Journal of Organometallic Chemistry 751 (2014) 306–313

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Platinum(II) complexes incorporating racemic and optically active 1-alkyl-3-phospholene P-ligands: Synthesis, stereostructure, NMR properties and catalytic activity

Péter Bagi [a], Tamara Kovács [a], Tibor Szilvási [b], Péter Pongrácz [c], László Kollár [c], László Drahos [d], Elemér Fogassy [a], György Keglevich [a,*]

[a] Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[b] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[c] Department of Inorganic Chemistry, University of Pécs and Szentágothai Research Center, 7624 Pécs, Hungary
[d] Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary

ARTICLE INFO

Article history:
Received 20 February 2013
Received in revised form
27 March 2013
Accepted 29 March 2013

Keywords:
3-Phospholene oxide
Optical resolution
P-ligand
Borane and platinum complexes
Theoretical calculations
Hydroformylation

ABSTRACT

Three 1-alkyl-3-phospholene 1-oxides, such as the P-ethyl, P-isobutyl and P-isopentyl derivative were prepared in racemic and enantiopure forms. After deoxygenation, the cyclic phosphines were converted to the corresponding phosphine–boranes and phosphine–platinum complexes ($PtCl_2L_2$, where L = 1-alkyl-3-phospholene). The new products were characterized by spectral methods, and the stereostructure of the complexes was also evaluated by high level quantum chemical calculations. The platinum complexes were tested in the hydroformylation of the styrene. The extent of the regioselectivity towards branched aldehyde exceeds that measured with earlier platinum complexes. However, the enantioselectivity remained below 29%.

1. Introduction

Phosphines form an important class among organophosphorous compounds as their transition metal complexes may be potential catalysts in homogenous catalytic reactions, such as hydrogenation and hydroformylation [1,2]. Platinum(II)–phosphine complexes are probably the best studied transition metal complexes due to their thermodynamic stability and kinetic inertness. Platinum(II)-complexes incorporating P-heterocyclic ligands form an interesting class of coordination compounds [3,4]. *Pringle* et al. synthesized several 5-, 6- and 7-membered P-heterocycles, as well as 9-phosphabicyclononanes (Phobanes) and studied their complexation reactions [5,6]. Several bidentate heterocyclic P-ligands, such as DuPhos [7], PennPhos [8], BIPNOR [9] have also been reported in the literature.

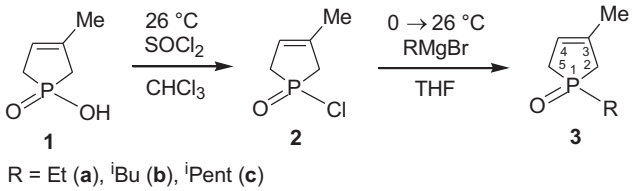
The complexation reactions of several 5- and 6-membered P-heterocycles were investigated by *Keglevich* and co-workers; arylphospholes, 3-phospholenes, phospholanes, a 1,4-dihydrophosphinine and a 1,2,3,6-tetrahydrophosphinine were converted to the corresponding Pt-complexes [10–14].

Recently, resolution methods were developed for aryl-, alkyl- and alkoxy-3-phospholene oxides using TADDOL derivatives and the Ca^{2+}-salts of dibenzoyl- and di-*p*-toluoyl-tartaric acid [15–18], that allowed us to synthesize 1-phenyl-, 1-*n*-propyl and 1-*n*-butyl-3-phospholene–platinum complexes in optically active form. Besides the synthetic interest, it was a question how the change of the aryl-substituent of the phospholenes to alkyl-substituent influences the catalytic selectivity in the hydroformylation reaction. The complexes were used as catalysts in the asymmetric hydroformylation reaction of styrene and showed high chemo-, and regioselectivity towards the branched aldehyde. The enantioselectivity obtained with the novel *n*-propyl-3-phospholene was significantly higher than that obtained with the corresponding phenyl derivative [12,19].

In this paper, novel platinum complexes incorporating racemic and optically active 1-ethyl-, 1-isobutyl and 1-isopentyl-3-phospholene ligands are described that were tested as catalysts in the hydroformylation of styrene.

* Corresponding author. Tel.: +36 1 4631111/5883; fax: +36 1 4633648.
E-mail addresses: gkeglevich@mail.bme.hu, keglevich@mail.bme.hu (G. Keglevich).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.03.045



Scheme 1.

2. Results and discussion

2.1. Synthesis of 1-alkyl-3-phospholene 1-oxides in racemic and enantiopure form

The 1-ethyl-3-methyl-3-phospholene 1-oxide (**3a**) was prepared from cyclic phosphinic acid **1** via chloride **2**, as described earlier [20]. This method was then extended to the synthesis of the 1-isobutyl and 1-isopentyl derivatives (**3b** and **3c**) (Scheme 1). The 1-isobutyl and 1-isopentyl-3-methyl-3-phospholene 1-oxides (**3b** and **3c**) were characterized by ^{31}P, ^{13}C and ^{1}H NMR spectroscopy.

The resolution of the 1-ethyl-3-methyl-3-phospholene 1-oxide (**3a**) with calcium hydrogen (−)-*O*,*O*′-di-*p*-toluoyl-(2*R*,3*R*)-tartrate was accomplished as described earlier [18]. The (*S*)-**3a** was obtained in an ee of 83% after two recrystallizations. As a further extension, calcium hydrogen (−)-*O*,*O*′-di-*p*-toluoyl-(2*R*,3*R*)-tartrate was also suitable for the resolution of 1-isopentyl-3-phospholene 1-oxide (**3c**) to provide the (*S*)-isomer of **3c** in an ee of 95% after the typical work-up procedure including filtration of the diastereomeric species formed, its purification by digestions and recovery of the phospholene oxide by treatment of the chloroform solution of the diastereomeric complex with aqueous ammonia (Scheme 2).

The (*R*)-1-isobutyl-3-phospholene 1-oxide ((*R*)-**3b**) was obtained by another method of ours [15], namely by resolution with (2*R*,3*R*)-(−)-α,α,α′,α′-tetraphenyl-1,4-dioxaspiro[4.5]decan-2,3-dimethanol (spiro-TADDOL). This procedure comprising filtration and recrystallizations of the diastereomeric complex formed and finally regeneration of the phospholene oxide by chromatography furnished compound (*R*)-**3b** in an ee of 96% (Scheme 3).

This was the first case that the 1-isobutyl- and 1-isopentyl-3-methyl-3-phospholene 1-oxides were prepared in optically active (*R* or *S*) forms. Details for the determination of the absolute P-configuration of 1-isobutyl and 1-isopentyl-3-phospholene oxides (**3c** and **3b**) by an X-ray study, CD investigations and high level quantum chemical calculations will form the subject of another paper.

2.2. Synthesis of 1-alkyl-3-phospholene-borane and platinum complexes

The racemic and optically active 3-phospholene oxides (**3a**–**c**, (*S*)-**3a**, (*R*)-**3b** and (*S*)-**3c**) were treated with trichlorosilane to give the corresponding P(III) derivatives (**4a**–**c**, (*R*)-**4a**, (*S*)-**4b** and (*R*)-**4c**). It is known that the deoxygenation of phosphine oxides with trichlorosilane, at least in the presence of pyridine, goes with retention of the configuration of the P-atom [21].

The phospholenes (**4a**–**c**, (*R*)-**4a**, (*S*)-**4b** and (*R*)-**4c**) were then converted to the corresponding phospholene–borane adducts (**5a**–**c**, (*R*)-**5a**, (*S*)-**5b** and (*R*)-**5c**) by reaction with dimethylsulfide-borane (Schemes 4 and 5). The phosphine–borane complexes (**5a**–**c**, (*R*)-**5a**, (*S*)-**5b** and (*R*)-**5c**) so obtained can be regarded phosphine precursors, as the phosphines can be liberated from them [22].

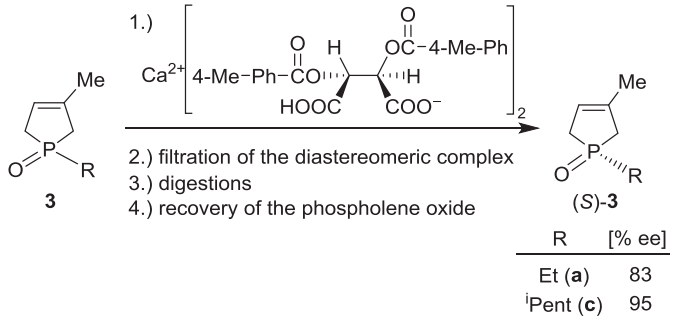
The 1-alkyl-3-phospholenes (**4a**–**c**, (*R*)-**4a**, (*S*)-**4b** and (*R*)-**4c**) were also converted to the corresponding platinum complexes (**6a**–**c**) by reaction with dichlorodibenzonitrileplatinum at 26 °C in benzene. Starting from racemic phospholene oxides (**3a**–**c**), a mixture of the homochiral (*R*,*R*- and *S*,*S*) and the heterochiral (*R*,*S*) complexes were formed. In case of the ethyl- and isopentyl-substituted derivatives (**6a** and **6c**), the ratio of the two forms was 1:1, while the 1-isobutyl-3-phospholene platinum complex (**6b**) was obtained as a 3:1 mixture of the two forms (Scheme 4). Starting from the corresponding optically active phospholenes ((*R*)-**4a**, (*S*)-**4b** and (*R*)-**4c**), platinum complexes (**6a**–**c**) were obtained in the corresponding homochiral forms (Scheme 5).

