ACADEMIA ROMÂNĂ
*Revue Roumaine de Chimie*
http://web.icf.ro/rrch/

*Rev. Roum. Chim.*,
**2013**, *58*(2-3), 265-273

*Dedicated to Professor Bogdan C. Simionescu on the occasion of his 65th anniversary*

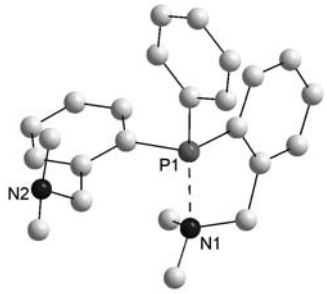
# COBALT(II) COMPLEXES WITH HYPERVALENT TRIARYLPHOSPHANES

Raluca MITEA, Ancuta COVACI, Cristian SILVESTRU and Anca SILVESTRU*

Supramolecular Organic and Organometallic Chemistry Centre (CCSOOM), Chemistry Department, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, RO-400028 Cluj-Napoca, Roumania

*Received December 20, 2012*

Reactions between triarylphosphanes of type $P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}$ [x = 1 (**1**), 2 (**2**), 3 (**3**)] and $CoCl_2{\cdot}6H_2O$ in a 1:1 molar ratio resulted in cobalt(II) complexes of type $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ [x = 1 (**4**), 2 (**5**), 3 (**6**)]. The new species were isolated as blue solids and they were investigated by $^1H$ and $^{31}P$ NMR, mass spectrometry and electronic spectroscopy. X-ray diffraction studies revealed a monomeric structure in case of the starting phosphane $P(C_6H_4CH_2NMe_2\text{-}2)_2Ph$ (**2**), in which one 2-$(Me_2NCH_2)C_6H_4$ pendant arm is involved in an intramolecular N→P interaction. The oxidized species $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ [x = 2 (**5a**), 3 (**6a**)] were also isolated as blue solids. A similar coordination pattern as in case of the related $[ZnCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ (**7**) might be proposed for such oxidized species.




## INTRODUCTION

Triorganophosphanes are well known as stabilizing ligands for different transition metals.[1-3] Moreover, species containing both soft phosphorus and hard nitrogen donor atoms attracted a considerable raising interest due to their potential to build metal complexes with applications in homogeneous catalysis or electronics.[4-8] Triarylphosphanes of type $P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}$ (x = 1-3) have already been reported and at some extent they were used as ligands towards several transition metals (Cu, Ag, Pd, Pt, Rh, Co, Ir).[9-20]

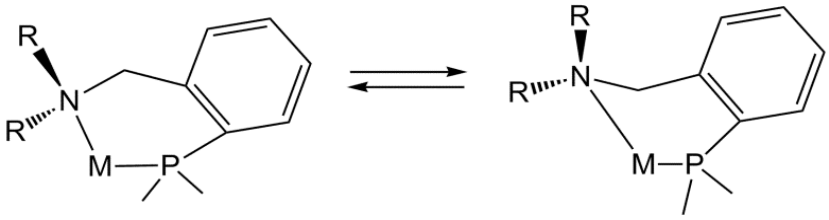
The nitrogen atoms in the pendant arms are capable for intramolecular coordination either to phosphorus or to a metal centre. In this way low oxidation states of the central atoms are stabilized, a conformational rigidity is induced to the molecule and polymeric associations generally are avoided.[21,22]

For several transition metal (Rh, Pd, Pt)[11,17-19] complexes with such ligands a fluxional behaviour in solution was observed by NMR, according to a conformation exchange of the six-membered chelate ring formed through P→M and N→M coordination, as depicted in Scheme 1.

Taking into account the recent increased interest in the catalytic activity of cobalt complexes,[23-28] we focused our studies on the reactivity of triarylphospanes of type $P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}$ towards cobalt(II). Here we report on the synthesis and spectroscopic characterization of the complexes

* Corresponding author: ancas@chem.ubbcluj.ro

$[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ [x = 1 (**4**), 2 (**5**), 3 (**6**)] as well as the oxidation products $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ [x = 2 (**5a**), 3 (**6a**)]. We have to note that compound **4** was already previously obtained, but it was not fully characterized.[10] The crystal and molecular structures of the starting triarylphosphane $P(C_6H_4CH_2NMe_2\text{-}2)_2Ph$ (**2**) and the related oxidation product $[ZnCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ are also described.




Scheme 1

## RESULTS

### Synthesis

Reactions between $CoCl_2 \cdot 6H_2O$ and the corresponding triarylphosphanes in a 1:1 molar ratio were performed in ethanol in order to obtain adducts of type $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ (Scheme 2). When phosphane **1** was used, only the product **4**, soluble in ethanol was isolated and characterized, while the use of phosphanes **2** and **3** resulted in isolation, besides the desired complexes **5** and **6**, also of the oxidation products **5a** and **6a** formed by initial oxidation of the parent phosphorus ligands (Scheme 2).

All species were obtained as blue solids, soluble in alcohols (**4**, **5a** and **6a**) and both in alcohols and chlorinated solvents (**5** and **6**).

