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Synthesis, Characterization, and Application of Platinum(II) Complexes Incorporating Racemic and Optically Active 4-Chloro-5-Methyl-1-Phenyl-1,2,3,6-Tetrahydrophosphinine Ligand

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ABSTRACT: *An efficient resolution method was elaborated for the preparation of (+)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine oxide using the acidic Ca^{2+} salt of (–)-O,O-di-p-toluoyl-(2R,3R)-tartaric acid. Crystal structure of the diastereomeric complex was evaluated by single crystal X-ray analysis. Beside this, the absolute P-configuration was also determined by a circular dichroism (CD) spectroscopic study including theoretical calculations. The tetrahydrophosphinine oxide was then converted to the corresponding platinum complex whose stereostructure was investigated by high-level quantum chemical calculations. The Pt complex was tested as a catalyst in the hydroformylation of styrene.* © 2016 Wiley Periodicals, Inc. Heteroatom Chem. 27:91–101, 2016; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21305

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INTRODUCTION

The phosphines are important, as their transition metal complexes are widely applied catalysts in homogeneous catalytic reactions (e.g., hydrogenation and hydroformylation) [1, 2]. Among the P(III) ligands, the derivatives incorporating a P-heterocyclic moiety are of great importance [3, 4]. Chiral phosphines also form an important class, as they are potential ligands in asymmetric syntheses. Most of such ligands contain C-chirality center(s), and only a few of them possess a P-stereogenic center [5, 6].

Enantioselective hydroformylation that can be applied in the synthesis of anti-inflammatory drugs (e.g., ibuprofen and naproxen) is a direct method to obtain optically active derivatives [7, 8]. Among the ligands used in asymmetric hydroformylations, several P-chiral heterocyclic phosphines were described that were employed mainly in rhodium complexes [4, 9–14]. Optically active P-heterocyclic ligands were rarely used in platinum-catalyzed hydroformylations [13]. Gouygou and co-workers synthesized a few platinum complexes incorporating optically active bisphosphole ligands that were tested in enantioselective hydroformylations [15].

Our research group synthesized a series of optically active 1-aryl- and 1-alkyl-3-methyl-3-phospholenes that were then converted to the corresponding platinum complexes, which were tested as catalysts in the hydroformylation of styrene. Enantiomeric excess (Ee-s) up to 29% were obtained [16–20]. The key step of the ligand synthesis is the optical resolution of the corresponding racemic phospholene oxides [21–24]. These methods developed were then extended to the preparation of optically active six-membered phosphine oxides, including a 3-phenyl-3-phosphabicyclo[3.1.0]hexane oxide, a 1-phenyl-1,2-dihydrophosphinine oxide, and a 1-phenyl-1,2,3,6-tetrahydrophosphinine oxide [25, 26]. A few platinum complexes incorporating racemic P-heterocyclic ligands, such as 1,2,3,6-tetrahydrophosphinine and a 1,4-dihydrophosphinine derivative, were also prepared by us [16].

Our research group also synthesized platinum complexes of bidentate P-ligands incorporating five- and six-membered P-heterocycles with an exocyclic P-function, such as 3-diphenylphosphino-1-phenylphospholane (LuPhos), 3-diphenylphosphino-1-phenyl-1,2,3,6-tetrahydrophosphinine, and 3-diphenylphosphino-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine. These platinum complexes were also tested as catalysts in the hydroformylation of styrene. The catalytic activity of the complexes incorporating six-membered P-ligand was significantly higher than those with five-membered P-rings [17, 25, 27, 28].

Inspired by the results obtained with the optically active 3-phospholene platinum complexes, we were interested in if the ring size influences the catalytic activity and selectivity of the platinum complexes. For this, we synthesized the optically active platinum complex of 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine to be tested as catalyst in the hydroformylation of styrene.

RESULTS AND DISCUSSION

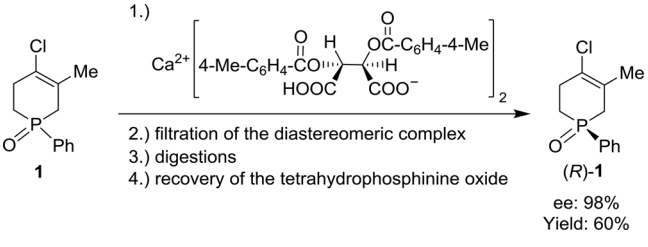
Synthesis of Optically Active 4-Chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-Oxide (*1*)

The racemic 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**) was prepared as described earlier [26]. The resolution of the phenyl-tetrahydrophosphinine oxide (**1**) was carried out applying the acidic Ca^{2+} salt of (−)-*O*,*O*'-di-*p*-toluoyl-(2*R*,3*R*)-tartaric acid [Ca(H-DPTTA)$_2$] in a mixture of ethanol and water (Scheme 1) [26]. However, a better purification of the corresponding diastereomeric associates was elaborated performing the digestion in ethanol. This modification led to a more efficient resolution, as the (+)-(*R*)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-oxide [(*R*)-**1**] was obtained in a yield of 60% and with an enantiomeric excess (ee) of 98%, whereas in the previous study [26], the yield and the ee were 28% and 99%, respectively.

Moreover, it became possible to characterize the diastereomeric intermediate of the resolution and identify the P-stereogenic center.