The borane and platinum complexes (**5a**–**c** and **6a**–**c**) were characterized by ^{31}P, ^{13}C and ^{1}H NMR spectroscopy, as well as HRMS. The relative position of the phospholene ligands in the platinum complexes was confirmed by ^{31}P NMR spectroscopy. The $^{1}J_{Pt-P}$ couplings of 3449–3454 MHz were in agreement with the *cis* orientation of the hetero rings in platinum complexes **6** [23].

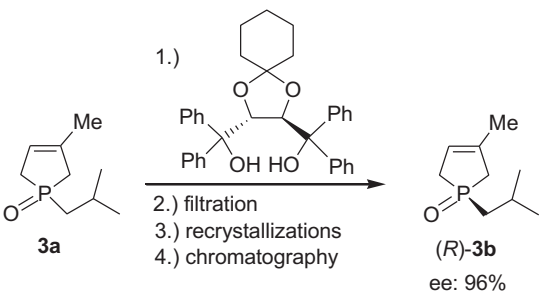
The ^{13}C NMR spectra of the platinum complexes are complicated due to the ^{195}Pt and the ^{31}P splittings. The ^{195}Pt nucleus with a 1/2 nuclear spin occurs in 33.8% abundance. The J_{Pt-C} and J_{P-C} coupling constants were determined by a first-order analysis of the splittings found in the ^{13}C NMR spectra of the platinum complexes (**6**).

2.3. Stereostructure of the 3-phospholene–platinum complexes

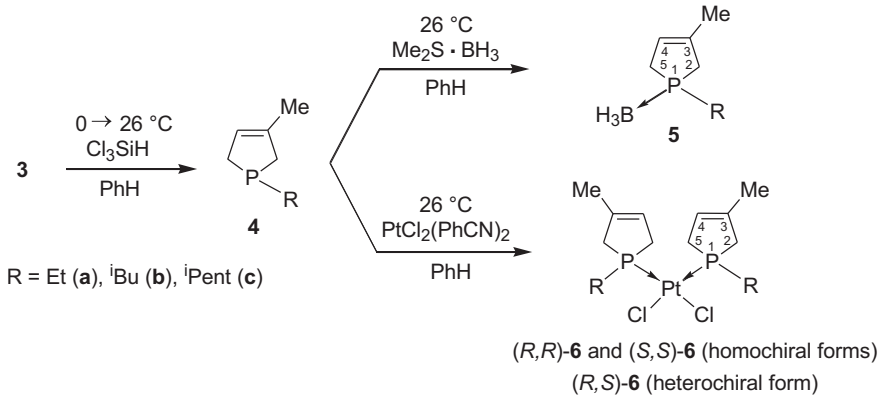
Stereostructures of 3-phospholene–platinum complexes were evaluated by the ωB97X-D/cc-pVTZ//RI-B97-D/6-31G(d) method with cc-pVTZ-PP pseudopotential on Pt atoms. The most stable structures of the *cis*-bis(1-ethyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*S*,*S*)-**6a**), the *cis*-bis(1-isobutyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*R*,*R*)-**6b**) and the *cis*-bis(1-isopentyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*S*,*S*)-**6c**) complexes are shown in Figs. 1–3, respectively. It has been found that the conformer with a rotational symmetry (C_2 symmetry group) is the favourable structure, which is determined by the intramolecular nonbonding interactions between the alkyl ligands. The geometry around the Pt atom is considered square planar as the P-Cl-Cl-P dihedral angles are in the range of −0.8 to −6.0. The newly calculated bond lengths/angles were in good agreement with earlier data of similar Pt-complexes. Regarding the



Scheme 2.



Scheme 3.



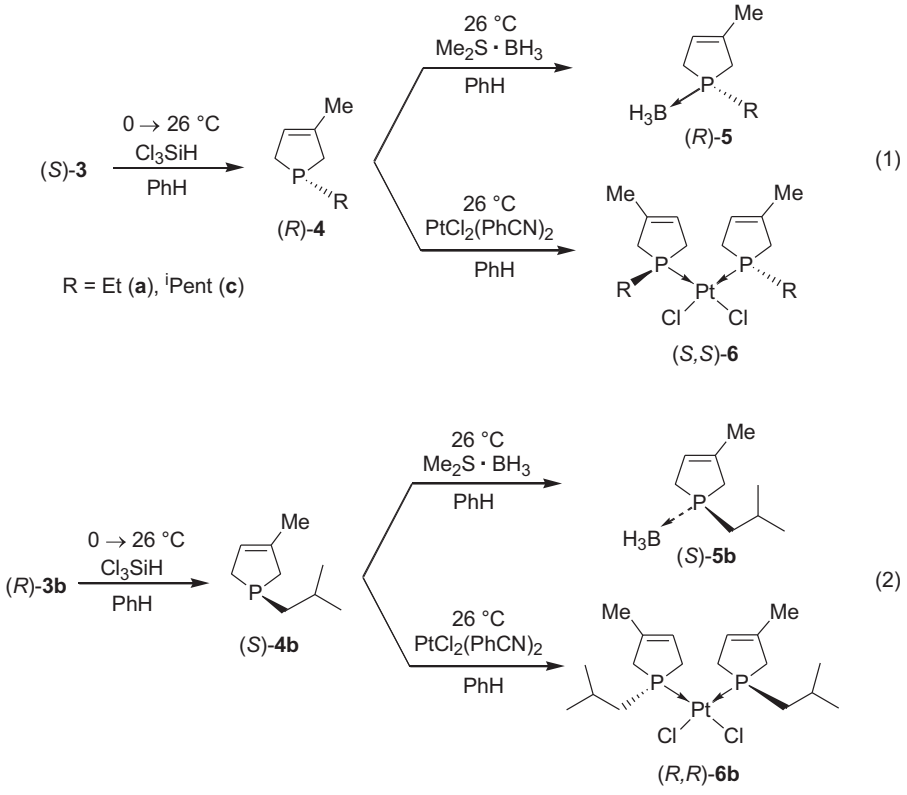
Scheme 4.

earlier described phenyl-phospholene–Pt-complex [12] and the newly introduced ethyl-phospholene–Pt-complex (**6a**), the P–Pt distances were 2.300 Å and 2.231 Å, respectively, while the Pt–Cl distances were 2.421 Å and 2.401 Å, respectively. On the basis of our earlier experiences, the stereostructure and geometrical data of the platinum complexes of the type PtP_2Cl_2 (where P = P-heterocyclic ligand) may be adequately described by high level quantum chemical calculations. The validation was based on the comparison of the X-ray structure and the calculated structure of a PtP_2Cl_2 complex, where P is a dibenzo[*c,e*] [1,2]oxaphosphorine. In respect of the P–Pt and Pt–Cl distances, the deviation between the results of the two methods was ca. 3–4% [24,25].

Accurate ωB97X-D single point energy calculations suggested that the relative energies of the stereostructures of 3-phospholene–platinum complexes are close to each other within 0.5 kcal/mol. This energetics is in accordance with the experimentally observed 1:1 ratio of the heterochiral and homochiral complexes.

2.4. Catalytic activity of the *cis*-$PtCl_2(L)_2$ complexes (L = **4a–e**) in the hydroformylation of styrene

The *cis*-$PtCl_2(L)_2$-type complexes (where L stands for 1-alkyl-3-methyl-3-phospholenes, **4a–e**, Fig. 4) were tested as catalyst precursors in the hydroformylation of styrene. The platinum-containing *in situ* catalysts formed from *cis*-$PtCl_2(L)_2$ and tin(II) chloride were used under standard 'oxo-conditions' (at $p(CO) = p(H_2) = 40$ bar, and reaction temperature 60 °C or 100 °C). As generally observed in the hydroformylation of styrene, in addition to the branched and linear formyl regioisomers (2-phenylpropanal (**A**) and 3-phenylpropanal (**B**), respectively) the hydrogenation by-product ethylbenzene (**C**) was also formed (Eq. (1)).



Scheme 5.

$$PhCH{=}CH_2 \xrightarrow{CO/H_2} \underset{\mathbf{A}}{PhCH(CHO)CH_3} + \underset{\mathbf{B}}{PhCH_2CH_2CHO} + \underset{\mathbf{C}}{PhCH_2CH_3} \quad (1)$$

The catalytic activity of the above system was comparable to the platinum-monophosphole-tin(II) chloride catalysts [4,26]. It is worth noting that it is behind the most investigated platinum-(chiral) diphosphine-tin(II) halide systems [27,28].

