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A New Family of Platinum(II) Complexes Incorporating Five- and Six-Membered Cyclic Phosphine Ligands

Andrea Kerényi,[1] Viktória Kovács,[1] Tamás Körtvélyesi,[2] Krisztina Ludányi,[3,4] László Drahos,[4] and György Keglevich[1]

[1]*Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

[2]*Department of Physical Chemistry and Material Sciences, University of Szeged, 6701 Szeged, Hungary*

[3]*Semmelweis University, Faculty of Pharmacy, Department of Pharmaceutics, 1092 Budapest, Hungary*

[4]*Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary*

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ABSTRACT: *New platinum complexes of the type cis-Pt(L)$_2$Cl$_2$ have been synthesized from five- and six-membered cyclic phosphines, which were prepared after deoxygenating a series of phosphine oxides (3-phospholene oxides, phospholane oxides, a 1,4-dihydrophosphinine oxide, and a 1,2,3,6-tetrahydrophosphinine oxide). The complexes were characterized by NMR and mass spectral data, and their stereostructures were elucidated by B3LYP/6-31G(d)-LANL2DZ ECP calculations. The phosphine intermediates were characterized as the corresponding phosphine-boranes.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:63–70, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20579

Correspondence to: György Keglevich; e-mail: keglevich@mail.bme.hu.

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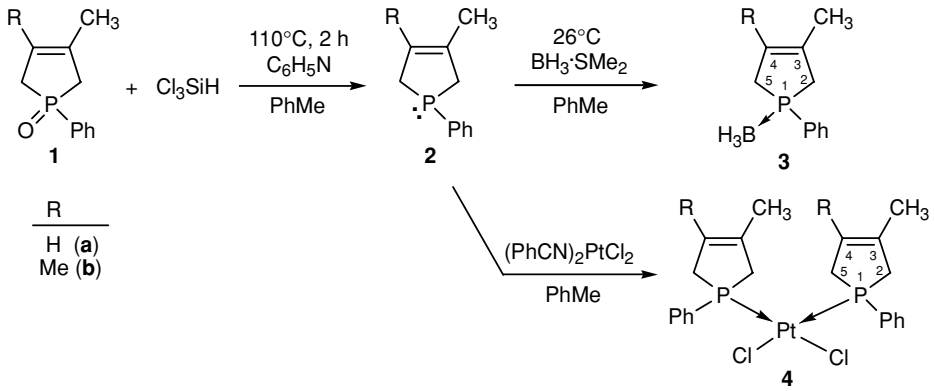
INTRODUCTION

Transition metal complexes incorporating P(III)-ligands are of increasing importance due to their applicability as catalysts in homogeneous catalytic processes [1,2]. Owing to their practical importance, platinum complexes form a well-studied segment within transition metal chemistry. However, relatively not much is known about platinum complexes with P-heterocyclic ligands [3]. As regard to cyclic phosphines, arylphospholes were transformed to the related platinum complexes by Kollár and Keglevich [4–6]. Pringle et al. described the platinum complexes of a few phospholanes, phosphorin's, and phosphepanes [7], as well as 9-phosphabicyclononanes (Phobanes) [8] and 6-phospha-2,4,8-trioxaadamantanes [9]. Among the bidentate heterocyclic P-ligands, DuPhos [10], PennPhos [11], and BIPNOR [12] are well-known representatives, from among which only DuPhos has been applied in platinum complexes [13–15]. In addition, 3-diphenylphosphino-1,2,3,6-tetrahydrophosphinine and 3-diphenylphosphino-1,2,3,4,5,6-hexahydrophosphinine served as bidentate P-ligands in the corresponding cis chelate platinum