Single Crystal X-Ray Analysis of Diastereomeric Complex Ca(*1*)$_2$(H-DPTTA)$_2$

As turned out from the experiment, Ca(**1**)$_2$(H-DPTTA)$_2$ crystallized as an ethanol inclusion species with two partially occupied (one-third of approximate populations) and disordered alcohol molecules in the asymmetric unit of the crystal. Figure 1 shows the catemer subunit from



SCHEME 1

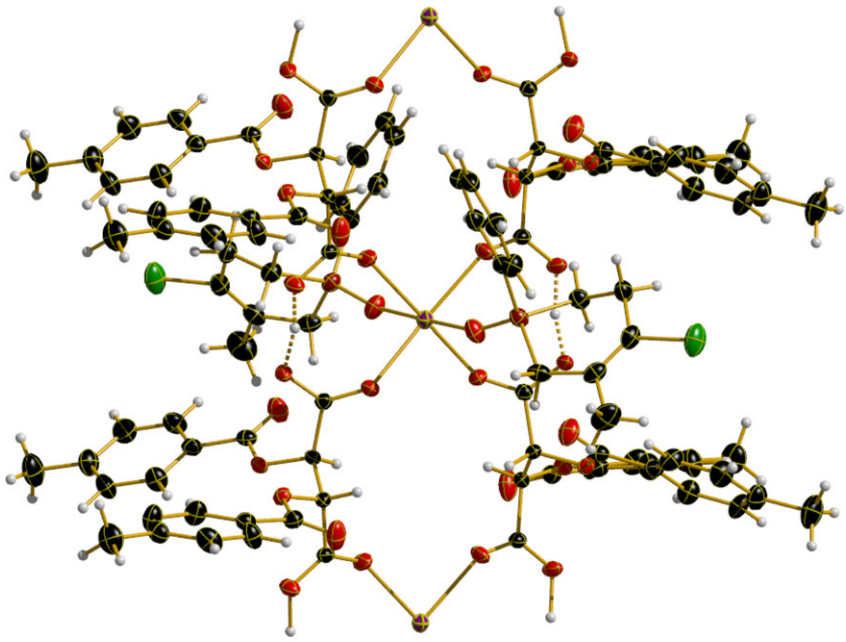


FIGURE 1 Fifty percent atomic displacements plot of Ca(**1**)$_2$(H-DPTTA)$_2$ showing carboxyl/carboxylate H-bridge contacts in broken lines. Disordered ethanol molecules are omitted for clarity from this drawing.

the polymer chain that makes up the crystal. Most basic feature of this coordination salt assembly is its perfect twofold symmetry that matches a crystallographic C_2 symmetry axis going through the Ca^{2+} ion. The coordination sphere of the Ca^{2+} ion is made up from six O atoms and can be described as a slightly distorted tetragonal bipyramid. The Ca–O1=P coordination distance is the shortest one (2.291(2)Å) around the Ca^{2+} ion. This distance value falls on the slightly shorter side than the mean of 13 (out of 15) such Ca—O distances (2.306 Å, sample s.d. 0.028 Å) distribution from the Cambridge Structural Database (CSD) [29]. It is not only significantly shorter than the other two independent distances (2.342(2)Å and 2.354(2)Å, Δ = 0.051 Å and 0.063 Å, i.e., 25σ and 31σ differences), but those longer contacts are maintained by partial negative charged carboxyl/carboxylate pairs. In other words, it seems from these distances that the O1 = P oxygen atom is more negatively polarized than those in the COOH/COO^- pair. Otherwise, the covalent bonds largely conform to the database mean values as attested by a MOGUL analysis [30] of corresponding bonds and angles.

The *H*-principal O—H···O H-bridges may ideally form a symmetric COOH/COO^- H-bridge, apart from which there are a few C—H···O contacts in the crystal. The Cl atom also maintains numerous C—H···Cl short contacts.

The chirality of the P-center was established as *R* with high confidence marked by a Flack parameter of 0.01(5).

*CD Spectroscopic Investigation of the Optically Active 4-Chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-Oxide (**1**)*

The theoretical calculations were performed on the randomly selected (*R*)-isomer of 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**). It was started with a molecular mechanics (MM) conformation analysis, which resulted in 14 stable conformers lying at most at 10 kJ/mol above the lowest energy one. Geometry optimizations were performed at the density functional theory (DFT) level for the low-energy conformers, and accurate conformational energies were calculated with the direct random-phase approximation (dRPA) approach at the DFT-optimized structures. Three low-energy conformers were identified differing in the orientation of the phenyl group with the two higher energy ones lying at around 1.1 and 4.4 kJ/mol above the most stable conformer. Other conformers were higher by at least 15 kJ/mol in energy and were not considered in the further calculations. The optimized geometry for the most stable conformer is presented in Fig. 2; the geometrical parameters are given in Table 1. These calculated data are compared with the parameters obtained from the single crystal X-ray analysis of the optically active P-heterocyclic moiety in the diastereomer complex Ca(**1**)$_2$(H-DPTTA)$_2$. As can be seen, the theoretically calculated data generally agree within the usual 3*sigma (3σ) criteria. The only notable exceptions concern the bonds around the P atom.

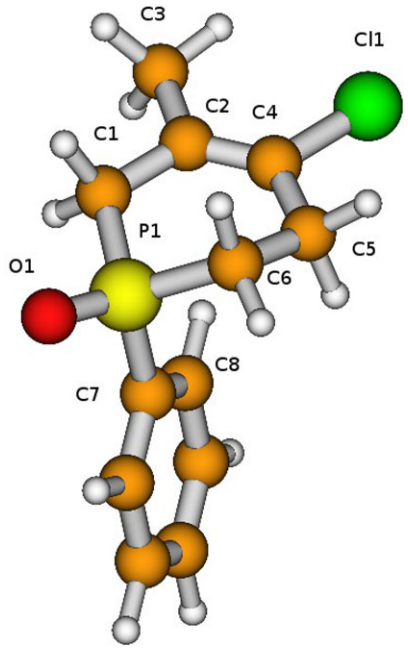


FIGURE 2 Optimized geometry for the lowest energy conformer of (*R*)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide [(*R*)-**1**].

