Research Article

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Coordination behavior of $\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}$: Case study $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}]$

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Abstract: The reaction between CdCl_2 and $\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}$ (**1**) in a 1:1 molar ratio resulted in the cadmium(II) complex $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}]$ (**2**). The complex **2** was characterized in solution by NMR spectroscopy (^1H , ^{13}C , and ^{31}P). Single-crystal X-ray diffraction studies revealed no intramolecular $\text{N} \rightarrow \text{P}$ interaction in **1**. The phosphane ligand behaves as a P,N chelating moiety in the cadmium complex **2**, thus resulting in a species containing distorted tetrahedral environments around cadmium and phosphorus. Short intermolecular interactions $\text{CH} \cdots \pi$ aryl and $\text{CH} \cdots \text{O}$ in **1** and $\text{CH} \cdots \pi$ aryl and $\text{CH} \cdots \text{Cl}$ in **2** resulted in supramolecular networks.

Keywords: triarylphosphane ligand, cadmium complexes, chelating behavior, NMR spectroscopy, crystal and molecular structure

1 Introduction

Homo- and heteroleptic triorganophosphanes were frequently used as ligands for transition metal complexes with significant catalytic properties (Alonso et al., 2003; Brunner et al., 1999; Fierro-Arias et al., 2005; Selvakumar et al., 2000). In order to increase both the stability and the specific activity of the metal complexes, new species were developed, containing aryl groups with pendant arms bearing nitrogen atoms capable for intramolecular

coordination, e.g., $\text{PPh}_x[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_{3-x}$ ($x = 0-2$). Such phosphanes are expected to behave as P,N chelating ligands. Several structural features should be mentioned with regard to the metal complexes with such ligands: (i) the intramolecular $\text{N} \rightarrow \text{M}$ coordination results in six membered MPC_3N metallacycles which undergo a conformational exchange in solution (Scheme 1), as it was observed for the mononuclear Pd, Pt, and Rh derivatives (Alonso et al., 2003; Fierro-Arias et al., 2005; Kapteijn et al., 1996; Pfeiffer et al., 2000); (ii) the crystals of these complexes usually contain λ and δ isomers, as a result of the chirality induced to the metal by the $\text{N} \rightarrow \text{M}$ interaction (Connelly et al., 2005). (iii) the phosphanes containing two or three organic groups with pendant arms behave as P,N chelating moieties in mononuclear metal complexes, in most cases with only one nitrogen involved in coordination to the metal centre. Polynuclear species with bridging P,N ligands were also described (Lang et al., 2001).

During last years we reported several metal complexes with triaryl phosphanes capable for a P,N coordination, e.g., $\text{CoCl}_2\text{PPh}_x[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_{3-x}$ (Mitea et al., 2013) and $\text{CuXPPh}_x[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_{3-x}$ ($\text{R} = \text{Me}$, $\text{X} = \text{Cl, Br, I}$; Covaci et al., 2014; $\text{R} = \text{Et}$, $\text{X} = \text{Cl}$; Şuteu et al., 2018), as well as the group 12 metal complexes $\text{MCl}_2\text{PPh}_x[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_{3-x}$ ($x = 0-2$, $\text{M} = \text{Zn, Cd, Hg}$; Dobri et al., 2020). As a continuation of our studies upon group 12 metal complexes, we report here the synthesis and structural characterization of the new cadmium(II) complex $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}]$ (**2**). The crystal and molecular structure of the starting phosphane $\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]-2\}$ (**1**) is also discussed.

2 Results

2.1 Synthesis and spectroscopic characterization

The cadmium complex **2** was synthesised by reacting CdCl_2 with the triarylphosphane **1** in a 1:1 molar ratio,

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using a 1:1 (v:v) mixture of methanol and CH_2Cl_2 as solvent, as depicted in Eq. 1.