The cobalt(II) complexes were investigated by $^1H$ and $^{31}P$ NMR, mass spectrometry, electronic spectroscopy and magnetic measurements in order to determine the coordination behaviour of the phosphane ligands towards the metal centre.

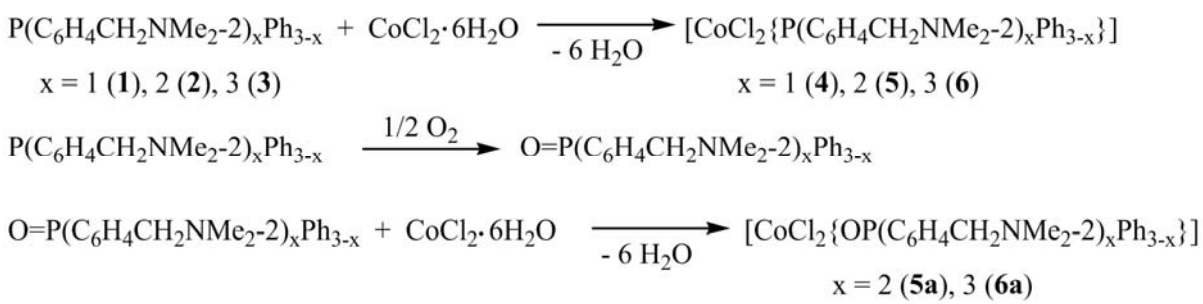
## DISCUSSION

### Spectroscopy

Compound **4** was soluble only in alcohols (methanol or ethanol), while compounds **5** and **6** were soluble both in alcohols, acetonitrile and chlorinated solvents. The methanol solution of compound **4** is blue, while for the other species pink solutions in methanol and blue solutions in $CH_2Cl_2$, $CDCl_3$ or $CH_3CN$, were obtained. This is consistent with a tetrahedral environment about cobalt in case of the blue species and an octahedral one in case of the pink species. When the solvent was completely removed from the pink solutions, blue solids were recovered.

Both by NMR and mass spectrometry it was observed that the phosphane ligand is readily oxidized in alcohol solution to the phosphine oxides $OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}$, which finally result in the formation of a mixture of $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ and $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ (x = 2, 3). The phosphineoxide complexes were almost insoluble in chlorinated solvents, so that compounds **5** and **6** soluble in $CH_2Cl_2$ could be separated from the oxidized species **5a** and **6a**, respectively, based on their different solubilities.

The NMR resonances are broad, due to paramagnetic nature of the Co(II) complexes. The $^1H$ NMR spectra for species **5** revealed in the aliphatic region a broad singlet resonance corresponding to the $NCH_3$ protons and two large resonances centred at $\delta$ 4.02 and 4.15 ppm, respectively, corresponding to the $CH_2N$ protons. This pattern is characteristic for an AB spin system for the $CH_2N$ protons. For the other species the diastereotopic nature of the $CH_2N$ protons could not be evidenced by NMR at room temperature. The aromatic region contains the expected resonances for the aromatic groups in the compound. The $^{31}P$ NMR is indicative for the presence in solution of P(III)-containing species in case of compounds **4** – **6**, slightly shifted from the respective $\delta$ values of the free ligands, while for the oxidized compounds **5a** and **6a** chemical shifts characteristic for P(V) were observed (see Table 1).




Scheme 2

*Table 1*

Analytical data for the investigated compounds

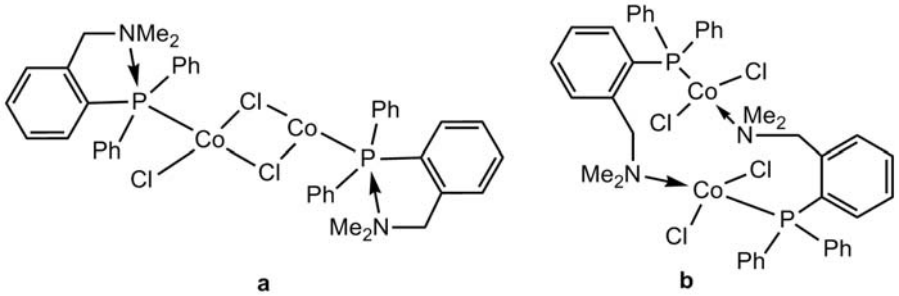
| | Compound | $^{31}$P NMR δ [ppm] (solvent) | μ [BM] | Electronic spectra $\lambda_{max}$ [nm] (solvent) |
|---|---|---|---|---|
| **1** | $P[C_6H_4(CH_2NMe_2)\text{-}2]Ph_2$ | -15.3 ($CDCl_3$) | - | |
| **2** | $P[C_6H_4(CH_2NMe_2)\text{-}2]_2Ph$ | -25.1 ($CDCl_3$) | - | |
| **3** | $P[C_6H_4(CH_2NMe_2)\text{-}2]_3$ | -35.3 ($CDCl_3$) | - | |
| **4** | $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)Ph_2\}]$ | -16.4 ($CD_3OD$) | 4.49 | 624; 671 (EtOH) |
| **5** | $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ | -22.8 ($CDCl_3$) | 4.02 | 628; 644 (EtOH) |
| **6** | $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_3\}]$ | -34.9 ($CD_3OD$) | 3.74 | 654; 693 (EtOH) |
| **5a** | $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ | 42.5 ($CD_3OD$) | 3.92 | 651 (EtOH)<br>589; 688 ($CH_3CN$) |
| **6a** | $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_3\}]$ | 47.2 ($CD_3OD$) | 3.84 | 662 (EtOH) |

A similar sensitivity to oxidation was observed in case of the reaction between $P(C_6H_4CH_2NMe_2\text{-}2)_2Ph$ and $ZnCl_2$, when about 10% from the isolated solid adduct was $[ZnCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ (**7**), with a $^{31}$P NMR chemical shift at $\delta$ 45.8 ppm in $CDCl_3$ solution. For this species also the X-ray single-crystal structure was determined by X-ray diffractometry (see subsequent discussion).