TABLE 1 Comparison of bonds and angles of tetrahydrophosphinine **1**, obtained by theoretical calculations (d_T) against the X-ray data (d_X) from [32] and the data obtained from the Ca(**1**)$_2$(H-DPTTA)$_2$ crystal structure at 173K (d_{Xn}) with the standard uncertainties in parentheses (σ)

	d_T (Å/°)	d_X (Å/°) [32]	d_{Xn} (Å/°)	$\lvert\Delta/\sigma\rvert$[a]
P1-O1	1.508	1.484	1.489(3)	*6.3*
P1-C6	1.811	1.798	1.792(4)	*4.8*
P1-C1	1.818	1.801	1.798(4)	*5*
C5-C6	1.526	1.536	1.535(6)	1.5
C4-C5	1.501	1.488	1.499(5)	0.4
C2-C4	1.338	1.323	1.320(5)	*3.6*
C1-C2	1.512	1.513	1.501(6)	1.8
P1-C7	1.811		1.784(4)	*6.8*
C2-C3	1.497		1.511(6)	2.3
C4-Cl1	1.761		1.761(4)	0
C7-C8	1.398		1.407(6)	1.2
O1-P1-C6	114	114.8	113.6(2)	2
C1-P1-C6	101	100.1	102.4(2)	7
O1-P1-C7	112	112.5	112.0(2)	2.5
O1-P1-C1	114	114.1	113.2(2)	*4*
C6-P1-C7	107	106.5	107.3(2)	1.5
C1-P1-C7	107	107.9	107.7(2)	3
P1-C7-C8	123		121.3	*6.3*
P1-C1-C2	118		116.9(3)	*3.7*
C1-C2-C4	122		123.0(4)	2.5
C2-C4-Cl1	120		119.6(3)	1.3
C1-C2-C3	113		112.7(4)	0.8

[a] Δ is defined as $\Delta = |d_T - d_{Xn}|$, while d_{Xn} values from the Ca(**1**)$_2$(H-DPTTA)$_2$ crystal are averaged for the two *o*-position bonds and angles. Values of $|\Delta/\sigma|$ that are larger than the $3^*\sigma$ level are printed in italics.

The theoretical absorption and CD spectra for the selected three conformers were evaluated at the time-dependent DFT (TD-DFT) level. The theoretical spectra of the mixture of conformers obtained as the Boltzmann-weighted sum of their spectra, together with the experimental spectra of the tetrahydrophosphinine oxide (**1**), are displayed in Fig. 3. The agreement of the measured and calculated UV and CD spectra of the compound is satisfactory. The measured and calculated CD spectra are rather similar, and the sign of the dominant features in the two spectra are identical, and their positions are very close to each other that indicates that the absolute P-configuration of the compound synthesized is identical to that of the molecule considered in the calculations, that is the (*R)* P-configuration. Moreover, this absolute P-configuration is also confirmed by the result of the single crystal X-ray analysis.

Synthesis of 4-Chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine Borane and Platinum Complexes

The deoxygenation of racemic and optically active 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide [**1** and (*R*)-**1**] was carried out with trichlorosilane at 0°C. In case of optically active phosphine oxides, the deoxygenation with trichlorosilane takes place with retention of the configuration of the P-stereogenic center [33]. Earlier, the deoxygenation of phenyl-tetrahydrophosphinine oxide was carried out with a mixture of trichlorosilane and pyridine at 110°C [16].

The racemic and optically active phenyl-tetrahydrophosphinines [**2** and (*S*)-**2**] obtained were then reacted with dichlorodibenzonitrile platinum to give the corresponding platinum complexes [**3** and (*R,R*)-**3**] (Schemes 2 and 3). Starting from racemic phenyl-tetrahydrophosphinine (**2**), the corresponding platinum complexes were obtained as a ca. 2:1 mixture of the racemic [(*R,R*)-**3** and (*S,S*)-**3**] and meso [(*R,S*)-**3**] forms.

The (*S*)-phenyl-tetrahydrophosphinine [(*S*)-**2**] was reacted with dimethylsulfide-borane to furnish the corresponding optically active borane complex [(*S*)-**4**] (Scheme 3). The importance of the optically active phosphine boranes lies in the fact that they can be regarded as protected phosphines, since the P(III)-compounds may be liberated from them using secondary amines (e.g., diethylamine) [31].

The structure of the platinum and borane complexes [**3**, (*R,R*)-**3** and (*S*)-**4**] was characterized by ^{1}H, ^{13}C, and ^{31}P NMR, as well as high resolution MS (HRMS). In case of the phenyl-tetrahydrophosphinine platinum complexes [**3** and