The cadmium(II) complex was isolated as a crystalline, colourless solid, with a moderate yield. The compound has a poor solubility in chlorinated solvents, but it has a slightly better solubility in methanol. The elemental analysis and the room temperature NMR spectra (^1H , ^{13}C , and ^{31}P) confirmed the formation of complex **2**.

2.2 X-ray diffraction studies

Selected bond lengths and angles for the phosphane **1** and the cadmium(II) complex **2** are given in Tables 1 and 2, while the thermal ellipsoids representations along with the atom numbering schemes for **1** and **2** are depicted in Figures 1 and 2, respectively.

3 Discussion

3.1 NMR spectroscopy

The NMR spectra of the cadmium complex **2** were recorded in CD_3OD . The ^1H NMR spectrum shows the expected resonances in the aliphatic and the aromatic region, respectively. The resonances in the aliphatic region are broad singlets, two of them determined by the protons $H_{8,11}$ and $H_{9,10}$, respectively in the morpholinyl ring (for numbering see Scheme 2) and a third one assigned to the $\text{C}_6\text{H}_4\text{CH}_2\text{N}$ methylene protons in the pendant arm, thus suggesting a dynamic behaviour in solution, which might be determined by (i) a conformation exchange of the formed six membered metallacycle, as depicted in Scheme 1, and/or (ii) a decoordination/recoordination process accompanied by a conformation exchange of the morpholinyl ring as well (Kulcsar *et al.*, 2007), both of them too fast to be observed at the NMR time scale at

Scheme 1: Conformational exchange of the MPC_3N metallacycle.

Table 1: Selected interatomic distances (Å) and bond angles (deg.) in **1**

1			
C(1)–P(1)	1.848(3)	C(1)–P(1)–C(12)	103.73(15)
C(12)–P(1)	1.835(3)	C(1)–P(1)–C(18)	101.64(15)
C(18)–P(1)	1.838(3)	C(12)–P(1)–C(18)	101.56(15)

Table 2: Selected interatomic distances (Å) and bond angles (deg.) in **2**

2			
Cd(1)–P(1)	2.593(2)	N(1)–Cd(1)–Cl(1)	102.10(18)
		N(1)–Cd(1)–Cl(2)	123.76(16)
		Cl(1)–Cd(1)–Cl(2)	104.05(8)
		N(1)–Cd(1)–P(1)	90.58(17)
		Cl(1)–Cd(1)–P(1)	116.00(8)
Cd(1)–Cl(1)	2.313(2)	Cl(2)–Cd(1)–P(1)	119.65(7)
		C(1)–P(1)–C(12)	111.9(3)
Cd(1)–Cl(2)	2.4366(19)	C(1)–P(1)–C(18)	101.7(4)
Cd(1)–P(1)	2.585(8)	C(12)–P(1)–C(18)	103.4(4)
		Cd(1)–P(1)–C(1)	105.21
C(1)–P(1)	1.911(8)	Cd(1)–P(1)–C(12)	116.64
C(12)–P(1)	1.882(8)	Cd(1)–P(1)–C(18)	117.36
C(18)–P(1)	1.703(8)

Figure 1: Thermal ellipsoids representation at 30% probability and atom numbering scheme of phosphane **1**. Hydrogen atoms are omitted for clarity.

room temperature. Anyway, the ^1H NMR spectrum of this compound gives no clear evidence for a possible $\text{N} \rightarrow \text{P}$ or $\text{N} \rightarrow \text{Cd}$ intramolecular coordination in solution. The ^{13}C NMR spectrum showed the expected resonances, singlets in the aliphatic region and doublets, determined by ^{31}P - ^{13}C couplings in the aromatic region. The ^{31}P NMR resonance is a slightly broad singlet at δ 35.16 ppm. After several hours the ^{31}P NMR spectrum of the same CD_3OD solution revealed the presence of free phosphane (δ -16.02 ppm) formed by decomposition.

