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Rhodium(III) and palladium(II) complexes of some P-heterocycles; synthesis and X-ray structures

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Abstract

Deoxygenation of the *syn*-3-phosphabicyclo[3.1.0]hexane 3-oxides bearing a 3-phenyl or a 3-(4-methylphenyl) substituent (**1a**,**b**) by trichlorosilane took place already at mild condition and resulted in the corresponding phosphines (**2a**,**b**) with retention of configuration at phosphorus, while in the case of 3-(2-methylphenyl)-3-phosphabicyclo[3.1.0]hexane (**2c**), the inversion of the phosphorus atom was observed in solution under ambient conditions that was evaluated by quantum chemical calculations. A further phosphine ligand (**5**) was obtained by the reduction of 4-dichloromethylene-1,4-dihydrophosphinine oxide (**4**). The phosphine ligands (**2** and **5**) were used in the preparation of Rh(III) complexes (**3** and **6**). A Pd(II) complex of type $PdCl_2(\mathbf{5})_2$ (**7**) was also prepared. The stereostructures of a series of Rh(III) complexes of 3-aryl-3-phosphabicyclo[3.1.0]hexanes (**3b**-*syn*, **3c**-*syn* and **3c**-*anti*) were elucidated by single crystal X-ray analysis confirming the relative position of the dichlorocyclopropane and the P-substituent.

Keywords: Cyclic phosphine oxides; Deoxygenation; Cyclic phosphines; Rhodium and palladium complexes; Stereostructure

1. Introduction

Transition metal complexes incorporating phosphines and diphosphines as the ligands are frequently used catalysts in hydroformylations and hydrogenations [1]. Many catalysts involve phosphole or phosphole-based ligands, the most pregnant example of which is BIPNOR [2]. One of us developed a simple method for the synthesis of a variety of six-membered P-heterocycles, such as 3-phosphabicyclo[3.1.0]hexane 3-oxides and 1,2- or 1,4-dihydrophosphinine oxides making thus available a valuable pool for novel P-ligands that have never been prepared and studied [3,4].

For the preparation of phosphines, the reduction of the corresponding phosphine oxides by silane hydrides [5] is the best choice due to the selectivity and efficiency. This simple methodology was applied to obtain a series of heterocyclic phosphine ligands referred also as λ^3-phosphacyclanes in order to prepare their Rh(III) and Pd(II) complexes and to introduce them for tests in catalytic reactions.

In this paper, our interesting findings on the deoxygenation of the phosphine precursors and on the stereostructure of the P-ligands, as well as the transition metal (Rh(III) and Pd(II)) complexes based on the cyclic phosphines are discussed. The results of the catalytic activity

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of a variety of such complexes in hydroformylation and hydroalkoxycarbonylation are described elsewhere [6].

2. Results and discussion

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

Earlier, one of us reported on the facile synthesis of 6,6-dichloro-1-methyl-3-phenyl-3-phosphabicyclo[3.1.0] hexane 3-oxide (**1a**) by dichlorocyclopropanation of the corresponding 2,5-dihydrophosphole oxide under phase transfer catalytic conditions [3,7]. In contrast to the similar P-alkoxy derivatives [3,8], dichlorocarbene adduct **1a** was obtained as a single isomer with *syn* disposition of the cyclopropane ring and the P-phenyl substituent [9]. The aryl-analogues (**1b**,**c**) were obtained by a similar procedure, but the *o*-tolyl derivative (**1c**) was formed as a 6:4 mixture of *syn* and *anti* isomers, which were separated by chromatography [10]. The structure of the *syn*-isomer **1c** was independently confirmed by X-ray crystallography [10]. For further reduction procedure to be discussed in this paper, the pure *syn*-isomers **1a**–**c** were utilised. We wished to prepare the rhodium(III) and the palladium(II) complexes of the novel ligands and to study their peculiarities.

It was shown that the deoxygenation of phosphine oxides **1a**,**b** with trichlorosilane proceeded very easily even at 0 °C in the 1:1 mixture of dichloromethane and benzene to afford the desired phosphine **2a**,**b** as the only reaction product (Scheme 1). It should be noted that at a higher temperature (even at ambient conditions), the formation of a variety of side-products (up to 45–50% in total) could be observed.

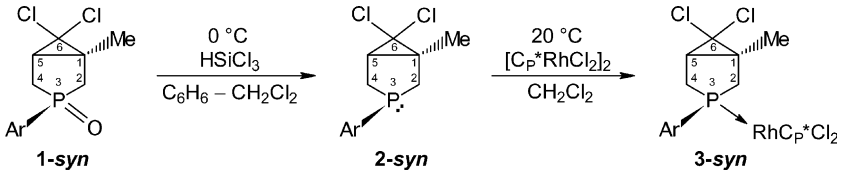
Phosphines **2a**,**b** have upfield δ_P shifts of ca. 25 ppm in $CDCl_3$ as compared with those of the P-oxides **1a** and **1b** (δ_P ca. 77 ppm). In the ^{13}C NMR spectra of **2a**,**b**, the signals of the skeletal carbon atoms can be found in about the same regions as that for **1a**,**b**. In phosphines **2a**,**b**, the signal of C(1) is shifted downfield ($\Delta\delta$ ~4 ppm), while on the contrary, C(2) and C(4) are shifted upfield, as compared with the oxides **1a**,**b**. Going from λ^5 to λ^3 phosphorus derivatives, the usual decrease in J_{PC} coupling costants could be observed.

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 structure of complex **3b** was independently confirmed by single crystal X-ray analysis suggesting the *cis* disposition of the P-*p*-tolyl substituent and the cyclopropane ring (**3b**-*syn*) (Fig. 1). A comparison of the spectral features of complexes **3a** and **3b** allowed us to conclude that complex **3a** also has the *syn*-geometry. Thus the reduction of phosphines **1a**,**b** proceeds with the retention of configuration.

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 δ_P signals in the phosphine region (in $CDCl_3$ at 22.6 and 27.9 ppm) 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. It was assumed to have the *syn* and *anti* diastereomers of **2c** in hands (Scheme 2, showing in the first approach a tentative assignment).