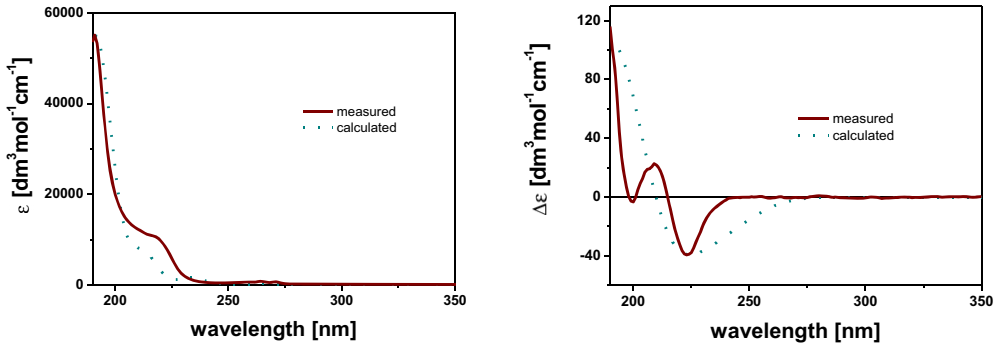
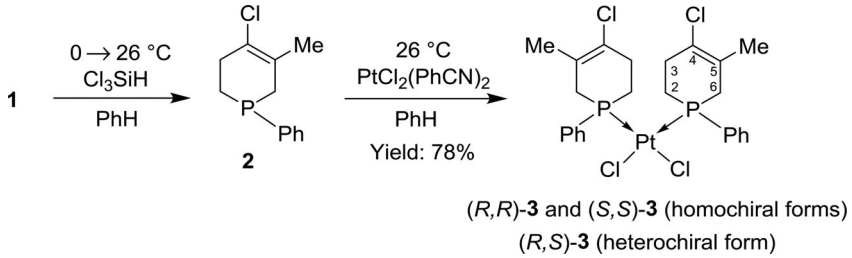
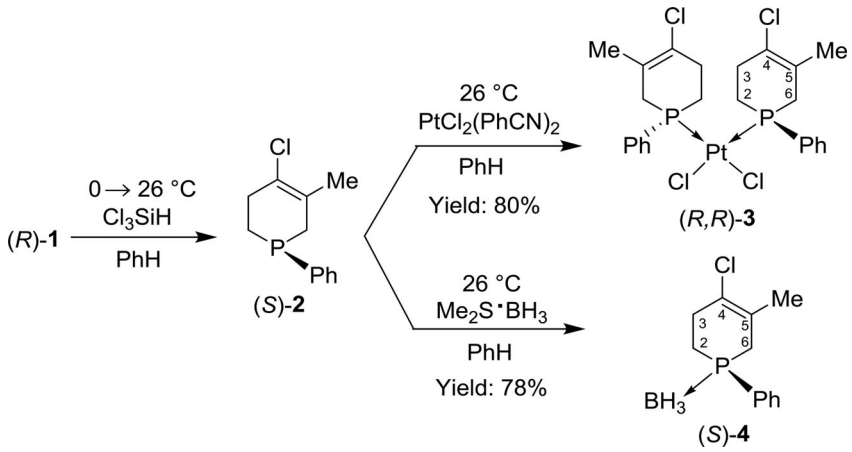


FIGURE 3 Calculated (dashed line) UV absorption (a) and CD (b) spectra of (*R*)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide [(*R*)-**1**] together with the measured (solid line) spectra of (+)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide [(+)-**1**]. The solvent was acetonitrile.



SCHEME 2



SCHEME 3

(*R*,*R*)-**3**], 2D ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and HMBC spectra were also recorded to verify the structures. The relative position of the tetrahydrophosphinine ligands in the platinum complexes [**3** and (*R*,*R*)-**3**] was confirmed by the stereospecific $^{1}J_{\text{Pt-P}}$ couplings that were 3567 and 3568 Hz for **3** and (*R*,*R*)-**3**, respectively. It is known that the coupling constants of ca. 3500 Hz indicate that the corresponding coordinated phosphorus donor atom and chloro ligand are in the *trans* disposition. All relevant heteronuclear coupling constants, including the ^{195}Pt–^{13}C and ^{31}P–^{13}C couplings of the optically active platinum complex [(*R*,*R*)-**3**], were determined by first-order analysis.

Stereostructure of the (R,R)-4-Chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine Platinum Complex [(R,R)-3]

Stereostructure of the 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine platinum complex (**3**) was calculated at the ωB97X-D/cc-pVTZ//