Figure 2: Thermal ellipsoids representation at 30% probability and atom numbering scheme of λ -**2**. Hydrogen atoms are omitted for clarity.

3.2 X-ray diffraction studies

3.2.1 Crystal and molecular structure of **1**

The starting triarylphosphane **1** crystallizes in the triclinic $P\bar{1}$ space group. The pendant arm containing the morpholinyl ring is twisted in such a way that no $\text{N} \rightarrow \text{P}$ intramolecular interaction could be observed in the molecule of **1** [$\text{N}(1) \cdots \text{P}(1)$ nonbonding distance is 4.53 Å, vs. $\Sigma r_{\text{vdW}}(\text{P}, \text{N})$ 3.45 Å (Emsley, 1994), by contrast with the situation found in $\text{P}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_3$, for which three different crystalline forms were determined with either all three or only two of the organic groups intramolecularly coordinated to phosphorus ($\text{N} \rightarrow \text{P}$ 3.095(3), 3.032(3), 3.056(3) Å and 3.017(2), 3.007(2) Å, respectively; Chandrasekaran et al., 2002), $\text{PPh}[\text{C}_6\text{H}_4\{\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}\}_2]_2$ (3.038(4) and 3.105(4) Å (Covaci et al, 2009a) or the *N*-methyl piperazinyl substituted derivative $\text{PPh}_2[\text{C}_6\text{H}_4\{\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NMe}\}_2]$ with a $\text{N} \rightarrow \text{P}$ intramolecular interaction of 3.051(3) Å (Covaci et al, 2009b). The coordination geometry of the phosphorus atom is distorted pseudo-tetrahedral, with $\text{C}-\text{P}-\text{C}$ bond angles of an average value of 102.31°, close to that found in the monoclinic modification of triphenylphosphane (102.87°) (Liang et al., 2003) The morpholinyl ring has a *chair* conformation. A closer check of the crystal packing of **1** revealed $\text{C}-\text{H} \cdots \pi$ ($\text{Ph}_{\text{centroid}}$) distances which suggest weak intermolecular contacts. Aromatic $\text{CH}(14) \cdots \text{C}_g[\text{C}(1)-\text{C}(6)]$ 2.92 Å and aliphatic $\text{HCH}(7\text{A}) \cdots \text{C}_g[\text{C}(1)-\text{C}(6)]$ 2.68 Å generate polymeric chains, which are further connected in 2D layers (Figure 3) by $\text{HCH}(9\text{B}) \cdots \text{C}_g[\text{C}(18)-\text{C}(23)]$ contacts of 2.94 Å. Finally, $\text{CH}(4) \cdots \text{O}(1)$ contacts (2.67 Å vs. $\Sigma r_{\text{vdW}}(\text{O}, \text{H}) = 2.72$ Å) generates a 3D network.

3.2.2 Crystal and molecular structure of **2**

The cadmium(II) complex **2** crystallizes in the monoclinic $P2(1)/n$ space group. In this compound the phosphane **1** behaves as a P,N -chelating ligand, with the nitrogen atom in the pendant arm coordinated to cadmium. In this way a six membered CdPC_3N ring is formed, with a boat conformation and the atoms $\text{C}(7)$ and $\text{P}(1)$ in apices. Both cadmium and phosphorus have a distorted tetrahedral geometry with angles ranging from 90.58(17)° to 123.76(16)° around cadmium and from 101.69° to 117.36° around phosphorus. Similarly with the phosphane ligand **1**, the morpholinyl ring has a *chair* conformation, with oxygen and nitrogen in apices. The intramolecular $\text{N} \rightarrow \text{Cd}$ coordination induces chirality to metal and, as a consequence, the compound crystallizes as a mixture of λ and δ isomers (Connolly et al., 2005). The $\text{P}-\text{Cd}$ and $\text{N}-\text{Cd}$ distances are of a similar magnitude as in other closely related cadmium complexes of triarylphosphane ligands (Dobri et al., 2020).

