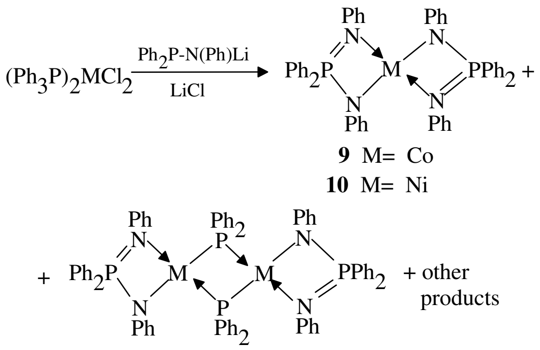


Fig. 3. Molecular structure of $[(Bu^tC_6H_4N{=}Ph_2P{-}NC_6H_4Bu^t)_2Co] \cdot (C_7H_8)$ (**11**). The H atoms and solvent molecule are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for $[Bu^tC_6H_4N{=}Ph_2P{-}NC_6H_4Bu^t]_2Co$ (C_7H_8) (**11**)

Co(1)–N(1)	2.025(4)
Co(1)–N(2)	2.017(5)
Co(1)–N(3)	1.999(4)
Co(1)–N(4)	2.020(4)
Co(1)–P(1)	2.6730(16)
Co(1)–P(2)	2.6704(16)
P(1)–N(1)	1.602(5)
P(1)–N(2)	1.624(5)
P(2)–N(3)	1.603(5)
P(2)–N(4)	1.623(5)
N(1)–Co(1)–N(2)	73.62(18)
N(1)–Co(1)–N(3)	126.96(19)
N(1)–Co(1)–N(4)	125.85(18)
N(2)–Co(1)–N(3)	124.75(18)
N(2)–Co(1)–N(4)	141.33(19)
N(3)–Co(1)–N(4)	73.59(18)
N(1)–Co(1)–P(2)	133.38(13)
N(2)–Co(1)–P(2)	151.56(13)
N(3)–Co(1)–P(1)	132.95(14)
N(4)–Co(1)–P(1)	152.31(13)
P(1)–Co(1)–P(2)	164.87(6)
N(1)–P(1)–N(2)	97.3(2)
N(3)–P(2)–N(4)	96.5(2)
C(13)–N(1)–P(1)	130.0(4)
C(13)–N(1)–Co(1)	135.1(4)
P(1)–N(1)–Co(1)	94.2(2)
C(23)–N(2)–P(1)	128.6(4)
C(23)–N(2)–Co(1)	137.9(3)
P(1)–N(2)–Co(1)	93.8(2)
C(45)–N(3)–P(2)	128.7(4)
C(45)–N(3)–Co(1)	135.6(4)
P(2)–N(3)–Co(1)	95.1(2)

Note, cobalt and nickel cyclophosphazane complexes (**9**, **10**) were isolated and characterized earlier as products of the reaction of lithium diphenylphosphinophenylamide ($Ph_2P{-}NPh{-}Li$) with metal halides (Eq. (10)) [21].



(10)

In the course of these non-stoichiometric reactions a cleavage and a formation of new P–N bonds occurred.

We explored also another approaches to **9**. The heating of free ligand $Ph_2P{-}NPh{-}NPhH$ with cobalt(II) silylamide cleanly affords fine crystalline **9**:

$$Co[N(SiMe_3)_2]_2 + 2Ph_2P{-}NPh{-}NPhH \rightarrow \underset{\mathbf{9}}{Co[NPh{-}PPh_2{=}NPh]_2} + 2(Me_3Si)_2NH \tag{11}$$

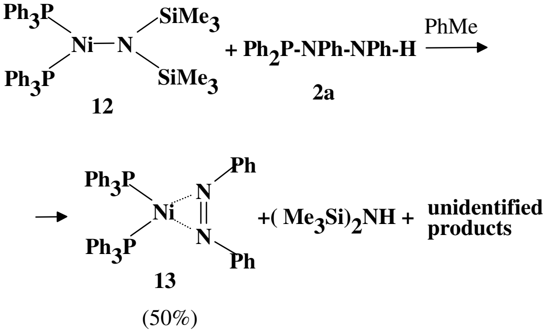
The reaction of $CoCl_2$ with lithium salts of aminoiminophosphorane **4** in THF gave the same final product **9**.

$$CoCl_2 + 2Li[NPh{-}PPh_2{=}NPh] \rightarrow \underset{\mathbf{9}}{Co[NPh{-}PPh_2{=}NPh]_2} + 2LiCl \tag{12}$$

It is necessary to notice that the last reaction proceeds slower than reaction (9), perhaps due to less nucleophility of the $[PhN{-}PPh_2{=}NPh]^-$ anion caused by the charge delocalization in this fragment.

The reason of the rearrangement (Eq. (9)) is not completely clear since nickel and cobalt as a late transition metals usually form strong coordination bonds to tertiary phosphines. Perhaps, the formation of the NPN-moiety with tetracoordinate phosphorus combined with the *N*,*N*′-amidinate-like bonding to nickel (cobalt) are thermodynamically more favorable than the phosphorus pπ–dπ back donation to nickel atom together with week a single amido-bond N–Ni (N–Co).