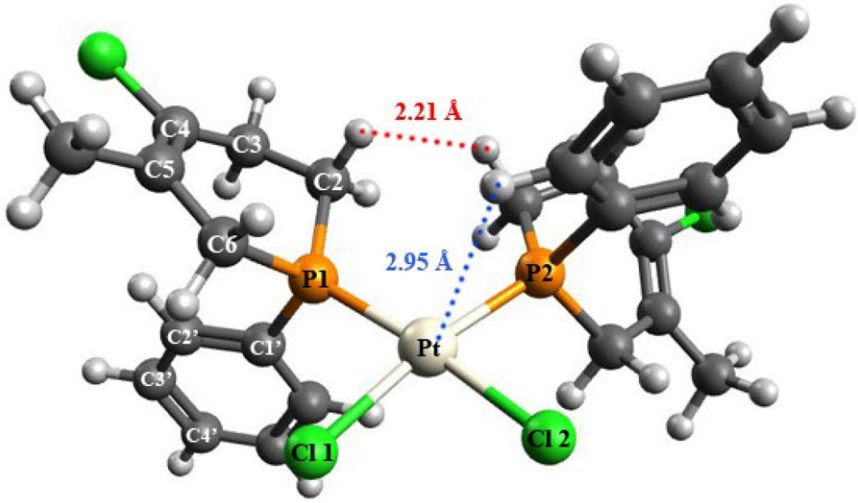


FIGURE 4 Perspective view of *cis-bis*(4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinino)-dichloro-platinum(II) [(*R*,*R*)-**3**] calculated by the ωB97X-D/cc-pVTZ//RI-B97-D/6-31G(d) method. For Pt atoms, cc-pVTZ-PP pseudopotential was applied in all cases. Gray, white gray, orange, green, and white colors are referred to carbon, hydrogen, phosphorus, chlorine, and platinum atoms, respectively. Selected bond lengths (Å), bond angles (°), and torsion angles (°) are as follows: Pt-Cl(1) 2.394, Pt-P(1) 2.252, P(1)-C2 1.858, C2-C3 1.542, C3-C4 1.515, C4-C5 1.351, C5-C6 1.523, P(1)-C6 1.861, P(1)-C1' 1.832, C1'-C2' 1.411, C2'-C3' 1.403, C3'-C4' 1.404; Cl(1)-Pt-Cl(2) 88.7, Cl(1)-Pt-P(1) 83.8, Pt-P(1)-C2 121.7, Pt-P(1)-C6 110.8, Pt-P(1)-C1' 113.0, P(1)-C2-C3 112.7, C2-C3-C4 114.7, C3-C4-C5 127.5, C4-C5-C6 123.0, C5-C6-P1 119.4, C2-P(1)-C6 98.8, C2-P(1)-C1' 104.0, C6-P(1)-C1' 106.8; P(1)···Cl(1)···Cl(2)···P(2) –4.6, Cl(1)-Pt-P(1)-C2 170.8, Pt-P(1)-C2-C3 –172.4, P(1)-C2-C3-C4 52.5, C2-C3-C4-Cl 158.5, C2-C3-C4-C5 –24.5, C3-C4-C5-C6 –0.5.

RI-B97-D/6-31G(d) level of theory with cc-pVTZ-PP pseudopotential on the Pt atom. Accurate ωB97X-D single point energy calculations suggested that the relative energies of the corresponding homochiral [(*R*,*R*) and (*S*,*S*)] and heterochiral (*R*,*S*)-1,2,3,6-tetrahydrophosphinine platinum complexes (**3**) are close to each other as the values are within 0.9 kcal/mol. The most stable structure of the (*R*,*R*)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine platinum complex [(*R*,*R*)-**3**] synthesized is displayed in Fig. 4. The geometry around the Pt atom is considered square planar, as the P(1)···Cl(1)···Cl(2)···P(2) pseudo-torsion angle is –3.9°. It was found that the conformer with rotational symmetry (C_2 symmetry group) is the most favorable structure, which is stabilized by intramolecular nonbonding interactions between the phosphinine rings.

CH···HC interactions were identified between the C(2)H_2 moieties of the two phosphinine rings (the shortest H···H distance is 2.21 Å, see Fig. 4, red dashed line). These secondary interactions also define the conformation of the phenyl groups, and thus the environment of the platinum. In case of (*R*,*R*)-**3**, due to the C_2 symmetry, one *ortho*-H of each phenyl rings is situated close to the platinum center significantly influencing the environment of the platinum that is shown by the H···Pt···Cl(2) ···Cl(1) dihedral angle of 116.9° and the *ortho-H*···Pt distance of 2.95 Å (where *ortho-H* is the corresponding H of the phenyl group, see Fig. 4, blue dotted line).

*Catalytic Activity of the cis-$PtCl_2(L)_2$ (where L Stands for **2** or (S)-**2**) Complex in the Hydroformylation of Styrene*

The "preformed" $PtCl_2L_2$-type complexes (**3** or (*R*,*R*)-**3** containing ligands **2** or (*S*)-**2**, respectively) were tested as a catalyst precursors in the hydroformylation of styrene. The catalysts formed in situ from **3** (or (*R*,*R*)-**3**) and two equivalents of tin(II) chloride were used at 80 bar [syngas; p(CO) = $p(H_2)$ = 40 bar]. In addition to the branched and linear formyl regioisomers (2-phenylpropanal (**A**) and 3-phenylpropanal (**B**), respectively), ethylbenzene (**C**) as hydrogenation by-product was also formed (Eq. 1).

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

As expected, both catalytic systems formed either from the racemic or enantiomerically pure tetrahydrophosphinine ligand (**2** or (*S*)-**2**, respectively) provided similar catalytic activity (compare, for instance, entries 2 and 6, as well as 4 and 9,

TABLE 2 Hydroformylation of Styrene in the Presence of In Situ Formed Catalysts from $PtCl_2(L)_2$ Complex (L = **2** or (*S*)-**2**) and Tin(II) Chloride[a]

Entry	*L*	*Temperature (°C)*	*Reaction time (h)*	*Conversion (%)*	R_c [b] *(%)*	R_{br} [c] *(%)*	*ee (%)*
1	**2**	40	20	11	83	62	–
2	**2**	60	20	91	82	58	–
3	**2**	100	5	91	87	55	–
4	**2**	100	10	98	84	54	–
5	(*S*)-**2**	40	20	20	84	64	29 (*R*)
6	(*S*)-**2**	60	20	90	81	61	17 (*R*)
7	(*S*)-**2**	100	2	54	87	59	10 (*R*)
8	(*S*)-**2**	100	4	96	88	57	9 (*R*)
9	(*S*)-**2**	100	10	99	85	58	8 (*R*)

[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 toward aldehydes (**A**, **B**). [(moles of **A** + moles of **B**)/(moles of **A** + moles of **B** + moles of **C**) × 100], where **A** is 2-phenylpropanal, **B** is 3-phenylpropanal, and **C** is ethylbenzene.
[c]Regioselectivity toward branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) × 100].

Table 2). Reasonable activity was observed even at 40°C (entries 1 and 5).

The formation of the aldehydes (**A** and **B**) was highly preferred in all cases, i.e., chemoselectivities above 81% were obtained in all cases. A slight increase in chemoselectivity (up to 88%) was obtained at higher temperature (entry 8).

The formation of branched aldehyde (**A**) is predominated in all cases; however, slightly higher branched selectivities were obtained at lower temperatures (entries 1, 2 and 5, 6) than at 100°C (entries 3, 4 and 8, 9). It is worth noting that the major trends regarding chemo- and regioselectivities keep in line with those observed for Pt catalysts with 5-membered P-heterocycles as P-ligands in hydroformylation [17–19].