In the crystal of this complex the monomeric units are associated by intermolecular $\text{Cl} \cdots \text{H}$ interactions [$\text{Cl}(1) \cdots \text{H}(15)$ 2.85, $\text{Cl}(2) \cdots \text{H}(5)$ 2.75 Å] in a ladder-like polymer built of λ and δ isomers. Further $\text{HCH}(9\text{B}) \cdots \text{C}_g[\text{C}(12)-\text{C}(17)]$ contacts of 2.84 Å result in a supramolecular layered network (Figure 4). No $\text{Cd} \cdots \text{Cl}$ intermolecular interactions were observed in the crystal of **2**, by contrast with the related complex $\text{CdCl}_2\{\text{PPh}_2[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]\}_2 \cdot \text{CH}_2\text{Cl}_2$ where dimeric units are formed by bridging chlorine atoms (Dobri et al., 2020).

4 Conclusions

A new cadmium(II) complex, namely $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}\}_2]$ (**2**), was prepared and structurally characterized. The room temperature ^1H NMR spectrum suggested no intramolecular coordination of nitrogen to either phosphorus or cadmium in CD_3OD solution. The solid-state structure of both the starting phosphane $\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}\}_2$ (**1**) and the cadmium(II) complex **2**, determined by single crystal X-ray diffraction, revealed no $\text{N} \rightarrow \text{P}$ interactions. The phosphane acts as a P,N chelating ligand towards cadmium in **2**, thus resulting in a six membered non-planar CdNC_3P metallacycle. In both compounds short intermolecular contacts generate supramolecular assemblies.

Experimental

The triarylphosphane $\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}\}_2$ (**1**) was prepared according to the procedure reported

Figure 3: A layer built by C–H... π ($\text{Ph}_{\text{centroid}}$) interactions in the crystal of the phosphane **1**. Hydrogen atoms, except those involved in intermolecular interactions, are omitted for clarity. Symmetry equivalent positions $1-x, -y, 1-z$; $1-x, -y, 2-z$ and $x, 1+y, z$ are given by *prime*, *second*, and *tert*, respectively.

Figure 4: Supramolecular network in the crystal of **2**. Hydrogen atoms, except those involved in intermolecular interactions, are omitted for clarity. Symmetry equivalent positions $2-x, -y, 1-z$; $-1/2+x, 1/2-y, -1/2+z$ and $3/2-x, -1/2+y, 1/2-z$ are given by *prime*, *second*, and *tert*, respectively.

previously (Covaci et al., 2014). CdCl_2 was commercially available and used as purchased from Aldrich. Solvents were dried (MeOH on magnesium, CH_2Cl_2 on CaCl_2 and n-hexane on sodium) and distilled under argon prior to use. Elemental analysis were performed on a VarioEL 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 operating at 300.13 and 121.48 MHz, respectively. The chemical shifts are reported in δ units (ppm) relative to TMS [ref. CH_3OH : ^1H 3.31 ppm (qv), 4.87 ppm (s)] and H_3PO_4 85% (^{31}P). The assignments of the ^1H chemical shifts were made according to the numbering scheme depicted in Scheme 2.

Preparation of $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}-2\}]$ (2)

