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# Novel functionalised P-ligands: advances and application

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**Abstract**

Novel endo- and exocyclic phosphine ligands possessing different functionalities obtained by reduction of the P=O precursors with desired stereochemistry are discussed. The diastereoselective deoxygenation including the catalytic reduction processes, the factors defining the reactivity and the role of the substituents on the stability of phosphorus atom configuration in a series of 3-aryl-3-phosphabicyclo[3.1.0]hexanes are reported. The complexation features of the ligands with Rh(III) and Pd(II) were examined and Rh(III) complexes were tested in styrene hydroformylation showing the structure–activity dependence.


*Keywords:* Cyclic and acyclic phosphine oxides; Deoxygenation; Cyclic phosphines; 3-Cyano-1,2-thiaphosphacyclanes, 1-(Phosphino)cyclopropane carbonitriles, Rhodium and palladium complexes; Stereostructure; Hydroformylation; Homogeneous catalysis

## 1. Introduction

Transition metal complexes incorporating σ-donor phosphines as the ligands are frequently used as catalyst precursors in hydroformylation and hydrogenation reactions [1]. Taking into account that search of novel effective catalysts for a variety of applied processes is a never-ending story we would like to demonstrate our results in this field.

In principle phosphine oxides are the most important precursors of a variety of phosphine ligand-blocks as it is much easier to carry out the modification of chemical and stereochemical structure using stable in any sense compounds of the tetracoordinated phosphorus atom and such approach is widely used.

In this paper, our findings on the deoxygenation of the phosphine precursors bearing both endo- and exocyclic phosphorus atom and on the stereostructure of the P-ligands, as well as the transition metal (Rh(III) and Pd(II)) complexes based on the phosphines obtained along with their catalytic activity are discussed.

## 2. Results and discussion

For the preparation of phosphines, the reduction of the corresponding phosphine oxides by silane hydrides [2] is the best choice due to the selectivity and efficiency. To the best of our knowledge the general limitations of the method and comparison of the reactivity with the

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compound structures are not discussed in literature. To elucidate this problem three types of P=O precursors were involved in trichlorosilane reduction, namely saturated and non-saturated phosphacyclanes (**1a**–**c**, **4**), 2-oxo-1,2$\lambda^5$-thiaphosphacyclanes (**8c**, **9f**) which present phosphacyclanes having the heteroatom in the α-position to the phosphorus atom, and compounds (**14**–**16**) with the exocyclic phosphorus atom bearing carbocycle in α-position.

### 2.1. Synthesis of the 3-phosphabicyclo[3.1.0]hexane and dihydrophosphinine ligands and their $Rh^{III}$ and $Pd^{II}$ complexes

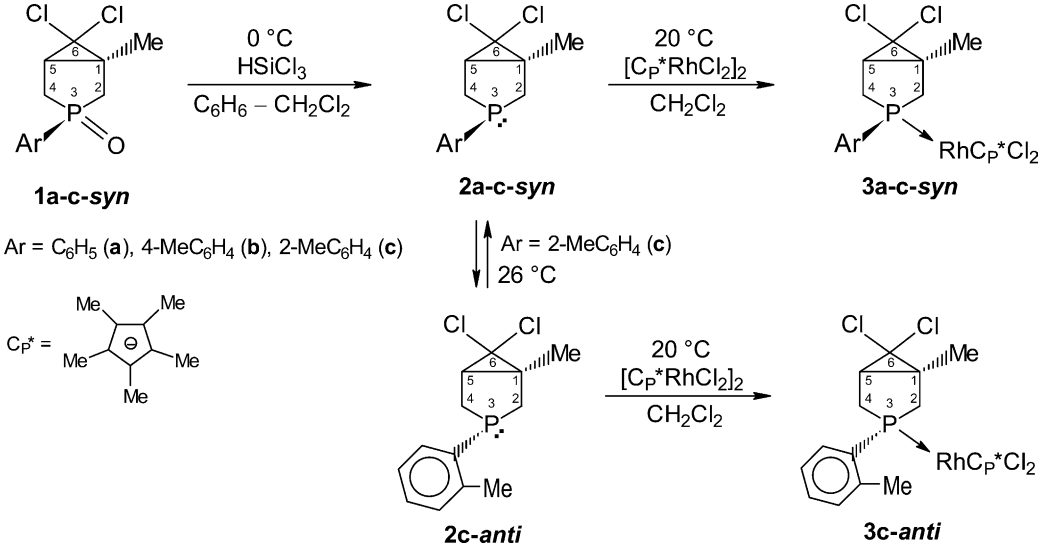
The facile synthesis of 6,6-dichloro-1-methyl-3-aryl-3-phosphabicyclo[3.1.0]hexane 3-oxides (**1a**–**c**) used as starting substrates of the first type by dichlorocyclopropanation of the corresponding 2,5-dihydrophosphole oxide under phase transfer catalytic conditions was reported by one of us earlier [3–5]. Such synthesis resulted in single isomers with *syn* disposition of the cyclopropane ring and the P-aryl substituent when the latter presents phenyl or *p*-tolyl. The corresponding *o*-tolyl derivative (**1c**) was formed as a 6:4 mixture of *syn*- and *anti*-isomers, which were separated by chromatography [5]. For further reduction procedure the pure *syn*-isomers **1a**–**c** were utilized.

The deoxygenation of phosphine oxides **1a**,**b** with trichlorosilane proceeded very easily even at 0 °C to afford the desired phosphines **2a**,**b** as the only reaction product, Scheme 1 [6]. At a higher temperature (even at ambient conditions), the formation of side-products presenting according to the NMR data a series of primary and secondary phosphines (up to 45–50% in total, $\delta_P$ of ca. $-40 \div -68$ ppm and the $^1J_{PH}$ coupling constants of ca. 480–500 Hz) could be observed apparently due to the rupture of the endocyclic P–C bonds.

At the same time, a similar reduction procedure used for **1c** possessing *o*-tolyl substituent at the phosphorus atom led to two closely related forms of product (**2c**), having $\delta_P$ signals in the phosphine region and the same pattern of signals in the $^{13}C$ NMR spectra. The ratio of the components depended on the reaction time and was 95:5 after the standard procedure (2 h at 0 °C followed by 2 h at 20 °C) and changed to 38:62 after a 6 days' standing. These two products were assigned to *syn*- and *anti*-diastereomers of **2c** (Scheme 1).

The interaction of phosphines **2a**,**b** with dimeric pentamethylcyclopentadienyl rhodium dichloride resulted in the typical formation of complexes of type $C_P$*$RhCl_2L$ (**3a**,**b**) in high yield. The single crystal X-ray analysis performed for **3b**-*syn* confirmed the *cis* disposition of the P-*p*-tolyl substituent and the cyclopropane ring and similarity in spectral features of phosphines **2a**,**b** and their complexes **3a** and **3b** allowed us to conclude that complex **3a** also has the *syn*-geometry [6]. On addition of the Rh(III) precursor to the mixture of phosphine isomers (**2c**-*syn* and **2c**-*anti*) in different times, the two different Rh(III) complexes (**3c**-*syn* and **3c**-*anti*) were formed in the same ratio observed for the phosphines **2c**-*syn* and **2c**-*anti* used in the complexation reaction. The stereostructure of both isomers of complex **3c** was confirmed by X-ray analysis (Figs. 1 and 2) justifying the tentative assignment, the *syn* or the *anti* disposition of the P-aryl substituent and the cyclopropane ring [6].

It should be noted that according to the X-ray and elemental analysis data rhodium (III) complexes **3a**–**c** were found to form strong solvates with dichlorometh-




Scheme 1.