The use of 1% catalyst related to the substrate resulted in moderate conversion in 24–72 h at 100 °C (Table 1, entries 1, 5, 8, 12 and 16). All of the *in situ* catalysts have shown activity even at 60 °C (entries 2, 6, 9, 13 and 17). Decreased activity with increasing size of the *P*-substituent was observed. The only exception is the isopentyl-substituted ligand (**4c**) whose application resulted in a catalyst with comparable activities with that of 1-ethyl-3-methyl-3-phospholene (**4a**) (entries 16 and 1).

The formation of the aldehydes (**A** and **B**) was preferred in all cases and the chemoselectivity towards aldehydes varied typically in the range of 76–92%. The known tendency of increasing chemoselectivity towards aldehydes with decreasing reaction temperature was observed. Generally, the chemoselectivities obtained at 60 °C are 3–10% higher than those obtained at 100 °C. For example, in case of catalytic precursor *cis*-$PtCl_2$(**4a**)$_2$, chemoselectivities of 76% and 86% were obtained at 100 °C and 60 °C, respectively (entries 1 and 2).

As for the regioselectivity, the branched aldehyde (**A**) predominated over the linear one (**B**) in all cases. Regarding platinum-catalyzed hydroformylations, surprisingly high regioselectivities towards the branched aldehyde (**A**), varied between 65% and 82%, were obtained. It has to be mentioned that these values are below those ones obtained with the corresponding Rh-catalysts, however, they are among the best results achieved in the presence of catalysts formed from Pt-precursors. With all catalytic precursors incorporating ligands **4a**–**e**, the dependence of the regioselectivities on the reaction temperature has shown the same tendency. That is, the application of lower reaction temperature favours the formation of the branched aldehyde (**A**). For example, branched regioselectivities of 74/82, 71/77, 72/78, 73/80 and 70/77% were obtained at 100 °C/60 °C using precursors *cis*-$PtCl_2(L)_2$ (L = **4a**–**e**), respectively (entries 1/2, 5/6, 8/9, 12/13 and 16/17, respectively).

All five ligands were also tested in enantiomerically highly enriched (ee > 83%) form ((*R*)-**4a**, (*S*)-**4b**, (*R*)-**4c**, (*R*)-**4d**, (*R*)-**4e**). Their *cis*-$PtCl_2P_2$-type complexes were used as precursors in the enantioselective hydroformylation of styrene. In general, low enantioselectivities (up to 29%) were achieved. Despite the fact that the enantiomeric purity of (*R*)-ethyl-phospholene ligand **4a** was only 83%, the highest enantioselectivity was obtained with this ligand ((*R*)-**4a**). Slight increase in the ee-s was observed by decreasing the temperature from 100 °C to 60 °C. Surprisingly, (*S*)-2-phenylpropanal was found to be the predominating enantiomer in all cases, despite the fact that the absolute P-configuration of ligand (*S*)-**4b** was opposite, than that of the other ones ((*R*)-**4a**, (*R*)-**4c**–**e**).

It has to be added that, in general, rhodium-containing catalysts provide higher activities and higher branched regioselectivities than the platinum-containing ones in the hydroformylation of styrene [28]. It is true not only for phosphine and phosphite ligands, but for *P*-heterocycles as well [4]. For example, considering 5-

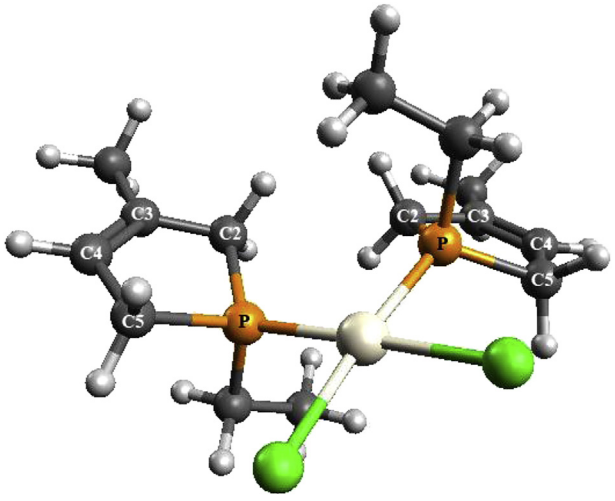


Fig. 1. Perspective view of *cis*-bis(1-ethyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*S*,*S*)-**6a**) calculated by ωB97X-D/cc-pVTZ//RI-B97-D/6-31G(d) method. For Pt atoms, cc-pVTZ-PP pseudopotential was applied in all cases. Grey, white grey, orange, green and white colours are referred to carbon, hydrogen, phosphorus, chlorine and platinum atoms, respectively. Selected bond lengths (Å) and angles (°) are as follows: Pt–Cl 2.401, Pt–P 2.231, P–C2 1.873, C2–C3 1.521, C3–C4 1.348, C4–C5 1.510, P–C5 1.870, P–C1′ 1.856, C1′–C2′ 1.539, P–Pt–P 100.4, Cl–Pt–Cl 91.1, Cl–Pt–P 84.4, Pt–P–C2 122.4, Pt–P–C5 116.6, Pt–P–C1′ 112.6, P–C2–C3 104.9, C2–C3–C4 116.1, C3–C4–C5 118.5, C2–P–C5 94.0, C2–P–C1′ 103.9, C5–P–C1′ 104.9, P–Cl–Cl–P −4.0, Cl–Pt–P–C2 162.4, Pt–P–C1′–C2′ −56.1, Pt–P–C2–C3 −139.0, P–C2–C3–C4 10.7, P–C2–C3–CH_3 −170.4, C2–C3–C4–C5 −0.1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

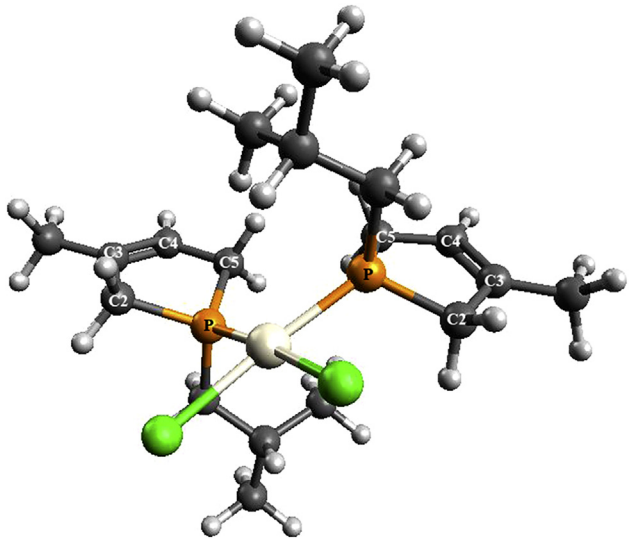


Fig. 2. Perspective view of *cis*-bis(1-isobutyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*R*,*R*)-**6b**) calculated by ωB97X-D/cc-pVTZ//RI-B97-D/6-31G(d) method. For Pt atoms, cc-pVTZ-PP pseudopotential was applied in all cases. Grey, white grey, orange, green and white colours are referred to carbon, hydrogen, phosphorus, chlorine and platinum atoms, respectively. Selected bond lengths (Å) and angles (°) are as follows: Pt–Cl 2.407, Pt–P 2.234, P–C2 1.866, C2–C3 1.518, C3–C4 1.349, C4–C5 1.514, P–C5 1.879, P–C1′ 1.862, C1′–C2′ 1.546, C2′–C3′ 1.541, C2′–C4′ 1.539, P–Pt–P 103.1, Cl–Pt–Cl 90.6, Cl–Pt–P 83.1, Pt–P–C2 115.4, Pt–P–C5 124.4, Pt–P–C1′ 112.3, P–C2–C3 104.9, C2–C3–C4 116.0, C3–C4–C5 118.1, C2–P–C5 93.5, C2–P–C1′ 104.6, C5–P–C1′ 103.8, P–Cl–Cl–P −0.8, Cl–Pt–P–C2 118.1, Pt–P–C1′–C2′ −36.3, Pt–P–C2–C3 148.3, P–C2–C3–C4 −12.4, P–C2–C3–CH_3 168.3, C2–C3–C4–C5 −1.5, P–C1′–C2′–C3′ 176.1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

