Note

The rearrangement of phosphitohydrazide ligand [(ArO)$_2$P–NPh–NPh–] into iminophosphoranate anion [(PhN=P(OAr)$_2$–NPh–] {(ArO)$_2$P = [CH$_2$(^{t}BuMeC$_6$H$_2$O)$_2$P]} in coordination sphere of divalent cobalt

Natalia V. Belina, Alexander N. Kornev *, Vyacheslav V. Sushev, Georgy K. Fukin, Eugene V. Baranov, Gleb A. Abakumov

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

A R T I C L E   I N F O

A B S T R A C T

The reaction of bromophosphite (ArO)$_2$PBr {(ArO)$_2$P = CH$_2$(6-^{t}Bu-4-Me-C$_6$H$_2$O)$_2$P} with lithium salt of 1,2-diphenylhydrazine gave phosphitohydrazine (ArO)$_2$P–NPh–NPhH (**2**) in 64% yield. The last one reacted with Co[N(SiMe$_3$)$_2$]$_2$ to afford cobalt(II) iminophosphoranate (PhN=P(OAr)$_2$–NPh–)$_2$Co (**3**), which is the result of isomerisation of the phosphitohydrazide ligand in coordination sphere of divalent cobalt.

1. Introduction

Rearrangements play a key role in phosphorus chemistry being a practical tool for synthesizing a great variety of useful compounds. Recently it was shown that rearrangements of mono-, bis- and tris(diphenylphosphino)hydrazide ligands, Ph$_2$P–NPh–NPh–, (Ph$_2$P)$_2$N–NPh–, (Ph$_2$P)$_2$N–N(PPh$_2$)–, in the coordination sphere of nickel(II), cobalt(II) and iron(III) result in the formation of metal complexes of the phosphazene and phosphinoamide type depending on the starting ligand [1–3] (see Scheme 1).

Note, however, that similar phosphinohydrazide complexes, containing more hindered diisopropylphosphino group, (*i*-Pr$_2$P–NPh–NPh)$_2$M (M = Co, Ni), do not undergo rearrangement [4] whereas lithium salt of bis(diisopropylphosphine)methylhydrazine, (*i*-Pr$_2$P–NMe–NLi–P*i*Pr$_2$) rearranges quickly to iminophosphoranate salt *i*-Pr$_2$P–NMe–P*i*Pr$_2$=NLi [4]. The reason of such differences still is not clear in details. Nevertheless, it is obvious that the tendency of the phosphinohydrazide system toward rearrangement depends on several factors: (1) the energy of the N–N bond, which is strongly depended on the nature of the substituents and a charge on the nitrogen atoms; (2) the energy of the M–P bond, which is determined by a combination of electronic effects of direct and back bonding between both atoms; (3) the energy of the M–N σ bond, which is usually weaker going from early to late transition metals. All these factors influence each other, that complicates prediction of the rearrangement, leaving an intrigue in research of a new ligands. Here we report the first example involving rearrangement of phosphitohydrazide ligand {CH$_2$(6-^{t}Bu-4-Me-C$_6$H$_2$O)$_2$P–NPh–NPh–} in coordination sphere of divalent cobalt.
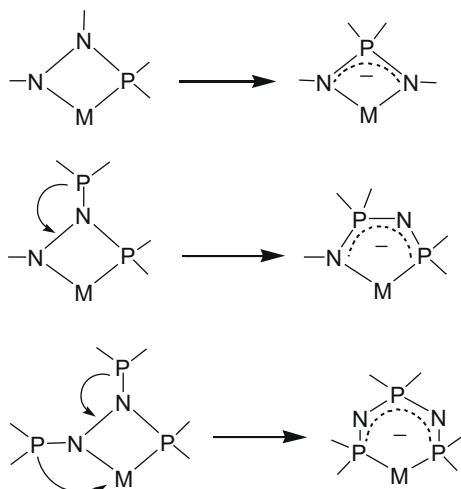
2. Results and discussion

Starting phosphitohydrazine **2** was prepared in good yield by the reaction of bromophosphite **1** with an equivalent of monolithium salt of 1,2-diphenylhydrazine:

(1)
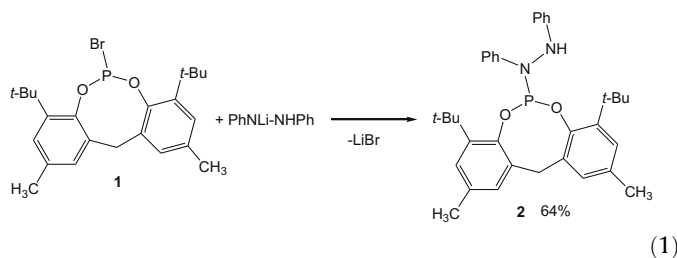
The molecular structure of **2**, recorded at 100 K, shows discrete molecular units (Fig. 1).

Scheme 1. Rearrangements of mono-, di- and triphosphinohydrazides in transition metal coordination sphere (M = Fe³⁺, Co²⁺, Ni²⁺).
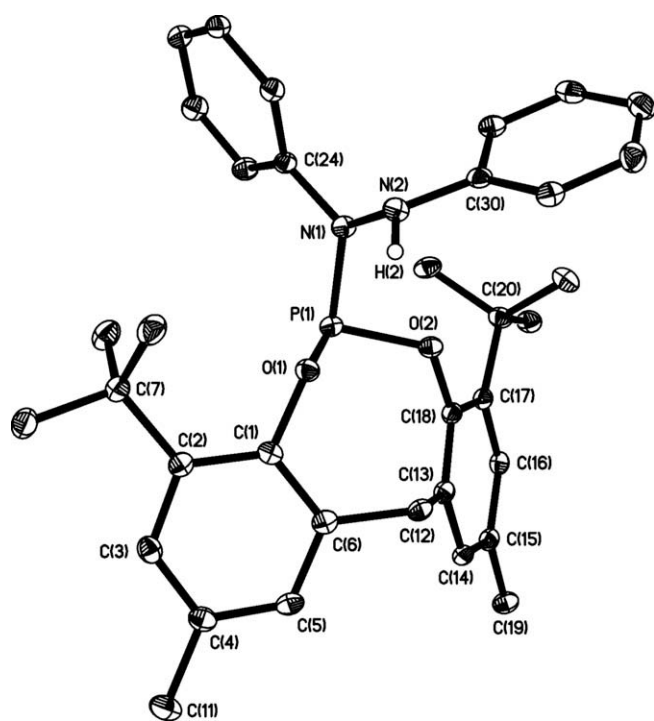

Fig. 1. The molecular structure of **2**. Hydrogen atoms except H(2) were omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: N(1)–N(2) 1.420(3), P(1)–N(1) 1.698(2), P(1)–O(1) 1.660(2), P(1)–O(2) 1.646(2), N(1)–C(24) 1.432(3), N(2)–C(30) 1.407(3), O(2)–P(1)–O(1) 101.30(8), O(1)–P(1)–N(1) 95.79(9), O(2)–P(1)–N(1) 95.95(9), C(1)–O(1)–P(1) 119.3(1), N(2)–N(1)–C(24) 115.6(2), N(2)–N(1)–P(1) 119.1(2), C(24)–N(1)–P(1) 121.8(2), C(30)–N(2)–N(1) 116.7(2), C(6)–C(12)–C(13) 114.8(2).

In the unit cell, hexane solvate molecules were localized in special positions. Table 1 displays the crystal data for **2**. The nitrogen atom N(1) in **2** has a trigonal nearly planar environment (sum of the angles is 356, 45°). The P(1)–N(1) and N(1)–N(2) bond lengths in the molecule (1.698(2) and 1.420(3) Å, respectively) are typical for phosphazanes and phosphinohydrazines [2,5]. Note, however, the N–N bond distance in **2** is somewhat longer than that found in monophosphinohydrazine analog PhNH–NPh–PPh₂ (1.401(2)) [1]. Eight-membered heterocycle in **2** demonstrates chair-like conformation.