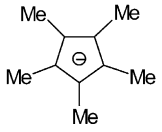
We note that in the ^{13}C NMR spectra of phosphines **2c**-*syn* and **2c**-*anti*, the signal pattern is also close to that of their precursor **1c**, but the high $^3J_{PC}$ value for the *o*-methyl substituent (15.5 and 23.1 Hz in **2c**-*syn* and **2c**-*anti* isomers, respectively) should also be mentioned, in comparison with the 3.5 Hz detected on the *o*-methyl substituent of **1c**.

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. Both phosphine **2c**-*syn* and complex **3c**-*syn* revealed upfield ^{31}P NMR chemical shifts, as compared with those for the other isomers (**2c**-*anti* and **3c**-*anti*). The stereostructure of both isomers of complex **3c** was confirmed by X-ray analysis justifying the



Ar = Ph (**a**), 4-MeC_6H_4 (**b**)

C_P* =



Scheme 1.

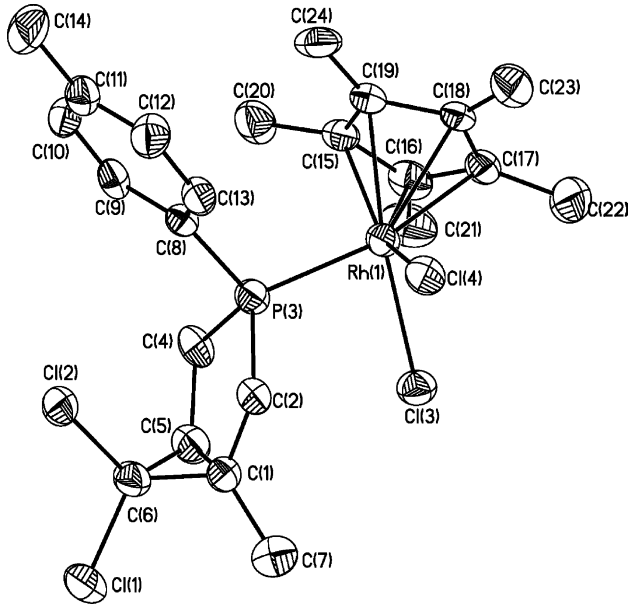


Fig. 1. The general view of **3b**-*syn* in representation of atoms by thermal motion ellipsoids at 50% probability level.

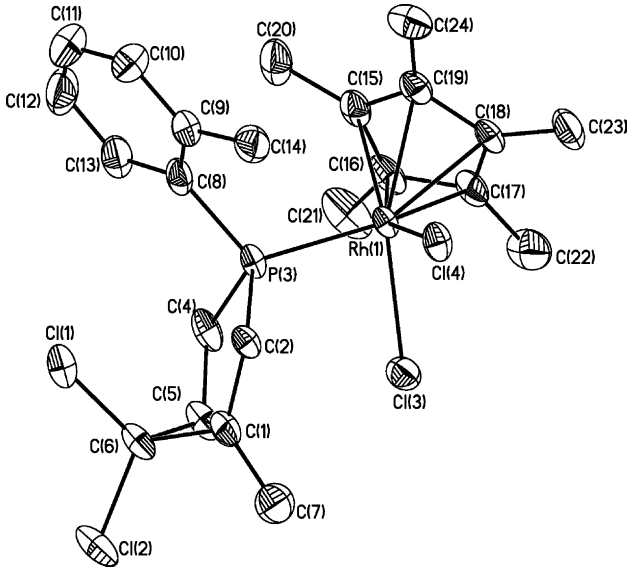
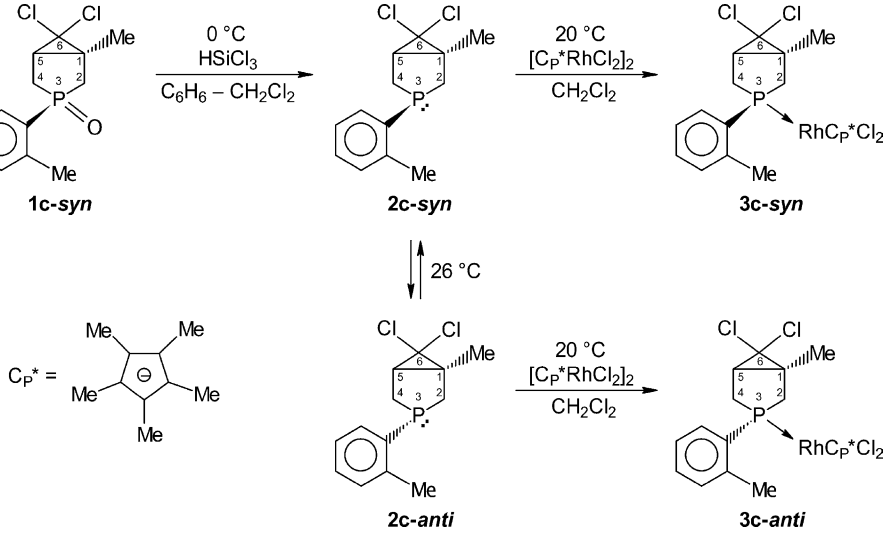


Fig. 2. The general view of **3c**-*syn* in representation of atoms by thermal motion ellipsoids at 50% probability level.

tentative assignment, the *syn* or the *anti* disposition of the P-aryl substituent and the cyclopropane ring, both in the complex (**3c**), and in the phosphine (**2c**) (Figs. 2 and 3). Hence, the assignment of the second signal at δ_P 27.9 (or at δ_P 20.1 for a crude mixture) in the ^{31}P NMR spectrum of the mixture of phosphines to species **2c**-*anti* was also confirmed.