It is noteworthy that for the related oxidized phosphane $OP[C_6H_4CH_2N(O)Me_2\text{-}2]_3$ it was reported a $^{31}$P NMR resonance at $\delta$ 40.3 ppm in methanol, similarly with the values found in our species containing triorganophosphorus(V) ligands.[9]

All compounds gave blue solutions in ethanol or acetonitrile which show in the visible region of their electronic spectra absorption bands in the range 589-693 nm (see Table 1), typical for tetrahedral Co(II) species.[29,30] The magnetic moments of the blue solid compounds at room temperature have values ranging from 3.74 to 4.49 B.M., consistent with a tetrahedral Co(II) environment in solid state (Table 1).

In all cases the mass spectra show peaks of high intensity of type $[CoCl\{P(C_6H_4CH_2NMe_2\text{-}2)_x Ph_{3-x}\}]^+$ corresponding to the desired species. Due to the oxidation process, ions of type $[OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}]^+$ are also present. The presence of ions of a higher mass than that one corresponding to the monomer in case of compound **4**, suggested intermolecular associations leading probably to dimeric units. Taking into account a tetrahedral coordination geometry around both cobalt atoms, a dinuclear structure with either chlorine atoms or the phosphane ligands bridging the two metal centres (Scheme 3) might be proposed.




Scheme 3

Unfortunately, our attempts to grow single-crystals of these adducts were unsuccessful.

*Crystal and molecular structure of P[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$Ph* (**2**)

Even if all three phosphanes used as ligands in our study were already described, only the molecular structure of P[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_3$ (**3**) was reported till now.[9] We manage to obtain single-crystals of P[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$Ph (**2**) and to determine its structure by X-ray difractometry. The compound crystallizes in the *P-1* space group and the crystal contains two independent monomeric molecules (**2'** and **2''**) in the unit cell. The ORTEP-like diagram with the numbering scheme for this ligand is depicted in Fig. 1, while interatomic distances and bond angles are given in Table 2.

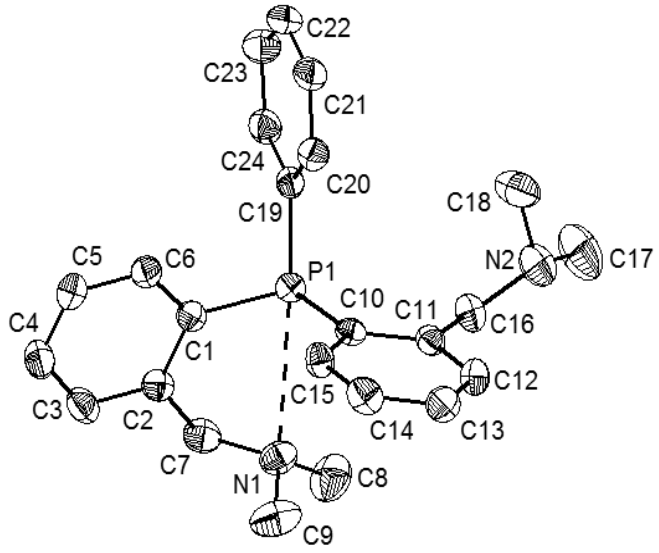



Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for the $S_{N1}C_{P1}$-**2'** isomer.

*Table 2*

Selected interatomic distances (Å) and angles (°) in P[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$Ph (**2**)

| **2'** | | **2''** | |
|---|---|---|---|
| P1–C1 | 1.850(3) | P2–C25 | 1.843(3) |
| P1–C10 | 1.842(3) | P2–C34 | 1.836(3) |
| P1–C19 | 1.840(3) | P2–C43 | 1.839(3) |
| P1···N1 | 2.912(3) | P2···N3 | 2.971(3) |
| | | | |
| C1–P1–C10 | 103.28(14) | C25–P2–C34 | 102.71(14) |
| C1–P1–C19 | 99.96(14) | C25–P2–C43 | 100.47(15) |
| C10–P1–C19 | 101.10(14) | C34–P2–C43 | 101.62(14) |
| N1···P1–C1 | 74.19(12) | N3···P2–C25 | 73.11(12) |
| N1···P1–C10 | 77.17(11) | N3···P2–C34 | 76.44(11) |
| N1···P1–C19 | 173.15(13) | N3···P2–C43 | 172.45(13) |
| C7–N1–C8 | 112.9(3) | C31–N3–C32 | 112.4(4) |
| C7–N1–C9 | 112.8(4) | C31–N3–C33 | 112.4(3) |
| C8–N1–C9 | 111.9(4) | C32–N3–C33 | 112.2(4) |
| C16–N2–C17 | 110.3(3) | C40B–N4B–C41B | 105.2(10) |
| C16–N2–C18 | 111.7(3) | C40B–N4B–C42A | 111.80(7) |
| C17–N2–C18 | 110.6(4) | C41B–N4B–C42A | 109.66(8) |