A mixture of CdCl_2 (0.183 g, 1 mmol) and $\text{PPh}_2[\text{C}_6\text{H}_4\{\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}-2\}]$ (0.361 g, 1 mmol) in a 1:1 (v:v) $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture (50 mL) was stirred for 2 h at room temperature. From the clear solution, the solvents were removed in vacuum and the remaining sticky solid was treated with n-hexane (20 mL). The title compound precipitated and it was isolated by filtration as a colourless powder. Yield: 0.392 g (72%). M.p. 135–136°C. Anal. calcd. for $\text{C}_{23}\text{H}_{24}\text{CdCl}_2\text{NOP}$ ($M = 544.74$): C 50.71, H 4.44, N 2.57; Found: C 50.48, H 4.39, N 2.62. ^1H NMR (CD_3OD): $\delta = 2.18$ (br., 4H CH_2 , morph, $H_{8,11}$), 3.16 (br., 4H CH_2 , morph, $H_{9,10}$), 3.78 (s, br., 2H, $\text{C}_6\text{H}_4\text{CH}_2\text{N}$, H_7), 7.02 (dd, 1H, $\text{P}-\text{C}_6\text{H}_4$, H_6 , $^3J_{\text{HH}} = 7.6$, $^3J_{\text{PH}} = 13.5$ Hz), 7.20 (t, 1H, $\text{P}-\text{C}_6\text{H}_4$, $H_{4/5}$, $^3J_{\text{HH}} = 7.7$ Hz), 7.31 (t, 1H, $\text{P}-\text{C}_6\text{H}_4$, $H_{4/5}$, $^3J_{\text{HH}} = 7.2$ Hz), 7.44–7.64 (m, 1H, $\text{P}-\text{C}_6\text{H}_4$, H_3 , + 10H $\text{P}-\text{C}_6\text{H}_5$); ^{13}C NMR (CD_3OD): $\delta = 54.10$ (s, $\text{N}(\text{CH}_2)_2$), 52.29 (d, CH_2N , $^3J_{\text{PC}} = 6.9$ Hz), 67.32 (s, $\text{O}(\text{CH}_2)_2$), 128.18 (d, $\text{P}-\text{C}_6\text{H}_4$, $^3J_{\text{PC}} = 8.7$ Hz), 129.62 (d, $\text{P}-\text{C}_6\text{H}_5$, $^4J_{\text{PC}} = 5.4$ Hz), 129.92 (d,

Scheme 2: Numbering scheme for ^1H NMR assignments.

$\text{P}-\text{C}_6\text{H}_5$, $^3J_{\text{PC}} = 12.3$ Hz), 132.74 (d, $\text{P}-\text{C}_6\text{H}_5$, $^2J_{\text{PC}} = 9.8$ Hz), 133.39 (br., $\text{P}-\text{C}_6\text{H}_4$), 134.77 (d, $\text{P}-\text{C}_6\text{H}_4$, $^3J_{\text{PC}} = 13.2$ Hz), 135.74 (d, $\text{P}-\text{C}_6\text{H}_4$, $^4J_{\text{PC}} = 6.5$ Hz). The resonances for ipso carbon atoms could not be assigned. ^{31}P NMR (CD_3OD): $\delta = 35.16$ (s).

Crystal structure determination

Single-crystals of compounds **1** and **2** suitable for X-ray diffraction studies were obtained from CH_2Cl_2 and were attached with Paratone N oil on cryoloops. The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The details of the crystal structure determination and refinement are given in Table 3. The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined

Table 3: Crystal data and structure refinement for $\text{PPh}_2[\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}-2]$ (**1**) and $\text{CdCl}_2[\text{PPh}_2\{\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}-2\}]$ (**2**)