The application of (*R,R*)-**3** complex with the optically active P-ligand, (*S*)-**2** resulted in low enantioselectivities by the predominance of the *R* enantiomer of the branched aldehyde. The ee-s obtained at low temperature (40–60°C) are definitely higher, than those detected at 100°C (compare entries 5, 6 and 7–9).

CONCLUSIONS

Absolute configuration of (+)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine oxide was determined by single crystal X-ray investigation of the diastereomeric associate obtained by resolution with the acidic Ca^{2+} salt of (–)-*O*,*O*-di-*p*-toluoyl-(2*R*,3*R*)-tartaric acid. An independent CD spectroscopic study also suggested "*R*" configuration of the P-stereogenic center of the tetrahydrophosphinine oxide that was then converted to the corresponding platinum complex after deoxygenation. The Pt complex showed moderate enantioselectivity as catalyst in the hydroformylation of styrene, and its stereostructure was evaluated by theoretical calculations.

EXPERIMENTAL

General (Instruments)

The ^{31}P NMR spectra were recorded on a Bruker AV-300 (Wien, Austria) spectrometer operating at 121.5 MHz for ^{31}P, whereas the ^{13}C and ^{1}H NMR spectra were obtained on a Bruker DRX-500 (Wien, Austria) spectrometer operating at 125.7 for ^{13}C and 500 MHz for ^{1}H, respectively. 2D ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and HMBC spectra of platinum complexes [**3** and (*R,R*)-**3**] were acquired on a Bruker Avance II (Wien, Austria) spectrometer operating at 500 MHz ^{1}H frequency equipped with a BBI or a TXI z-gradient probe. The couplings are given in hertz. The exact mass measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode. The ee of the 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**) was determined by chiral HPLC using Kromasil® 5-Amycoat 250 × 4.6 mm ID, hexane/ethanol 85/15 as an eluent with a flow rate of 0.8 mL/min, T = 20°C, UV detector α = 254 nm. Retention times: 15.8 min for (+)-**1** and 23.2 min for (−)-**1**. The determination of the ee-s of 2-phenylpropanal (**A**) was carried out on a Thermo Scientific FOCUS gas-chromatograph equipped with a Cyclodex column (20 m × 0.25 mm, 0.25 μm film, FID detector, helium as carrier gas, injector 250°C, detector 280°C, head pressure: 14.5 psi). (*S*)-2-Phenylpropanal was eluted before the (*R*)-enantiomer. Optical rotations were determined on a Perkin-Elmer 241 polarimeter (Boston, MA).

The 4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**) was synthesized

as described earlier [32]. The (–)-*O*,*O*′-di-*p*-toluoyl-(2*R*,3*R*)-tartaric acid was purchased from Aldrich (Budapest, Hungary).

*Preparation of (R)-4-Chloro-1-Phenyl-5-Methyl-1,2,3,6-Tetrahydrophosphinine 1-Oxide [(R)-**1**]*

To 0.55 g (1.4 mmol) of (−)-(*R*,*R*)-di-*p*-toluoyl-tartaric acid monohydrate and 0.039 g (0.68 mmol) of CaO in a mixture of 1.8 mL of ethanol and 0.35 mL of water, 0.65 g (2.7 mmol) of racemic 4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**) was added in 1.8 mL of ethanol. After standing at 26°C for 24 h, the crystals were filtered off to give 0.67 g (76%) of complex Ca[(*R*)-**1**]$_2$(H-DPTTA)$_2$ with a diastereomeric excess (de) of 86%. The complex was purified by two digestions, the crystals were taken up in 3.6 mL of ethanol and the suspension was stirred for 24 h at 26°C to afford 0.60 g (69%) of complex Ca[(*R*)-**1**]$_2$(H-DPTTA)$_2$ with a de of 98%. The (*R*)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-oxide [(*R*)-**1**] was recovered by treating the dichloromethane solution (4 mL) of the complex with 2 mL of 10% aqueous ammonia. The organic phase was washed with 1 mL of water, dried (Na_2SO_4), and concentrated to give 0.20 g (60%) of (*R*)-**1** with an ee of 98%. ^{31}P NMR ($CDCl_3$) δ: 27.8, (δ_P [26] 27.9); $[\alpha]_D^{25} = +19.5$ (c 0.7; $CHCl_3$). (In this experiment, the yields were based on the half of the racemate that is regarded to be 100% for each antipode.)

*Preparation of cis-[Bis(4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinino)-dichloro-platinum(II)] (**3**)*

The solution of 0.070 g (0.29 mmol) of racemic 4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**1**) in 2 mL of benzene was degassed and cooled to 0°C, then 0.18 mL (1.7 mmol) of trichlorosilane was added. The mixture was stirred at 0°C for 3 h, and then at 26°C for 3 h under nitrogen to afford the corresponding phenyltetrahydrophosphinine (**2**). Then, 0.068 g (0.15 mmol) of dichlorodibenzonitrile platinum(II) was added to the reaction mixture under nitrogen. The mixture was stirred at 26°C for 1 day, whereupon the complex precipitated. Separation by filtration led to 0.081 g (78%) of complex **3** as a 2:1 mixture of the homo- [(*R*,*R*) and (*S*,*S*)] and heterochiral (*R*,*S*) forms.