Compound **2** was found to be quite resistant to oxygen. Bubbling of O_2 through a solution of **2** in THF did not result in formation of any products during 24 h according ³¹P NMR analysis.

Phosphitohydrazine **2** was allowed to react with 0.5 equivalent of cobalt(II) bis(trimethylsilyl)amide in toluene. The color of green solution slowly turned brown–violet. After keeping the reaction mixture for 3 days at room temperature pink crystals of complex **3** were formed. Crystals suitable for X-ray analysis were obtained from diethyl ether/toluene mixture. The molecular structure of **3** with the atom numbering scheme is shown in Fig. 2. Crystal data and some details of the data collection and refinement for **3** are given in Table 1. The X-ray investigation reveals formation the spirocyclic complex **3** as Et₂O solvate with central cobalt atom in tetrahedral environment.

Two nearly planar four-membered metallacycles CoNPN unfolded relatively to each other to 53.8°. The bond angles N(2A)–Co(1)–N(1A) 74.0(1)° and N(2B)–Co(1)–N(1B) 74.0(1)° are very close to that found in similar iminophosphoranate [Ph₂P(NC₆H₄Bu^t)₂Co]₂ [1]. The P–N bond lengths all lie between the values 1.575(1) Å and 1.596(1) Å, as they occur in phosphazenes [6]. Comparing the structural parameters of the compounds **2** and **3** it may notice that the P–O bonds are shortened going from free ligand **2** (1.646(2), 1.660(2) Å) to the complex **3** (1.587(1)–1.595(1) Å). Contraction of the P–O bonds may be explained by more strong interaction of the oxygen atoms with positively charged phosphorus(V) in **3**.

(2)
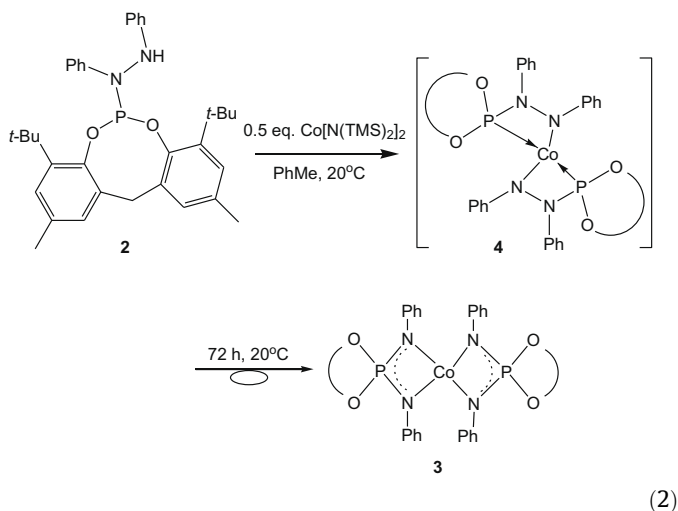
The IR spectrum of **3** shows an intense absorption bands at 1300 and 1130 cm⁻¹ assigned to the ν_s and ν_{as}(PN) stretching vibration. The UV–vis spectrum of the solution of **3** in methylene chloride contains two absorptions with λ_{max} 384 and 565 nm. The complex **3** is the single product separated in the reaction (2). It is appeared impossible to separate the proposed intermediate(s) **4** during this slow reaction. On the other hand, in the related reaction of cobalt(II) bromide with lithium salt of **2** in equimolar ratio, the formation of cobalt phosphinohydrazide-monobromide **5** was observed soon after mixing the reagents (Eq. (3)). Tentatively we proposed dimeric structure for **5**.
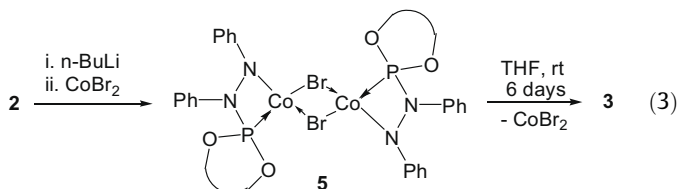

(3)

Table 1
Crystal and structure refinement.