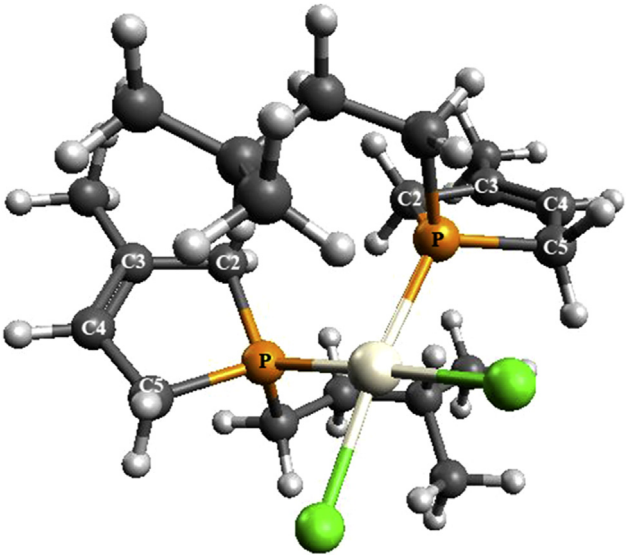


Fig. 3. Perspective view of *cis*-bis(1-isopentyl-3-methyl-3-phospholeno)-dichloro-platinum(II) ((*S*,*S*)-**6c**) calculated by ωB97X-D/cc-pVTZ//RI-B97-D/6-31G(d) method. For Pt atoms, cc-pVTZ-PP pseudopotential was applied in all cases. Grey, white grey, orange, green and white colours are referred to carbon, hydrogen, phosphorus, chlorine and platinum atoms, respectively. Selected bond lengths (Å) and angles (°) are as follows: Pt–Cl 2.404, Pt–P 2.231, P–C2 1.878, C2–C3 1.519, C3–C4 1.348, C4–C5 1.509, P–C5 1.873, P–C1′ 1.855, C1′–C2′ 1.544, C2′–C3′ 1.546, C3′–C4′ 1.540, C3′–C5′ 1.538, P–Pt–P 99.6, Cl–Pt–Cl 90.7, Cl–Pt–P 85.0, Pt–P–C2 120.9, Pt–P–C5 114.0, Pt–P–C1′ 115.4, P–C2–C3 105.3, C2–C3–C4 116.4, C3–C4–C5 118.7, C2–P–C5 94.3, C2–P–C1′ 104.6, C5–P–C1′ 104.8, P–Cl–Cl–P −6.0, Cl–Pt–P–C2 160.5, Pt–P–C1′–C2′ −68.0, Pt–P–C2–C3 −128.1, P–C2–C3–C4 5.1, P–C2–C3–CH_3 −176.5, C2–C3–C4–C5 0.2, P–C1′–C2′–C3′ 64.4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

membered *P*-heterocycles, the hydroformylation of styrene with platinum and rhodium complexes incorporating 1-arylphospholes with 2,4,6-trialkylphenyl substituents of various sterical hindrance resulted in a high preference for branched aldehyde in both cases. The activity of the platinum–phosphole–tin(II)chloride *in situ* systems were behind most of the platinum–diphosphine systems described earlier. In spite of the slight selectivities towards the linear aldehyde (3-phenylpropanal), with most platinum-diphosphine systems excellent regioselectivities towards the branched aldehyde were obtained in the case of the Pt-phosphole-$SnCl_2$ *in situ* catalyst [11,26].

As for the enantioselective hydroformylation of styrene, the Rh-BINAPHOS system, developed by the group of Takaya, opened a way even to practical applications due to its high enantioselectivity accompanied by high branched regioselectivity [29,30]. Among *P*-heterocycles, chiral bis(phospholanes), belonging to the DuPHOS and BPE ligand families, proved to be highly efficient in the rhodium-catalyzed enantioselective hydroformylation of styrene providing excellent regio- and enantioselectivities, as well as high turnover rates [31].

Although the application of several Pt-diphosphine-tin(II) chloride systems resulted in promising enantioselectivities in the eighties [32–36], the last two decades have shown the clear dominance of rhodium catalysts in asymmetric hydroformylation [28].

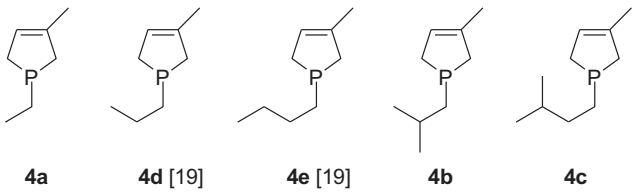


Fig. 4. Ligands used in platinum-catalyzed hydroformylation.

Table 1
Hydroformylation of styrene in the presence of *in situ* formed catalysts from $PtCl_2(L)_2$ complexes (L = **4a**–**e**) and tin(II) chloride.[a]

Entry	L	Temp. (°C)	R. time (h)	Conv. (%)	R_c[b] (%)	R_{br}[c] (%)	e.e. (%)
1	**4a**	100	24	54	76	74	–
2	**4a**	60	72	17	86	82	–
3	(*R*)-**4a**	100	24	52	80	75	25 (*S*)
4	(*R*)-**4a**	60	72	17	84	76	29 (*S*)
5	**4d**	100	24	48	82	71	–
6	**4d**	60	110	24	85	77	–
7	(*R*)-**4d**	100	48	83	92	69	21 (*S*)
8	**4e**	100	24	41	85	72	–
9	**4e**	60	72	22	89	78	–
10	(*R*)-**4e**	100	24	67	83	70	7 (*S*)
11	(*R*)-**4e**	60	72	33	87	76	5 (*S*)
12	**4b**	100	24	31	87	73	–
13	**4b**	60	72	11	84	80	–
14	(*S*)-**4b**	100	24	38	83	72	11 (*S*)
15	(*S*)-**4b**	60	72	19	86	86	15 (*S*)
16	**4c**	100	24	54	80	70	–
17	**4c**	60	72	25	86	77	–
18	(*R*)-**4c**	100	24	54	83	73	16 (*S*)
19	(*R*)-**4c**	60	72	14	83	82	22 (*S*)

[a] Reaction conditions: Pt/styrene = 1/100, Pt/$SnCl_2$ = 1/2; p(CO) = p(H_2) = 40 bar, 1 mmol of styrene, solvent: 10 mL of toluene.
[b] Chemoselectivity towards aldehydes (**A**, **B**). [(moles of **A** + moles of **B**)/(moles of **A** + moles of **B** + moles of **C**) × 100].
[c] Regioselectivity towards branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) × 100].

3. Conclusions

1-Alkyl-3-phospholene oxides were prepared in racemic and optically active forms and were utilized, after deoxygenation, in the synthesis of *cis*-$PtCl_2(L)_2$-type complexes (where L represents 1-alkyl-3-methyl-3-phospholenes). The platinum complexes form active *in situ* hydroformylation catalysts with tin(II) chloride as the cocatalyst. The hydroformylation of styrene is regioselective (69–86%) towards the branched aldehyde (2-phenylpropanal), however low ee-s (up to 29%) could be achieved.

4. Experimental

4.1. General (instruments)

The ^{31}P, ^{13}C, ^{1}H NMR spectra were taken on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5 and 300 or 202.4, 125.7 and 500 MHz, respectively. The couplings are given in Hz. The exact mass measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode. The enantiomeric excess (ee) values of the phospholene oxides **3a**–**c** were determined by chiral GC on Agilent 4890D instrument equipped with a BETA DEX™ 120 column (30 m × 0.25 mm, 0.25 um film, FID detector, nitrogen as carrier gas, injector 240 °C, detector 300 °C, head pressure: 5–10 psi, at 1:100 split ratio). The determination of the ee-s of 2-phenylpropanal (**A**) was carried out on Thermo Scientific FOCUS gas-chromatograph equipped with a Cyclodex-column (20 m × 0.25 mm, 0.25 um film, FID detector, helium as carrier gas, injector 250 °C, detector 280 °C, head pressure: 14.5 psi). Optical rotations were determined on a Perkin–Elmer 241 polarimeter.

The 1-ethyl-3-methyl-3-phospholene 1-oxide (**3a**) [20] and the (−)-(2*R*,3*R*)-α,α,α′,α′-tetraphenyl-1,4-dioxaspiro[4.5]decan-2,3-dimethanol (spiro-TADDOL) [37] were synthesized as described earlier. The (−)-*O*,*O*′-di-*p*-toluoyl-(2*R*,3*R*)-tartaric acid was purchased from Aldrich Chemical Co.