^{1}H NMR ($CDCl_3$) δ: 1.58 (bs, 6H, CH_3 of the homochiral form), 1.70 (bs, 6H, CH_3 of the heterochiral form), 1.86–2.04 (m, 4H) and 2.40–2.60 (m, 4H) C_3-H_2 of the homo- and heterochiral forms, 2.09–2.20 (m, 2H) and 2.84–2.94 (m, 2H) C_6-H_2 of the homochiral form, 2.21–2.29 (m, 2H) and 2.76–2.85 (m, 2H) C_2-H_2 of the homochiral form, 2.27–2.35 (m, 2H) and 3.01–3.14 (m, 2H) C_6-H_2 of the heterochiral form, 2.31–2.38 (m, 2H) and 2.62–2.72 (m, 2H) C_2-H_2 of the heterochiral form, 7.25–7.34 (m, 8H, $C_{2'}$-H of the homo- and heterochiral forms), 7.27–7.36 (m, 8H, $C_{3'}$-H of the homo- and heterochiral forms), 7.39–7.47 (m, 4H, $C_{4'}$-H of the homo- and heterochiral forms); ^{13}C NMR ($CDCl_3$) δ 22.0–22.4 (m, C_2), 22.5–22.6 (m, CH_3), 27.5–27.9 (m, C_6 of the homochiral form), 28.0–28.4 (m, C_6 of the heterochiral form), 30.3–30.6 (m, C_3), 123.9–124.2 (m, C_5 of the homochiral form), 124.4–124.5 (m, C_5 of the heterochiral form), 127.7–127.8 (m, C_4), 128.0–128.7 (m, $C_{1'}$), 129.2 (m, $C_{3'}$), 131.5–131.7 (m, $C_{2'}$), 131.8 ($C_{4'}$ of the heterochiral form), 131.9 ($C_{4'}$ of the homochiral form); ^{31}P NMR ($CDCl_3$) δ: –14.3 ($J_{Pt-P} = 3568$, 65%), –14.7 ($J_{Pt-P} = 3568$, 35%), (δ_P [16] –14.7); HRMS $[M-Cl]^+_{found}$ = 677.0370, $C_{24}H_{28}P_2Cl_3Pt$ requires 677.0359 for the ^{35}Cl and ^{195}Pt isotopes.

The optically active *cis*-[bis-(*R*)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinino]-dichloro-platinum(II) [(*R*,*R*)-**3**] was prepared in a similar manner from (*R*)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine-1-oxide [(*R*)-**1**] with an ee of 98%. Yield of (*R*,*R*)-**3**: 80%.

^{1}H NMR ($CDCl_3$) δ: 1.58 (bs, 6H, CH_3), 1.86–1.99 (m, 2H) and 2.44–2.60 (m, 2H) C_3-H_2, 2.10–2.22 (m, 2H) and 2.84–2.94 (m, 2H) C_6-H_2, 2.22–2.33 (m, 2H) and 2.75–2.85 (m, 2H) C_2-H_2, 7.26–7.33 (m, 4H, $C_{2'}$-H), 7.28–7.35 (m, 4H, $C_{3'}$-H), 7.41–7.46 (m, 2H, $C_{4'}$-H); ^{13}C NMR ($CDCl_3$) δ 22.3 ($^1J_{P-C}$ = 48.7, $^3J_{P-C} = 6.9$, C_2), 22.5 ($^3J_{P-C} = 4.0$, $^5J_{P-C} = 4.0$, CH_3), 27.7 ($^2J_{Pt-C} = \sim 36$, $^1J_{P-C} = 45.6$, $^3J_{P-C} = 6.6$, C_6), 30.4 ($^3J_{Pt-C} = \sim 24$, $^2J_{P-C} = 3.4$, $^4J_{P-C} = 3.4$, C_3), 124.0 ($^3J_{Pt-C} = \sim 29$, $^2J_{P-C} = 4.0$, $^4J_{P-C} = 4.0$, C_5), 127.7 ($^4J_{Pt-C} = \sim 39$, $^3J_{P-C} = 5.6$, $^5J_{P-C} = 5.6$, C_4),128.2 (m, $C_{1'}$), 129.2 ($^4J_{Pt-C} = \sim 39$, $^3J_{P-C} = 5.4$, $^5J_{P-C} = 5.4$, $C_{3'}$), 131.6 ($^3J_{Pt-C} = \sim 35$, $^2J_{P-C} = 5.0$, $^4J_{P-C} = 5.0$, $C_{2'}$), 131.9 ($C_{4'}$); ^{31}P NMR ($CDCl_3$) δ: –14.3 ($J_{Pt-P} = 3567$); HRMS $[M-Cl]^+_{found} = 677.0381$, $C_{24}H_{28}P_2Cl_3Pt$ requires 677.0359 for the ^{35}Cl and ^{195}Pt isotopes; $[\alpha]_D^{25} = +33.6$ (c 1; $CHCl_3$).

*Preparation of (S)-4-Chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine-borane [(S)-**4**]*

The deoxygenation of 0.064 g (0.27 mmol) of (*R*)-4-chloro-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine-1-oxide [(*R*)-**1**] was carried out in

benzene using 0.16 mL (1.6 mmol) of trichlorosilane according to the procedure described above. Then, 0.13 mL of 2 M dimethyl sulfide borane in tetrahydrofuran (0.27 mmol) was added and the solution was stirred at 26°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 dichloromethane) to give 0.050 g (78%) of (*S*)-4-chloro-1-phenyl-5-methyl-1,2,3,6-tetrahydrophosphinine-borane [(*S*)-**4**].