The Rh(III) complexes **3a**,**b** are characterized by δ_P shifts that are close to the corresponding values of the P-oxides **1a**,**b**. For **3c**, the complex with *syn* geometry has an upfield chemical shift (δ_P 67.8 ppm), as compared with that of the starting oxide **1c** (δ_P 80.3 ppm), while the signal for the **3c**-*anti* is shifted downfield (δ_P 91.6 ppm). It is noted that the signals of the rhodium complexes appeared as sharp doublets with characteristic coupling constant ($^1J_{PRh}$) in the ^{31}P NMR spectra. This constant comprises a value of ca. 138 Hz for 138 Hz for **3**(**a**–**c**)-*syn* and is a little bit higher (143.0 Hz) for **3c**-*anti*. In the ^{13}C NMR spectra, the $^1J_{PC}$ coupling constants for **3a**–**c** are approximately one and a half higher than for **2a**–**c**, but twice as much lower than for **1a**–**c**.

The geometry of the ligand in complexes **3b**-*syn* and **3c**-*syn* (Figs. 1 and 2) is practically identical having the aryl ring and the dichlorocyclopropane moiety in *cis* orientation (Table 1). The 5-membered hetero ring in **3b**-*syn* and **3c**-*syn* adopts an envelope conformation with a deviation of 0.205–0.344 Å of the P(3) atom from



Scheme 2.

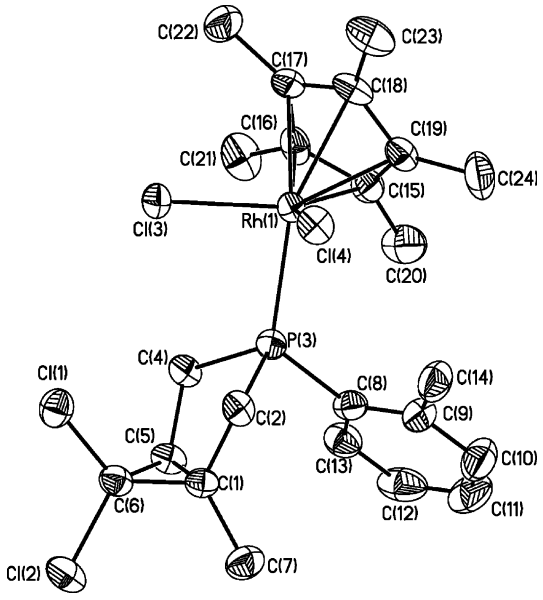


Fig. 3. The general view of one of independent molecules of **3c**-*anti* in representation of atoms by thermal motion ellipsoids at 50% probability level.

the C(2)C(1)C(5)C(4) plane towards the metal atom. The dihedral angle between the "base" of envelope and the cyclopropane moiety in both complexes is equal to 70°. The angle between the Cp* and the aryl moiety is slightly different and is equal to 23.6° and 18.9° for **3b**-*syn* and **3c**-*syn*, respectively. The only difference observed for **3b**-*syn* and **3c**-*syn* is the orientation of the Cp* in respect to the $RhCl_2P$ moiety (see the P(1)Rh(1)C(15)C(20) torsion angle).

As it may be seen, the relative position of the P-aryl substituent and the cyclopropane moiety in complex **3c**-*anti* is *trans*. Despite the difference in the configuration of the phosphorus atom, the principal geometry of complex **3c**-*anti* (two independent molecules per unit cell) is quite similar to the above mentioned *syn* analogues (Table 1, Fig. 3). The main differences are reflected in the pronounced increase in the deviation of the P(3) atom from the C(2)C(1)C(5)C(4) plane up to 0.709 Å, as well as in an increase in the C(2)P(3)C(8)C(9) angle corresponding to the mutual disposition of the aryl and the hetero rings.

It should be noted that complexes **3** form stable solvates with chlorine containing solvents (CH_2Cl_2 or $CHCl_3$), which in some cases we failed to remove even at prolonged drying in vacuo at an elevated temperature. Apparently, the solvates are stabilized by numerous H...Cl interactions formed between the $RhCl_2$ moiety and the dichloromethane or the chloroform molecules. Moreover, recrystallization of **3c**-*syn* · $2CH_2Cl_2$ from chloroform gave the corresponding pseudopolymorph modification with a chloroform solvate, which structure was also confirmed by X-ray diffraction investigation (Table 1).

2.2. P-inversion in 6,6-dichloro-1-methyl-3-(2-methylphenyl)-3-phosphabicyclo[3.1.0]hexane; quantum chemical calculations

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 pK_b 5, such as triethylamine, the inversion was observed to take place predominantly in silane reductions [11]. Thus, one may assume that reduction of 3-phosphabicyclohexan-3-oxides **1a**–**c** by trichlorosilane alone resulted in the formation of the corresponding phosphine with

Table 1
Selected bond lengths [Å] and bond angles [°] of rhodium complexes **3b** and **3c**

	3b-*syn* · CH_2Cl_2	**3c**-*syn* · $2CH_2Cl_2$	**3c**-*syn* · $2CHCl_3$	**3c**-*anti* · $2CHCl_3$
Rh(1)–P(3)	2.283(1)	2,3207(8)	2.323(1)	2.300(1)
P(3)–C(2)	1.825(6)	1,848(3)	1.844(4)	1.834(4)
P(3)–C(4)	1.834(5)	1.854(3)	1.854(4)	1.838(4)
P(3)–C(8)	1.797(5)	1.828(3)	1.808(5)	1.826(4)
Rh–Cp_{cent}[a]	1.802	1.813	1.819	1.815
Rh–C(Cp)	2.143(5)–2.203(5)	2.155(3)–2.223(3)	2.152(4)–2.232(4)	2.146(4)–2.223(4)
Rh–Cl	2.393(1)–2.399(1)	2.402(1)–2.412(1)	2.408(1)–2.414(1)	2.383(1)–2.404(1)
P(3)Rh(1)Cp	130.4	124.1	132.6	131.7
Cl(1)Rh(1)Cl(2)	90.90(5)	88.75(3)	88.93(4)	87.29(4)
C(2)P(3)C(4)	96.6(2)	95.9(1)	95.5(2)	91.6(1)
$\delta_{P(1)}$[b]	0.205	0.266	0.344	0.79
$\delta_{C(6)}$[c]	–1.19	–1.22	–0.99	–1.18
P(3)Rh(1)C(15)C(20)	–13.6	8.3	7.3	7.4/–9.9
C(2)P(3)C(8)C(9)	56.9	61.3	59.5	71.1
Cp/Ph[d]	23.6	18.9	22.0	16.4