In both molecules **2'** and **2''** only one nitrogen atom interacts with phosphorus: N(1)···P(1) 2.912(3) Å in molecule **2'** and N(3)···P(2) 2.971(3) Å in molecule **2''**. The other nitrogen atom *per* molecular unit is pushed far away from the coordination sphere of phosphorus, at a distance (4.35 and 4.30 Å in molecules **2'** and **2''**, respectively) much larger than the sum of the van der Waals radii of the corresponding atoms [$\Sigma r_{vdW}$(N,P) = 3.44 Å].[31] It is noteworthy that in case of P[$C_6H_4(CH_2NMe_2)$-2]$_3$, in one of the two crystallographic forms all three nitrogen atoms from the pendant arms are coordinated to phosphorus, while in the other only two nitrogens are interacting with phosphorus. In the molecules of compound **2** the N···P intramolecular interactions are of a similar magnitude as those observed in P[$C_6H_4(CH_2NMe_2)$-2]$_3$ [range 3.007(2) – 3.095(3) Å].[9] As a result of the N→P intramolecular coordination a five-membered $PC_3N$ ring is formed. The ring is not planar, but folded along the P···$C_{methylene}$ axis, with the nitrogen atom lying out of the best plane defined by the residual $PC_3$ system. This induces planar chirality [with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively]. As a consequence, the compound crystallizes as a mixture of $R_N$ and $S_N$ isomers. If we consider also the phosphorus lone pair of electrons, the coordination geometry around this atom might be described as distorted *pseudo*-trigonal bipyramidal, with N(1) and C(19) (in molecule **2'**) and N(3) and C(43) (in molecule **2''**), respectively, in apices [N(1)···P(1)–C(19) 173.15(13)$^o$ and N(3)···P(2)–C(43) 172.45(13)$^o$, respectively]. The trigonal plane is determined by the other two carbon atoms attached to phosphorus and the lone pair. In this way, a second type of chirality is induced to the phosphorus centre in the trigonal-bipyramidal environment and thus the crystal of **2** contains a mixture of $S_{N1}C_{P1}$, $R_{N1}A_{P1}$, $R_{N3}C_{P2}$ and $S_{N3}A_{P2}$ isomers.

### *Crystal and molecular structure of [$ZnCl_2${$OP(C_6H_4CH_2NMe_2$-2)$_2$Ph}]* (**7**)

The compound crystallizes in the *P2(1)/c* monoclinic space group and has a monomeric structure. The ORTEP-like diagram with the numbering scheme for this complex is depicted in Fig. 2, while interatomic distances and bond angles are given in Table 3.

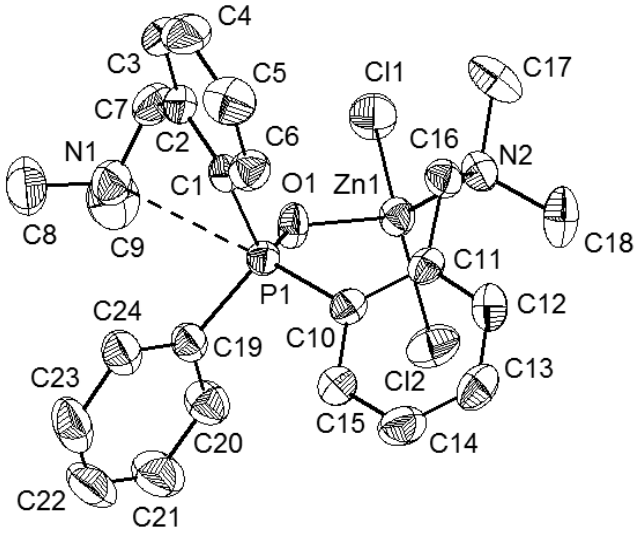



Fig. 2 – ORTEP representation at 50% probability and atom numbering scheme for $S_{N1}R_{N2}A_P$ -7 isomer.

*Table 3*

Selected interatomic distances (Å) and angles ($^o$) in [$ZnCl_2${$OP(C_6H_4CH_2NMe_2$-2)$_2$Ph}] (**7**)

| **7** | | | |
|---|---|---|---|
| P1–C1 | 1.803(4) | N1···P1–C10 | 175.45(12) |
| P1–C10 | 1.817(3) | N1···P1–C19 | 73.54(12) |
| P1–C19 | 1.787(3) | N1···P1–O1 | 74.80(11) |
| P1···N1 | 2.995(4) | C16–N2–C17 | 106.3(3) |