^{1}H NMR ($CDCl_3$) δ: 0.28-1.33 (m, 3H, BH_3), 1.99 (bs, 3H, CH_3), 2.07–2.20 (m, 2H, C_3–H_2), 2.44–2.85 (m, 4H, C_2–H_2 and C_6–H_2), 7.44–7.54 (m, 3H, Ar–H), 7.61–7.68 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$) δ: 21.2 ($^1J_{P-C}$ = 35, C_2), 23.0 ($^3J_{P-C}$ = 7, CH_3), 27.8 ($^1J_{P-C}$ = 36, C_6), 30.0 ($^2J_{P-C}$ = 6, C_3), 124.6 ($^2J_{P-C}$ = 7, C_5), 127.8 ($^2J_{P-C}$ = 11, C_4), 128.4 ($^1J_{P-C}$ = 52, $C_{1'}$), 129.1 ($^3J_{P-C}$ = 10, $C_{3'}$), 131.4 ($^3J_{P-C}$ = 9, $C_{2'}$), 131.7 ($^4J_{P-C}$ = 3, $C_{4'}$); ^{31}P NMR ($CDCl_3$) δ: –0.3 (bs); $[M + Na]^+_{found}$ = 261.0752, $C_{12}H_{17}PBClNa$ requires 261.0747 for the ^{35}Cl ^{11}B isotope; $[\alpha]_D^{25}$ = +46.7 (c 1; $CHCl_3$).

Hydroformylation Experiments

In a typical experiment, a solution of *cis*-$PtCl_2(L)_2$ (where L stands for **2** or (*S*)-**2**), 0.01 mmol) and tin(II) chloride (3.8 mg; 0.02 mmol) in toluene (10 mL) containing styrene (0.115 mL, 1.0 mmol) 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 constant temperature. The mixture was stirred with a magnetic stirrer for the given reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by gas chromatography.

X-Ray Measurements

X-ray quality crystals of the diastereomeric complex Ca(**1**)$_2$(H-DPTTA)$_2$ were grown from a saturated ethanol solution of 5.2 mg (0.022 mmol) of (*R*)-**1** and 4.4 mg (0.0054 mmol) of Ca(H-DPTTA)$_2$ prepared in situ as described above.

A crystal of the complex Ca(**1**)$_2$(H-DPTTA)$_2$ was mounted on a glass fiber. Cell parameters were determined by least-squares from the respective setting angles of reflections. Space group was determined as chiral orthorhombic $P2_12_12$ (No. 18). Diffraction data were collected at 173 K using monochromatized Mo Kα radiation. Completeness were equal or greater to 2θ = 98.7%. Semiempirical absorption correction from equivalents was applied to the data with minimum and maximum transmission factors of 0.958 and 0.983. Initial structure models were obtained by direct methods [34, 35] and subsequent difference syntheses. Anisotropic full-matrix least-squares refinement on F^2 were applied [34, 35] for all nonhydrogen atoms except the disordered solvent atomic sites and the model was refined to convergence. Final R indices [$I > 2\sigma(I)$] are R_1 = 0.0534, wR^2 = 0.1288; absolute structure parameter value of 0.01(5) shows assignments of the correct hand and of the absolute configuration. Hydrogen atomic positions were calculated from assumed geometries where appropriate; O–H hydrogen atoms were located from difference electron density maps. Hydrogen atoms were included in structure factor calculations and only the nontrivial hydrogen positions and their isotropic displacements were refined. Other H atoms were kept riding on their anchor atoms, with isotropic displacement parameters of these hydrogen atoms were approximated from the U(eq) value of the atom they were bonded. The maximum and minimum residual electron densities in the final difference maps are 0.87 and –0.25 e.Å^{-3} and are acceptable due to solvent disorder. All further calculations and drawings were done by using PLATON [36] and SCHAKAL [37]. Crystal structure data are deposited with the Cambridge Crystallographic Data Centre under CCDC 1409703 and can be obtained free of charge upon application.

CD Measurements

The UV and CD spectra were measured in acetonitrile solutions at 25°C. The UV spectra were recorded on an Agilent 8453 diode array spectrometer. The CD spectra were obtained on a Jasco J-810 spectropolarimeter.

Theoretical Calculations

The MM, DFT, and dRPA calculations were carried out using the Marvin [38], Gaussian 09 [39], and MRCC [40] programs, respectively. The Merck Molecular Force Field (MMFF) [41] was employed at the MM conformational analysis. DFT geometry optimizations were performed with the PBE0 [42, 43] functional and the 6–311++G** [44] basis set. The absorption and CD spectra were computed using the TD-DFT [45] method and the same functional and basis set. Rotator strengths were calculated in the velocity gauge. The DFT calculations

were performed invoking the polarized continuum model [46] with acetonitrile as the solvent since the latter was employed in the experiments. The dRPA energies were evaluated with the aug-cc-pVTZ basis set using PBE0 Kohn-Sham orbitals. Temperature corrections, entropy contributions, and Gibbs energies of solvation evaluated at the DFT level with the above functional and basis set were added to the gas-phase dRPA energies to obtain 298 K Gibbs energies of the conformers in the solvent. For all the three conformers, the absorption (CD) spectra were simulated as superpositions of Gaussian functions placed at the wavelengths of the computed transitions with heights proportional to the corresponding computed oscillator (rotator) strengths. To obtain the final theoretical spectra, the spectra of the individual conformers were weighted using the Boltzmann factors calculated from the conformational energies. The averaged curves were normalized so that the height of the dominant band will be identical to that of the experimental spectra, and the spectra were shifted by –2 nm so that the most intense band in the theoretical and experimental absorption spectra will appear at the same wavelength (191 nm).

Geometries were computed at the RI-B97-D/6-31G(d) level of theory [47–50], then single point energy calculations were performed at the optima using ωB97X-D/cc-pVTZ level [51, 52]. For Pt atoms, cc-pVTZ-PP pseudopotential [53] was applied for both geometry optimization and single point energy calculations. Minima on the potential energy surface were characterized by harmonic vibrational frequency calculations. Calculations were carried out using Gaussian09 [39] program. Avogadro was utilized for visualization [54].

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