The course of PNN-ligand transformation essentially depends on metal oxidation state and metal environment. When nickel(I) bis(triphenilphosphine)–bis (trimethylsilyl)amide (**12**) reacts with free phosphinohydrazine **2a** we find a single isolated crystalline product – bis(triphenylphosphino)azobenzene nickel(0) complex (**13**). The structure of **13** was confirmed by the X-ray analysis (Fig. 4)



(13)

The molecule **13** is an analogue of known bis(tritolylphosphino)azobenzene nickel(0) [22], so the structural parameters of the both molecules are very similar. Selected bond distances and angles for **13** are shown in Table 5. We could not isolate any other products of this reaction. According to the ^{31}P NMR spectrum of the residue, a complex mixture of phosphorus-containing products was formed.

2.7.2. Fe

The phosphinohydrazine ligands show quite different behavior dependent on the oxidation state of iron. Ferrous bis(trimethylsilyl)amide slowly reacts with phosphinohydrazine **2a** in toluene to form a thermally stable dark green solution of **14**. The solvent and hexamethyldisilazane were removed in vacuum yielding a black-green powder of **14**

$$\mathrm{Fe[N(SiMe_3)_2]_2 + 2Ph_2P\text{–}NPh\text{–}NPhH} \\ \rightarrow \underset{\mathbf{14}}{\mathrm{Fe[NPh\text{–}NPh\text{–}PPh_2]_2}} + 2\mathrm{(Me_3Si)_2NH} \qquad (14)$$

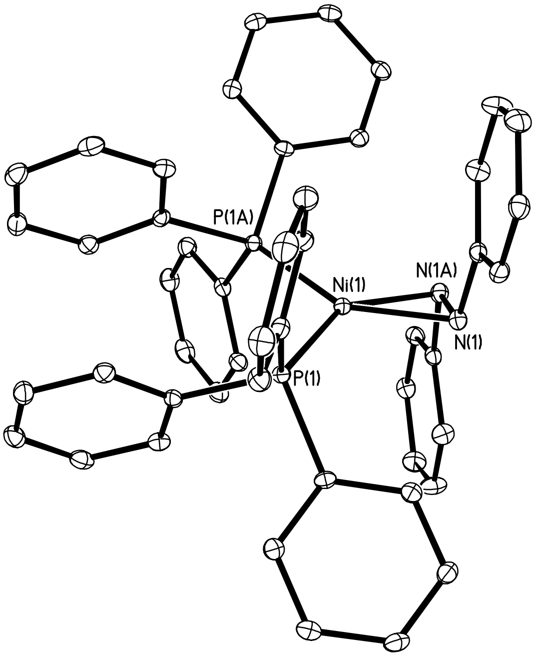


Fig. 4. Molecular structure of $\mathrm{(Ph_3P)_2Ni(PhN{=}NPh)}$ (**13**). The H atoms are omitted for clarity.

Table 5
Selected bond lengths (Å) and angles (°) for **13**

Ni(1)–N(1)	1.9450(15)
Ni(1)–P(1)	2.1985(5)
P(1)–C(13)	1.8269(17)
P(1)–C(7)	1.8312(17)
P(1)–C(19)	1.8424(17)
N(1)–N(1a)	1.371(3)
N(1)–C(1)	1.437(2)
N(1)–Ni(1)–N(1a)	41.26(8)
N(1a)–Ni(1)–P(1)	144.65(4)
N(1)–Ni(1)–P(1)	105.74(4)
P(1)–Ni(1)–P(1a)	109.00(3)
N(1a)–N(1)–C(1)	110.66(16)
N(1a)–N(1)–Ni(1)	69.37(4)
C(1)–N(1)–Ni(1)	101.21(10)

The same product was prepared by the reaction of iron(II) bromide with the lithium salt of phosphinohydrazine (**2a**). Compound **14** is moderately moisture and oxygen sensitive. An alkaline hydrolysis of **14** under anaerobic conditions in a water–ether mixture gives pure phosphinohydrazine **2a** and ferrous hydroxide. All attempts to obtain the crystals of **14** using various solvents (including coordinated ones) were in vain. We suppose it might be due to a simultaneous formation of several labile conformers (or coordination oligomers) of this compound. The IR spectrum of **14** differs significantly from the spectra of aminoiminophosphoranides **9**, **10** and contains a set of the bands of low to moderate intensity in the 1300–800 cm^{-1} region and strong peaks at 740 and 690 cm^{-1}.

In contrast to the iron(II) compound, iron(III) silylamide reacts with **2a** to form aminnoiminophosphoranate **15**

$$\mathrm{Fe[N(SiMe_3)_2]_3 + 3Ph_2P\text{–}NPh\text{–}NPhH} \\ \rightarrow \underset{\mathbf{15}}{\mathrm{Fe[NPh\text{–}PPh_2{=}NPh]_3}} + 3\mathrm{(Me_3Si)_2NH} \qquad (15)$$

Iron(III) complex **15** was separated as air stable, poor soluble, fine yellow crystals. The IR spectrum of **15** is identical to the spectra, obtained for nickel and cobalt aminoiminophosphoronates **9** and **10**. The main feature of these spectra is very strong absorptions at 1300 and 1270 cm^{-1}, assigned to the stretching vibrations of the N–P$^{\mathrm{V}}$=N moiety.