	1	2
Empirical formula	$\text{C}_{23}\text{H}_{24}\text{NOP}$	$\text{C}_{23}\text{H}_{24}\text{CdCl}_2\text{NOP}$
Formula weight	361.40	544.70
Temperature (K)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	P-1	P2(1)/n
<i>a</i> (Å)	8.417(3)	9.937(3)
<i>b</i> (Å)	10.648(3)	15.982(4)
<i>c</i> (Å)	11.364(3)	14.714(4)
α (°)	88.595(6)	90
β (°)	75.145(5)	90.014(5)
γ (°)	86.045(5)	90
Volume (Å ³)	982.1(5)	2336.8(11)
<i>Z</i>	2	4
Density (calculated) (g/cm ³)	1.222	1.548
Absorption coefficient (mm ⁻¹)	0.151	1.246
<i>F</i> (000)	384	1096
Crystal size (mm)	0.33 x 0.22 x 0.21	0.51 x 0.36 x 0.23
θ range for data collections (°)	2.51 to 25.00	1.88 to 25.00
Reflections collected	9521	12014
Independent reflections	3448	4106
	[<i>R</i> (int) = 0.0550]	[<i>R</i> (int) = 0.0375]
Max. and min. transmissions	0.9710 and 0.9519	0.751 and 0.590
Refinement method		
Data/restraints/parameters	3448/0/235	4106/0/250
Goodness-of-fit on <i>F</i> ²	1.121	1.098
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0778, w <i>R</i> 2 = 0.1573	<i>R</i> 1 = 0.0753, w <i>R</i> 2 = 0.2140
<i>R</i> indices (all data)	0.1061, w <i>R</i> 2 = 0.1683	<i>R</i> 1 = 0.0874, w <i>R</i> 2 = 0.2229
Largest diff. peak and hole (eÅ ⁻³)	0.300 and -0.214	1.787 and -1.002

with a riding model and a mutual isotropic thermal parameter. The structures were solved and refined using the software package SHELX-97 (Sheldrick, 2008) and the drawings were created with the Diamond program (Brandenburg, 2006). Short C–H $\cdots\pi$ (Ph_{centroid}), H $\cdots$ O and H $\cdots$ Cl intermolecular contacts were found with PLATON (Spek, 2009).

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 751323 and 751322 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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References