[a] Distance to centroid of the cyclopentadienyl ring.
[b] Deviation of the P(3) atom from the C(2), C(3), C(4) and C(5) plane.
[c] Deviation of the C(6) atom from the C(2), C(3), C(4) and C(5) plane.
[d] Dihedral angle between the Ph and the cyclopentadienyl rings.

preserved P-configuration that was followed by inversion only in the case of compound **2c** bearing an *o*-tolyl substituent. The ease of the inversion for **2c** is a noteworthy observation of us, as common phosphines are not known to undergo P-inversion at 26 °C. For example, the barrier of inversion for a phospholane bearing a hydrogen atom on the phosphorus atom is 39.4 kcal/mol [12].

To consider such a possibility and to estimate the reasons for the inversion observed only in the case of **2c**, quantum chemical calculations were carried out at the 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 data, 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** (1.79 kcal/mol) than that for **2c** (0.83 kcal/mol). At the same time, the inversion barrier is somewhat smaller for **2c** than that for **2a** in the *syn* to *anti* direction [ΔE_a(**2a**) − E_a(**2c**) = 0.687 kcal/mol]. Although the difference is not significant, the tendency read from the energy values is in accord with the observation.

In the transition state for the inversion of **2a** and **2c**, the planarization of the phosphorus atom leads to significant shortening of the P–C'_1 bond lengths (where C'_1 is the ipso carbon atom). The above mentioned bond length is slightly different in transitions states of **2a** and **2c** (1.772 and 1.782 Å, respectively) that is the consequence of some decrease of conjugation in **2c** due to the steric repulsion of the *o*-methyl substituent of the Ph-ring and the methylene hydrogens of the α-carbon atoms. Apparently such decrease of conjugation in **2c** intermediate planar state shifts the equilibrium to the thermodynamically more preferred *anti*-isomer of phosphine.

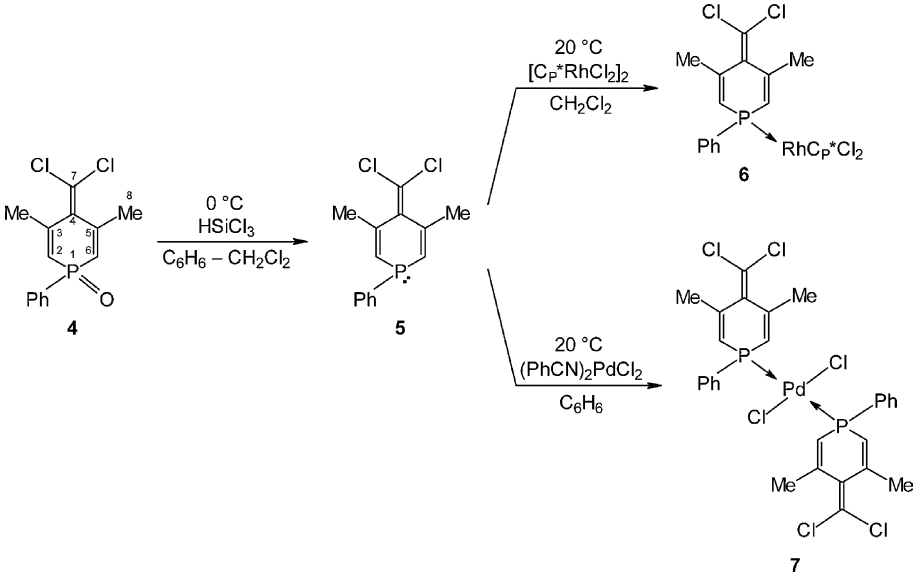
Thus, our preliminary results based on simplified calculations neglecting the specific and nonspecific solvatations (that may have a considerable impact on the final outcome) fit well the experimental observation that the inversion proceeds more readily in the case of *ortho*-methylphenyl substituted phosphine **2c** than for that with the P-phenyl phosphine (**2a**).

2.3. Preparation of a dihydrophosphinine ligand and its complexation with Rh(III) and Pd(II)

The analogous series of reactions (reduction by trichlorosilane followed by complexation) was applied to 4-dichloromethylene-1,4-dihydrophosphinine 1-oxide **4** [12]. In this case, the reduction and the subsequent complexation with dimeric pentamethylcyclopentadienyl rhodium dichloride furnished phosphine **5** and complex **6**, respectively (Scheme 3).

The reaction of phosphine **5** with with *trans*-dichloro(dibenzonitrile)palladium in benzene solution at 0 °C led to the formation of ML_2 type complex **7**. At a higher temperature, the exothermic complexation reaction proceeded to yield at least three different products which were not isolated and identified. Complex **7** precipitated from the dichloromethane solution as fine yellow crystals after the addition of pentane. The structure of the complexes (**6** and **7**) were unambiguously confirmed by NMR and MS data.

The ^{31}P NMR signals for both the phosphine oxide **4** and the corresponding phosphine **5** are shifted upfield as compared with those for the λ^5- and λ^3-phosphacyclanes **1** and **2**, e.g., the δ_P for the latter one appears at –30.6, at the same time, the δ_P for Rh(III) and Pd(II) complexes **6** and **7** can be found at −0.89 and −5.18, respectively. In **6**, the $^1J_{PRh}$ coupling constant is approximately the same



Scheme 3.