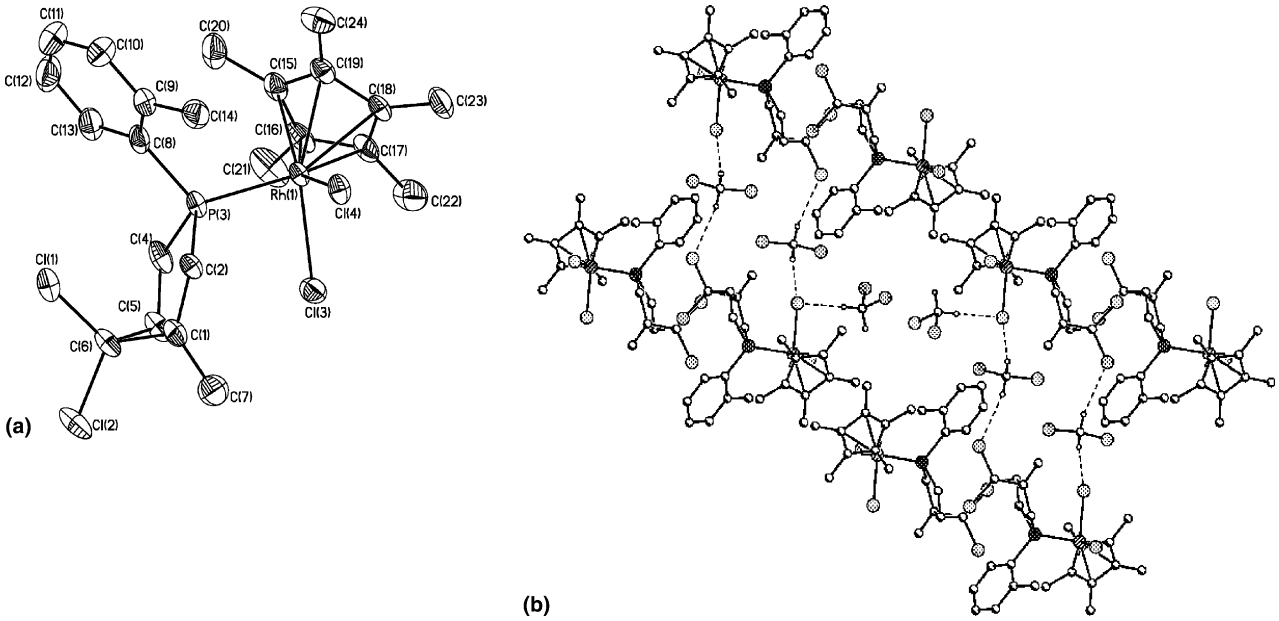



Fig. 1. (a) The general view of **3c**-*syn*-$2CH_2Cl_2$ in representation of atoms by thermal motion ellipsoids at 50% probability level. Hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond lengths (Å): P(3)–Rh(I) 2.3207(8), P(3)–C(2) 1.848(3), P(3)–C(4) 1.854(3), P(3)–C(8) 1.828(3). Selected bond angles and torsion angles (°): P(1)Rh(1)–centre(Cp*) 124.1, C(2)P(3)C(4) = 95.9(1), P(3)Rh(1)C(15)C(20) = 8.3(4), C(2)P(3)C(8)C(9) = 61.3(3). (b) The scheme illustrating the crystal packing pattern of the $CH_2Cl_2$ solvate.

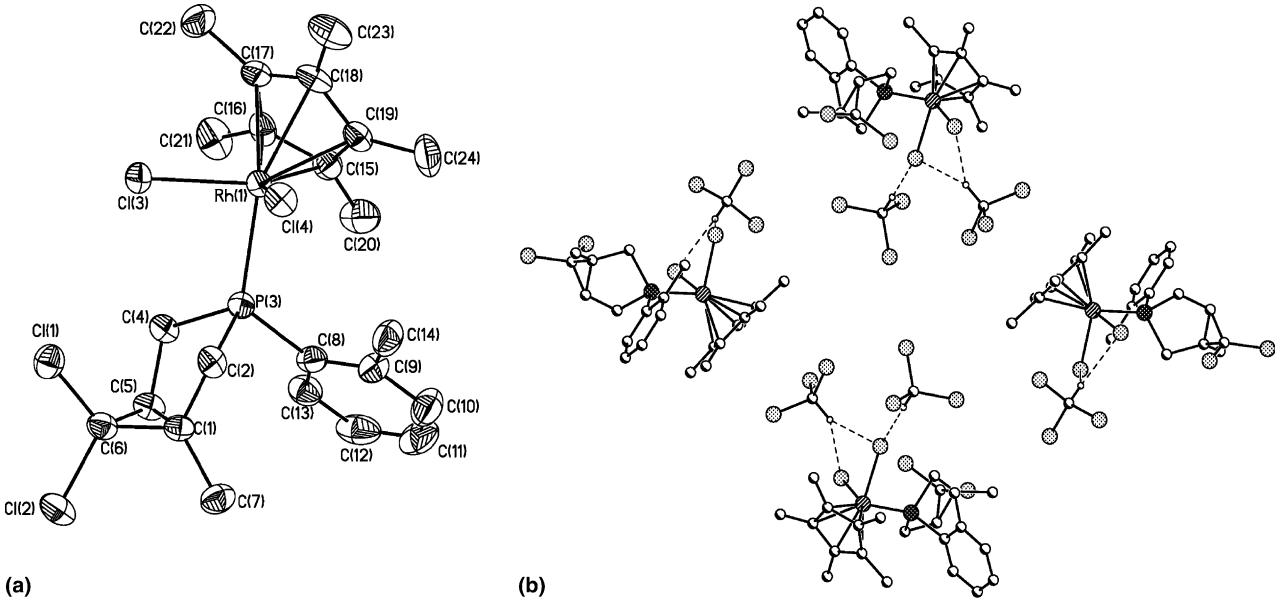



Fig. 2. (a) The general view of one of independent molecules of **3c**-*anti*-$2CHCl_3$ in representation of atoms by thermal motion ellipsoids at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å): P(3)–Rh(I) 2.300(1), P(3)–C(2) 1.834(4), P(3)–C(4) 1.838(4), P(3)–C(8) 1.826(4). Selected bond and torsion angles (°): P(1)Rh(1)–centre(Cp*) 131.7, C(2)P(3)C(4) 91.6(1), P(3)Rh(1)C(15) C(20) 7.4(3)/−9.9(3), C(2)P(3)C(8)C(9) 71.1(4). (b) The scheme illustrating the crystal parking pattern of the $CHCl_3$ solvate.

ane used as a solvent for complexation and in some cases we failed to remove the solvent even at prolonged drying in vacuo at an elevated temperature. Moreover, recrystallization of **3c**-*syn* from chloroform gave the corresponding pseudopolymorph modification as a chloroform solvate, which structure was also confirmed by X-ray diffraction investigation. Apparently, the solvates are stabilized by numerous H···Cl interactions formed between the $RhCl_2$ moiety and the dichloromethane or the chloroform molecules. Figs. 1(b) and 2(b) show the crystal packing pattern of solvates obtained for both isomers of **3c**.

The phosphines **2a**,**b**-*syn* demonstrate chemical shifts $\delta_P$ of ca. 25 ppm in $CDCl_3$, signals of both isomers of **2c** are situated in the same region and at that **2c**-*syn* has upfield shift (22.6 ppm) as compared with the one for **2c**-*anti* (27.9 ppm). The Rh(III) complexes are characterized by $\delta_P$ shifts close to those for P═O precursors **1a**–**c** and characteristic disposition of signals for *syn*- and *anti*-isomers of **3c** is the same as that observed for the corresponding isomers of phosphine **2c** (**3c**-*syn* has upfield chemical shift at 67.8 ppm in comparison with **3c**-*anti* (91.6 ppm)). In the $^{13}C$ NMR spectra of **2a**–**c** and **3a**–**c** the signals of the skeletal carbon atoms are situated in about the same regions that were observed for their P═O precursors **1a**–**c** with normal decrease in $J_{PC}$ coupling constants passing from phosphine oxides **1a**–**c** to Rh(III) complexes **3a**–**c** and further to phosphines **2a**–**c**. The large value $\Delta\delta$ between **2** and **3** suggested a rather strong coordination between the phosphorus and Rh(III) atoms in this series.

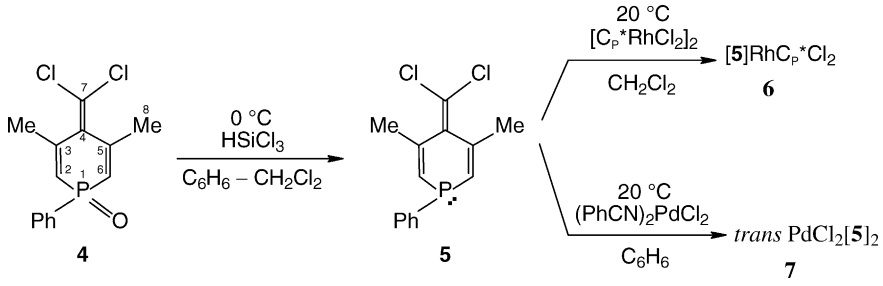
It is known that trichlorosilane alone or more conveniently its pyridine complex reduces phosphine oxides with retention of configuration. Only in the presence of amines of base strength greater than about p$K_b$ 5, such as triethylamine, the inversion was observed to take place predominantly [7]. Detailed mechanisms of both processes with different stereochemistry outcome are still unclear, but it was suggested [7] that in the absence of amine the first step is the complexation of phosphoryl oxygen by the silicon atom of the silane. Such complex transfers oxygen to silicon leaving protonated phosphine. At using the mixture trichlorosilane/$Et_3N$ the first step include the transfer of proton to the oxygen atom of P═O moiety and subsequent attack by $SiCl_3^-$ anion resulting in inversion.