*Table 3 (continued)*

| | | | |
|---|---|---|---|
| P1–O1 | 1.491(2) | C16–N2–C18 | 110.6(3) |
| O1···Zn1 | 1.943(2) | C17–N2–C18 | 108.5(3) |
| N2···Zn1 | 2.102(3) | C16–N2–Zn1 | 112.4(2) |
| | | | |
| C1–P1–C10 | 106.67(16) | C17–N2–Zn1 | 108.9(2) |
| C1–P1–C19 | 113.22(16) | C18–N2–Zn1 | 110.0(2) |
| C10–P1–C19 | 103.93(16) | O1–Zn1–N2 | 101.83(11) |
| O1–P1–C1 | 111.12(15) | O1–Zn1–Cl1 | 104.52(8) |
| O1–P1–C10 | 109.71(15) | O1–Zn1–Cl2 | 107.04(9) |
| O1–P1–C19 | 111.78(16) | N2–Zn1–Cl1 | 110.20(9) |
| N1···P1–C1 | 71.41(12) | N2–Zn1–Cl2 | 110.20(9) |

The ligand acts as a bidentate moiety, being attached to zinc by oxygen and the nitrogen atom from one of the pendant arms [O(1)···Zn(1) 1.943(2) Å and N(2)···Zn(1) 2.102(3) Å, *vs.* $\Sigma r_{vdW}$(O,Zn) = 2.80 Å, $\Sigma r_{vdW}$(N,Zn) = 2.95 Å]. The second nitrogen of the ligand is coordinated to phosphorus [N(1)···P(1) 2.995(4) Å]. In this way a distorted trigonal-bipyramidal coordination geometry, with N(1) and C(10) in apices [N(1)···P(1)–C(10) 175.45(12)$^o$] is realized around phosphorus, while the zinc atom is in a distorted tetrahedral environment. The phosphorus-oxygen distance corresponds to a double bond [P(1)=O(1) 1.491(2) Å, cf. P=O 1.486(6) and P=O 1.526 Å in $Ph_2P(=O)OH$].[32] The intramolecular N(1)→P(1) and respectively N(2)→Zn(1) coordination resulted in two chelate rings, one of five members ($NC_3P$), folded along the P···$C_{methylene}$ axis, and the other one of seven atoms ($ZnOPC_3N$), with an envelope conformation, folded as well on the corresponding P···$C_{methylene}$ axis. In the latter case, the O(1) atom is displayed out of the best plane P(1)C(16)Zn(1)N(2) at 0.41 Å. The intramolecular N(1)→P(1) and N(2)→Zn(1) interactions induce planar chirality, thus determining the formation of a racemic mixture of $R_{N1}S_{N2}$ and $S_{N1}R_{N2}$ isomers. Taking into account also the chirality induced to phosphorus, the stereoisomerism of this species might be considered in terms of $R_{N1}S_{N2}C_P$ and $S_{N1}R_{N2}A_P$ isomers.

We have to note that three triarylphosphane oxides containing organic groups with nitrogen potential donor atoms were structurally characterized before our studies: $OP[C_6H_4(CH_2NOMe_2)\text{-}2]_3$,[9] $OP[C_6H_4(CHMeNMe_2)\text{-}2]_3$,[33] and tris[2-(2′-benzothiazolyl)phenyl]phosphane oxide.[34] Only in the last compound one of the nitrogen atoms interacts with phosphorus [N···P 2.888(4) Å], while in the other two species the nitrogen atoms are placed at distances much longer (range 4.148 – 4.175 Å in $OP[C_6H_4(CH_2NOMe_2)\text{-}2]_3$,[9] and 4.395 – 4.517 Å in $OP[C_6H_4(CHMeNMe_2)\text{-}2]_3$,[33]) than the sum of the corresponding van der Waals radii of the two elements.

## EXPERIMENTAL

The starting triarylphosphanes were prepared according to literature procedures: $P(C_6H_4CH_2NMe_2\text{-}2)Ph_2$ (**1**), $P(C_6H_4CH_2NMe_2\text{-}2)_2Ph$ (**2**)[11] and $P(C_6H_4CH_2NMe_2\text{-}2)_3$ (**3**).[9] Elemental analysis was performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. $^1H$ and $^{31}P$ NMR spectra were recorded on a BRUKER Avance 300 instrument. The chemical shifts are reported in δ units (ppm) relative to TMS (ref. $CHCl_3$: $^1H$ 7.26 ppm, $CD_3OD$: $^1H$ 3.31 and 4.84 ppm) and $H_3PO_4$ 85%, respectively. Mass spectra were performed on a LTQ Orbitrap - XL instrument, while magnetic moments were determined on a Sherwood MSB AUTO magnetometer and electronic spectra were recorded on a Jasco V-550 spectrometer.