(142.1 Hz), as that in Rh(III) complexes **3**. In the ^{13}C NMR spectra **5** and **6**, the signal pattern is similar to that of starting compound **4** with an expected decrease in the J_{PC} constants for the carbon atoms of heterocyclic ring. The $^{1}J_{PC}$ coupling constant for **6** is approximately six time higher than that is for **5**, but is twice as much lower than that is for **4** [13]. For phosphine **5**, the increase in the $^{2}J_{PC}$ and in the $^{3}J_{PC}$ values for the *o*- and the *m*-carbon atoms of the phenyl group that are even higher than the $^{1}J_{PC}$ value for the *ipso*-carbon is also noteworthy. This fact may be explained by the violation of conjugation due to the difference in the mutual disposition of the unsaturated hetero ring and the phenyl group in **5**. For complex **6**, the large $^{3}J_{PC}$ value detected on C_4 and on C_7 atoms is to be mentioned. As the ^{1}H NMR spectra are concerned, the downfield shift for the CH═ proton in complexes **6** and **7** along with the increase in the $^{2}J_{PH}$ value seems to be interesting.

As regards the EI-mass spectra of all Rh(III) complexes obtained (**3a**–**c** and **6**), despite their stability under usual conditions, they underwent immediate rupture of the P–Rh bond resulting in two series of fragments. Thus, the spectra revealed independent decompositions for the ligand part and for the metal containing moiety. It should be mentioned that not only the principle fragmentation patterns, but the intensities for the rhodium containing moieties were quite similar for compounds **3** and **6**.

The complexes obtained have been tested as catalysts in the hydroformylation and hydroalxoxycarbonylation reaction of styrene. The chemoselectivity of hydroformylation was found to be excellent (higher than 99%) in all cases. A strong dependence of the regioselectivity on the P-substituents was observed and the introduction of a tolyl group instead of the phenyl one caused an unexpectedly high increase of the catalytic activity [6].

2.4. Concluding remarks

In summary, the reduction of 3-phosphabicyclo[3.1.0]hexane oxides and dihydrophosphinine oxides by $HSiCl_3$ was found to proceed easily at 0 °C in contrast to the acyclic phosphine oxides that require reflux at least in benzene solution [5]. In the case of 1-methyl-3-(2-methylphenyl)-3-phosphabicyclo[3.1.0]hexane, a novel inversion at the phosphorus atom was observed at ambient conditions.

The new type of heterocyclic P-ligands were utilized in the synthesis of Rh(III) and Pd(II) complexes. The large $\Delta\delta$ (>50 ppm) between **2** and **3** suggested a rather strong coordination between the phosphorus and the Rh(III) atoms in the above series. At the same time, for rhodium(III) complex **6**, the $\Delta\delta_P$ of 29.7 suggested only a weaker phosphorus–rhodium coordination, as compared with that in complexes **3**.

3. Experimental section

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 (^{1}H, ^{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 mass-spectra were obtained on a Varian MAT-311A spectrometer at 70 eV. The starting phosphine oxides used as precursors for the ligands were obtained as described earlier [3,7,10,13].

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

To a cooled (0 °C) solution of 0.3 mmol of precursor **1a**–**c** or **4** in 10 ml of a 1:1 mixture of CH_2Cl_2–C_6H_6 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.

The phosphines **2a**–**c** and **5** were used in the subsequent complex formation without further purification.

Compound **2a**-*syn*: ^{31}P NMR ($CDCl_3$) δ 25.2, (δ_P lit[14] 25.4); ^{13}C NMR ($CDCl_3$) δ 21.2 ($^{3}J_{PC}$ = 2.9, C_1–CH_3), 27.0 ($^{1}J_{PC}$ = 18.6, C_4), 32.8 ($^{1}J_{PC}$ = 17.6, C_2), 40.5 ($^{2}J_{PC}$ = 4.9, C_5), 40.9 (C_1), 72.6 (C_6), 128.6 ($^{2}J_{PC}$ = 7.8, C'_2), 129.5 ($^{1}J_{PC}$ = 9.4 C'_1), 130.23 ($^{3}J_{PC}$ = 13.5, C'_3), 132.3 (C'_4); FAB-MS, *m*/*z* 259 (M + H).

Compound **2b**-*syn*: ^{31}P NMR ($CDCl_3$) δ 24.5; ^{13}C NMR ($CDCl_3$) δ 21.2 (C_1–CH_3), 21.4 (Ar–CH_3), 27.2 ($^{1}J_{PC}$ = 11.8, C_4), 33.1 ($^{1}J_{PC}$ = 10.8, C_2), 40.3 (C_1), 40.8 (C_5), 73.4 (C_6), 126.02 ($^{1}J_{PC}$ = 15.4, C'_1), 129.34 ($^{2}J_{PC}$ =7.2, C'_2), 131.22 ($^{3}J_{PC}$ = 13.5, C'_3), 140.62 (C'_4); FAB-MS, M^+ found = 273.0342; $C_{13}H_{16}Cl_2P$ requires 273.0367 for the ^{35}Cl isotopes.

Compound **2c**-*syn*: ^{31}P NMR ($CDCl_3$) δ 22.6 (95%); ^{13}C NMR ($CDCl_3$) δ 21.6 (Ar–CH_3), 21.6 (C_1–CH_3), 26.6 ($^{1}J_{PC}$ = 3.7, C_4), 37.7 ($^{1}J_{PC}$ = 5.3, C_2), 40.6 (C_5), 40.6 (C_1), 74.3 ($^{3}J_{PC}$ = 7.2, C_6), 125.64 (C'_5), 128.43

($^1J_{PC}$ ~7, C'_1), 128.49 ($^3J_{PC}$ = 2.8, C'_3), 128.55 (C'_4), 129.97 ($^2J_{PC}$ = 4.0, C'_6), 139.71 ($^2J_{PC}$ = 18.6, C'_2); FAB-MS, M^+ found = 273.0346, $C_{13}H_{16}Cl_2P$ requires 273.0367 for the ^{35}Cl isotopes.

Compound **2c**-*anti*: ^{31}P NMR ($CDCl_3$) δ 27.9 (60%), ^{13}C NMR ($CDCl_3$) δ 21.1 (C_1–CH_3), 21.3 ($^3J_{PC}$ = 23.1, Ar–CH_3), 37.4 ($^1J_{PC}$ = 16.9, C_2), 39.3 ($^1J_{PC}$ = 14.6, C_4), 39.8 ($^2J_{PC}$ = 5.7, C_5), 45.2 ($^2J_{PC}$ = 5.3, C_1), C_6 overlapped with the signals of $CDCl_3$, 125.83 (C'_5), 128.43–128.49 (C'_1 and C'_3 of both isomers overlapped), 128.75 (C'_4), 130.29 ($^2J_{PC}$ = 4.2, C'_6), 135.48 ($^2J_{PC}$ = 13.1, C'_2).