4.2. Preparation of 1-isobutyl-3-methyl-3-phospholene 1-oxide (**3b**)

To 10.2 g (77.0 mmol) of 1-hydroxy-3-phospholene 1-oxide **1** in 30 mL of chloroform was added 6.9 mL (94.0 mmol) of thionyl chloride and the solution was stirred overnight. The volatile components were removed *in vacuo*, and the residue was dissolved in 40 mL of THF. To the solution so obtained was added dropwise 85.0 mmol of isobutylmagnesium bromide in 40 mL of THF (prepared from 2.5 g (85.0 mmol) of magnesium and 9.2 mL (85.0 mmol) of isobutyl-bromide) at 0 °C and the mixture was stirred overnight. The reaction was then quenched with a 3 M HCl at 0 °C. The two phases were separated, and the organic layer was washed with $NaHCO_3$, brine and then dried with Na_2SO_4. After evaporating the solvent, the residue so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 10.0 g (76%) of **3b** as a dense oil. ^{31}P NMR ($CDCl_3$) δ 68.4; ^{13}C NMR ($CDCl_3$) δ 20.2 ($^3J_{P-C}$ = 10.4, C_3—CH_3), 23.9 ($^2J_{P-C}$ = 4.3, $CHMe_2$), 24.4 ($^3J_{P-C}$ = 8.8, $CH(CH_3)_2$), 33.6 ($^1J_{P-C}$ = 62.7, PCH_2), 36.8 ($^1J_{P-C}$ = 65.6, C_5), 38.9 ($^1J_{P-C}$ = 62.1, C_2), 120.7 ($^2J_{P-C}$ = 7.4, C_4), 136.7 ($^2J_{P-C}$ = 12.1, C_3); ^{1}H NMR ($CDCl_3$) δ 1.10 (d, J = 6.6, 3H) and 1.11 (d, J = 6.6, 3H) $CH(CH_3)_2$, 1.80 (bs, 3H, C_3—CH_3), 1.77—1.83 (m, 2H, PCH_2), 2.15—2.29 (m, 1H, $CHMe_2$), 2.33—2.65 (m, 4H, CH_2PCH_2), 5.49 (d, J = 29.5, 1H, CH=); HRMS $[M + Na]^+_{found}$ = 195.0908, $C_9H_{17}OPNa$ requires 195.0915.

4.3. Preparation of 1-isopentyl-3-methyl-3-phospholene 1-oxide (**3c**)

1-Hydroxy-3-phospholene 1-oxide **1** (10.2 g (77.0 mmol)) was converted to 1-isopentyl-3-methyl-3-phospholene 1-oxide (**3c**) analogously to the **1** → **3b** transformation using the Grignard reagent prepared from 2.5 g (85.0 mmol) of magnesium and 10.6 mL (85.0 mmol) of isopentyl-bromide in 40 mL of THF. Yield: 73%; ^{31}P NMR ($CDCl_3$) δ 70.1; ^{13}C NMR ($CDCl_3$) δ 20.3 ($^3J_{P-C}$ = 10.5, C_3—CH_3), 22.0 ($CH(CH_3)_2$), 27.8 ($^1J_{P-C}$ = 63.1, PCH_2), 29.1 ($^3J_{P-C}$ = 13.9, $CHMe_2$), 30.5 ($^2J_{P-C}$ = 4.1, CH_2CH_2CH), 32.2 ($^1J_{P-C}$ = 63.0, C_5), 35.3 ($^1J_{P-C}$ = 65.8, C_2), 120.8 ($^2J_{P-C}$ = 7.6, C_4), 136.8 ($^2J_{P-C}$ = 12.3, C_3); ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.5, 6H, $CH(CH_3)_2$), 1.47—1.70 (m, 3H, $CHMe_2$ and CH_2CH_2CH), 1.80 (bs, 3H, C_3—CH_3), 1.79—1.88 (m, 2H, PCH_2), 2.31—2.62 (m, 4H, CH_2PCH_2), 5.48 (d, J = 29.8, 1H, CH=); HRMS $[M + Na]^+_{found}$ = 209.1070, $C_{10}H_{19}OPNa$ requires 209.1071.

4.4. Preparation of (*S*)-1-ethyl-3-methyl-3-phospholene 1-oxide ((*S*)-**3a**)

The (*S*)-1-ethyl-3-methyl-3-phospholene 1-oxide (**3a**) was prepared as described earlier [18] by resolution with Ca(H-DPTTA)$_2$. Yield of (*S*)-**3a**: 7%; ee: 83%.

4.5. Preparation of (*R*)-1-isobutyl-3-methyl-3-phospholene 1-oxide ((*R*)-**3b**)

1.5 g (9.0 mmol) of racemic 1-isobutyl-3-methyl-3-phospholene 1-oxide (**3b**) and 2.3 g (4.5 mmol) of (*R*,*R*)-spiro-TADDOL was dissolved in 14 mL of hot methanol. The solution was allowed to cool down to 26 °C. After 24 h, the crystals were separated by filtration to give 2.3 g (14%) of complex [((*R*)-**3b**)(spiro-TADDOL)$_7$] with a de of 71%. The diastereomer complex was purified further by two recrystallizations from 14 mL of methanol to afford complex [((*R*)-**3b**)(spiro-TADDOL)$_7$] in a yield of 6% with a de of 96%. Column chromatography (silica gel, chloroform) of the complex regenerated 71 mg (5%) of the enantiomerically pure (+)-(*R*)-1-isobutyl-3-methyl-3-phospholene 1-oxide [(*R*)-**3b**] with an ee of 96%. $[\alpha]_D^{25}$ = +7.8 (c 1.3, $CHCl_3$).

4.6. Preparation of (*S*)-1-isopentyl-3-methyl-3-phospholene 1-oxide ((*S*)-**3c**)

To 1.8 g (4.6 mmol) of DPTTA·H_2O in a mixture of 6.0 mL of ethanol and 1.2 mL of water was added 0.13 g (2.3 mmol) of CaO, and the mixture was kept at reflux until it became clear. 1.7 g of racemic 1-isopentyl-3-methyl-3-phospholene 1-oxide (**3c**) in 6.0 mL of ethanol was then added to the solution of the *in situ* formed resolving agent. After standing at 26 °C for 3 h, the crystals were filtered off to give 2.0 g (62%) of $Ca_{2.5}$[((*S*)-**3c**)$_4$(H-DPTTA)$_5$] with a de of 69%. The diastereomer complex was purified further with two digestions in 13.2 mL of a 10:1 mixture of ethanol—water to afford the diastereomer complex $Ca_{2.5}$[((*S*)-**3c**)$_4$(H-DPTTA)$_5$] in a yield of 50% with a de of 95%. The phospholene oxide (*S*)-**3c** was recovered by treatment of the 10 mL chloroform solution of the complex with 10 mL of a 10% aqueous ammonia. The organic phase was washed with 2 mL of water, dried (Na_2SO_4), and concentrated to give 0.27 g (32%) of (*S*)-1-isopentyl-3-methyl-3-phospholene 1-oxide [(*S*)-**3c**] with an ee of 95%. $[\alpha]_D^{25}$ = −15.6 (c 3.2, $CHCl_3$).

4.7. Preparation of 1-ethyl-3-methyl-3-phospholene-borane (**5a**)

The solution of 0.31 g (2.2 mmol) of racemic 1-ethyl-3-methyl-3-phospholene 1-oxide (**3a**) in 4 mL of toluene was degassed and cooled to 0 °C, then 1.3 mL (12.9 mmol) of trichlorosilane was added. The mixture was stirred at 0 °C for 3 h and then at 25 °C for 3 h under nitrogen to afford the corresponding phospholene (**4a**) that was immediately reacted further. 1.3 mL of 2 M dimethylsulfide-borane in tetrahydrofuran (2.6 mmol) was added and the solution was stirred at 25 °C for 3 h under nitrogen. Then the mixture was treated with 3 mL of water and stirred for 15 min. The precipitated boric acid was removed by filtration and the organic phase dried (Na_2SO_4). Volatile components were removed under reduced pressure and the residue so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 0.04 g (13%) of **5a**.

^{31}P NMR ($CDCl_3$) δ 35.2 (broad); ^{13}C NMR ($CDCl_3$) δ 7.1 ($^2J_{P-C}$ = 2.8, CH_2CH_3), 18.7 ($^1J_{P-C}$ = 31.5, PCH_2), 19.2 ($^3J_{P-C}$ = 7.5, C_3—CH_3), 29.5 ($^1J_{P-C}$ = 34.0, C_5), 33.3 ($^1J_{P-C}$ = 35.7, C_2), 122.0 (C_4), 138.0 ($^2J_{P-C}$ = 2.3, C_3); ^{1}H NMR ($CDCl_3$) δ 0.27—0.88 (m, 3H, BH_3), 1.09—1.16 (m, 3H, CH_2CH_3), 1.65—1.72 (m, 2H, PCH_2), 1.79 (bs, 3H, C_3—CH_3), 2.30—2.58 (m, 4H, CH_2PCH_2), 5.42 (d, J = 21.3, 1H, CH=); MS m/z: $[M + Na]^+$ = 165.