First of all one may assume that reduction of 3-phosphabicyclohexane 3-oxides **1a**–**c** by trichlorosilane alone resulted in the formation of the corresponding phosphine with preserved P-configuration that unexpectedly was followed by the inversion only in the case of compound **2c** bearing an *o*-tolyl substituent. As commonly phosphines do not undergo P-inversion at ambient conditions, in order to estimate the possibility of easy inversion in the case of **2c** we carried out quantum chemical calculations at the B3PW91 DFT level of theory with the 6-31G* basis set for both the *syn*- and the *anti*-isomers of phosphines **2a** and **2c**. According to these calculations the corresponding *anti*-isomers are thermodynamically more stable in both cases. The difference in energy between the two isomers is higher for the unsubstituted phosphine **2a** in comparison with **2c** (1.79 kcal/mol (**2a**) and 0.83 kcal/mol (**2c**)). At the same time, going in the *syn*- to *anti*-direction the inversion barrier estimated as the difference in energy between *syn*-isomer and the transition planar state is somewhat smaller for **2c** than that for **2a** ($E_{syn} - E_{TS}$ 33.256 and 33.943 kcal/mol correspondingly). Although the difference between these values is not significant (0.687 kcal/mol), the tendency read from the energy values fits the observation. Nevertheless, the rather high value of the inversion barrier calculated suggests that one should not exclude that reduction in the case of **1c** proceeds via the different mechanism (with partially inversion of configuration) in comparison with its phenyl or *p*-tolyl analogues **2a**,**b** or is accompanied by the formation of an intermediate with the pentacoordinated phosphorus atom which may undergo the bipyramidal inversion. This question is currently under detail investigation.

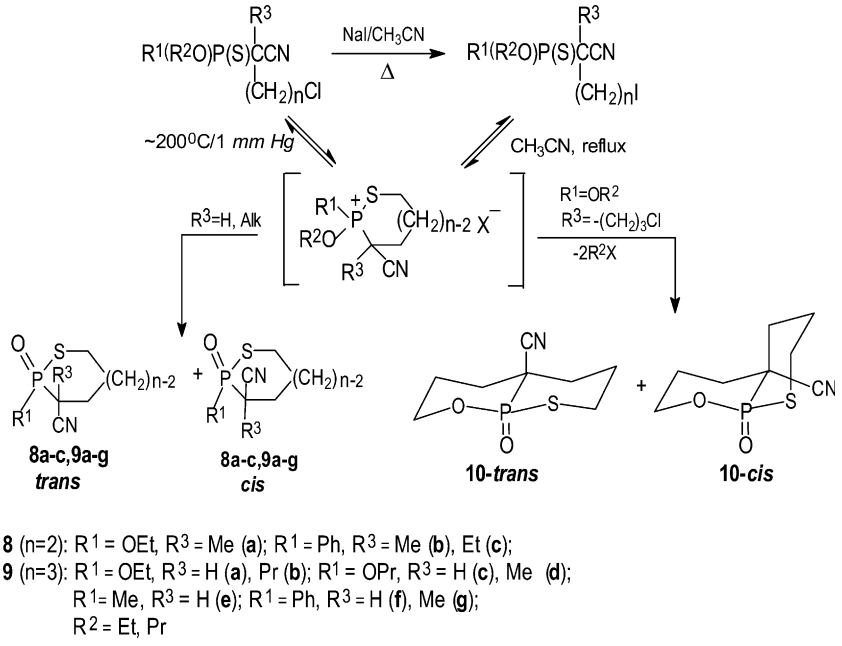
The analogous series of reactions (reduction by trichlorosilane followed by complexation) was applied to 4-dichloromethylene-1,4-dihydrophosphinine 1-oxide **4** [8]. In this case, the reduction at 0 °C and the subsequent complexation with dimeric pentamethylcyclopentadienyl rhodium dichloride or with *trans*-dichloro(dibenzonitrile)palladium furnished phosphine **5** and complexes **6**, **7**, respectively (Scheme 2).

### 2.2. Synthesis of 3-cyano-1,2$\lambda^3$-thiaphosphacyclanes

Recently we have shown that the intramolecular cyclization in a series of ω-haloalkyl substituted thiophosphoryl compounds which mechanism involves the S-alkylation of the P═S group followed by the dealkylation of the P-alkoxy group in the quasiphosphonium salt formed, represents a convenient general route to 2-oxo-1,2$\lambda^5$-thiaphosphacyclanes both functionalized or not [9]. In the case of ω-haloalkyl substituted thiophosphorylacetonitriles, such methodology gave rise to either mono or bicyclic cyanosubstituted thia-




Scheme 2.

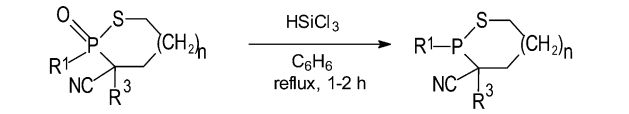



**8** (n=2): R1 = OEt, R3 = Me (**a**); R1 = Ph, R3 = Me (**b**), Et (**c**);
**9** (n=3): R1 = OEt, R3 = H (**a**), Pr (**b**); R1 = OPr, R3 = H (**c**), Me (**d**);
R1 = Me, R3 = H (**e**); R1 = Ph, R3 = H (**f**), Me (**g**);
R2 = Et, Pr

Scheme 3.

phosphacyclanes (Scheme 3) [10]. Compounds **8a**–**c**, **9a**–**g** and **10** were formed as mixtures of $R^*_P, R^*_C$-*cis* and $R^*_P, S^*_C$-*trans* isomers differing in the mutual disposition of the phosphoryl oxygen atom and the cyano group in relation to the ring plane and separated by chromatography. The *cis*- and *trans*-arrangements of the substituents was unambiguously confirmed by the X-ray data [9] and corresponded well to typical $^1$H NMR spectroscopic analysis based on the deschielding effect of the P=O bond on all the kinds of protons situated in the *cis*-position to the P=O group according to [11]. Moreover, it was shown that a *cis*-isomer is characterized by a downfield chemical shift for **8** while for six-membered compounds **9** a downfield chemical shift in the $^{31}$P NMR spectrum correspond to the *trans* disposition of the mentioned substituents [10]. The similar characteristic disposition of the signals in the $^{31}$P NMR spectra was observed for cyano substituted cyclic compounds with tricoordinated phosphorus atom [12]. Thus, $^{31}$P NMR spectroscopy allows one to assign unambiguously the type of geometric isomer and therefore the configuration of the asymmetric centers in the case of 3-cyano-1,2-thaiphosphacyclanes bearing both P(III) and P(IV) atoms.

As in the previous case, for further reduction we used merely individual isomers. In contrast to the above mentioned phosphacyclanes **1a**–**c**, **4**, more severe conditions are required for the reduction of 3-cyano-2-oxo-1,2-thiaphosphacyclanes **8c**, **9f** by trichlorosilane, namely refluxing in benzene solution over 1–2 h (Scheme 4). Nevertheless, side products were not observed in the reaction mixtures and the target 3-cyano-1,2$\lambda^3$-thiaphosphacyclanes **11**, **12** are formed in practically quantitative yields as a single isomer. [1] Surprisingly, the reduction either in presence of triethylamine, or in the absence of the latter one resulted in the products with the same stereochemical configuration which was ascertained by $^{31}$P NMR spectroscopic analysis. As the formal seniority of the substituents changes passing from tetracoordinated phosphorus compounds to the three coordinated ones, in all the cases, $R^*_P, R^*_C$-*cis* isomers of 2-oxo-derivatives yielded the $R^*_P, S^*_C$-*trans* isomers of 1,2$\lambda^3$-thiaphosphacyclanes and vice versa. That is to say, the ring structure remained intact in the reaction course.