The total yield for the two isomers of **2c** is 100%.

Compound **5**: ^{31}P NMR (C_6D_6) δ –30.6; ^{13}C NMR (C_6D_6) δ 23.1 ($^3J_{PC}$ = 5.6, CH_3), 128.7 ($^1J_{PC}$ = 8.2, C_2), 129.8 (C'_4), 131.8 ($^3J_{PC}$ = 16.0, C'_3), 134.4 ($^1J_{PC}$ = 16.2, C'_1), 134.5 ($^2J_{PC}$ = 21.5, C'_2), 134.7 (C_3), 136.8 ($^3J_{PC}$ = 11.4, C_4), 144.4 (C_7); FAB-MS, M^+ found = 283.0191; $C_{14}H_{14}Cl_2P$ requires 283.0210 for the ^{35}Cl isotopes.

3.3. Preparation of rhodium (III) complexes *3a–c* and *6*

To the solution of 0.30 mmol of ligand **2a**–**c** in 6 ml of CH_2Cl_2 was added 89 mg (0.14 mmol) of $[Cp^*RhCl_2]_2$ in 10 ml of CH_2Cl_2 at 25 °C over a period of 10–15 min. The red solution formed immediately was stirred for 0.5 h. According to ^{31}P NMR, the formation of the complex(es) was completed during this time. In the case of **2c**, the mixtures of isomers of the starting phosphines were used in the ratio **2c***syn*:**2c**-*anti* = 95:5 and 38:62 to obtain **3c**-*syn* and **3c**-*anti*, respectively. Then the solvent was evaporated to dryness and 3 ml of CH_2Cl_2 was added. The mixture was filtered and ~1 ml of pentane was added dropwise to the filtrate. The solution was allowed to stand at 26 °C for overnight. The red crystals precipitated from the solution were filtered off and dried in vacuo. For isolation of **3c**-*anti*, the precipitated 35:75 mixture of the two **3c** isomers was again recrystallized using the same system of solvents (CH_2Cl_2-pentane).

Compound **3a**-*syn*: yield: 87%; m.p. 191–195 °C; ^{31}P NMR ($CDCl_3$) δ 70.3 (J_{PRh} = 137.3), ^{13}C NMR ($CDCl_3$) δ 8.6 (Cp^*–CH_3), 20.1 ($^3J_{PC}$ = 6.6, C_1–CH_3), 30.3 ($^1J_{PC}$ = 31.5, C_4), 36.3 ($^1J_{PC}$ = 30.1, C_2), 42.0 (C_1), 43.1 (C_5), 72.1 (C_6), 98.0 (C_P^*), 127.9 ($^3J_{PC}$ = 9.6, C'_3), 130.2 ($^4J_{PC}$ = 2.5, C'_4), 130.7 ($^2J_{PC}$ = 7.8, C'_2), 133.0 ($^1J_{PC}$ = 31.0, C'_1); ^1H NMR ($CDCl_3$) δ 1.42 (d, 15H, CH_3–Cp*, J = 3.6); 1.63 (s, 3H, CH_3), 2.23 (dd, 1H, C_2–H_b, $^2J_{HH}$ = 7.6, $^2J_{PH}$ = 18.4), 2.70 (dd, 1H, *cis*-C_2–H_a, $^2J_{HH}$ = 7.6, $^2J_{PH}$ = 15.2), 2.90 (part of ABDX system, 1H, C_4–H_b, J = 8.4, 8.4, 14.8), 3.01 (part of ABDX system, 1H, C_4–H_B, J = 7.6, 7.6, 14.8), 3.32 (m, 1H, C_5–H, J = 8.4, 8.0, 14.8), 7.35–7.39 and 7.81–7.85 (2m, 3H + 2H, Ph). MS, *m*/*z* (rel. int.) 258 ($[M - Cp^*RhCl_2]^+$, 6), 223 ($[M - Cp^*RhCl_2 - Cl]^+$, 30), 187 ($[M - Cp^*RhCl_2 - Cl - HCl]^+$, 9) and independently 308 ($[Cp^*RhCl_2]^+$, 8), 273 ($[Cp^*RhCl]^+$, 8), 272 ($[Cp^*RhCl - H]^+$, 10), 237 ($[Cp^*Rh - H]^+$, 18), 134 ($[Cp^* - H]^+$, 27). Anal. Calc. for $C_{22}H_{28}Cl_4RhP$: C, 46.51; H, 4.97; P, 5.45. Found: C, 46.16, 46.48; H, 5.21, 5.17; P, 5.80, 5.87%.

Compound **3b**-*syn*: yield: 87%; m.p. 187–188 °C; ^{31}P NMR ($CDCl_3$) δ 70.6 (J_{PRh} = 136.6); ^{13}C NMR ($CDCl_3$) δ 8.6 (C_P^*–CH_3), 20.2 ($^3J_{PC}$ = 7.2, C_1–CH_3), 21.3 (Ar–CH_3), 30.4 ($^1J_{PC}$ = 31.7, C_4), 36.4 ($^1J_{PC}$ = 30.3, C_2), 42.0 (C_1), 43.2 (C_5), 72.2 (C_6), 98.0 ($^1J_{CRh}$ = 4.1, Cp*), 128.6 ($^3J_{PC}$ = 9.9, C'_3), 129.4 ($^1J_{PC}$ = 33.7, C'_1) 130.8 ($^2J_{PC}$ = 8.2, C'_2), 140.5 (C'_4); ^1H NMR ($CDCl_3$) δ 1.39 (d, 15H, CH_3–Cp*, J = 3.6); 1.60 (s, 3H, CH_3–C_1), 1.99 (dd, 1H, C_2–H_b, $^2J_{HH}$ = 8.0, $^2J_{PH}$ = 18.0), 2.34 (s, 3H, *m*-CH_3–Ar), 2.64 (dd, 1H, *cis*-C_2–H_a, $^2J_{HH}$ = 7.0, $^2J_{PH}$ = 15.2), 2.86 (part of ABDX system, 1H, C_4–H_b, J = 8.8, 8.8, 14.8), 2.96 (part of ABDX system, 1H, C_4–H_B, J = 7.2, 7.2, 14.8), 3.29 (m, 1H, C_5–H), 5.27 (2H, CH_2Cl_2-solvate), 7.17 (d, 2H, *o*-$C_6H_4CH_3$, $^3J_{HH}$ = 7.2), 7.68 (d, 1H, *m*-$C_6H_4CH_3$, $^3J_{HH}$ = 7.2), 7.71 (d, 1H, *m*-$C_6H_4CH_3$, $^3J_{HH}$ = 7.2); Anal. Calc. for $C_{23}H_{30}Cl_4RhP \cdot CH_2Cl_2$: C, 43.21; H, 4.83. Found: C, 43.18; H, 4.74%.