|	2	3
Empirical formula	$C_{38}H_{48}N_2O_2P$	$C_{72}H_{85}CoN_4O_{4.5}P_2$
Formula weight	595.75	1199.31
Temperature (K)	100(2)	100(2)
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	*P*$\bar{1}$
Unit cell dimensions		
a (Å)	15.6685(5)	12.8688(5)
b (Å)	17.1886(6)	15.5278(6)
c (Å)	24.2235(8)	18.2691(7)
α (°)	90	108.3670(10)
β (°)	90	91.7030(10)
γ (°)	90	103.1760(10)
Volume (Å^{-3})	6523.9(4)	3353.0(2)
Z	8	2
Density (calculated) (Mg/m^3)	1.213	1.188
Absorption coefficient (mm^{-1})	0.12	0.354
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.10$	$0.85 \times 0.38 \times 0.15$
Reflections collected	34226	20158
Independent reflections	5747 [R(int) = 0.0460]	13060 [R(int) = 0.0151]
Absorption correction	Semi-empirical from equivalents, sadabs	Semi-empirical from equivalents, sadabs
Max./min. transmission	0.9881/0.9648	0.9488/0.7529
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5747/3/552	13060/72/823
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0548$, $wR_2 = 0.1390$	$R_1 = 0.0609$, $wR_2 = 0.1788$
R indices (all data)	$R_1 = 0.0730$, $wR_2 = 0.1492$	$R_1 = 0.0750$, $wR_2 = 0.1910$
Largest diff. peak and hole (e Å^{-3})	1.074 and −0.674	1.408 and −0.606
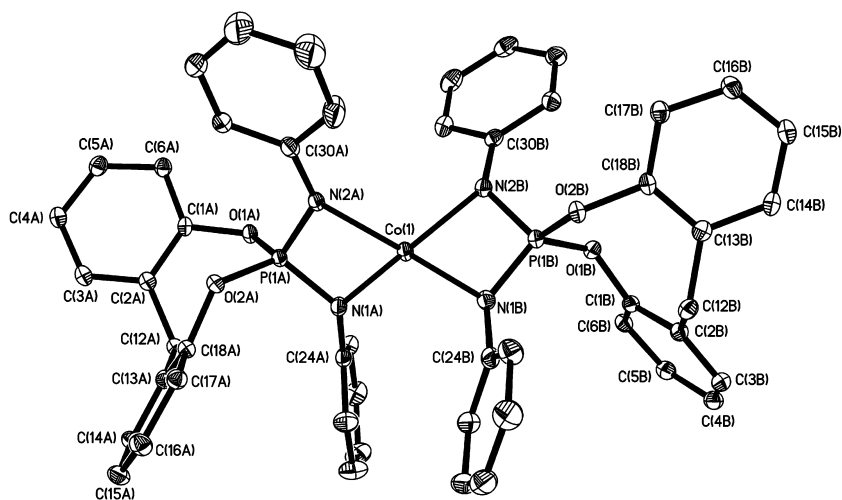
Fig. 2. The molecular structure of **3**. The *t*Bu groups at C(6), C(17) and the methyl groups at C(4) and C(15) carbon atoms as well as hydrogen atoms and solvate molecule (Et$_2$O) were omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: Co(1)–N(2B) 2.012(1), Co(1)–N(2A) 2.021(1), Co(1)–N(1A) 2.025(1), Co(1)–N(1B) 2.032(1), Co(1)–P(1B) 2.6288(4), Co(1)–P(1A) 2.6357(4), P(1A)–N(1A) 1.584(1), P(1A)–N(2A) 1.587(1), P(1A)–O(2A) 1.593(1), P(1A)–O(1A) 1.595(1), P(1B)–N(1B) 1.575(1), P(1B)–O(1B) 1.589(1), P(1B)–O(2B) 1.592(1), P(1B)–N(2B) 1.596(1); N(2B)–Co(1)–N(2A) 111.6(1), N(2B)–Co(1)–N(1A) 146.3(1), N(2A)–Co(1)–N(1A) 74.0(1), N(2B)–Co(1)–N(1B) 74.1(1), N(2A)–Co(1)–N(1B) 150.1(1), N(1A)–Co(1)–N(1B) 118.4(1), P(1B)–Co(1)–P(1A) 176.7(1), N(1A)–P(1A)–N(2A) 100.0(1), N(1B)–P(1B)–N(2B) 100.4(1), N(1A)–P(1A)–O(2A) 119.3(1), O(2A)–P(1A)–N(2A) 108.0(1), N(1A)–P(1A)–O(1A) 110.6(1), O(2A)–P(1A)–O(1A) 104.1(1), N(2A)–P(1A)–O(1A) 115.4(1), C(1B)–O(1B)–P(1B) 134.3(1), C(1A)–O(1A)–P(1A) 127.1(1), P(1A)–N(1A)–Co(1) 93.0(1), P(1B)–N(1B)–Co(1) 92.7(1), P(1B)–N(2B)–Co(1) 92.8(1), P(1A)–N(2A)–Co(1) 92.9(1).