**8c**-*cis*, **8c**-*trans*, **9f**-*cis*, **9f**-*trans* — **11**-*trans*, **11**-*cis*, **12**-*trans*, **12**-*cis*

R1=Ph, R3=Et, n=0 (**8c**, **11**); R1=Ph, R3=H, n=1 (**9f**,**12**)

Scheme 4.

It should be mentioned that the linear analogue of 2-oxo-1,2-thiaphosphacyclanes, e.g. diphenyl(thiopropyl) phosphine oxide – remains invariable either under the same reduction conditions or more severe ones (refluxing in xylene). This fact clearly indicates that cyclic phosphine oxides are much more reactive than the linear ones.

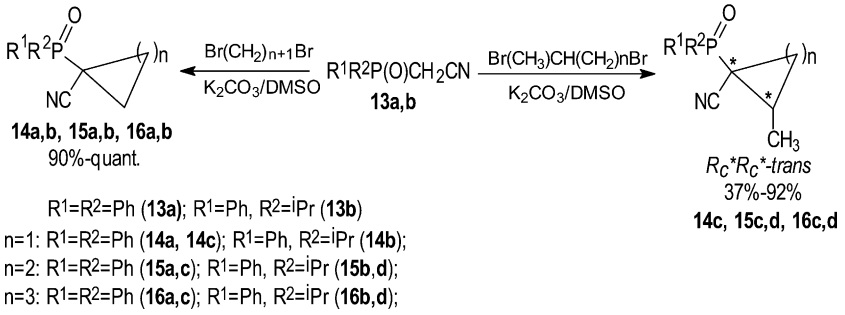
[1] The complexation features of the 1,2$\lambda^3$-thiaphosphacyclanes will be published elsewhere.

### 2.3. Synthesis of the 1-(phosphino)cyclopropane carbonitriles

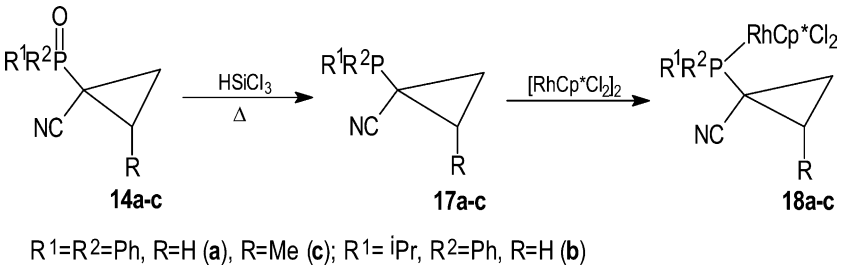
Among functionalized phosphine ligands, those containing phosphorus and nitrogen complexing centers in a molecule are of special interest showing high catalitic activity in many reactions [1a]. Nevertheless, only a limited number of such ligands including sp-hybridized nitrogen atom as a coordination site are reported in literature, e.g. cyanomethylphosphines [13–15] and cyanoethylphosphines [16–18]. Cyanosubstituted phosphines with rather rigid stereochemical structure advantageous for metal complex catalysis were of undoubted interest.

1-(Phosphino)cycloalkane carbonitriles potentially containing a few stereogenic centers in the molecule meet these conditions. Therefore the third group of compounds involved in reduction presented 1-(phosphoryl)cycloalkane carbonitriles. The precursors were obtained by cycloalkylation of phosphorylacetonitriles 13a,b with α,ω- and α,ψ-dihaloalkanes under phase transfer catalysis conditions (Scheme 5). The reaction with α,ω-dihaloalkanes was carried out according to procedure elaborated by us earlier [19]. Despite in the case of α,ψ-dihaloalkanes one could expect the formation of reaction products as statistic mixture of *cis*- and *trans*-isomers, unexpectedly such reaction of phosphoryl and thiophosphorylacetonitriles turned out to proceed in a diastereoselective way, yielding only *trans*-isomer with the identical configuration of asymmetric carbon atoms ($C^*_RC^*_R$). In the case of additional asymmetric phosphorus atom in the starting substrate, *trans*-isomers are formed as a mixture of diastereomers differing in phosphorus atom configuration ($P^*_SC^*_RC^*_R$ and $P^*_RC^*_RC^*_R$) [20].

As for the reduction of the cycloalkanecarbonitriles **14–16**, the reduction rate is significantly lower in comparison with the above discussed phosphacyclanes being in direct correlation with the ring size (Scheme 6). For comparison, the reduction of diphenylphosphoryl acetonitrile proceeds with about the same rate as in the case of 2-oxo-1,2-thiaphosphacyclanes (1 h, $C_6H_6$, 80 °C) yielding the corresponding phosphine in a nearly quantitative yield. Passing from the corresponding cyclopropane to cyclopentane derivatives not only elongation of the reaction time, but also higher reaction temperatures are necessary. Nevertheless, the reaction was not completed even under rather severe conditions (140 °C, 37 h) in the case of cyclopentane derivatives. Such result cannot be explained due to the difference in electronic factors in a series of 1-(phosphoryl)cycloalkane carbonitriles **14–16**, as they are practically the same in the all compounds. Therefore the main reason of such behavior is likely connected with increase of the steric hindrances growing up with the increase of the cyclic size and preventing the formation of the intermediate with the hypervalent silicon atom. The influence of steric hindrances on the reduction of phosphine oxides by $HSiCl_3$ was confirmed by the model reaction, namely we failed to reduce even at 140 °C (40 h) 1-diphenylphosphoryl-1-methylpropane nitrile which is the direct linear structural analogue of the above mentioned phosphorylated cycloalkanecarbonitriles.




Scheme 5.




Scheme 6.

The attempt to carry out the catalytic reduction of 1-(phosphoryl)cycloalkane carbonitriles using $(EtO)_3SiH$ and catalytic amount of $Ti(O^iPr)_4$ according to [21] resulted in about 40% formation of secondary phosphines (either $Ph_2PH$ or $Ph^iPrPH$ depending on the substituents at the phosphorus atom of the precursor) as side products due to the rupture of P–C bond between the phosphorus atom and carbocycle.

Thus, in comparison with phosphacyclanes the reactivity of linear phosphine oxides in the reaction with $HSiCl_3$ is decreased and steric hindrances in the nearest vicinity at the P═O group inhibit the reduction.

1-(Phosphino)cyclopropane carbonitriles **17a–c** obtained in practically quantitative yields after the reduction were further used in the subsequent complexation with dimeric pentamethylcyclopentadienyl rhodium dichloride resulting in the complexes **18a–c** which structures were confirmed by a single crystal X-ray analysis (Figs. 3 and 4).

As regards the spectroscopic analysis, the phosphines **17a–c** show signals in 12–14 ppm region in their $^{31}P$ NMR spectra. Complexation with Rh(III) results in coordination shift $\Delta\delta = 21$–25 ppm and the signals of **18a–b** represent the typical doublets with the coupling constants $^1J_{PRh}$ in the range of 146–150 Hz. In the $^1H$ and $^{13}C$ NMR spectra of **17a–c** and **18a–c** the patterns of the corresponding signals are similar in principle to those of the P═O precursors with typical changes in $J_{PC}$ coupling constants. It should be noted also that methyl groups of the P-isopropyl radical in **17b**, **18b** are observed as separated signals both in the $^1H$ and $^{13}C$ NMR spectra indicating on the hindered rotation relative to the P–C bond. An insignificant shift of the CN absorbtion band in the IR spectra of **18a–c** in comparison with the corresponding ligands means that nitrogen atom is not involved in the coordination with rhodium.