Compound **3c**-*syn*: yield: 67%; m.p. 169–170 °C; ^{31}P NMR ($CDCl_3$) δ 67.8 ($^1J_{PRh}$ = 139.9); ^{13}C NMR ($CDCl_3$) δ 8.5 (Cp^*–CH_3), 20.2 (C_1–CH_3), 22.8 (Ar–CH_3), 30.0 (C_4), 34.5 (C_2), 44.0 (C_5), 73.9 (C_6), 98.1 (Cp*), 124.75 ($^2J_{PC}$ = 7.8, C'_6), 130.3 (C'_4), 130.5 ($^1J_{PC}$ = 108.5, C'_1), 130.7 ($^3J_{PC}$ = 4.5, C'_3), 131.5 ($^3J_{PC}$ = 8.4, C'_5), 141.7 ($^2J_{PC}$ = 10.2, C'_2–Me); ^1H NMR ($CDCl_3$) δ 1.35 (d, 15H, CH_3–Cp*, J = 3.6), 1.59 (s, 3H, CH_3–C_1), 1.95–2.06 (br.m, 1H, C_2–H), 2.50 (br.s, 4H, *o*-CH_3–Ar overlapped with C_2–H), 2.92–3.12 (br.m, 2H, C_2–H_2), 3.62–3.70 (br.m, 1H, C_5–H), 5.27 (2H, CH_2Cl_2-solvate), 7.21 (d, 1H, C'_6-H, $^3J_{HH}$ = 7.4), 7.24 (d, 1H, C'_2–H, $^3J_{HH}$ = 7.2), 7.35 (dd, 1H, C'_5–H, $^3J_{HH}$ = 7.4, 7.6), 7.50 (t, 1H, C'_4–H, $^3J_{HH}$ = 7.6). Anal. Calc. for $C_{23}H_{30}Cl_4RhP$: C, 47.45; H, 5.19. Found: C, 47.75, 47.60; H, 5.19, 5.27%.

Compound **3c**-*anti*: yield: 32%; m.p.: 166–168 °C; ^{31}P NMR ($CDCl_3$) δ 91.6 ($^1J_{PRh}$ = 143.4); ^{13}C NMR ($CDCl_3$) 20.7 (C_1–CH_3), 22.6 (Ar–CH_3), 29.5 (C_4), 34.2 ($^1J_{PC}$ = 27.4, C_2), 40.4 (C_1), 41.9 (C_5), 75.1 ($^3J_{PC}$ = 14.0, C_6), 98.6 (d, Cp*, J = 2.6), 125.4 ($^2J_{PC}$ = 6.8, C'_6), 130.9 (C'_4), 130.5 ($^1J_{PC}$ = 88.5, C'_1), 131.4 ($^3J_{PC}$ = 8.4, C'_5), 131.6 ($^3J_{PC}$ = 8.6, C'_5), 132.3 ($^2J_{PC}$ = 8.0, C'_2–Me); Anal. Calc. for $C_{23}H_{30}Cl_4RhP$: C, 47.45; H, 5.19. Found: C, 47.85; H, 5.08%.

Complex **6** was obtained by the analogous procedure using the appropriate amounts of $[Cp^*RhCl_2]_2$ and phosphine **5**. Yield: 80%; m.p. >350 °C; ^{31}P NMR ($CDCl_3$) δ –0.89 ($^1J_{RhP}$ = 142.1); ^{13}C NMR ($CDCl_3$) δ 8,7 (CH_3–Cp*), 22.9 ($^3J_{PC}$ =9.3, C_8), 98.3 (Cp*), 121.7 ($^1J_{PC}$ = 48.9, C_2), 127.0 ($^1J_{PC}$ = 86.0, C'_1-*ipso*), 127.8 ($^3J_{PC}$ = 10.2, C'_3), 130.2 (C'_4), 131.1 ($^3J_{PC}$ = 42.5, C_4), 131.6 ($^3J_{PC}$ = 9.2, C'_2), 140.4 (C_3), and 152.4 ($^4J_{PC}$ = 8.8, C_7); ^1H NMR ($CDCl_3$) δ 1.49 (d, CH_3Cp*,

J = 3.6, 15H), 2.29 (s, C_8H_3, 6H), 6.48 (d, $^2J_{PH}$ = 27.2, C_2H, 2H), 7.32–7.51 (m, *m*-, *p*-C_6H_5P, 3H), 7.78 (d, $^3J_{HH}$ = 7.6, *o*-C_6H_5P, 1H), 7.80 (d, $^3J_{HH}$ = 7.2, *o*-C_6H_5P, 1H); IR (KBr) ν C=C 1610–1625(br) cm^{-1}. MS, *m/z* (rel. int.) 282 ([M − Cp*$RhCl_2$], 21), 247 ([M − Cp*$RhCl_2$ − Cl], 30), 211 ([M − Cp*$RhCl_2$ − Cl − HCl], 25), 196 ([M − Cp*$RhCl_2$ − Cl − HCl − CH_3], 13), 181 ([M − Cp*$RhCl_2$ − Cl − HCl − $2CH_3$], 15) and independently 308 ($[Cp^*RhCl_2]^+$, 7), 273 ($[Cp^*RhCl]^+$, 8), 237 ($[Cp^*Rh - H]^+$, 17), 236 ($[Cp^*Rh - H]^+$, 23), 134 ($[Cp^* - H]^+$, 34). Anal. Calc. for $C_{24}H_{28}Cl_4RhP$: C, 48.68; H, 4.77; P, 5.23. Found: C, 49.16, 49.48; H, 5.21, 5.17; P, 4.80, 4.87%.