Sparingly soluble brown crystals of **5** have analytical data corresponding to the formula **5** and IR spectrum similar to the starting ligand **2**. Basic hydrolysis of **5** in THF with equimolar amount of water gave Co-containing precipitate and a solution, containing phosphitohydrazine **2** according to the ^{31}P NMR spectrum. No other phosphor-containing products were detected over a period of 3 h. Unfortunately, we failed in our attempts to obtain crystals of **5** that were suitable for X-ray crystallography, apparently because of slow disproportionation and rearrangement of this substance. Keeping the solution of **5** in THF at room temperature for about a week gave cobalt bromide and pink crystals of the complex

3 described above in quantitative yield. Formation of the rearranged ligand, containing NPN iminophosphorane system is clearly seen from IR spectrum. In this case a strong absorption ($v_{P=N}$) at 1300 cm^{-1} occurs.

3. Conclusion

In summary, we have reported the first example of rearrangement of the phosphitohydrazide ligand, (ArO)$_2$P–NPh–NPh–, into

iminophosphoranate anion, PhN=P(OAr)$_2$–NPh–, which takes place in the coordination sphere of Co(II).

4. Experimental part

4.1. General

Solvents were purified following standard methods [7]. Toluene was thoroughly dried and distilled over sodium prior to use. Diethyl ether and THF were dried and distilled over Na/benzophenone. Cobalt silylamide [Co{N(SiMe$_3$)$_2$}$_2$] [8,9] was prepared according to a known methods. 2,2′-Methylenebis(4-methyl-6-tert-butylphenol) was purchased from Sigma–Aldrich Chemical Co. and used as received. 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 a 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 cobalt in the prepared compounds was carried out by the methods described in [10]. Infrared spectra were recorded on a Perkin–Elmer 577 spectrometer from 4000 to 400 cm^{-1} in Nujol on a Perkin–Elmer FT-IR spectrometer System 2000 as KBr mulls. NMR spectra were recorded in CDCl$_3$ or C$_6$D$_6$ solutions using a Bruker DPX-200 spectrometer.

4.2. X-ray crystallography

X-ray data for **2** and **3** were collected on a Bruker AXS SMART APEX diffractometer (graphite-monochromator, Mo Kα radiation (λ = 0.71073 Å), φ–ω scan). All structures were solved by direct methods and were refined on F^2 using SHELXTL [10] package. All non-hydrogen atoms were refined anisotropically. H atoms in **2** were refined with mixed treatment: hydrogen atoms in molecule of **2** were located from Fourier synthesis and refined isotropically, H atoms of solvate hexane molecule in **2** were included into the model at geometrically calculated positions and refined using a riding model. All hydrogen atoms in **3** were placed in calculated positions and were refined in the riding model. One of t-Bu-groups in **3** was found to be disordered over two positions and was refined with a population in each position of 0.5. In crystal of **3** one solvate Et$_2$O molecule is disordered over two positions so that one part of Et$_2$O occupies a general position and another part of this one lies in a special position. SADABS [11] was used to perform absorption corrections. The main crystallographic data and structure refinement details for **2** and **3** are presented in Table 1.