Finally, the catalytic reduction using $(EtO)_3SiH/Ti(O^iPr)_4$ turned out to be highly effective in the case of phosphorylmethyl arenes bearing either one or two phosphoryl groups and known to be reduced with difficulties by trichlorosilane [22] (Scheme 7). These phosphines **21**, **22** were also involved in the complexation with rhodium(III) yielding complexes **23** and **24** correspondingly. A representation of mononuclear complex **23** is shown in Fig.5. The complex **24** has a composition $M_2L$ but the phosphorus atoms are completely equivalent and appear in the $^{31}P$ NMR spectrum as a single doublet with the $J_{PRh}$ coupling constant equal to ca. 142 Hz. In the IR spectrum of **24** two absorption bands of the cyano group are observed. One of them at 2220 $cm^{-1}$ corresponds to the non-coordinated cyano group whereas the second one shifted up to 2250 $cm^{-1}$ indicates apparently on the

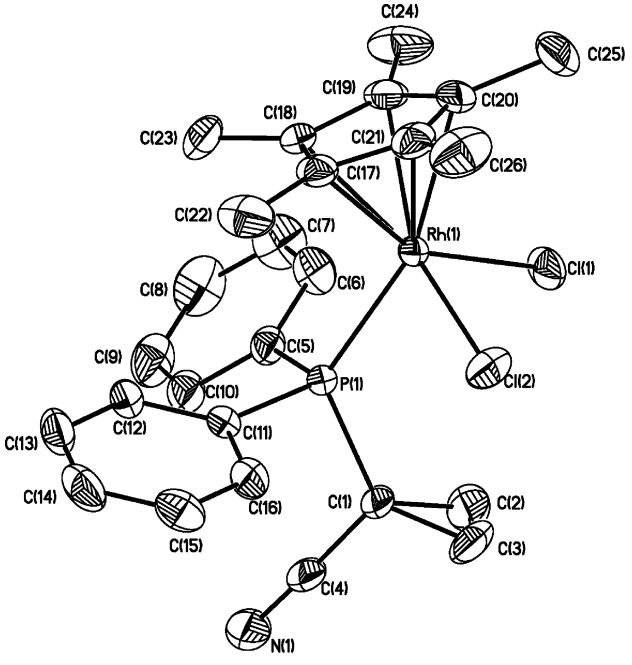



Fig. 3. The general view of molecules of {[(1-diphenylphosphino)cyclopropane carbonitrile]pentamethylcyclopentadienyl} rhodium dichloride **18a** in representation of atoms by thermal motion ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–P(1) 2.3461(8), P(1)–C(1) 1.838(3), Rh(1)–centre(Cp*) 1.815. Selected torsion angles (°): Rh(1)P(1)C(1)C(4) 171.3(4), Rh(1)P(1)C(1)C(2) 51.7(4).

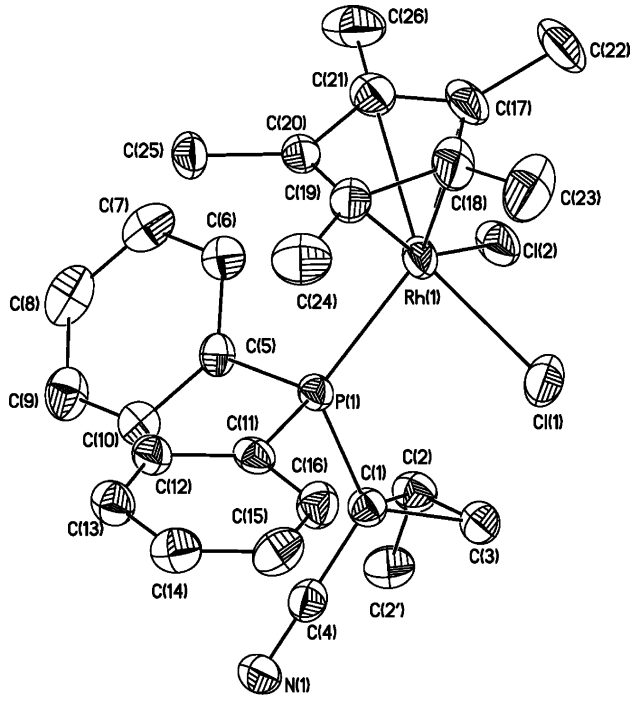
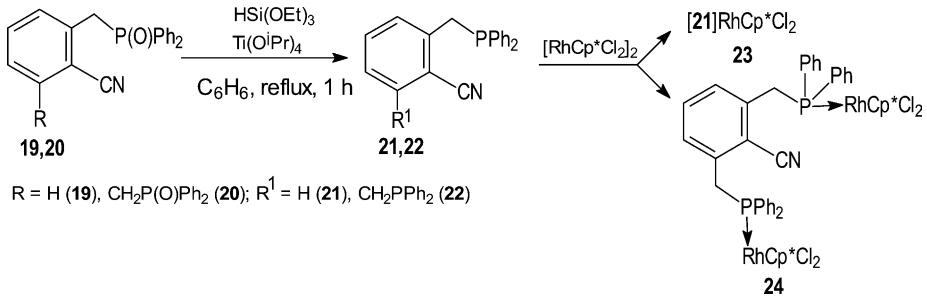



Fig. 4. The general view of molecule of {[[(1-diphenylphosphino)-2-methyl]cyclopropane carbonitrile]pentamethylcyclopentadienyl} rhodium dichloride **18c** in representation of atoms by thermal motion ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–P(1) 2.333(2), P(1)–C(1) 1.846(6), Rh(1)–centre(Cp*) 1.813. Selected torsion angles (°): Rh(1)P(1)C(1)C(4) 151.3(4), Rh(1)P(1)C(1)C(2) 66.1(4).




Scheme 7.

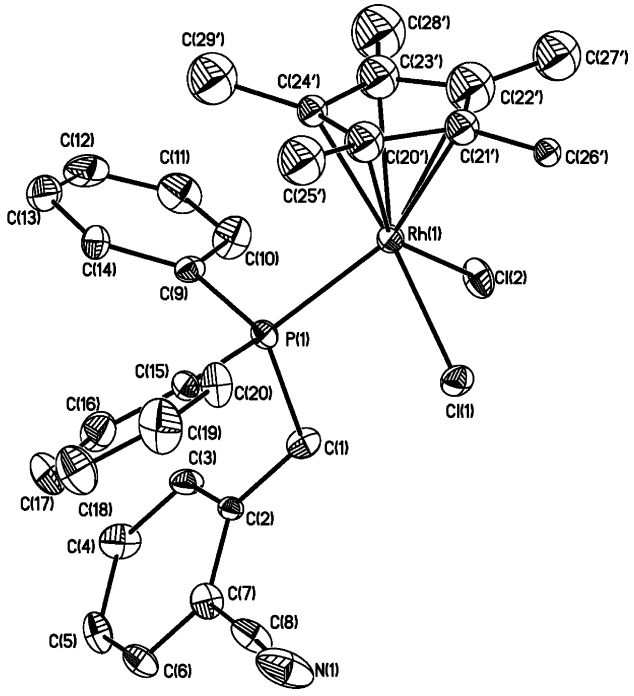



Fig. 5. The general view of molecule of Rh(III) complex **23** in representation of atoms by thermal motion ellipsoids at 50% probability level. Hydrogen atoms and the second position of the disodered Cp* are omitted for clarity. Selected bond lengths (Å): Rh(1)–P(1) 2.336(2), P(1)–C(1) 1.841(8), Rh(1)–centre(Cp*) 1.821. Selected torsion angles (°): Rh(1)P(1)C(1)C(2) 177.0(4), P(1)C(1)C(2)C(7).

coordination of the cyano group nitrogen atom with rhodium in either intra- or intermolecular mode.

### *2.4. Hydroformylation reaction catalyzed by rhodium (III) complexes containing the phosphine ligands under investigation*

Due to their high practical importance, hydroformylation catalysts have received particular attention. Thus, we estimated the catalytic activity of rhodium complexes **3a**–**c**, **6**, **18a**–**c** of the $RhCl_2(Cp^*)(L)$-type, where L presents monodentate either P-heterocyclic or cyclopropane-based P-ligand, as catalyst precursors in hydroformylation reaction [23]. Styrene displaying a relatively high reactivity among the alkenes was chosen as the model substrate that was reacted with $CO/H_2$ (1/1) in toluene at 40–100 °C and at a pressure of 100 bar in the presence of one of the catalyst precursors (Rh/styrene = 1:4000). The reaction solutions were analyzed immediately after the reaction by GC–MS analysis.

In such reaction in addition to the formyl linear and branched regioisomers, some hydrogenation product is also expected. Surprisingly, in all the cases the formation of $PhCH_2CH_3$ was negligible (less than 0.5% and, in most cases, less than the detection limit). Therefore the chemoselectivity of the styrene hydroformylation was excellent in all cases where the catalyst was active at all.