2.7.3. Cr, Mn

Chromium and manganese phosphinohydrazides **16a**, **16b** can be prepared by the reaction of anhydrous $\mathrm{CrCl_3}$ or $\mathrm{MnCl_2}$ with lithium salt **6a** in THF solution.

$$\mathrm{MCl}_n + n\underset{\mathbf{6a}}{\mathrm{Ph_2P\text{–}NPh\text{–}NPhLi(Et_2O)}} \\ \rightarrow \underset{\mathbf{16,17}}{\mathrm{M[NPh\text{–}NPh\text{–}PPh_2]}_n} + n\mathrm{LiCl} \qquad (16)$$

16 M = Cr, $n = 3$

17 M = Mn, $n = 2$

Chromium phosphinohydrazide (**16**) is a dark brown powder, stable in air. The toluene solutions of **16** are not decomposed by aqueous acids (!) (AcOH, HCl), but **16** reacts easily with a 25% aqueous ammonia solution to form chromium hydroxide and free ligand **2a**. Manganese (II) phosphinohydrazide, in contrast to **16**, is easily oxidized in air. An anaerobic treatment of **17** with a 25% aqueous ammonia solution yields manganese hydroxide (II) and free ligand as well. Unfortunately, manganese(II) phosphinohydrazide (**17**) cannot be considered as an individual compound, since chlorine content was found to be 3%.

2.7.4. Cu

Copper is known of its tendency to form more reliable coordination bonds with phosphines as compared to amines in the complexes containing ambidentate aminophosphine ligands.

The reaction of copper(I) silylamide with hydrazophosphine Ph2P–NPh–NPhH leads to the formation of orange crystalline adduct $(Me_3Si)_2NCu(Ph_2P–NPh–NPhH)_2$ (**18**) which gives red insoluble copper diphenylphosphide (**19**), azobenzene and initial ligand on heating in toluene solution.

$$\begin{aligned}&[CuN(SiMe_3)_2]_n + 2Ph_2P–NPh–NPhH\\&\xrightarrow{20\ ^\circ C} \underset{\mathbf{18}}{(Me_3Si)_2NCu(Ph_2P–NPh–NPhH)_2}\end{aligned}\tag{17}$$

$$\begin{aligned}&\mathbf{18} \xrightarrow{PhMe,\ 80^\circ C} \underset{\mathbf{19}}{[Ph_2PCu]_n} + PhN{=}NPh\\&+ Ph_2P–NPh–NPhH + (Me_3Si)_2NH\end{aligned}\tag{18}$$

Compound **19** was prepared earlier by another way in the reaction of Ph_2PSiMe_3 with CuCl [23].

As a rule the reactions involving transition metal silylamides require more acidic reagents than $(Me_3Si)_2NH$ to substitute silylamide function with another group. Phosphinohydrazines seem to be not much more acidic than hexamethyldisilazane. However, the reactions of **2a** with copper, nickel and cobalt silylamides proceed quite rapidly. Apparently this is due to formation of a coordination metal–phosphorus bond on the first stage of the reaction. This is confirmed by formation of compound **18**.

Possessing two different coordination sites and relatively week P–N and N–N bonds, phosphinohydrazide-ligand shows a variable behavior depending on a transition metal, its oxidation state and a ligand surrounding. For example, it is known that the reaction of bisphosphinohydrazine $(MeO)_2PN(Me)N(Me)P(MeO)_2$ with tricobalt cluster $PhCCo_3(CO)_9$ produced an unexpected compound with the phosphorus–phosphorus bond, $[PhCCo_3(CO)_8]_2[(MeO)_2PP(OMe)_2]$, suggesting the formal loss of the "N(Me)N(Me)" fragment [24,25].

3. Experimental

3.1. General considerations

Solvents were purified following standard methods [26]. Toluene and methylene chloride were thoroughly dried and distilled over P_2O_5 prior to use. Ether and THF were dried and distilled over Na/benzophenone.

Metal silylamides $Fe[N(SiMe_3)_2]_2$ [27], $Co[N(SiMe_3)_2]_2$ [27,28], $(Ph_3P)_2NiN(SiMe_3)_2$ [29], $[CuN(SiMe_3)_2]_n$ [30,31] 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 transition metals (Mn, Cr, Fe, Co, Ni, Cu) in the prepared compounds was provided by the methods described in [32].

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

NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions using "Bruker DPX-200" device, with Me_4Si as internal standard.

3.2. X-ray structure determinations

A summary of crystal data collection and refinement parameters for **2a**, **7**, **11** and **13** are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX CCD (**7**, **11**, **13**) and a Bruker P4 diffractometer equipped with a CCD detector (**2a**) (Mo Kα (λ = 0.71073 Å)) at 223(2) (**2a**), 243(2) (**7**) and 100 (**13**) K. X-ray diffraction experiment for **11** was carried out at room temperature (293 K) because crystals shattered at low temperature. Space groups of symmetry for **7**, **11** and **13** were determined based on systematic absences. All data sets were treated with SADABS absorption corrections (Sheldrick, G., Bruker-AXS, 2001). The structures were solved using direct methods and difference map techniques, and were refined by full-matrix least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms in **2a** were found on the F-map and refined with isotropic thermal parameters. In the other structures the H atoms were treated as idealized contributions. Disordered toluene molecules in **11** was treated by SQUEEZE [34]; corrections of the X-ray data by SQUEEZE (495 electron/cell) was slightly larger than the required value (400 electron/cell). All software and sources of scattering factors are contained in the

SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

3.3. Synthesis

*3.3.1. [p-^{t}Bu–C_6H_4–NH]$_2$ (**1b**)*

Zinc powder (14 g) was added stepwise to a boiling mixture of *p-tert*-butylnitrobenzene (6.3 g) in 35 ml of isopropyl alcohol and 10 g of NaOH in 30 ml of water. Hot colorless organic lawyer was decanted under argon atmosphere. Colorless crystals of **1b** were precipitated by cooling the solution to room temperature. The crystals were washed with cold hexane and dried in vacuum. Yield: 2.76 g (53%). Anal. Calc. for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52. Found: C, 80.63; H, 9.44%. ^{1}H NMR, δ 1.29 (18H, *t*-Bu); 5.53 (2H, N**H**); 7.25 and 6.82 (DD, 8H, $J^3_{\mathrm{H,H}} = 8.0$ Hz, –C_6**H_4**–). IR (Nujol), v (cm^{-1}): 3320 (m), 1600 (s), 1520 (m),1510 (m); 1380, 1370 (m) (D, *t*-Bu); 1280 (w), 1260 (vw), 1250 (m) (*t*-Bu), 1170 (m), 1100 (m), 820 (s), 720 (m), 620 (w), 550 (m), 530 (m).

*3.3.2. Ph_2P–NPh–NHPh (**2a**)*

A hexane solution of *n*-BuLi (1.0 M, 8.2 ml) was added to a stirred solution of 1,2-diphenylhydrazine (**1a**) (1.51g, 8.2 mmol) in 15 ml of toluene at 0 °C. After stirring for 10 min Ph_2PCl (1.81 g, 8.2 mmol) in 10 ml of toluene was added dropwise. A colorless solution turned orange. The reaction mixture was kept at room temperature for 30 min and washed with water to remove LiCl. The resulting solution was dried over Na_2SO_4, the major part of the solvent was removed in vacuum and 15 ml of abs. ethanol was added. A slow crystallization at 20 °C was completed in about 5 h to leave colorless crystals of **2a**. Yield: 1.60 g (53%). Anal. Calc. for $C_{24}H_{21}PN_2$: C, 78.24; H, 5.75; P, 8.41. Found: C, 78.12; H, 5.43; P, 8.73%. ^{31}P NMR ($CDCl_3$), δ (ppm): 63.62, ^{1}H NMR δ (ppm): 5.97 (s, 1H, NH), 6.3–7.4 (m, 20H). IR (Nujol), v, cm^{-1}: 3330 (m), (NH), 1580 (s), 1430 (w), 1300 (w), 1270 (m), 1225 (m), 1190 (m), 1120 (m), 1100 (m), 1020 (m), 1000 (w), 950 (m), 910 (m), 880 (w), 740 (s), 730 (sh), 690 (s), 530 (w), 500 (vw).

Thermal destruction of **2a**. A sample of **2a** (0.15 g, 0.4 mmol) was placed into a long glass tube. The thermolysis was carried out in vacuum (0.1 mm Hg) at slow heating (2 °C/min) up to 150 °C and maintaining for 30 min at this temperature. Destruction of **2a** begins at 140 °C. Azobenzene sublimes at the top of the ampoule. It was isolated (0.036 g, ~0.2 mmol) and identified by HPLC (Silasorb C_{16}T, 64 × 2; CH_3OH:H_2O = 75:25; $F = 100$ mkl/min, $\lambda = 210$ nm, retention time 8′05″). Brown solid residue was analysed by ^{31}P NMR spectroscopy. The main signals were (δ, ppm): 29.4 (18%, tentatively PhNH–PPh_2 [7,33]), 19.9 (8%), 11.1 (8%), −4.08 (37%, PhNH–PPh_2═NPh (**4**)), −13.7 (8%, tentatively Ph_2P–PPh_2). Note, that Ph_3P shows resonance at $\delta = -4$, 08 (the same those found for compound **4**). Triphenylphosphine, however, was not found by HPLC analysis.

*3.3.3. Ph_2P–$NC_6H_4Bu^t$–$NHC_6H_4Bu^t$ (**2b**)*

A solution of 0.96 M *n*-buthyllithium in hexane (5.1 ml, 4.9 mmol) was added to a stirred solution of **1b** (1.46 g, 4.9 mmol) in 15 ml of toluene at room temperature. After the mixture was kept for 0.5 h, a solution of Ph_2PCl (1.08 g, 4.9 mmol) in 5 ml of toluene was added. The mixture was stirred for ca. 1 h when washed with water to remove LiCl. The resulting solution was dried over Na_2SO_4. Toluene was removed in vacuum and 15 ml of abs. ethanol was added. A crystallization overnight at 0 °C yields large colorless crystals of **2b** (1.23 g, 52%). Anal. Calc. for $C_{32}H_{37}PN_2$: C, 79.97; H, 7.76; P, 6.44. Found: C, 79.63; H, 7.80; P, 6.38%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 62.9 (s). ^{1}H NMR, δ 1.17 (9H, *t*-**Bu**$C_6H_4NPPh_2$), 1.29 (9H, *t*-**Bu**C_6H_4NH); 6.01 (1H, N**H**); 6.28 and 6.87 (DD, $J^3 = 8.5$ Hz, 4H, *t*-BuC_6**H_4**NH); 7.1–7.7 (m, 14H, (C_6**H_5**)$_2$P and *t*-BuC_6**H_4**NP). IR (Nujol) v(cm^{-1}): 3350 (m), 3320 (w), 1610 (s), 1510 (s); 1380 (m), 1370 (m) (*t*-Bu), 1180 (m), 1120 (m), 1100 (w), 1000 (w), 920 (m), 830 (s), 750 (m), 730 (m), 700 (s), 560 (m), 530 (w), 500 (m).