4.3. CH$_2$[(t-Bu)MeC$_6$H$_2$O]$_2$PBr (1)

A mixture of 2,2′-methylenebis(4-methyl-6-tert-butylphenol) (5.0 g, 14.7 mmol) and 1.5 equiv. of tribromophosphine (5.9 g, 22.0 mmol) in 15 mL of chlorobenzene was heated at 135 °C for 3 h in argon atmosphere. Chlorobenzene and excess of PBr$_3$ were removed under reduced pressure at 50 °C. The residue was dissolved in equal amount of toluene; concentrating of the resulted solution gave colorless crystals (4.12 g, 62%) of **1**. Anal. Calc. for C$_{23}$H$_{30}$BrO$_2$P: C, 61.47; H, 6.73; Br, 17.78. Found: C, 61.52; H, 6.69; Br, 17.72%. ^{1}H NMR (200 MHz, CDCl$_3$) 7.3–7.0 (m, 4H), 3.85 (dd, J = 13 Hz, CH$_2$, 2H), 2.3 (s, Me, 6H), 1.4 (s, tBu,18H). ^{31}P NMR (80 MHz, PhCl), ppm: 174.7. IR (v, cm^{-1}): 1286w, 1260w, 1202m, 1186m, 1123w, 1098m, 915w, 854sh, 837s, 797w, 775w, 697m, 593m, 552w, 530m, 482m, 452m.

Note, that bromophosphite **1** is easily oxidized by dioxygen at 20 °C in solution to give bromophosphate showing a ^{31}P shift at 7.4 ppm.

4.4. {CH$_2$(6-^{t}Bu-4-Me-C$_6$H$_2$O)$_2$P–NPh–NPhH} (2)

A solution of n-BuLi in hexane (9.0 mL, 1.0 M) was added to a stirred solution of 1,2-diphenylhydrazine (1.66 g, 9.0 mmol) in 15 mL of toluene at 0 °C. After stirring for 10 min, a solution of CH$_2$[(t-Bu)MeC$_6$H$_2$O]$_2$PBr (4.04 g, 9.0 mmol) in 20 mL of toluene was added dropwise. A colorless solution turned orange. The reaction mixture was kept at room temperature for 30 min, the major part of the solvent was removed in vacuum and 20 mL of hexane was added. The precipitate (LiBr) was filtered out; the filtrate was concentrated to 10 mL. A slow crystallization at 20 °C was completed in about 5 h to leave colorless crystals of **2**. Yield: 3.43 g (64%). Anal. Calc. for C$_{38}$H$_{48}$N$_2$O$_2$P (**2**·½C$_6$H$_{14}$): C, 76.61; H, 8.12; P, 5.20. Found: C, 76.55; H, 8.20; P, 8.76%. ^{31}P NMR (80 MHz, CDCl$_3$), ppm: 139.5; ^{1}H NMR (200 MHz, CDCl$_3$): 7.6–6.7 (m,14H), 4.35 (CH$_a$H$_b$ dd, $^2J_{H,H}$ = 12 Hz, J$_{H,P}$ = 3 Hz, 1H), 3.35 (CH$_b$H$_a$ d, $^2J_{H,H}$ = 12 Hz, 1H), 2.28 (s, 6H, CH$_3$), 1.23 (s, 18H, tBu), 6.92 (s, 1H, NH). IR (v, cm^{-1}): 3370w, 1597s, 1290w, 1261w, 1209s, 1114s, 1030w, 932m, 910m, 846s, 832 (sh), 801w, 748m, 693m, 676m, 628ww, 596w, 573w, 528w, 485w, 458w.

Alternatively, phosphitohydrazine **2** may be obtained using CH$_2$[(t-Bu)MeC$_6$H$_2$O]$_2$PCl [12] instead bromide as a starting material in similar yield.