It was demonstrated that activity of **3a**-*syn* and **6** in this reaction is moderate and the conversions are very similar to each other and do not exceed 28%. At that the regioselectivity towards the branched regioisomer $R_{br}$ was rather high at 100 °C (83–85%) and in the case of 6 increased up to 95% at lower temperature.The complexes **3a**-*syn* and **3c**-*syn* formed by the *syn*-isomers of 6,6-dichloro-1-methyl-3-*p*-tolyl- or 3-*o*-tolyl-3-phosphabicyclo[3.1.0]hexanes **2b** and **2c** correspondingly, can be considered as inactive at low temperatures (40 °C), but they provided excellent conversions (>99%) at 100 °C in comparison with the catalyst precursor **3a**-*syn* containing ligand **2a** with similar structure but bearing phenyl group at the phosphorus atom. Thus, the introduction of tolyl groups instead of the phenyl one caused an unexpectedly high increase in activity in a series of Rh(III)–Cp* complexes formed by 6,6-dichloro-1-methyl-3-aryl-3-phosphabicyclo[3.1.0]hexanes. At the same time the usage of **3b**, **3c** yielded in noticeable decrease in the regioselectivity $R_{br}$ (33–42%).

In comparison with the complexes formed by phosphacyclanes, higher activities have been observed for the complexes of 1-(phosphino)cyclopropane carbonitriles **18a** and **18b** bearing an exocyclic phosphorus atom. For these compounds conversions was nearly quantitative at temperatures in the range of 70–100 °C. Moreover, in longer reaction time, the complex **18b** proved to be active even at 40 °C (the conversion was equal to 52.5% over 70 h) but this complex formed by the more basic phosphine **17b** resulted in lower regioselectivities ($R_{br}$ = 68% and 34% for **18a** and **18b** correspondingly at 100 °C) which changes in favor of the linear aldehyde.

Furthermore, for **18a** the lower the temperature was, the lower $R_{br}$ value was observed, i.e. decrease of the temperature increased the formation of the linear aldehyde. This tendency is opposite to that observed with well-known preformed (e.g. $HRh(CO)(PPh_3)_3$) or in situ prepared rhodium–$PPh_3$ systems [24]. The introduction of the methyl substituent in the cyclopropane ring (complex **18c**) in *trans* position to the phosphorus atom resulted in a drastic decrease of the catalytic activity: even at elevated temperature conversion is as small as 15%.

In those cases, when complexes of sterically demanding phosphorus ligands (**3b**, **3c** and **18b**) were used, good to excellent turnover frequences (TOFs) up to 1000 have been obtained referring to the determining role of coordinatively unsaturated $HRh(CO)_2(L)$ species of high activity.

Considering the whole ligand series investigated it turned out that the high activity was accompanied by practically complete chemoselectivities towards aldehydes.

### 2.5. Concluding remarks

In summary, the reduction of phosphine oxides by $HSiCl_3$ is a sterically sensitive reaction and reactivity of P═O precursors used decreases when going from saturated and non-saturated phosphacyclane oxides to 2-oxo-1,2-phosphacyclanes and further to compounds with exocyclic phosphorus atom. The former ones are reduced easily at 0 °C, while for the reduction of the linear phosphine oxides, the prolonged reflux in high-boiling solvents is required. The new type of P-ligands were utilized in the synthesis of Rh(III) complexes which activity was tested in the hydroformylation of styrene.

## 3. Experimental

### 3.1. General

All reactions were conducted under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. The NMR spectra were recorded on a "Bruker AMX-400" spectrometer in $CDCl_3$ solutions using residual proton signals of deutero solvent as an internal standard ($^1H$, $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$) as an external standard. IR spectra were recorded in KBr pellets on a Fourier spectrometer "Magna-IR750" (Nicolet) with a resolution of 2 $cm^{-1}$ after 128 scans. The starting phosphine oxides **1a–c** [3–5], **4** [8], **8c**, **9f** [10], **14a–c**, **15a–d**, **16a–d** [20] used as precursors for the ligands were obtained as described earlier. All the phosphines obtained had the purity >97% according NMR spectral analysis and were used in the subsequent complex formation without further purification. All the compounds have satisfactory elemental analysis data.

#### 3.1.1. General procedure for the preparation of phosphines *2a–c and 5*

To a cooled (0 °C) stirred solution of precursor **1a–c** or **4** (0.3 mmol) in of a 1:1 mixture of $CH_2Cl_2$–$C_6H_6$ (10 ml) was added 0.15 ml (1.45 mmol) of $HSiCl_3$ under argon atmosphere and on stirring. The mixture was stirred at the same temperature for 2 h and at ambient temperature for further 2 h. According to $^{31}P$ NMR, the deoxygenation proceeded with high selectivity. Then the volatile components were evaporated in vacuo to yield the phosphines **2a–c** and **5** quantitatively and in a pure form according to $^{31}P$ and $^{13}C$ NMR (**2c** consisted of a 95:5% mixture of the *syn*- and the *anti*-isomers). On standing at room temperature for 6 days, the isomeric mixture of **2c** was converted to a 38:62% mixture of the *syn*- and the *anti*-isomers. For the NMR parameters of **2a–c** and **5**, see [6].

#### 3.1.2. General procedure for the preparation of 3-cyano-2-phenyl-1,2$\lambda^3$-thiaphosphacyclanes (*11, 12*)

To a solution of the corresponding 3-cyano-2-oxo-1,2$\lambda^5$-thiaphosphocyclane **8c**-*cis*, **8c**-*trans*, **9f**-*cis* or **9f**-*trans* (1.00 mmol) in benzene (60 ml) trichlorosilane (5.00 mmol) was added at ambient temperature. The reaction mixture was refluxed under argon atmosphere for 2 h, cooled and evaporated to dryness. Acetonitrile (30 ml) was added to the residue and the precipitate of siloxane polymer was filtered off under argon. The filtrate was evaporated in vacuo yielding the yellowish solids of the phosphines **11**, **12** with high purity according the NMR analysis.

***11**-cis (obtained from **8c**-trans):* Yield: 98%; $^{31}P$ NMR ($CDCl_3$): 42.78; $^1H$ NMR ($CDCl_3$): $\delta$ 1.27 (t, $^3J_{HH}$ = 7.6 Hz, 3H, $CH_3$), 1.66–1.79 (m, 1H, $C\underline{H}_2CH_3$), 1.85–1.92 (m, 1H, $CH_2CH_3$), 2.27–2.34 (m, 1H, $CH_2C(CN)$), 1.98–2.07 (m, 1H, $CH_2C(CN)$), 2.87–2.94 (m, 1H, $SCH_2$), 3.34–3.39 (m, 1H, $SCH_2$), 7.42–7.46, 7.65–7.69 (two m, 5H, $C_6H_5P$); $^{13}C$ NMR ($CDCl_3$): 51.79 (d, $^1J_{PC}$ = 30.3 Hz, P–C), 10.67 (d, $^3J_{PC}$ = 13.4 Hz, $CH_3$), 26.96 (d,$^2J_{PC}$ = 13.4 Hz, $\underline{C}H_2CH_3$), 32.68 (d, $^2J_{PC}$ = 1.6 Hz, $C(CN)\underline{C}H_2$), 36.41 (d, $^2J_{PC}$ = 3.7 Hz, $SCH_2$), 119.51 (d, $^2J_{PC}$ = 8.3 Hz, CN), 128.00 (d, $^2J_{PC}$ = 6.5 Hz, *o*-C in $C_6H_5$–P), 129.88 (*p*-C in $C_6H_5$–P), 131.77 (d, $^3J_{PC}$ = 20.6 Hz, *m*-C in $C_6H_5$–P); IR ($CH_2Cl_2$): $\nu_{CN}$ 2220 $cm^{-1}$.

***12**-trans (obtained from **9f**-cis):* Yield: 95%. $^{31}P$ NMR ($CDCl_3$): $\delta$ 15.82. IR (KBr): $\nu_{CN}$ 2230 $cm^{-1}$.

***12**-cis (obtained from **9f**-trans):* Yield: 96%. $^{31}P$ NMR ($CDCl_3$): $\delta$ 13.00. IR (KBr): $\nu_{CN}$ 2232 $cm^{-1}$.

#### 3.1.3. General procedure for the preparation of (1-phosphino)cyclopropanecarbonitriles *17a–c*

The procedure was essentially the same as for **11**, **12**, except for the reaction time was 12–13 h.

For the characterization of **17a**, see [25].