The optically active (*R*)-1-ethyl-3-methyl-3-phospholene-borane ((*R*)-**5a**) was prepared analogously from (*S*)-1-ethyl-3-methyl-3-phospholene-1-oxide ((*S*)-**3a**) with an ee of 83%. Yield of **5a**: 24%. $[\alpha]_D^{25}$ = +2.8 (c 2.9, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ 35.2 (broad); ^{13}C NMR ($CDCl_3$) δ 7.1 ($^2J_{P-C}$ = 2.8), 18.6 ($^1J_{P-C}$ = 31.5), 19.1 ($^3J_{P-C}$ = 7.5), 29.5 ($^1J_{P-C}$ = 34.0), 33.3 ($^1J_{P-C}$ = 35.7), 121.9, 137.9 ($^2J_{P-C}$ = 2.3); ^{1}H NMR ($CDCl_3$) δ 0.24—0.85 (m, 3H), 1.07—1.13 (m, 3H), 1.63—1.69 (m, 2H), 1.77 (bs, 3H), 2.29—2.55 (m, 4H), 5.40 (d, J = 21.4, 1H); HRMS $[M + Na]^+_{found}$ = 165.0976, $C_7H_{16}PBNa$ requires 165.0980 for the ^{11}B isotope.

4.8. Preparation of cis-[bis(1-ethyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] (**6a**)

The deoxygenation of 0.084 g (0.58 mmol) of racemic 1-ethyl-3-methyl-3-phospholene-1-oxide (**3a**) was carried out in benzene using 0.35 mL (3.48 mmol) of trichlorosilane according to the procedure described in Section 4.7. Then, 0.14 g (0.29 mmol) of dichlorodibenzonitrileplatinum in 1 mL of degassed benzene was added to the reaction mixture under nitrogen. The mixture was stirred at 26 °C for 1 day, whereupon the complex gradually precipitated. Separation by filtration led to 0.14 g (94%) of crude product that was taken up in 2 mL of chloroform. The suspension

was filtered and the mother liquor was concentrated to give 0.13 g (85%) of **6a** as a 1:1 mixture of the homo- ((*R*,*R*) and (*S*,*S*)) and the heterochiral (*R*,*S*) forms.

^{31}P NMR ($CDCl_3$) δ 21.19 (J_{Pt-P} = 3450, 50%), 21.21 (J_{Pt-P} = 3451, 50%); ^{13}C NMR ($CDCl_3$) δ 8.9 ($^3J_{Pt-C}$ = 25, CH_2CH_3), 18.8–19.1 (m, C_3-CH_3), 21.3 ($^2J_{Pt-C}$ = 37, $^1J_{P-C}$ = 43, $^3J_{P-C}$ = 7, PCH_2), 31.8–32.6 (m, C_5), 35.5–36.3 (m, C_2), 122.1–122.5 (m, C_4), 138.6–139.0 (m, C_3); ^{1}H NMR ($CDCl_3$) δ 1.15–1.22 (m, 3H, CH_2CH_3), 1.83 (bs, 3H, C_3-CH_3), 2.02–2.09 (m, 2H, PCH_2), 2.67–3.05 (m, 4H, CH_2PCH_2), 5.50 (d, J = 23.0, 1H, CH=); HRMS $[M - Cl]^+_{found}$ = 485.0810, $C_{14}H_{26}P_2ClPt$ requires 485.0825 for the ^{35}Cl and ^{195}Pt isotopes.

The optically active cis-[bis(1-ethyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] ((*S*,*S*)-**6a**) was prepared similarly from (*S*)-1-ethyl-3-methyl-3-phospholene-1-oxide ((*S*)-**3a**) with an ee of 83%. Yield of (*S*,*S*)-**6a**: 55%; $[\alpha]_D^{25}$ = −1.3 [c 1.2, $CHCl_3$]; ^{31}P NMR ($CDCl_3$) δ 21.2 (J_{Pt-P} = 3451); ^{13}C NMR ($CDCl_3$) δ 8.9 ($^3J_{Pt-C}$ = 25, CH_2CH_3), 18.9 ($^4J_{Pt-C}$ = 30, $^3J_{P-C}$ = 5, $^5J_{P-C}$ = 5, C_3-CH_3), 21.3 ($^2J_{Pt-C}$ = 37, $^1J_{P-C}$ = 42, $^3J_{P-C}$ = 7, PCH_2), 32.2 ($^2J_{Pt-C}$ = 53, $^1J_{P-C}$ = 47, $^3J_{P-C}$ = 6, C_5), 35.7 ($^2J_{Pt-C}$ = 41, $^1J_{P-C}$ = 48, $^3J_{P-C}$ = 6, C_2), 122.2 ($^3J_{Pt-C}$ = 30, C_4), 138.7 ($^3J_{Pt-C}$ = 31, $^3J_{P-C}$ = 2, $^5J_{P-C}$ = 2, C_3); ^{1}H NMR ($CDCl_3$) δ 1.16–1.23 (m, 3H, CH_2CH_3), 1.82 (bs, 3H, C_3-CH_3), 2.01–2.11 (m, 2H, PCH_2), 2.53–2.75 (m, 4H, CH_2PCH_2), 5.52 (d, J = 23.5, 1H, CH=); HRMS $[M - Cl]^+_{found}$ = 485.0828, $C_{14}H_{26}P_2ClPt$ requires 485.0825 for the ^{35}Cl and ^{195}Pt isotopes.

4.9. Preparation of 1-isobutyl-3-methyl-3-phospholene-borane (**5b**)

Racemic 1-isobutyl-3-methyl-3-phospholene 1-oxide (**3b**) (0.38 g (2.2 mmol)) was transformed to phospholene-borane **5b** analogously to the **3a**→**4a**→**5a** conversion. Yield: 25%; ^{31}P NMR ($CDCl_3$) δ 32.9 (broad); ^{13}C NMR ($CDCl_3$) δ 19.1 ($^3J_{P-C}$ = 7.6, C_3-CH_3), 24.37 ($^3J_{P-C}$ = 7.9) and 24.39 ($^3J_{P-C}$ = 7.9) $CH(CH_3)_2$, 25.0 ($CHMe_2$), 31.5 ($^1J_{P-C}$ = 34.5, C_5), 35.1 ($^1J_{P-C}$ = 28.3, PCH_2), 35.4 ($^1J_{P-C}$ = 36.2, C_2), 121.7 (C_4), 137.7 ($^2J_{P-C}$ = 2.9, C_3); ^{1}H NMR ($CDCl_3$) δ 0.30–0.90 (m, 3H, BH_3), 1.00 (d, J = 6.7, 3H) and 1.01 (d, J = 6.7, 3H) $CH(CH_3)_2$, 1.61–1.64 (m, 2H, PCH_2), 1.77 (bs, 3H, C_3-CH_3), 2.00–2.10 (m, 1H, $CHMe_2$), 2.32–2.59 (m, 4H, CH_2PCH_2), 5.40 (d, J = 21.7, 1H, CH=); HRMS $[M + Na]^+_{found}$ = 193.1297, $C_9H_{20}PBNa$ requires 193.1293 for the ^{11}B isotope.

The optically active (*S*)-1-isobutyl-3-methyl-3-phospholene-borane ((*S*)-**5b**) was prepared analogously from (*R*)-1-isobutyl-3-methyl-3-phospholene-1-oxide ((*R*)-**3b**) with an ee of 96%. Yield of (*S*)-**5b**: 32%; $[\alpha]_D^{25}$ = −0.7 [c 1.3, $CHCl_3$]; ^{31}P NMR ($CDCl_3$) δ 31.4 (broad); ^{13}C NMR ($CDCl_3$) δ 19.2 ($^3J_{P-C}$ = 7.6), 24.34 ($^3J_{P-C}$ = 7.9), 24.47 ($^3J_{P-C}$ = 7.9), 25.1, 31.6 ($^1J_{P-C}$ = 34.5), 35.2 ($^1J_{P-C}$ = 28.3), 35.5 ($^1J_{P-C}$ = 35.5), 121.8, 137.8 ($^2J_{P-C}$ = 2.9); ^{1}H NMR ($CDCl_3$) δ 0.32–0.89 (m, 3H), 1.01 and 1.02 (d, J = 6.7, 6H), 1.62–1.66 (m, 2H), 1.79 (bs, 3H), 2.02–2.12 (m, 1H), 2.33–2.61 (m, 4H), 5.41 (d, J=21.7, 1H); HRMS $[M+Na]^+_{found}$ = 193.1298, $C_9H_{20}PBNa$ requires 193.1293 for the ^{11}B isotope.

4.10. Preparation of cis-[bis(1-isobutyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] (**6b**)

Racemic 1-isobutyl-3-methyl-3-phospholene-1-oxide (**3b**) (0.10 g (0.58 mmol)) was transformed to complex **6b** analogously to the **3a** → **4a** → **6a** conversion. Yield: 62% as a 3*:1* mixture of homo- ((*R*,*R*) and (*S*,*S*)) and the heterochiral (*R*,*S*) forms, * may be reversed; ^{31}P NMR ($CDCl_3$) δ 14.19 (J_{Pt-P} = 3450, 75%), 14.20 (J_{Pt-P} = 3449, 25%); ^{13}C NMR ($CDCl_3$) δ 18.9–19.1 (m, C_3-CH_3), 24.6–25.1 (m, $CH(CH_3)_2$), 25.7 ($^3J_{Pt-C}$ = 17, $CHMe_2$), 32.9–34.2 (m, PCH_2), 36.4–37.9 (m, C_2 and C_5), 121.8–122.5 (m, C_4), 138.5–139.1 (m, C_3); ^{1}H NMR ($CDCl_3$) δ 1.13–1.18 (m, 6H, $CH(CH_3)_2$), 1.84 (bs, 3H, C_3-CH_3), 1.89–2.05 (m, 2H, PCH_2), 2.08–2.15 (m, 1H, $CHMe_2$), 2.66–3.11 (m, 4H, CH_2PCH_2), 5.50 (d, J = 24.1, 1H, CH=); HRMS $[M - Cl]^+_{found}$ = 541.1465, $C_{18}H_{34}P_2ClPt$ requires 541.1451 for the ^{35}Cl and ^{195}Pt isotopes.