4.5. Reaction of 2 with Co{N(SiMe$_3$)$_2$}$_2$

A solution of Co[N(SiMe$_3$)$_2$]$_2$ (0.49 g, 0.85 mmol) in 5 mL of toluene was added to a solution of the phosphitohydrazine **2** (0.76 g, 1.7 mmol) in the same solvent (10 mL). Green solution slowly turned reddish brown during reaction time (72 h). The solution was concentrated at reduced pressure; pink crystals of **3** were formed after addition of diethyl ether. Yield 0.66 g, 67%.

Anal. Calc. for C$_{72}$H$_{85}$CoN$_4$O$_{4.5}$P$_2$: C, 72.10; H, 7.14; Co, 4.91. Found: C, 72.30; H, 7.28; Co, 4.86%. IR (v, cm^{-1}): 1595s, 1300s, 1210s, 1130m, 1050m, 1020m, 925s, 855s, 795m, 750m, 727m, 693s, 629w. UV/vis spectrum (THF): λ_{max} 384, 565 nm.

4.6. Reaction of CoBr$_2$ with lithium salt of 2

A solution of n-butyllithium in hexane (1.6 mL, 0.75 M) was added slowly to a solution of phosphitohydrazine **2** (0.66 g, 1.2 mmol) in 10 mL of toluene at 0 °C. The reaction mixture was concentrated under reduced pressure, and 5 mL of THF was added. The resulted solution of lithium phosphitohydrazide was added to a homogeneous solution of anhydrous CoBr$_2$ (0.26 g, 1.2 mmol) in 15 mL of THF. The mixture turned dark brown. Brown crystalline precipitate formed overnight at 0 °C was washed with cold THF and dried in vacuum. Yield 1.62 g, 98%. Anal. Calc. for C$_{70}$H$_{80}$Br$_2$Co$_2$N$_4$O$_4$P$_2$: C, 60.88; H, 5.84; Br, 11.57; Co, 8.53. Found: C, 61.03; H, 5.90; Br, 11.49; Co, 8.48%. IR (v, cm^{-1}): 1592m, 1206m, 1115m, 1026m, 927m, 830s, 744m, 685m, 594w.

5. Supplementary material

CCDC 746205 and 746206 contain the supplementary crystallographic data for compound **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

References

[1] Y.V. Fedotova, A.N. Kornev, V.V. Sushev, Y.A. Kursky, T.G. Mushtina, N.P. Makarenko, G.K. Fukin, G.A. Abakumov, L.N. Zakharov, A.L. Rheingold, J. Organomet. Chem. 689 (2004) 3060–3074.

[2] V.V. Sushev, A.N. Kornev, Y.A. Min'ko, N.V. Belina, Y.A. Kurskiy, O.V. Kuznetsova, G.K. Fukin, E.V. Baranov, V.K. Cherkasov, G.A. Abakumov, J. Organomet. Chem. 691 (2006) 879–889.

[3] V.V. Sushev, N.V. Belina, G.K. Fukin, Inorg. Chem. 47 (2008) 2608–2612.

[4] A.N. Kornev, N.V. Belina, V.V. Sushev, G.K. Fukin, E.V. Baranov, Y.A. Kurskiy, A.I. Poddelskii, G.A. Abakumov, P. Lönnecke, E. Hey-Hawkins, Inorg. Chem. 48 (2009) 5574–5583.

[5] V.A. Naumov, L.V. Vilkov, Molecular structures of organophosphorus compounds, (in Rus), Nauka, 1986, p. 320.

[6] H.R. Allcock, Chem. Res. 72 (1972) 315.

[7] R.A. Andersen, K. Faegri, J.C. Green, A. Haaland, M.F. Lappert, W.-P. Leung, K. Rypdal, Inorg. Chem. 27 (1988) 1782–1786.

[8] H. Burger, U. Wannagat, Monatsh. Chem. 94 (1963) 007.

[9] E. Upor, M. Mohai, G. Novak, Photometric Methods in Inorganic Trace Analysis, Academiai Kiado, Budapest, 1985.

[10] G.M. Sheldrick, SHELXTL v. 6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.

[11] G.M. Sheldrick, SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.

[12] D.J. Sherlock, A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 36 (1997) 5082–5089.