*1-(Isopropylphenylphosphino)cyclopropane carbonitrile **17b**:* Yield: 97%; $^{31}$P NMR ($CDCl_3$): $\delta$ 13.51; $^{1}$H NMR ($CDCl_3$): $\delta$ 0.86 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{PH}$ = 17.1 Hz, 3H, (C$\underline{H}_3$)CH), 0.95 (dd, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{PH}$ = 17.1 Hz, 3H, (C$\underline{H}_3$)CH), overlapped with 0.92–1.27 (m, 3H, $CH_2$), 1.37–1.46 (m, 1H, $CH_2$), 2.43–2.60 (m, 1H, CH), 7.31–7.69 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$): $\delta$ 5.00 (d, $^{1}J_{PC}$ = 27.1 Hz, P–$\underline{C}$(CN)), 12.61 (d, $^{2}J_{PC}$ = 11.3 Hz, $CH_2$), 16.96 (d, $^{2}J_{PC}$ = 18.8 Hz, $CH_2$), 18.88 (d, $^{2}J_{PC}$ = 20.3 Hz, ($\underline{C}$H$_3$)CH–P), 19.21 (d, $^{2}J_{PC}$ = 17.3 Hz, ($\underline{C}$H$_3$)CH–P), 25.25 (d, $^{1}J_{PC}$ = 6.0 Hz, PCH), 121.19 (d, $^{2}J_{PC}$ = 6.0 Hz, CN), 128.61 (d, $^{3}J_{PC}$ = 6.0 Hz, *m*-C in $C_6H_5P$), 130.11 (*p*-C in $C_6H_5P$), 132.97 (d, $^{2}J_{PC}$ = 20.6 Hz, *o*-C in $C_6H_5P$, tentative assignment), 134.18 (d, $^{1}J_{PC}$ = 12.8 Hz, *ipso*-C in $C_6H_5P$); IR (KBr): $\nu_{CN}$ 2224 cm$^{-1}$.

*1-(Diphenylphosphino)-2-methylcyclopropane carbonitrile **17c**:* Yield: 95%; $^{31}$P NMR ($CDCl_3$): $\delta$ 12.72; $^{1}$H NMR ($CDCl_3$): $\delta$ 1.23–1.32 (m, 1H, CH), 1.44 (d, 3H, $^{3}J_{PH}$ = 5.9 Hz, $CH_3$), 1.47–1.57, 1.61–1.73 (two m, 1H + 1H, $CH_2$), 7.37–7.43, 7.47–7.59 (two m, 6H + 4H, $C_5H_5P$); $^{13}$C NMR ($CDCl_3$): $\delta$ 12.98 (d, $^{1}J_{PC}$ = 24.9 Hz, P–$\underline{C}$–CN), 21.77 (d, $^{2}J_{PC}$ = 16.6 Hz, CH), 22.21 (d, $^{2}J_{PC}$ = 12.8 Hz, $CH_2$), 15.52 ($CH_3$), 120.03 (d, $^{2}J_{PC}$ = 4.5 Hz, CN); 127.57 (d, $J_{PC}$ = 7.5 Hz), 128.62 (d, $J_{PC}$ = 6.0 Hz), 129.25, 129.63, 132.06, 132.41, 132.80, 133.19, 134.71 (d, $^{1}J_{PC}$ = 10.1 Hz, *ipso*-C in $C_6H_5P$), 135.01 (d, $^{1}J_{PC}$ = 9.6 Hz, *ipso*-C in $C_6H_5P$); IR (KBr): $\nu_{CN}$ 2223 cm$^{-1}$.

### 3.1.4. General procedure for the preparation of 2-(diphenylphosphino)methyl substituted benzenecarbonitriles **21**, **22**

To a mixture of benzenecarbonitrile **19** or **20** (0.63 mmol) and triethoxysilane (0.70 ml; 3.79 mmol) in 10 ml of benzene 46.5 l of Ti(O$^{i}$Pr) (0.16 mmol) was added. The resulting suspension was refluxed for either 1 h (**19**) or 2 h (**20**) until the light green clear solution was formed. The mixture was evaporated to dryness and phosphines **21** and **22** correspondingly having the purity over 95% was used in subsequent complexation reactions without further purification.

**21**: $^{31}$P NMR ($C_6H_6$): $\delta$ −7.26 ppm (100% purity). IR ($C_6H_6$): $\nu_{CN}$ 2220 cm$^{-1}$ (br).

**22**: $^{31}$P NMR ($C_6H_6$): $\delta$ −7.86 ppm (95% purity). IR ($C_6H_6$): $\nu_{CN}$ 2225 cm$^{-1}$ (br).

### 3.1.5. General procedure for the preparation of rhodium(III) complexes of phosphines

To a stirred solution of the corresponding phosphine (0.30 mmol) in $CH_2Cl_2$ (25 ml) a solution of [Cp*$RhCl_2$]$_2$ (97.85 mg, 0.15 mmol (for P-monodentate phosphines **2a**–**c**, **5**, **17a**–**c**, **21** or 195.7 mg, 0.30 mmol in the case of **22**)) in $CH_2Cl_2$ (ca. 5 ml) was added under argon. The stirring was continued for 0.5 h. The reaction mixture was evaporated to the final volume of ca. 1 ml and 6-fold volume excess of pentane was added. The dark orange crystals of the complexes formed were filtered off and dried in vacuo.

For the physical–chemical data and spectral characterization of **3a**–**c**, **6**, **7**, see [6]. Complexes **18a**–**c** have satisfactory elemental analysis data.

**18a**: Yield: 76%; m.p. 160 °C (decomposition); $^{31}$P NMR ($CDCl_3$): 35.02 (d, $^{1}J_{PRh}$ = 148.3 Hz); $^{1}$H NMR ($C_6D_6$): $\delta$ 1.33 (15H, d, $J_{HPh}$ = 3.2 Hz, $CH_3$(Cp*)), 1.45–1.51 (2H, m, $CH_2$), 1.57–1.62 (2H, m, $CH_2$), 7.47–7.55, 7.97–8.03 (10H, m, $C_6H_5$); $^{13}$C NMR ($CDCl_3$): $\delta$ 8.52 (*C*H$_3$(Cp*)), 18.40–19.10 (br, $CH_2$). 99.82 (d, $J$ = 6.8 Hz, Cp*), 122.25 (CN), 128.20 (d, $^{3}J_{PH}$ = 9.8 Hz, *m*-C in $C_6H_5P$), 131.40 (*p*-C in $C_6H_5P$), 133.87 (d, $^{2}J_{PH}$ = 8.0 Hz, *o*-C in $C_6H_5P$), signal of the central carbon atom of the cyclopropane ring does not appear because of the rather low solubility of the complex; IR (KBr): $\nu_{CN}$ 2225 cm$^{-1}$.

**18b**: Yield: 54%; m.p. 232 °C; $^{31}$P NMR ($CDCl_3$): $\delta$ 37.83 (d, $^{1}J_{PRh}$ = 146.34 Hz). $^{1}$H NMR ($CDCl_3$): $\delta$ 1.28 (d, $J_{RhH}$ = 3.5 Hz, 15H, $CH_3$(Cp*)), 1.35 (dd, $^{3}J_{PH}$ = 9.4 Hz, $^{3}J_{HH}$ = 7.5 Hz, 3H, C*H*(CH$_3$)$_2$), 1.57 (dd, $^{3}J_{PH}$ = 15.7 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, C*H*$_3$(CH)), 1.57–1.63 (m, 1H, $CH_2$), 1.68–1.76 (m, 1H, $CH_2$), 1.82–1.91 (m, 1H, $CH_2$), 2.61–2.70 (m, 1H, $CH_2$), 3.36–3.50 (m, 1H, C*H*(CH$_3$)$_2$), 7.43–7.53, 7.90–7.95 (m, 5H, $C_6H_5$); $^{13}$C NMR ($CDCl_3$): $\delta$ 2.47 (d, $^{1}J_{PC}$ = 26.1 Hz, P*C*(CN)), 8.75 (*C*H$_3$(Cp*)), 16.09 ($CH_2$), 17.57 (d, $^{2}J_{PC}$ = 2.5 Hz, $CH_2$), 19.41 (d, $^{2}J_{PC}$ = 2.5 Hz, *C*H$_3$CH), 19.70 (d, $^{2}J_{PC}$ = 7.4 Hz, *C*H$_3$CH), 29.06 (d, $^{1}J_{PC}$ = 23.6 Hz, P*C*(CH$_3$)$_2$), 99.38 (dd, $J$ = 2.5 Hz, $J$ = 7.4 Hz, Cp*),122.55 (d, $^{2}J_{PC}$ = 5.0 Hz, CN), 128.46 (d, $^{3}J_{PC}$ = 8.7 Hz, *m*-C in $C_6H_5P$), 130.63 (d, $^{4}J_{PC}$ = 2.5 Hz, *p*-C in $C_6H_5P$), 131.45 (d, $^{1}J_{PC}$ = 38.0 Hz, *ipso*-C in $C_6H_5P$),131.46 (d, $^{2}J_{PC}$ = 8.2 Hz, *o*-C in $C_6H_5P$); IR (KBr): $\nu_{CN}$ 2225 cm$^{-1}$.