SCHEME 1

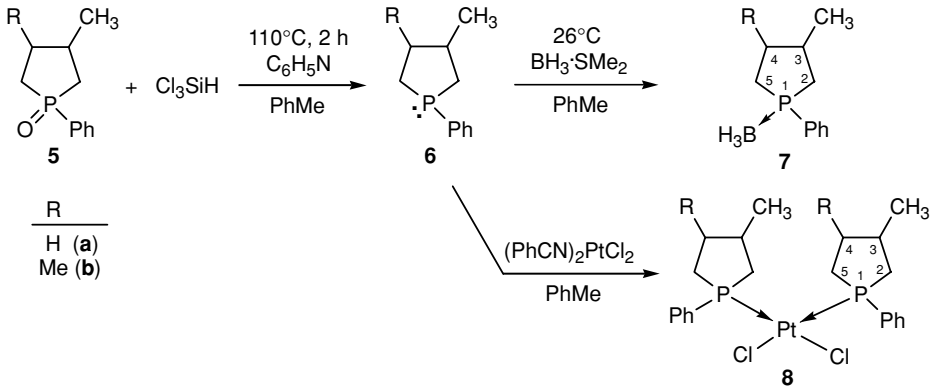
complexes [16–19]. Recently, P-aryl, P-amino, and P-alkoxy dibenzo[*c.e*][1,2]oxaphosphorines including optically active derivatives were made available by us and were converted to the corresponding bis(dibenzooxaphosphorino)dichloroplatinum complexes or related species [20–25]. These complexes incorporated mainly phosphinites, phosphonites, and phosphonous amides as P(III)-ligands.

In this paper, the discipline of platinum complexes with cyclic phosphines is broadened, and novel complexes of 3-phospholenes, phospholanes, a 1,4-dihydrophosphinine, and a 1,2,3,6-tetrahydrophosphinine are described that are potential catalysts in hydroformylations and hydrogenations.

RESULTS AND DISCUSSION

The chosen P-heterocycles, 3-methyl- and 3,4-dimethyl-1-phenyl-3-phospholene oxides (**1a** [26] and **1b** [27], respectively), 3-methyl- and 3,4-dimethyl-1-phenylphospholane oxides (**5a** [28] and **5b** [29], respectively), 4-dichloromethylene-3,5-dimethyl-1-phenyl-1,4-dihydrophosphinine oxide **9** [30], and 5-methyl-1-phenyl-4-chloro-1,2,3,6-tetrahydrophosphinine oxide **12** [31] were subjected to a standard deoxygenation procedure by trichlorosilane in the presence of pyridine in boiling toluene [32]. With one exception (**10**), the phosphines so obtained, **2a, 2b, 6a, 6b**, and **13** were reacted with dimethylsulfide borane and identified as the corresponding phosphine-boranes **3a, 3b, 7a, 7b**, and **14**, respectively. The phosphine boranes **3, 7**, and **14** can be regarded to be precursors of the corresponding phosphines **2, 6**, and **13**, respectively. In other experiments, the phosphines **2a, 2b, 6a, 6b, 10**, and **13** were reacted with a half equivalent of dichlorodibenzonitrileplatinum in toluene at 26°C to afford the corresponding platinum complexes **4a, 4b, 8a, 8b, 11**, and **15**, all incorporating two cyclic phosphine moieties. The above reaction sequences are shown in Schemes 1–4.

The new phosphine boranes **3, 7**, and **14** were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. The platinum complexes **4, 8, 11**, and **15** were characterized by ^{31}P and ^{1}H NMR as well as mass spectral data. On the basis of the stereospecific $J(^{195}Pt\text{-}^{31}P)$ couplings of 3490–3602 Hz, the heterocyclic rings



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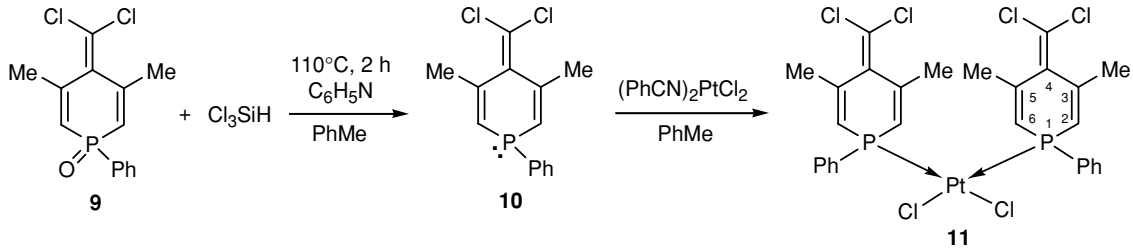