Thermal destruction of **2b** was carried out by analogy with **2a**. Only tentative suggestions may be done for some products, registrated by ^{31}P NMR sectroscopy: (δ, ppm) 29.3 (23%, ~*t*-BuC_6H_4–NH–PPh_2), 27.9 (9%), 12.4 (5%), 11.05 (19%), −4.43 (38%, ~^{t}BuC_6H_4–NH–PPh_2═$NC_6H_4Bu^t$).

*3.3.4. [PhNH–PPh_2═NPh] · 2HCl (**3**)*

A mixture of hydrazobenzene (1.85 g, 10.0 mmol) and Ph_2PCl (2.22 g, 10.0 mmol) in 20 ml of methylene chloride has been left for two days at 20 °C. The plentiful white crystalline residue has been filtered and dried up in vacuum. Yield of (**3**): 4.32 g (~ 98%). Anal. Calc. for $C_{24}H_{23}PN_2Cl_2$: C, 65.32; H, 5.25; Cl, 16.07; P, 7.02. Found: C, 65.41; H, 5.30; Cl, 16.21; P, 6.93%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 30.37 ppm. IR (Nujol) v(cm^{-1}): 1600 (s), 1500 (s), 1440 (m), 1420 (w), 1280 (m), 1210 (m), 1120 (s), 1030 (w), 1010 (w), 990 (m), 940 (m), 760 (s), 730 (s), 690 (s), 590 (w), 520 (w), 500 (w), 450 (w).

*3.3.5. PhNH–PPh_2═NPh (**4**)*

A solution of 10% ammonia (10 ml) is added to a suspension of **3** (4.32 g) in diethyl ether (30 ml). Dissolution of **3** and partial precipitation of a new crystalline product was observed. The suspension was washed with distilled water. Ether was removed in vacuum. The crystalline residue was pumped in vacuum. Crystallization from warm toluene gave 3.42 g (95%) of **4**. Anal. Calc. for $C_{24}H_{21}PN_2$: C, 78.26; H 6.79; P 8.42. Found: C 78.34; H 6.72; P 8.38%. ^{31}P {^{1}H} NMR ($CDCl_3$): δ-4.08 ppm. IR (Nujol) v(cm^{-1}): 3060 (w), 1600 (s), 1490 (s), 1410 (w), 1300 (vs), 1230 (m), 1170 (w), 1120 (m), 1060 (m), 1020 (w), 1000 (w), 930 (s), 760 (s), 720 (m), 700 (s), 580 (m), 525 (s). HPLC: $CH_3OH/H_2O = 90/10$; Diasorb $C_{16}T$, 7μ; colomn 64 × 2 mm, $F = 100$ μl/min; $\lambda = 210$ nm. Retention time 3′50″ and 4′20″.

3.3.6. Ph_2P–NPh-NPh–Li (**5a**) and Ph_2P–NPh–NPh–Li(Et_2O) (**6a**)

A hexane solution of *n*-BuLi (1.0 M, 4.2 ml) was added to a stirred solution of **2a** (1.55 g; 4.2 mmol) in 15 ml of toluene. The solvent was removed in vacuo. The oily residue (**5a**) shows ^{31}P NMR resonance (C_6D_6) δ 55.0 ppm and ^7Li NMR δ 2.90 ppm.

To a prepared toluene solution of **5a** (15 ml), 1 ml of Et_2O was added. The mixture was maintained overnight at 0 °C. The solvent was decanted; colorless crystals of **6a** were washed with toluene and dried in vacuo. Yield: 1.8 g (96%). Anal. Calc. for $C_{28}H_{30}PN_2LiO$: C, 74.99; H, 6.74; Li, 1.55. Found: C, 74.78; H, 6.79; Li, 1.50%.

3.3.7. Ph_2P–N($C_6H_4Bu^t$)–N($C_6H_4Bu^t$)Li(Et_2O) (**6b**)

The procedure is similar to **5a**. Colorless crystals. Yield: 0.72 g (68%). Anal. Calc. for $C_{36}H_{46}PN_2LiO$: C, 77.12; H, 8.27; Li, 1.24. Found: C, 77.06; H, 8.32; Li, 1.21%.

3.3.8. Ge(NPh–NPh–PPh_2)$_2$ (**7**)

A solutions of $GeCl_2(C_4H_8O_2)$ (0.46 g, 2.0 mmol) in 15 ml of THF, and **5a** (1.79 g, 4.0 mmol) in 15 ml THF were mixed at −50 °C. Colorless solution immediately turned orange-red. After stirring for 1 h at 0 °C the solvent was removed in vacuum and changed for toluene. The precipitate (LiCl) was filtered off, toluene was removed in vacuum and changed for Et_2O. Bright-yellow fine-crystalline precipitate was formed for 2 h at 20 °C. Mother liquor was decanted; the precipitate was recrystallized from warm Et_2O and dried in vacuum. Yield: 1.22 g (76%). Anal. Calc. for $C_{48}H_{40}P_2N_4Ge$: C, 71.40; H, 4.99; P, 7.67; Ge, 8.99. Found: C, 71.70; H, 5.00; P, 7.81; Ge, 9.15%. IR (Nujol) ν(cm^{-1}): 1580 (m), 1250 (w), 1230 (m), 1080 (m), 1020 (m), 870 (m), 840 (w), 730 (s), 700 (s), 500 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.2 (s). *T* dec 135 °C.