**18c**: Yield: 68%; m.p. 234–235 °C; $^{31}$P NMR ($CDCl_3$): $\delta$ 34.68 (d, $^{1}J_{PRh}$ = 149.6 Hz); $^{1}$H NMR ($CDCl_3$): $\delta$ 1.08–1.14 (1H, m, CH), 1.29 (d, $^{3}J_{PH}$ = 8.0 Hz, 3H, $CH_3$), 1.33 (15H, d, $J_{HRh}$ = 3.9 Hz, $CH_3$(Cp*)), 1.86–2.02, 2.12–2.32 (1H + 1H, two m, $CH_2$), 7.48–7.51, 7.91–7.99 (10H, m, $C_6H_5$). $^{13}$C NMR ($CDCl_3$): $\delta$ 8.35 (*C*H$_3$(Cp*)), 15.04 (s, $CH_3$), 19.90 ($CH_2$), 20.67 (*C*H(CH$_3$)), 99.62 (d, $J$ = 4.5 Hz, Cp*), 120.33 (d, $^{2}J_{PC}$ = 4.52 Hz, CN), 127.80 and 128.04 (both d, $^{3}J_{PC}$ = 9.9 Hz, *m*-C in $C_6H_5P$), 131.13 (d, $^{2}J_{PC}$ = 7.6 Hz, *o*-C in $C_6H_5P$), 133.37 (*p*-C in $C_6H_5P$), the signals of the central carbon atom of the cyclopropane ring and *ipso*-C in $C_6H_5P$ do not appear because of the rather low solubility of the complex; IR (KBr): $\nu_{CN}$ 2225 cm$^{-1}$.

**23**: Yield: 70%, m.p. 250 °C (dec.). $^{31}$P NMR ($CDCl_3$): $\delta$ 36.38 (d, $^{1}J_{PRh}$ = 143.95 Hz). $^{1}$H NMR ($CDCl_3$): $\delta$ 4.48 (d, $^{2}J_{PH}$ = 10.1 Hz, 2H, $CH_2$–P), 6.71 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, $C_6H_4P$), 6.97–7.04 (m, 2H, $C_6H_4P$), 7.22 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H,$C_6H_4P$), 7.33–7.36, 7.43–7.47, 7.72–7.77 (m, 10H, $C_6H_5P$). $^{13}$C NMR ($CDCl_3$): $\delta$ 8.49

Table 1
Crystallographic data for complexes **18a**, **18b** and **23**

| | **18a** | **18b** | **23** |
|---|---|---|---|
| Formula | $C_{26}H_{29}Cl_2NPRh$ | $C_{27}H_{31}Cl_2NPRh$ | $C_{30}H_{31}Cl_2NPRh$ |
| $T$ (K) | 298 | 120 | 163 |
| Diffractometer | Siemens P3/PC | Smart CCD | Syntex $P2_1$ |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/c$ | Orthorhombic, $P2_12_12_1$ |
| $a$ (Å) | 18.348(4) | 9.149(2) | 8.069(2) |
| $b$ (Å) | 8.479(2) | 36.287(8) | 15.752(3) |
| $c$ (Å) | 17.025(3) | 8.617(2) | 21.891(4) |
| $\beta$ (°) | 108.86(3) | 115.757(8) | |
| $V$ (Å$^3$) | 2506.6(9) | 2576.5(9) | 2782.3(10) |
| $Z(Z')$ | 4(1) | 4(1) | 4(1) |
| $M$ | 560.28 | 574.31 | 610.34 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 9.72 | 9.48 | 8.83 |
| $F(000)$ | 1144 | 1176 | 1248 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.485 | 1.481 | 1.457 |
| Scan type | $\omega$ | $\omega$ | $\omega$ |
| $2\theta_{max}$ (°) | 55.00 | 55.00 | 50.00 |
| No. of refl. measured ($R_{int}$) | 5947 (0.0252) | 18079 (0.0483) | 2778 (0.0) |
| No. of independent refl. | 5748 | 5883 | 2778 |
| No. of refl. with $I > 2\sigma(I)$ | 3759 | 4560 | 1978 |
| No. of parameters | 285 | 295 | 312 |
| $R_1$ | 0.0310 | 0.0733 | 0.0441 |
| $wR_2$ | 0.0730 | 0.1730 | 0.0824 |
| GOF | 0.932 | 1.101 | 0.893 |
| Max./min peak (e Å$^{-3}$) | 0.453/−0.352 | 1.134/−0.570 | 0.718/−0.519 |

($CH_3$), 34.49 (d, $^1J_{PC}$ = 21.3 Hz, $CH_2$), 98.67 (dd, $^1J_{CRh}$ = 2.8 Hz, $^1J_{PC}$ = 6.8 Hz, Cp*), 113.54 (d, $^3J_{PC}$ = 4.0 Hz, $C^1$ in $C_6H_4$), 116.96 (CN), 126.31 (d, $^3J_{PC}$ = 2.4 Hz, $C^3$ in $C_6H_4$), 127.29 (d, $^1J_{PC}$ = 40.5 Hz, *ipso*-C in$C_6H_5P$), 127.88 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C in $C_6H_5P$), 128.14 ($C^5$ in $C_6H_4$), 131.08 (d, $^4J_{PC}$ = 2.4 Hz, *p*-C in $C_6H_5P$), 131.46 (d, $^4J_{PC}$ = 4.9 Hz, $C^3$ in $C_6H_4$), 132.16 (d, $^4J_{PC}$ = 1.2 Hz, $C^4$ in $C_6H_5P$), 134.44 (d, $^2J_{PC}$ = 8.8 Hz, *o*-C in $C_6H_5P$), 139.35 (d, $^2J_{PC}$ = 12.8 Hz, $C^2$–$C_6H_4$). IR (KBr): $\nu_{CN}$ 2230 cm$^{-1}$. Anal. Calc. for $C_{30}H_{36}Cl_2NPRh \cdot 0.25\ CH_2Cl_2$: C, 56.95; H, 5.15; N, 2.19. Found: C, 56.97; H, 5.15; N, 2.13%.

**24**: Yield: 64%; m.p. >290 °C (dec.); $^{31}$P NMR ($CDCl_3$): $\delta$ 36.18 (d, $^1J_{PRh}$ = 142.34 Hz); $^1$H NMR ($CDCl_3$): $\delta$ 4.24 (d, $^2J_{PH}$ = 10.48 Hz, 4H, $CH_2P$), 6.25–6.27 (3H, m, $C_6H_3P$), 7.23–7.25, 7.34–7.35, 7.58–7.62 (3m, 20H, $C_6H_5P$). IR (KBr): $\nu_{CN}$ 2222, 2250 cm$^{-1}$. Anal. Calc. for $C_{53}H_{59}Cl_4NP_2Rh_2 \cdot CH_2Cl_2$: C, 54.62; H, 4.97; N, 1.16. Found: C, 53.79; H, 5.06; N, 1.16%.

The complexation features of the 1,2$\lambda^3$-thiaphosphacyclanes will be published elsewhere.

### 3.2. X-ray structure determination

The structures were solved by direct method and refined by the full-matrix least-squares against $F^2$ in anisotropic approximation for non-hydrogen atoms. The analysis of Fourier density synthesis revealed that Cp* ligand in **23** is disordered by two positions with equal occupancies. All atoms of the disordered ring were refined in isotropic approximation with the restraints on C–C bond lengths and angles (AFIX 5). Hydrogen atoms in all complexes were placed in geometrically calculated positions and included in final the refinement using the ''riding'' model with the $U_{iso}$(H) parameters equal to 1.2 $U_{eq}(C_i)$ or 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are, respectively, the equivalent thermal parameters of the aromatic and methylene carbon atoms to which corresponding H atoms are bonded. Crystal data and structure refinement parameters for **18a**, **18b** and **23** are given in Table 1. All calculations were performed using the SHELXTL software [26].

## 4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as Supplementary Nos. CCDC-225065 for **3c**-*anti*·2$CHCl_3$, CCDC-225066 for **3c**-*syn*·2$CH_2Cl_2$, CCDC-225067 for **3c**-*syn*·2$CHCl_3$; CCDC-249192 for **18a**; CCDC-249193 for **18b**; CCDC-249191 for **23**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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