*Synthesis of* $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)Ph_2\}]$ **(4)**

A reaction mixture of $P[C_6H_4(CH_2NMe_2)\text{-}2]Ph_2$ (0.213 g, 0.66 nmol) in 20 mL ethanol and (0.159g, 0.66 mmol) $CoCl_2{\cdot}6H_2O$ in 10 mL ethanol was stirred for 24 hours at room temperature. From the blue solution the solvent was removed in vacuum and the resulted blue solid product was washed with n-hexane. Yield: 0.29g (78%). M.p. 244°C (243°C[10]). Elem. Anal.: Calcd. for $C_{21}H_{22}NPCl_2Co$ (M = 449.21) C 56.15, H 4.94, N 3.12%; Found C: 55.83, H 4.89, N 3.24%. MS (ESI+, MeCN) m/z (%): 320.1 (100) $[P\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]^+$, 336.2 (11) $[OP\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]^+$, 413.0 (52) $[Co(Cl)P\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]^+$, 437.0 (12) $[Co_2P\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]^+$, 472.0 (5) $[Co_2(Cl)P\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]^+$, 863.0 (5) $[Co(Cl)P\{C_6H_4(CH_2NMe_2)\text{-}2\}Ph_2]_2 + Cl]^+$. $^1H$ NMR ($CD_3OD$): 2.46s (br, 6H, $NCH_3$), 4.03s (br, 2H, $CH_2N$), 6.95s (br, 1H, $C_6H_4$), 7.22 – 7.72m (3H, $C_6H_4$ + 10H, $C_6H_5$). $^{31}P$ NMR ($CD_3OD$): -16.4 [P(III)].

*Synthesis of* $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ *(5) and* $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ **(5a)**

A reaction mixture of $P[C_6H_4(CH_2NMe_2)\text{-}2]_2Ph$ (0.301g, 0.79 mmol) in 30 mL ethanol and (0.188g, 0.79 mmol) $CoCl_2{\cdot}6H_2O$ in 10 mL ethanol was stirred for 5 hours. The solvent was removed in vacuum and a viscous blue oily product resulted. It was treated with dichloromethane, when a clear blue solution and a blue precipitate formed, which was filtered off. The solution was dried over $Na_2SO_4$ and than the solvent was removed in vacuum. The resulted blue solid products, both from the solution (**5**) and the initial precipitate (**5a**) were washed with n-hexane and dried in vacuum. Yield: 0.40g (82%, **5**) and 0.092g (18%, **5a**). M.p. 108°C (**5**), 223°C (**5a**). **5**: Elem. Anal.: Calcd. for: $C_{24}H_{29}N_2PCl_2Co$ (M = 506.31) C 56.93, H 5.77, N 5.53%; Found C 56.82, H 6.02, N 5.68%. MS (ESI+, MeCN) m/z (%): 506 (11) $[M]^+$, 470.11 (56) $[Co(Cl)P\{C_6H_4(CH_2NMe_2)\text{-}2\}_2Ph]^+$, 393 (100) $[OP\{C_6H_4(CH_2NMe_2)\text{-}2\}_2Ph]^+$, 377.21 (83) $[P\{C_6H_4(CH_2NMe_2)\text{-}2\}_2Ph]^+$. $^1H$ NMR ($CDCl_3$): 2.48s (br, 12H, $NCH_3$), 4.02s (br, 2H, $CH_2N$), 4.15s (br, 2H, $CH_2N$), 6.88s (br, 2H, $C_6H_4$), 7.20 – 7.45m (4H, $C_6H_4$ + 5H, $C_6H_5$), 7.84s (br, 2H, $C_6H_4$). $^{31}P$ NMR ($CDCl_3$): -22.8 [br, P(III)]. **5a**: Elem. Anal.: Calcd. for: $C_{24}H_{29}N_2OPCl_2Co$ (M = 522.32) C 55.19, H 5.60, N 5.36%; Found C 55.44, H 5.83, N 5.47%. $^1H$ NMR ($CD_3OD$): 2.74s (br, 12H, $NCH_3$), 4.13s (br, 2H, $CH_2N$), 4.39s (br, 2H, $CH_2N$), 6.97s (br, 2H, $C_6H_4$), 7.63m (br, 6H, $C_6H_4$ + 5H, $C_6H_5$). $^{31}P$ NMR ($CD_3OD$): 42.5 [br, P(V)].

Compounds *$[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_3\}]$* **(6)** and *$[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_3\}]$* **(6a)** were prepared similarly from $P[C_6H_4(CH_2NMe_2)\text{-}2]_3$ (0.23g, 0.53 mmol) in 20 mL ethanol and $CoCl_2{\cdot}6H_2O$ (0.126g, 0.53 mmol) in 10 mL ethanol, by stirring for 24 hours. Yield: 0.31g (87%, **6**) and 0.047g (13%, **6a**). M.p. 174°C (dec.) (**6**) and 201°C (**6a**). **6**: Elem. Anal.: Calculated for: $C_{27}H_{36}Cl_2CoN_3P$ (M = 563.40): C 57.56, H 6.44, N 7.46; Found: C 57.42, H 6.41, N 7.23%. MS (ESI+, MeOH) m/z (%): 434.2 (100) $[P\{C_6H_4(CH_2NMe_2)\text{-}2\}_3]^+$, 450.2 (32) $[OP\{C_6H_4(CH_2NMe_2)\text{-}2\}_3]^+$, 527.1 (47) $[Co(Cl)P\{C_6H_4(CH_2NMe_2)\text{-}2\}_3]^+$. $^1H$ NMR ($CD_3OD$): 2.87s (br, 18H, $NCH_3$), 4.52s (br, 6H, $CH_2N$), 6.84s (br, 3H, $C_6H_4$), 7.45s (br, 3H, $C_6H_4$), 7.79-7.93m (br, 6H, $C_6H_4$). $^{31}P$ NMR ($CD_3OD$): -34.9 [br, P(III)]. **6a**: Elem. Anal.: Calcd. for: $C_{27}H_{36}Cl_2CoN_3PO$ (M = 579.42) C 55.97, H 6.26, N 7.25%; Found C 55.62, H 6.41, N 6.97%. $^1H$ NMR ($CD_3OD$): 2.66s (br, 18H, $NCH_3$), 4.25s (br, 6H, $CH_2N$), 6.96s (br, 3H, $C_6H_4$), 7.53s (br, 3H, $C_6H_4$), 7.82s (br, 6H, $C_6H_4$). $^{31}P$ NMR ($CD_3OD$): 47.2 [br, P(V)].