3.3.9. Zn(NPh–NPh–PPh_2)$_2$ (**8a**)

A solutions of **5a** (3.74 g in 20 ml of THF (10.0 mmol)) and anhydrous $ZnCl_2$ (0.68 g in 10 ml of THF (5.0 mmol)) were mixed at 0 °C. Colorless solution rapidly turned bright yellow. After stirring for 30 min at 20 °C the solvent was removed in vacuum and changed for toluene. The precipitate (LiCl) was filtered off. The clean solution was concentrated to 15 ml and maintained overnight at 20 °C to give deep yellow crystals. Yield: 3.80 g (95%). Anal. Calc. for $C_{48}H_{40}P_2N_4Zn$: C, 72.05; H, 5.04; P, 7.74; Zn, 8.17. Found: C, 71.94, H, 5.12, P, 7.70, Zn, 8.20; Cl (remaining), 0.5%. IR (Nujol) ν(cm^{-1}): 1590 (s), 1300 (w), 1230 (m), 1150 (w), 1080 (m), 1020 (w), 910 (m), 850 (m), 730 (vs), 700 (vs), 500 (w), 480 (w), 450 (w). *T* dec 135 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 63.10$ and 63.16 ppm.

The alkaline hydrolysis of **8a** was carried out in water/ether mixture to form free base **2a** which were characterized by IR-spectroscopy and elemental analysis.

3.3.10. Zn(NAr–NAr–PPh_2)$_2$, Ar = *p*-Bu^t–C_6H_4– (**8b**)

Compound **8b** was prepared by analogy with **8a**. Yellow viscous oil. Yield: 94%. Anal. Calc. for $C_{64}H_{72}P_2N_4Zn$: C, 75.02; H, 7.08; Zn, 6.38. Found: C, 75.10; H, 6.95; Zn, 6.23; Cl (remaining), 0.4%. IR (Nujol) ν(cm^{-1}): 1320 (w), 1280 (w), 1240 (m), 1110 (m), 1000 (m), 945 (m), 830 (m), 730 (s), 690 (s), 550 (m), 500 (m). T dec 135 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 63.0$ and 62.91 ppm.

3.3.11. Co(NPh–PPh_2=NPh)$_2$ (**9**)

(A) A solution of $CoCl_2$ (0.13 g, 1.0 mmol) in 20 ml of THF was added to a stirred solution of **5a** (0.75 g; 2.0 mmol) in 10 ml of the same solvent. The mixture immediately turned dark-brown. The color of the solution slowly turned violet-green at heating. Maintaining of the mixture at 80 °C during 12 h led to a fine crystalline pink precipitate of **9** (the precipitation of LiCl was not observed). The solvent was decanted; the crystals were washed with THF and dried in vacuum. Yield: 0.75 g (95%). Anal. Calc. for $C_{48}H_{40}P_2N_4Co$: C, 72.63; H, 5.08; Co, 7.42. Found: C, 72.80; H, 5.11; Co, 7.38; Cl (remaining), 0.2%. IR (Nujol) ν(cm^{-1}): 1590 (s), 1300 (vs), 1270 (s), 1170 (m), 1100 (s), 1030 (m), 1000 (m), 980 (m), 800 (s), 760 (m), 720 (m), 700 (m), 640 (m), 500 (s).

(B) A toluene solution containing 0.38 g of $Co[N(SiMe_3)_2]_2$ (1.0 mmol), 0.74 g (2.0 mmol) of phosphinohydrazine **2a** was heating at 80 °C for 6 h. The formed pink crystalline residue was washed with THF and dried in vacuum. Yield: 0.77 g (97%).

(C) A hexane solution of *n*-BuLi (1.0 M, 2.0 ml) was added to a stirred solution of PhNH–PPh_2=NPh **(4)** (0.75 g, 2.0 mmol) in 15 ml of toluene. The solvent was removed in vacuum and changed for THF. A solution of $CoCl_2$ (0.13 g; 1.0 mmol) in 20 ml of THF was added. The mixture turned dark-brown. Maintaining of the mixture at 80 °C during 12 h led to a fine crystalline pink precipitate of **9** (The precipitation of LiCl was not observed). The solvent was decanted; the crystals were washed with THF and dried in vacuum. Yield: 0.71 g (90%).

3.3.12. Ni(NPh–PPh_2=NPh)$_2$ (**10**)

The procedure is similar to the synthesis of **9a** by the method A. Ruby-brown fine crystals. Yield: 95%. Anal. Calc. for $C_{48}H_{40}P_2N_4Ni$: C, 72.65; H, 5.08; Ni, 7.40. Found: C, 72.73; H, 5.13; Ni, 7.31; Cl (remaining), 0.1%. IR (Nujol) ν(cm^{-1}): 1580 (s), 1290 (vs), 1260 (s), 1130 (w), 1100 (m), 1020 (w), 990 (w), 970 (w), 780 (m), 730 (m), 700 (w), 680 (m), 500 (m).