SCHEME 3

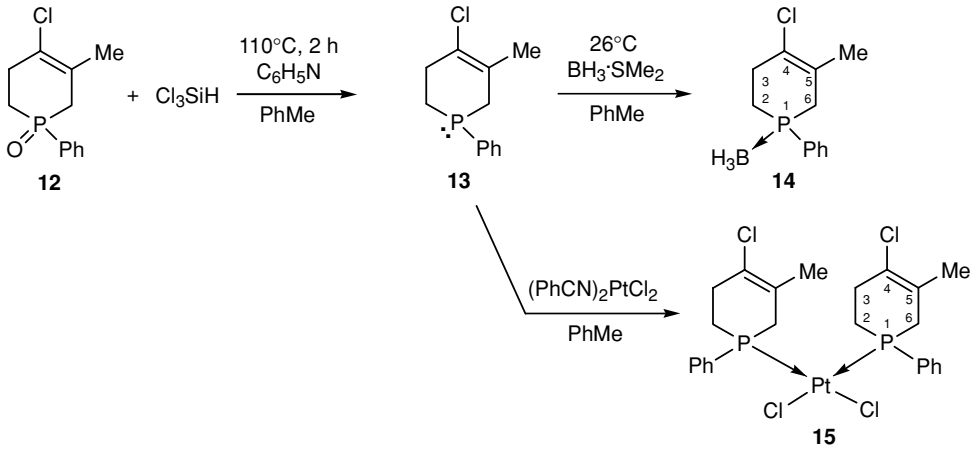
of the complexes are in the cis relationship to each other. Earlier studies [5,6,20,22,23,25] well demonstrated the selective formation of the corresponding *cis*-PtP_2Cl_2 complexes, only in the case of considerable steric hindrance was the *trans*-PtP_2Cl_2 species formed as the exclusive product [20,24]. This is in full agreement with the thesis of Pringle et al. that in solution the *cis*-PtP_2Cl_2 complexes are generally more stable than the corresponding trans species. This statement was supported by high-level quantum chemical calculations [33]. In our cases, ^{31}P NMR analysis of the crude reaction mixtures revealed only the presence of the cis complexes (**4, 8, 11**, and **15**), the trans isomer was not present, not even in traces. This observation together with, in most cases, the high (81–96%) yield confirms the selective formation of the cis complexes in the instance under discussion.

The best structures of **4a**-*R,R*, **4b, 8a**-*S,S*, **8b, 11**, and **15**-*S,S* are described in Figs. 1–6. The cis structures of the complexes are stabilized by a π–π stacking and, where relevant (in the case of complexes **4a, 4b, 11**, and **15**), by $\pi\cdots$HCP weakly polar interactions. No classical H-bonds were identified.

In the phospholene–platinum complex **4a**, the five-membered rings adopt an envelope-like conformation with the P atom on the flap. The distance between C(α) of one of the phenyl groups and C(β') of the other phenyl group is 3.70 Å, supporting a weak polar π–π interaction between the aromatic rings. The carbon atom of the $C(2)H_2$ moiety of the hetero ring is 3.38 Å from the C(α') atom of the corresponding phenyl ring. In the phospholene–platinum complex **4b**, the distance between the C(2) and C(α') atoms is 4.11 Å. There is a slight symmetrical interaction between the π-system of the corresponding phenyl ring and the carbon atom of the $C(2)H_2$ moiety of the hetero ring.

The hetero rings of phospholane–platinum complex **8a** adopt a deformed envelope conformation, and the distance between the C(5) atom of the hetero ring and the C(α') atom of the corresponding phenyl group (as well as that of C(5′) and C(α)) is 4.00 Å. A similar distance of 3.99 Å is observed in **8b**. The distance between the C(α) and C(β') atoms is 3.61 Å, indicating a slight π–π interaction.

In **11**, the 1,4-dihydrophosphinine ring is nonplanar. The calculations predict a boat-like phosphacyclohexadiene ring. The presence of the two methyl



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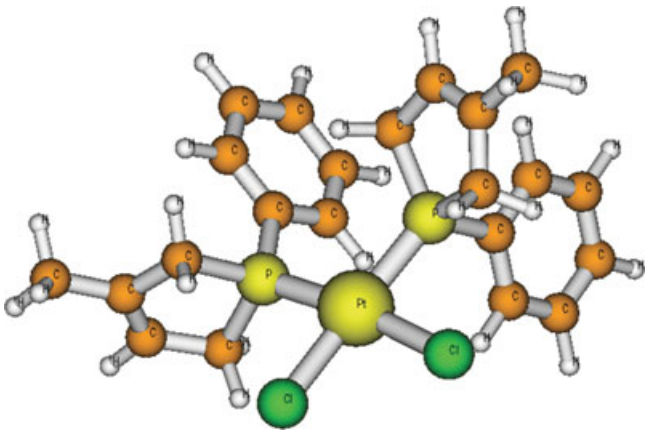