The optically active cis-[bis(1-isobutyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] ((*R*,*R*)-**6b**) was prepared analogously from (*R*)-1-isobutyl-3-methyl-3-phospholene-1-oxide ((*R*)-**3b**) and was obtained with an ee of 96%. Yield of (*R*,*R*)-**6b**: 91%; $[\alpha]_D^{25}$ = −8.6 [c 0.9, $CHCl_3$]; ^{31}P NMR ($CDCl_3$) δ 16.2 (J_{Pt-P} = 3449); ^{13}C NMR ($CDCl_3$) δ 19.0 ($^4J_{Pt-C}$ = 40, $^3J_{P-C}$ = 4, $^5J_{P-C}$ = 4, C_3-CH_3), 24.8 ($^4J_{Pt-C}$ = 34, $^3J_{P-C}$ = 4, $^5J_{P-C}$ = 4) and 24.9 ($^4J_{Pt-C}$ = 34, $^3J_{P-C}$ = 4, $^5J_{P-C}$ = 4) $CH(CH_3)_2$, 25.7 ($^3J_{Pt-C}$ = 16, $CHMe_2$), 33.5 ($^2J_{Pt-C}$ = 57, $^1J_{P-C}$ = 44, $^3J_{P-C}$ = 5, PCH_2), 36.9 ($^2J_{Pt-C}$ = 48, $^1J_{P-C}$ = 41, $^3J_{P-C}$ = 7, C_5), 37.3 ($^2J_{Pt-C}$ = 42, $^1J_{P-C}$ = 48, $^3J_{P-C}$ = 5, C_2), 122.0 ($^3J_{Pt-C}$ = 31, C_4), 138.9 ($^3J_{Pt-C}$ = 31, $^2J_{P-C}$ = 2, $^4J_{P-C}$ = 2, C_3); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J = 6.5, 3H) and 1.17 (d, J = 6.5, 3H) $CH(CH_3)_2$, 1.84 (bs, 3H, C_3-CH_3), 1.89–2.05 (m, 2H, PCH_2), 2.08–2.17 (m, 1H, $CHMe_2$), 2.72–3.11 (m, 4H, CH_2PCH_2), 5.50 (d, J = 22.6, 1H, CH=); HRMS $[M - Cl]^+_{found}$ = 541.1454, $C_{18}H_{34}P_2ClPt$ requires 541.1451 for the ^{35}Cl and ^{195}Pt isotopes.

4.11. Preparation of 1-isopentyl-3-methyl-3-phospholene-borane (**5c**)

Racemic 1-isopentyl-3-methyl-3-phospholene 1-oxide (**3c**) (0.41 g (2.2 mmol)) was transformed to phospholene-borane **5c** analogously to the **3a** → **4a** → **5a** conversion. Yield: 44%; ^{31}P NMR ($CDCl_3$) δ 33.3 (broad); ^{13}C NMR ($CDCl_3$) δ 19.1 ($^3J_{P-C}$ = 7.5, C_3-CH_3), 22.1 ($CH(CH_3)_2$), 23.3 ($^1J_{P-C}$ = 30.7, PCH_2), 29.2 ($^3J_{P-C}$ = 12.2, $CHMe_2$), 29.9 ($^1J_{P-C}$ = 34.1, C_5), 31.7 ($^2J_{P-C}$ = 2.1, CH_2CH_2CH), 33.8 ($^1J_{P-C}$ = 35.8, C_2), 121.9 (C_4), 137.9 ($^2J_{P-C}$ = 2.5, C_3); ^{1}H NMR ($CDCl_3$) δ 0.07–1.13 (m, 3H, BH_3), 0.91 (d, J = 6.6, 6H, $CH(CH_3)_2$), 1.32–1.45 (m, 2H, CH_2CH_2CH), 1.52–1.70 (m, 3H, PCH_2 and $CHMe_2$), 1.81 (bs, 3H, C_3-CH_3), 2.30–2.62 (m, 4H, CH_2PCH_2), 5.44 (d, J = 21.2, 1H, CH=); HRMS $[M + Na]^+_{found}$ = 207.1452, $C_{10}H_{22}PBNa$ requires 207.1450 for the ^{11}B isotope.

The optically active (*R*)-1-isopentyl-3-methyl-3-phospholene-borane ((*R*)-**5c**) was prepared analogously from (*S*)-1-isopentyl-3-methyl-3-phospholene-1-oxide ((*S*)-**3c**) with an ee of 95%. Yield of (*R*)-**5c**: 30%; $[\alpha]_D^{25}$ = −2.1 [c 1.4, $CHCl_3$]; ^{31}P NMR ($CDCl_3$) δ 33.3 (broad); ^{13}C NMR ($CDCl_3$) δ 19.2 ($^3J_{P-C}$ = 7.7), 22.2, 23.5 ($^1J_{P-C}$ = 30.7), 29.3 ($^3J_{P-C}$ = 12.1), 30.1 ($^1J_{P-C}$ = 34.1), 31.8 ($^2J_{P-C}$ = 2.1), 33.9 ($^1J_{P-C}$ = 35.8), 122.0, 138.0 ($^2J_{P-C}$ = 2.6); ^{1}H NMR ($CDCl_3$) δ 0.30–0.72 (m, 3H), 0.91 (d, J = 6.6, 6H), 1.36–1.43 (m, 2H), 1.54–1.68 (m, 3H), 1.81 (bs, 3H), 2.29–2.60 (m, 4H), 5.43 (d, J = 20.8, 1H); MS *m*/*z*: $[M + Na]^+$ = 207.

4.12. Preparation of cis-[bis(1-isopentyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] (**6c**)

Racemic 1-isopentyl-3-methyl-3-phospholene-1-oxide (**3c**) (0.11 g (0.58 mmol)) was transformed to complex **6c** analogously to the **3a** → **4a** → **6a** conversion. Yield: 97% as a 1:1 mixture of homo- ((*R*,*R*) and (*S*,*S*)) and the heterochiral (*R*,*S*) forms on the basis of the ^{13}C NMR data; ^{31}P NMR ($CDCl_3$) δ 16.3 (J_{Pt-P} = 3452); ^{13}C NMR ($CDCl_3$) δ 18.9–19.0 (m, C_3-CH_3), 22.1–22.2 (m, $CH(CH_3)_2$), 26.0 ($^2J_{Pt-C}$ = 35, $^1J_{P-C}$ = 43, $^3J_{P-C}$ = 7, PCH_2), 28.9 ($^4J_{Pt-C}$ = 37, $^3J_{P-C}$ = 7, $^5J_{P-C}$ = 7, $CHMe_2$), 31.8–33.1 (m, C_5), 33.2 ($^3J_{Pt-C}$ = 24, CH_2CH_2CH), 35.6–36.8 (m, C_2), 122.0–122.5 (m, C_4), 138.3–138.9 (m, C_3); ^{1}H NMR ($CDCl_3$) δ 0.91 (d, J = 6.5, 6H, $CH(CH_3)_2$), 1.38–1.58 (m, 2H, CH_2CH_2CH), 1.60–1.72 (m, 1H, $CHMe_2$), 1.84 (bs, 3H, C_3-CH_3), 1.89–2.10 (m, 2H, PCH_2), 2.73–3.08 (m, 4H, CH_2PCH_2), 5.52 (d, J = 24.9, 1H, CH=); HRMS $[M - Cl]^+_{found}$ = 569.1785, $C_{20}H_{38}P_2ClPt$ requires 569.1784 for the ^{35}Cl and ^{195}Pt isotopes.