3.3.13. *Co[N($C_6H_4Bu^t$)–PPh_2=N–$C_6H_4Bu^t$]$_2$ (11)*

$CoBr_2$ (0.22 g; 1.0 mmol) in 10 ml of THF was added to a stirred solution of Ph_2P–$NC_6H_4Bu^t$–$NLiC_6H_4Bu^t$ (1.12 g; 2.0 mmol) in 20 ml of the same solvent. The starting green solution rapidly turned brown. The mixture was heated at 70 °C for 6 h. THF was removed and changed for toluene. LiBr was filtered off. The clean solution was concentrated to 10 ml and maintained overnight at 0 °C to give large pink-violet crystals. Yield: 0.88 g (86%). Anal. Calc. for $C_{64}H_{72}P_2N_4Co$: C, 75.50; H, 7.13; Co, 5.79. Found: C, 75.56; H, 7.08; Co, 7.73%; IR (Nujol) ν(cm^{-1}): 1600 (s), 1510 (s) (*t*-Bu), 1300 (vs), 1270 (s), 1180 (m), 1110 (s), 1370 (w), 1380 (w), 1000 (s), 1010 (w), 1000 (s), 830 (m), 800 (s), 750 (w), 730 (m), 710 (w), 700 (m), 640 (w), 590 (m), 550 (w), 520 (s).

3.3.14. *Reaction of $(Me_3Si)_2NNi(PPh_3)_2$ (12) with Ph_2P–NPh–NHPh (**2a**).*

A mixture of **12** (0.74 g, 1 mmol) and **2a** (0.37 g, 1 mmol) in toluene (20 ml) was maintained at room temperature for 24 h. Brown-red crystals were separated from mother liquor, washed with cold toluene and dried in vacuum. Yield: 0.38 g (50%). Anal. Calc. for $C_{48}H_{40}P_2N_2Ni[(Ph_3P)_2Ni(PhN{=}NPh)]$ (**13**): C, 75.31; H, 5.27; Ni, 7.67. Found: C, 75.26; H-5.35; Ni 7.60%. Crystals were investigated by X-ray analysis.

3.3.15. *[Ph_2P–NPh-NPh]$_2$Fe (14)*

(A) A solution of lithium phosphinohydrazaide (**5a**) (0.75 g, 2.0 mmol) in 10 ml of THF was added to a suspension of $FeBr_2$ (0.43 g, 1.0 mmol) in 10 ml of the same solvent. The mixture was heated at 50 °C for 12 h. The solvent was change for hexane, LiBr was filtered off. Hexane was removed in vacuum to leave black-green powder of **14**. Yield: 0.76 g (96%). Anal. Calc. for $C_{48}H_{40}P_2N_4Fe$: C, 72.92; H, 5.10; Fe, 7.06. Found: C, 72.80; H, 5.20; Fe, 7.14%. IR (Nujol) ν(cm^{-1}): 1570 (m), 1240 (m), 1160 (m), 1060 (w), 1020 (w), 920 (m), 830 (m) 765 (w), 720 (s), 680 (s).

Hydrolisis of **14**. An ether solution of **14** was treated with 10% NaOH. Ferrous hydroxide was filtered off, ether layer was separated, ether was removed in vacuum and change for ethanol. Colorless crystals of **2a** were characterized by ^{31}P, ^{1}H NMR and IR spectroscopy.

(B) A mixture of Fe[N$(SiMe_3)_2$]$_2$ (0.38 g, 1 mmol) and **2a** (0.73 g, 2 mmol) in toluene (15 ml) was maintained at 50 °C for 12 h. The solvent and hexamethyldisilazane were removed in vacuum, to form black-green powder of **14**. Yield: 0.79 g (~100%).

3.3.16. *Fe(NPh–PPh_2=NPh)$_3$ (15)*

A mixture of Fe[N$(SiMe_3)_2$]$_3$ (0.54 g, 1 mmol) and **2a** (1.10 g, 3 mmol) in toluene (20 ml) was maintained at 80 °C for 12 h. Yellow fine crystalline precipitate of **15** was filtered off, washed with toluene and dried in vacuum. Yield 0.94 g (81%). Anal. Calc. for $C_{72}H_{60}P_3N_6Fe$: C, 74,67; H, 5.22; Fe, 4.82. Found: C, 74.61; H, 5.18; Fe, 4,78%. IR (Nujol) ν(cm^{-1}): 1590 (s), 1300 (vs), 1270 (vs), 1170 (w), 1110 (m), 1130 (m), 1000 (m), 970 (m), 930 (w), 830 (w), 780 (m), 750 (m), 720 (w), 690 (m), 640 (m), 510 (s).

3.3.17. *[Ph_2P–NPh–NPh]$_3$Cr (16)*

A solution of Ph_2P–NPh–NLiPh (**5a**) (1.12 g, 3 mmol) in 20 ml of THF was added to a suspension of $CrCl_3$ (0.16 g, 1 mmol). Dissolution of $CrCl_3$ was observed and color of the mixture got dark brown rapidly. The mixture was heated for 2 h at 50 °C. The solvent was removed in vacuum and changed for toluene. LiCl was filtered off. Toluene was removed in vacuum to leave black-brown powder of **16**. Yield: 1.08 g (94%). Anal. Calc. for $C_{72}H_{60}P_3N_6Cr$: C, 74.99; H, 5.24; Cr, 4.42. Found: C, 74.86; H, 5.30; Cr, 4.37%. IR (Nujol) ν(cm^{-1}): 1590 (s), 1260 (m), 1110 (m), 1120 (w), 980 (w), 810 (w), 740 (vs), 690 (vs), 510 (m), 460 (w).