### X-ray structure determination

The details of the crystal structure determination and refinement for compounds **2** and **7** are given in Table 4.

*Table 4*

X-ray crystal data and structure refinement
for compounds $P[C_6H_4(CH_2NMe_2)\text{-}2]_2Ph$ (**2**) and $[ZnCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ (**7**)

| | **2** | **7** |
|---|---|---|
| Empirical formula | $C_{48}H_{58}N_4P_2$ | $C_{24}H_{29}Cl_2N_2OPZn$ |
| Formula weight | 752.92 | 528.73 |
| Temperature (K) | 297(2) | 297(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P-1* | *P2(1)/c* |
| Unit cell dimensions | | |
| *a* (Å) | 8.5044(7) | 10.328(4) |
| *b* (Å) | 16.0549(14) | 16.993(8) |
| *c* (Å) | 16.1837(14) | 14.670(7) |
| $\alpha$ (°) | 86.000(2) | 90 |
| $\beta$ (°) | 89.857(2) | 104.390(9) |
| $\gamma$ (°) | 81.950(2) | 90 |
| Volume ($Å^3$) | 2182.5(3) | 2493.9(19) |
| *Z* | 2 | 4 |
| $D_c$ ($g/cm^3$) | 1.146 | 1.408 |
| Absorption coefficient ($mm^{-1}$) | 0.136 | 1.282 |
| *F(000)* | 808 | 1096 |
| Crystal size, mm | 0.44 x 0.43 x 0.41 | 0.33 x 0.27 x 0.21 |
| θ range for data collections (°) | 1.26 to 25.00 | 1.87 to 25.00 |
| Reflections collected | 21171 | 12988 |
| Independent reflections | 7645 | 4392 |
| | [R(int) = 0.0379] | [R(int) = 0.0464] |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 7645 / 17 / 534 | 4392 / 0 / 284 |
| Goodness-of-fit on $F^2$ | 1.101 | 1.115 |
| Final *R* indices [$F^2>2\sigma(F^2)$] | R1 = 0.0759, | R1 = 0.0490 |
| | wR2 = 0.1760 | wR2 = 0.1063 |
| *R* indices (all data) | R1 = 0.0999, | R1 = 0.0629 |
| | wR2 = 0.1887 | wR2 = 0.1119 |
| Largest diff. peak and hole, $eÅ^{-3}$ | 0.789 and -0.239 3 | 0.399 and -0.283 |

Data were collected on a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The crystals were attached with paraton/N oil on cryoloops and the data were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[35] The drawings were created with the Diamond program.[36] In case of compound **2**, which contains two independent molecules in the unit cell, in molecule **2''** one $CH_2NMe_2$ group is disordered over two positions with 34 and 66% occupancies, respectively.

## CONCLUSIONS

New cobalt(II) compounds of type $[CoCl_2\{P(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ (x = 1 – 3) were obtained and structurally characterized by spectroscopic methods. A tetrahedral environment about cobalt was suggested by electronic spectra and the experimentally determined magnetic moments. The oxidized species $[CoCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}\}]$ (x = 2, 3) were also isolated. The structural investigations, in accordance also with their blue colour, suggested a tetrahedral coordination about Co(II) in case of these two species. For the starting ligand $P(C_6H_4CH_2NMe_2\text{-}2)_2Ph$ (**2**) the single-crystal X-ray diffraction studies revealed a monomeric structure with only one nitrogen atom coordinated to phosphorus. For the oxidized species **5a** and **6a** a similar behaviour of the phosphane oxide ligands $OP(C_6H_4CH_2NMe_2\text{-}2)_xPh_{3-x}$ (x = 2, 3) towards Co(II) as in case of the related Zn(II) compound $[ZnCl_2\{OP(C_6H_4CH_2NMe_2\text{-}2)_2Ph\}]$ (**7**) might be envisaged. In compound **7** only one pendant arm remained coordinated to phosphorus, while the other nitrogen atom in the molecule interacts with the metal.

*Acknowledgements:* Financial support from National University Research Council of Roumania (Research Project PNII-ID 0659/2011) is greatly appreciated.