The optically active cis-[bis(1-isopentyl-3-methyl-3-phospholeno)-dichloro-platinum(II)] ((*S*,*S*)-**6c**) was prepared analogously from (*S*)-1-isopentyl-3-methyl-3-phospholene-1-oxide ((*S*)-**3c**) and was obtained with an ee of 95%. Yield of (*S*,*S*)-**6c**: 56%; $[\alpha]_D^{25} = +9.2$ [c 0.7, $CHCl_3$]; ^{31}P NMR ($CDCl_3$) δ 18.7 ($J_{Pt-P} = 3454$); ^{13}C NMR ($CDCl_3$) δ 18.9 ($^3J_{P-C} = 4$, $^5J_{P-C} = 4$, C_3–CH_3), 22.1 and 22.2 ($CH(CH_3)_2$), 26.0 ($^2J_{Pt-C} = 34$, $^1J_{P-C} = 43$, $^3J_{P-C} = 7$, PCH_2), 29.0 ($^4J_{Pt-C} = 37$, $^3J_{P-C} = 7$, $^5J_{P-C} = 7$, $CHMe_2$), 32.5 ($^2J_{Pt-C} = 53$, $^1J_{P-C} = 45$, $^3J_{P-C} = 5$, C_5), 33.2 ($^3J_{Pt-C} = 21$, CH_2CH_2CH), 36.3 ($^2J_{Pt-C} = 40$, $^1J_{P-C} = 48$, $^3J_{P-C} = 5$, C_2), 122.1 ($^3J_{Pt-C} = 28$, C_4), 138.9 ($^3J_{Pt-C} = 33$, $^3J_{P-C} = 2$, $^5J_{P-C} = 2$, C_3); ^1H NMR ($CDCl_3$) δ 0.91 (d, $J = 6.6$, 6H), 1.44–1.55 (m, 2H), 1.61–1.70 (m, 1H), 1.84 (bs, 3H), 1.94–2.07 (m, 2H), 2.71–3.08 (m, 4H), 5.49 (d, $J = 23.3$, 1H).

4.13. Hydroformylation experiments

A solution of 0.01 mmol of $PtCl_2$(ligand)$_2$ (L = **4a**–**d**) and 3.8 mg (0.02 mmol) of tin(II) chloride in 10 mL of toluene containing 0.115 mL (1.0 mmol) of styrene was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$) and placed in an oil bath of appropriate temperature and the mixture was stirred with a magnetic stirrer. Samples were taken from the mixture and the pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC and chiral GC (on a capillary Cyclodex-column, (*R*)-2-phenylpropanal was eluted before the (*S*) enantiomer).

4.14. Theoretical calculations

Geometries were computed at the RI-B97-D/6-31G(d) level of theory [38–41] then single point energy calculations were performed at the optima using ωB97X-D/cc-pVTZ level [42,43]. For Pt atoms, cc-pVTZ-PP pseudopotential [44] was applied for both geometry optimization and single point energy calculations. Minima on the potential energy surface (PES) were characterized by harmonic vibrational frequency calculations. Calculations were carried out using Gaussian09 program [45]. Avogadro was utilized for visualization [46].

Acknowledgements

The above project was supported by the Hungarian Scientific and Research Fund (OTKA K83118, K104769 and CK78553). Tibor Szilvási thanks for the support of The New Széchenyi Plan TAMOP-4.2.2/B-10/1-2010-0009 and also thanks the HPC of BUTE for computational time.

References

[1] H. Brunner, W. Zettlmeier, Handbook of Enantioselective Catalysis with Transition Metal Compounds, VCH, Weinheim, 1993.
[2] C. Botteghi, M. Marchetti, S. Paganelli, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, 1998.
[3] F. Mathey, Phosphorus-carbon Heterocyclic Chemistry: The Rise of a New Domain, Pergamon/Elsevier, Amsterdam, 2001.
[4] L. Kollar, G. Keglevich, Chem. Rev. 110 (2010) 4257.
[5] R.A. Baber, M.F. Haddow, A.J. Middleton, A.G. Orpen, P.G. Pringle, A. Haynes, G.L. Williams, R. Papp, Organometallics 26 (2006) 713.
[6] M. Carreira, M. Charernsuk, M. Eberhard, N. Fey, R.V. Ginkel, A. Hamilton, W.P. Mul, A.G. Orpen, H. Phetmung, P.G. Pringle, J. Am. Chem. Soc. 131 (2009) 3078.
[7] T. Clark, C. Landis, Tetrahedron: Asymmetry 15 (2004) 2123.
[8] Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, Angew. Chem. Int. Ed. 37 (1998) 1100.
[9] F. Robin, F. Mercier, L. Ricard, F. Mathey, M. Spagnol, Chem. A Eur. J. 3 (1997) 1365.
[10] Z. Csók, G. Keglevich, G. Petőcz, L. Kollár, Inorg. Chem. 38 (1999) 831.
[11] Z. Csók, G. Keglevich, G. Petőcz, L. Kollár, J. Organomet. Chem. 586 (1999) 79.
[12] A. Kerényi, V. Kovács, T. Körtvélyesi, K. Ludányi, L. Drahos, G. Keglevich, Heteroatom Chem. 21 (2010) 63.
[13] K.M. Pietrusiewicz, A. Flis, V. Ujj, T. Körtvélyesi, L. Drahos, P. Pongrácz, L. Kollár, G. Keglevich, Heteroatom Chem. 22 (2011) 730.
[14] G. Keglevich, M. Sipos, D. Szieberth, G. Petőcz, L. Kollár, J. Organomet. Chem. 689 (2004) 3158.
[15] T. Novák, J. Schindler, V. Ujj, M. Czugler, E. Fogassy, G. Keglevich, Tetrahedron: Asymmetry 17 (2006) 2599.
[16] T. Novák, V. Ujj, J. Schindler, M. Czugler, M. Kubinyi, Z.A. Mayer, E. Fogassy, G. Keglevich, Tetrahedron: Asymmetry 18 (2007) 2965.
[17] V. Ujj, J. Schindler, T. Novák, M. Czugler, E. Fogassy, G. Keglevich, Tetrahedron: Asymmetry 19 (2008) 1973.
[18] V. Ujj, P. Bagi, J. Schindler, J. Madarász, E. Fogassy, G. Keglevich, Chirality 22 (2010) 699.
[19] G. Keglevich, P. Bagi, Á. Szöllősy, T. Körtvélyesi, P. Pongrácz, L. Kollár, L. Drahos, J. Organomet. Chem. 696 (2011) 3557.
[20] G. Keglevich, L. Tőke, C. Lovász, K. Újszászy, G. Szalontai, Heteroatom Chem. 5 (1994) 395.
[21] R. Engel, in: R. Engel (Ed.), Handbook of Organophosphorus Chemistry, Marcel Dekker, New York, 1992, p. 193.
[22] Y. Gourdel, A. Ghanimi, P. Pellon, M. Le Corre, Tetrahedron Lett. 34 (1993) 1011.
[23] G. Keglevich, L. Kollár, Lett. Org. Chem. 7 (2010) 612.
[24] G. Keglevich, A. Kerényi, B. Mayer, T. Körtvélyesi, K. Ludányi, Transit. Metal Chem. 33 (2008) 505.
[25] T. Holczbauer, G. Keglevich, A. Kerenyi, M. Czugler, Acta Crystallogr. Sect. E 65 (2009) 347.
[26] G. Keglevich, T. Kégl, T. Chuluunbaatar, B. Dajka, P. Mátyus, B. Balogh, L. Kollár, J. Mol. Catal. A: Chem. 200 (2003) 131.
[27] F. Agbossou, J.-F. Carpentier, A. Mortreux, Chem. Rev. 95 (1995) 2485 (and references cited therein).
[28] R. Franke, D. Selent, A. Boerner, Chem. Rev. 112 (2012) 5675 (and references cited therein).
[29] N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033.
[30] N. Sakai, K. Nozaki, H. Takaya, J. Chem. Soc. Chem. Commun. (1994) 395.
[31] A.T. Axtell, C.J. Cobley, J. Klosin, G.T. Whiteker, A. Zanotti-Gerosa, K.A. Abboud, Angew. Chem. Int. Ed. 44 (2005) 5834.
[32] G. Consiglio, P. Pino, L.I. Flowers, C.U. Pittmann Jr., J. Chem. Soc. Chem. Commun. (1983) 612.
[33] P. Haelg, G. Consiglio, P. Pino, J. Organomet. Chem. 296 (1985) 281.
[34] L. Kollár, G. Consiglio, P. Pino, J. Organomet. Chem. 330 (1987) 305.
[35] G. Parrinello, J.K. Stille, J. Am. Chem. Soc. 109 (1987) 7122.
[36] L. Kollár, J. Bakos, I. Tóth, B. Heil, J. Organomet. Chem. 350 (1988) 277.
[37] A.K. Beck, B. Bastani, D.A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi, L. Lavecchia, Chimia 45 (1991) 238.
[38] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.
[39] O. Vahtras, J. Almlöf, M.W. Feyereisen, Chem. Phys. Lett. 213 (1993) 514.
[40] A.D. Becke, J. Chem. Phys. 107 (1997) 8554.
[41] S. Grimme, J. Comput. Chem. 27 (2006) 1787.
[42] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[43] J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys. 10 (2008) 6615.
[44] K.L. Schuchardt, B.T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T.L. Windus, J. Chem. Inf. Model. 47 (2007) 1045.
[45] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
[46] Avogadro: An Open-source Molecular Builder and Visualization Tool. Version 1.00. http://avogadro.openmolecules.net/.