Hydrolisis of **16**. An toluene solution of **16** was treated with 25% NH_4OH for 30 min. Chromium hydroxide was filtered off, organic layer was separated, the solvent was removed in vacuum and changed for ethanol. Colorless crystals of **2a** were characterized by ^{31}P, ^{1}H NMR and IR spectroscopy.

3.3.18. *[Ph_2P–NPh–NPh]$_2$Mn (17) (attempt of the synthesis)*

The synthesis of **17** from anhydrous $MnCl_2$ and **5a** is analogous to **16**. Dark-yellow powder from toluene. Yield 0.73 g (93%). Anal. Calc. for $C_{48}H_{40}P_2N_4Mn$: C, 73.00; H, 5.11; Mn, 6.96. Found: C, 71.07; H, 5.23; Mn, 7.84; Cl (remaining) 3.1%. IR (Nujol) ν(cm^{-1}): 1600 (m), 1270 (w), 1230 (m) 1130 (m), 1100 (w), 1030 (m), 1000 (w), 920 (m), 740 (vs), 700 (vs), 570 (w).

Hydrolysis of **17**. A toluene solution of **17** was treated with an excess of 25% NH_4OH under argon atmosphere for 30 min. Manganese hydroxide was filtered off, organic layer was separated, the solvent was removed in vacuum and change for ethanol. Colorless crystals of **2a** were characterized by ^{31}P, ^{1}H NMR and IR spectroscopy.

3.3.19. *$(Me_3Si)_2NCu$(Ph_2P–NPh–NPhH)$_2$ (18)*

A solution of $(Me_3Si)_2NCu$ (0,22 g, 1 mmol) in 10 ml of toluene was added to a solution of phosphinohydrazine **2a** (0.74 g, 2 mmol) in the same solvent (10 ml). The colorless solution turned yellow-orange. The mixture was allowed to stay for 4 h before precipitation of the product **18**. Orange needle crystals were filtered, washed with toluene and dried in vacuum. Yield: 0.75 g (81%). Anal. Calc. for $C_{54}H_{60}P_2N_5Si_2Cu$: C, 67.51; H, 6.30; Cu, 6.61. Found: C, 67.55; H, 6.34; Cu, 6.68%. IR (Nujol) $\nu(\mathrm{cm}^{-1})$: 3320 (w), 1590 (s), 1310 (w), 1270 (m), 1235 (m), 1170 (w), 1090 (m), 1030 (w), 980 (w), 950 (w), 870 (w), 740 (vs), 700 (vs), 500 (m). $^{31}P\{^1H\}$ NMR (C_6D_6), δ (ppm) 59.61; ^1H NMR 7.8–7.0 (m, 40 H, Ph), 0.11 (s, 18 H, SiMe), 5.30 (s, 2H, NH).

Thermolysis of **18.** A solution of **18** (0.96 g, 1 mmol) in toluene (20 ml) was heated at 80 °C for 2 h. Red precipitate of $\{Ph_2PCu\}_n$ was filtered off, washed with toluene and dried in vacuum. Yield: 0.23 g (93%). Anal. Calc. for $C_{12}H_{10}PCu$: C, 57.95; H, 4.05; Cu, 25.55. Found: C, 57.89; H, 4.10; Cu, 25.48%. IR (Nujol) $\nu(\mathrm{cm}^{-1})$: 1580 (w), 730 (m), 690 (m), 550 (m), 500 (m).

The filtrate was analysed further. Toluene was removed in vacuum; the residue was extracted with hexane. The extract contained azobenzene according to the HPLC analysis: Separon SGX, 5 μ, 64×2; $F = 200$ μl/min, $\lambda = 220$ nm; hexane/THF = 200/1; retention time 1′35″. Other conditions: Silasorb $C_{16}T$, 64×2; CH_3OH: H_2O = 75:25; $F = 100$ mkl/min, $\lambda = 210$ nm, retention time 8′05″).

The residue was treated with ethanol. Colorless crystals of $Ph_2PNPhNPhH$ (**2a**) (0.3 g, 81%) were characterized by IR and NMR spectroscopy.

4. Conclusions

The present research has shown that the stability of the metal complexes containing σ-bonded phosphinohydrazide ligand {–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 $M[N(Ar)N(Ar)PPh_2]_n$ {M = Li, Zn, Ge(II), Mn(II), Cr(III), Fe(II)} while the late transition metals (Co, Ni, Cu) and metals with enhanced oxidation state (Fe^{3+}) cause transformation of phosphinohydrazide ligand. The rearrangement of –NPh–NPh–PPh_2 into aminoiminophosphorane moiety, –NPh–PPh_2═NPh, is observed on Fe^{3+}, Co^{2+}, Ni^{2+} centres. Compound of Ni(I), $(Ph_3P)_2NiN(SiMe_3)_2$, reacts with HNPh–NPh–PPh_2 to form azobenzene complex, $(Ph_3P)_2Ni(PhN{=}NPh)$ while copper(I) silylamide affords diphenylphosphide $\{Ph_2PCu\}_n$ and azobenzene. Probably, the paths of the last two reactions are defined by exclusive stability of azobenzene. It is possible to expect, that the replacement of phenyl groups at nitrogen atoms in –NPh–NPh–PPh_2 for another substituents or functional groups will cause an essential changes in template transformations of phosphinohydrazine ligands.

5. Supplymentary material

The CIF are available from the Cambridge Crystallographic Data Center under the depositary number CCDC 233897 (**2a**), 233900 (**7**), 233898 (**11**), 233899 (**13**).

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