*Supplementary material*

CCDC 939688 and 939689 contain the supplementary crystallographic data for compounds **2** and **7**, respectively. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

## REFERENCES

1. F. Mohr, S. H. Priver, S. K. Bhargava, M. A. Bennett, *Coord. Chem. Rev*., **2006**, *250*, 1851, and ref. therein.
2. M. Altaf, H. Stoeckli-Evans, *Inorg. Chim. Acta*, **2010**, *363*, 2567.
3. A. Bader, E. Lindner, *Coord. Chem. Rev.,***1991**, *108*, 27.
4. R. Kreiter, J. J. Firet, M. J.J. Ruts, M. Lutz, A. L. Spek, R. J.M. Klein Gebbink, G. van Koten, *J. Organomet. Chem*., **2006**, *691*, 422.
5. S. Maggini, *Coord. Chem. Rev*., **2009**, *253*, 1793, and ref. therein
6. A. A. Dabbawala, H. C. Bajaj, H. Bricout, E. Monflier, *Appl. Catal. A: General*, **2012**, *413-414*, 273.
7. K. Salvakumer, M. Valentini, P. S. Pregosin, *Organometallics*, **2000**, *19*, 1299.
8. Lan-Chang Liang, *Coord. Chem. Rev*., **2006**, *250*, 1152, and ref. therein.
9. A. Chandrasekaran, N. V. Timosheva, R. O. Day, R. R. Holmes, *Inorg. Chem.*, **2002**, *41*, 5235.
10. T. B. Rauchfuss, F. T. Patino, D. M. Roundhill, *Inorg. Chem.*, **1975**, *14*, 652.
11. M. A. Alonso, J. A. Casares, P. Espinet, K. Soulantica, A. G. Orpen, H. Phetmung, *Inorg. Chem*., **2003**, *42*, 3856.
12. C. Chuit, R. J. P. Corriu, P. Monforte, C. Reye, J. P. Declercq, A. Dubourg, *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 1430.
13. M. Leschke, H. Lang, M. Melter, G. Rheinwald, C. Weber, H. A. Mayera, H. Pritzkowb, L. Zsolnaib, A. Driess, G. Huttner, *Z. Anorg. Allg. Chem*., **2002**, *628*, 349.
14. H. Lang, Y. Shen, T. Ruffer, B. Walfort, *Inorg. Chim. Acta*, **2008**, *361*, 95.
15. J.G. Fierro-Arias, R. Redon, J.J. Garcia, S. Hernandez-Ortega, R.A. Toscano, D. Morales-Morales, *J. Mol. Catal. A: Chem.*, **2005**, *233*, 17.
16. W. de Graaf, S. Harder, J. Boersma, G. van Koten, J.A. Kanters, *J. Organomet. Chem.*, **1988**, *358*, 545.
17. G.M. Kapteijn, M.P.R. Spee, D.M. Grove, H. Kooijman, A.L. Spek, G. van Koten, *Organometallics,* **1996**, *15*, 1405.
18. J. Pfeiffer, G. Kickelbick, U. Schubert, *Organometallics*, **2000**, *19*, 62.
19. F. Carre, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reye, *J. Organomet. Chem.*, **1997**, *529*, 59.
20. S. E. Watkins, D. C. Craig, S. B. Colbran, *Dalton Trans*., **2002**, 2423.
21. K. Akiba (Ed.), Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999.
22. K. Akiba, *Heteroatom Chemistry*, **2011**, *22*, 207.
23. V. Rosa, S. A. Carabineiro, T. Aviles, P. T. Gomes, R. Welter, J. M. Campos, M. R. Ribeiro, *J. Organomet. Chem.*, **2008**, *693*, 769.
24. Lin Chen, Pengfei Ai, Jianming Gu, Suyun Jie, Bo-Geng Li, *J. Organomet. Chem.*, **2012**, *716*, 55.
25. T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Lo fgren, M. Leskela, *Macromol. Rapid Commun*., **1999**, *20*, 487.
26. M. Qian, M. Wang, B. Zhou, R. He, *Appl. Catal. A – Gen*., **2001**, *209*, 11.
27. C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, *Organometallics*, **2003**, *22*, 2545.
28. Z. Zhang, H. Sun, W. Xu, X. Li, *Polyhedron*, **2013**, *50*, 571.
29. R. Bou-Moreno, S. A. Cotton, V. Hunter, K. Leonard, A. W. G. Platt, P. R. Raithby, S. Schiffers, *Polyhedron*, **2011**, *30*, 2832.
30. A. A. A. Abu-Hussen, W. Linert, *Spectrochim. Acta Part A*, **2009**, *74*, 214.

31. J. Emsley, "Die Elemente", Walter de Gruyter, Berlin, 1994.
32. D. Fenske, R. Mattes, J. Loens, K.-F. Tebbe, *Chem. Ber.*, **1973**, *106*, 1139.
33. V. M. Dem'yanovich, I. N. Shishkina, K. A. Potekhin, E. V. Balashova, Yu. T. Struchkov, N.S. Zefirov, *Dokl. Akad. Nauk SSSR*, **1998**, *360*, 645.
34. D. W. Allen, D. Hibbs, M. B. Hursthouse, K. M. A. Malik, *J. Organomet. Chem*., **1999**, *572*, 259.
35. G.M. Sheldrick, *Acta Crystallogr. Sect. A*, **2008**, *64*, 112.
36. K. Brandenburg, DIAMOND – Visual Crystal Structure Information System, Release 3.1d, Crystal Impact GbR, Bonn, Germany, **2006**.