3.4. Preparation of palladium (II) complex 7

To a 10 ml C_6H_6 solution of crude ligand **5** obtained from **4** (0.10 mmol) was added 32.0 mg (0.084 mmol) of $(PhCN)_2PdCl_2$ in 5 ml of the same solvent at 0 °C in a period of 10 minutes and the solution was stirred for 0.5 h. According to ^{31}P NMR, only one signal of the corresponding complex was observed after this time. After warming up to room temperature, the solvent was evaporated and 3 ml of CH_2Cl_2 was added. The mixture was filtered and ~1 ml of pentane was added. The solution was allowed to stand at 26 °C for overnight. The pale yellow precipitate was filtered off and dried in vacuo to afford 57 mg (73%) of **7**; m.p. >350 °C; ^{31}P NMR ($CDCl_3$) δ –5.2; ^1H NMR ($CDCl_3$) δ 2.32 (s, 12H, CH_3), 6.4 ($^2J_{PH}$ = 18.4, 4H, CH), 7.41–7.47 (6H, *m*-, *p*-C_6H_5P), 7.70–7.74 (4H, *o*-C_6H_5P); IR (KBr) ν C=C 1605–1625 (br) cm^{-1}; Anal. Calc. for $C_{28}H_{26}Cl_6P_2Pd$: C, 45.23; H, 3.52; P, 8.33. Found: C, 45.45, 45.55; H, 3.83, 3.37; P, 8.21, 8.16%.

3.5. X-ray Crystallography

Crystallographic data for the complexes are presented in Table 2. All structures were solved by direct methods and refined by full-matrix least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation, using the SHELXTL-97 package [15]. The absorption correction for all structures with the exception of **3c**-*syn* · $2CH_2Cl_2$ was applied semi-empirically from equivalents using the SADABS v. 2.01 program [16]. The positions of hydrogen atoms in all structures were calculated from geometrical point of view and included in refinement in riding model approximation. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary No. CCDC-225064 for **3b**-*syn* · CH_2Cl_2, CCDC-225065 for **3c**-*anti* · $2CHCl_3$, CCDC-225066 for **3c**-*syn* · $2CH_2Cl_2$, CCDC-225067 for **3c**-*syn* · $2CHCl_3$. 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).

Table 2
Crystallographic data for complexes **3b**,**c**

	3b-*syn* · CH_2Cl_2	**3c**-*anti* · $2CHCl_3$	**3c**-*syn* · $2CHCl_3$	**3c**-*syn* · $2CH_2Cl_2$
Formula	$C_{23}H_{30}Cl_4PRh \cdot CH_2Cl_2$	$C_{23}H_{30}Cl_4PRh \cdot 2CHCl_3$	$C_{23}H_{30}Cl_4PRh \cdot 2CHCl_3$	$C_{23}H_{30}Cl_4PRh \cdot 2CH_2Cl_2$
T (K)	110	120	120	153
Crystal system, space group	Orthorhombic, Pbca	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Unit cell dimensions				
a (Å)	24.514(4))	12.505(2)	19.548(2)	19.234(4)
b (Å)	8.708(1)	16.558(2)	8.997(1)	8.835(2)
c (Å)	26.115(4)	17.540(2)	20.190(2)	20.353(4)
α (°)		102.814(2)		
β (°)		106.659(2)	110.164(2)	113.56(3)
γ (°)		90.395(2)		
V (Å^3)	5574.5(15)	3383.1(7)	3333.3(7)	3170.5(11)
$Z(Z')$	8(1)	4(2)	4(1)	4(1)
M	667.08	820.89	820.89	752.00
μ (cm^{-1})	12.58	13.58	13.78	12.78
$F(000)$	2704	1648	1648	1520
ρ_{calc} (g cm^{-3})	1.590	1.612	1.636	1.680
$2\theta_{max}$ (deg)	56.00	58.00	58.00	58.00
Diffractometer	Smart CCD	Smart CCD	Smart CCD	Syntex $P2_1$
Scan mode	ω	ω	ω	$\theta/2\theta$
Number of reflections measured (R_{int})	19,301 (0.0588)	28,192 (0.0540)	35,827(0.0888)	6415 (0.0299)
Number of independent reflections	6667	16,887	8760	6227
Number of reflections with $I > 2\sigma(I)$	3756	10,800	6970	4999
Number of parameters	296	673	341	323
R_1	0.0585	0.0579	0.0624	0.0346
wR_2	0.1209	0.1309	0.1467	0.0939
GOF	1.083	1.070	1.085	1.003
Max/min peak (e Å^{-3})	1.28/–0.61	1.038/–0.992	1.18/–0.300	0.70/–0.98

3.6. Quantum chemical calculations

For computational consistency no symmetry constrains were used for all calculated molecules. The calculations have been done with the B3PW91 DFT method and 6-31G* basis set. Transition state calculations also carried out within the same DFT method and basis set via QST3 transition state search. Frequencies for all molecules also were calculated to proof transition state geometry and to consider zero point energy for inversion barrier energy and activation energy for this process. For each transition state geometry was found only one negative frequency. All calculations were carried out with GAUSSIAN 98 program package [17] in which ultrafine grid (99590) and the (10^{-8} hartree) designation were used for the SCF convergence. As a convergence criteria threshold limit 2×10^{-6} and 4×10^{-6} a.u. were used for maximum force and displacement, respectively.

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