- Alonso M.A., Casares J.A., Espinet P., Soulantica K., Orpen A.G., Phetmung H., Conformational Preferences Driven by the C-Methyl Substituent in Chelated *o*-Diphenylphosphino- α -methyl-*N,N*-dimethylbenzylamine Rhodium Complexes. *Inorg. Chem.*, 2003, 42, 3856-3864. DOI: 10.1021/ic034117a
- Brandenburg K., DIAMOND – Visual Crystal Structure Information System, Release 3.1d. Crystal Impact GbR, Bonn, Germany, 2006.
- Brunner H., Deml I., Dimberger W., Ittner K.P., Reißer W., Zimmermann M., Synthesis of the Stereoisomers of Methohexital by Palladium-Catalyzed Allylation. *Eur. J. Inorg. Chem.*, 1999, 51-59. DOI: 10.1002/(SICI)1099-0682
- Chandrasekaran A., Timosheva N.V., Day R.O., Holmes R.R., Pseudoheptacoordination and Pseudohexacoordination in Tris(2-*N,N*-dimethylbenzylamino)phosphane. *Inorg. Chem.*, 2002, 41, 5235-5240. DOI: 10.1021/ic020153i
- Connelly N.G., Damhus T., Hartshorn R.M., Hutton A.T., Nomenclature of Inorganic Chemistry-IUPAC Recommendations 2005. RSC Publishing, Cambridge, 2005.
- Covaci A., Varga R.A., Silvestru C., Bis[2-(morpholinomethyl)phenyl]phenyl-phosphane. *Acta Crystallogr. E*, 2009a, 65, o3158-o3159. DOI: 10.1107/S1600536809048946
- Covaci A., Raț C.I., Silvestru C., [2-(4-Methyl-piperazin-1-yl)methyl]phenyl]diphenyl-phosphane. *Acta Crystallogr. E*, 2009b, 65, o3193. DOI: 10.1107/S1600536809049526
- Covaci A., Mitea R., Hosu I., Silvestru A., Copper(I) complexes with the triarylphosphanes $\text{PPh}_n(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_{3-n}$ ($n = 0-2$) and $\text{PPh}_2[\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}-2]$. Synthesis and structural characterization. *Polyhedron*, 2014, 72, 157-163. DOI: 10.1016/j.poly.2014.01.035
- Dobri A., Covaci A.I., Covaci A., Silvestru A., Group 12 metal complexes with P,N chelating triarylphosphanes. Solution behaviour and solid state structure. *Polyhedron*, 2020, 182, 114511. DOI: 10.1016/j.poly.2020.114511
- Emsley J., Die Elemente. Walter de Gruyter, Berlin, 1994.
- Fierro-Arias J.G., Redon R., Garcia J.J., Hernandez-Ortega S., Toscano R.A., Morales-Morales D., Pd catalyzed Heck reaction with the catalytic system $[\text{Pd}(\text{Ph}_2\text{PC}_6\text{H}_4-2-(\text{CH}_2\text{NMe}_2))(\text{SRF})_2]$: Examination of the electronic effects of fluorinated thiolates. *J. Mol. Catal. A-Chem.*, 2005, 233, 17-27. DOI: 10.1016/j.molcata.2005.02.007
- Kapteijn G.M., Spee M.P.R., Grove D.M., Kooijman H., Spek A.L., van Koten G., Chemistry of P,N-Ligated Methylpalladium(II) Alkoxide Complexes: Syntheses, Structural Features in the Solid State and in Solution, and Hydrogen-Bond Formation. *Organometallics*, 1996, 15, 1405-1413. DOI: 10.1021/om950661i
- Kulcsar M., Beleaga A., Silvestru C., Nicolescu A., Deleanu C., Todasca C., et al., Solid state structure and solution behaviour of organoselenium(II) compounds containing 2- $\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}$ C_6H_4 groups ($\text{E} = \text{O}, \text{NMe}$). *Dalton T.*, 2007, 29, 2187-2196. DOI: 10.1039/b702629c
- Lang H., Leschke M., Mayer H.A., Melter M., Weber C., Rheinwald G., et al., A new type of dicopper structure with side arm coordinating triarylphosphane ligands. *Inorg. Chim. Acta*, 2001, 324, 266-272. DOI: 10.1016/S0020-1693(01)00619-3
- Liang L.-C., Lee W.-Y., Hung C.-H., Amido Phosphine Complexes of Zinc. *Inorg. Chem.*, 2003, 42, 5471-5473. DOI: 10.1021/ic0346228
- Mitea R., Covaci A., Silvestru C., Silvestru A., Cobalt(II) complexes with hypervalent triarylphosphanes. *Rev. Roum. Chim.*, 2013, 58 (2-3), 265-273.
- Pfeiffer J., Kickelbick G., Schubert U., Transition Metal Silyl Complexes. Platinum Dimethyl Complexes with Hemilabile P,N-Chelating Ligands: Synthesis, Structure, and Reactions with Iodotrimethylsilane and 1,2-Bis(dimethylsilyl)benzene. *Organometallics*, 2000, 19, 62-71. DOI: 10.1021/om990665d
- Selvakumar K., Valentini M., Pregosin P.S., Albinati A., Eisentraeger F., Catalytic and Structural Studies on Complexes of a Binaphthyl-Phosphino-Oxazoline Auxiliary: The Meta Dialkyl Effect on Enantioselectivity. *Organometallics*, 2000, 19, 1299-1307. DOI: 10.1021/om990892f
- Sheldrick G.M., A short history of SHELX. *Acta Crystallogr.*, 2008, A64, 112-122. DOI: 10.1107/S0108767307043930.
- Spek A.L., Structure validation in chemical crystallography. *Acta Crystallogr.*, 2009, D65, 148-155. DOI: 10.1107/S090744490804362X
- Șuteu R., Shova S., Silvestru A., Triarylphosphanes with 2-(Et_2NCH_2) C_6H_4 groups. Copper(I) complexes and oxidation derivatives of type $\text{EP}(\text{C}_6\text{H}_4\text{CH}_2\text{NEt}_2-2)_n\text{Ph}_{3-n}$ ($\text{E} = \text{S}, \text{Se}; n = 1, 2$). *Inorg. Chim. Acta*, 2018, 475, 105-111. DOI: 10.1016/j.ica.2017.09.044