FIGURE 1 Stereostructure of **4a**-*R,R* calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.421, Pt–P1 2.300, P1–C(Ph) 1.842, P1–C2 1.865, C2–C3 1.517, C3–C4 1.341, C4–C5 1.510, C5–P1 1.858, Cl1–Pt–P1 84.12, P1–C2–C3 104.25, C2–C3–C4 116.26, C3–C4–C5 118.10, C4–C5–P1 103.81, Cl1–Pt–P1–C(Ph) −166.38, Pt–P1–C2–C3 −137.42, P1–C2–C3–C4 12.20, P1–C2–C3–CH_3 −169.79.

substituents results in a repulsive effect in the structure. The distance of 3.21 Å between the carbon atom of the CH=unit and the C(β') suggests a $\pi\cdots$HCP interaction between the carbon atom of the CH= unit and the phenyl ring.

Tetrahydrophosphinine–platinum complex **15** exhibits a deformed (slightly twisted) boat conformation for the six-membered hetero rings. On the basis of the distance of 3.79 Å between the C(3) and C(α') atoms, a stabilizing $\pi\cdots H_2C$ interaction could be observed between the phenyl ring and the corresponding six-membered hetero ring.

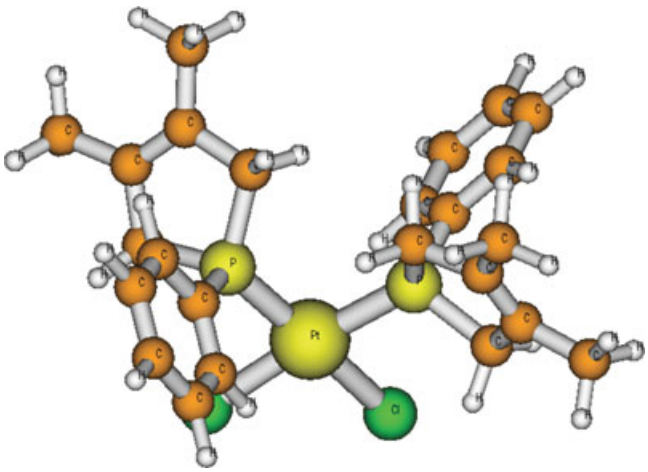


FIGURE 2 Stereostructure of **4b** calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.416, Pt–P1 2.293, P1–C(Ph) 1.834, P1–C2 1.867, C2–C3 1.518, C3–C4 1.348, C4–C5 1.515, C5–P1 1.859, Cl1–Pt–P1 85.53, P1–C2–C3 106.00, C2–C3-C4 116.49, C3–C4–C5 116.92, C4–C5–P1 106.10, Cl1–Pt–P1–C(Ph) 83.28, Pt–P1–C2–C3 131.71, P1–C2–C3–C4–6.79, P1–C2–C3–CH_3 −174.32.

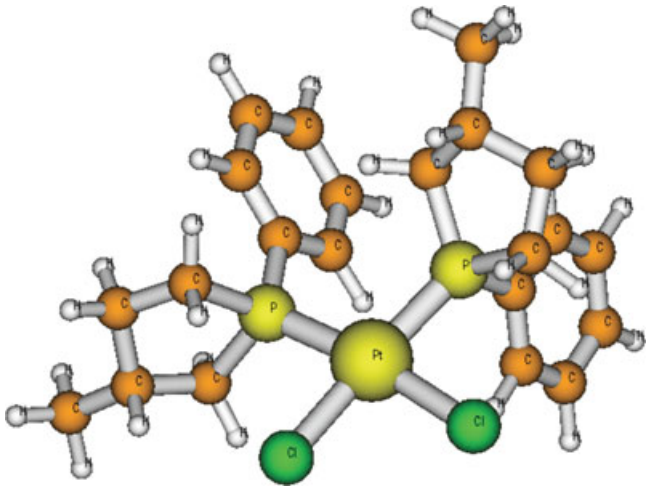


FIGURE 3 Stereostructure of **8a**-*S,S* calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.419, Pt–P1 2.300, P1–C(Ph) 1.837, P1–C2 1.866, C2–C3 1.542, C3–C4 1.541, C4–C5 1.541, C5–P1 1.876, Cl1–Pt-P1 86.75, P1–C2–C3 105.98, C2–C3–C4 106.34, C3–C4–C5 107.78, C4–C5–P1 106.16, Cl1–Pt–P1–C(Ph) −84.20, Pt–P1–C2–C3 105.60, P1–C2–C3–C4 39.41, P1–C2–C3–CH_3 164.27.

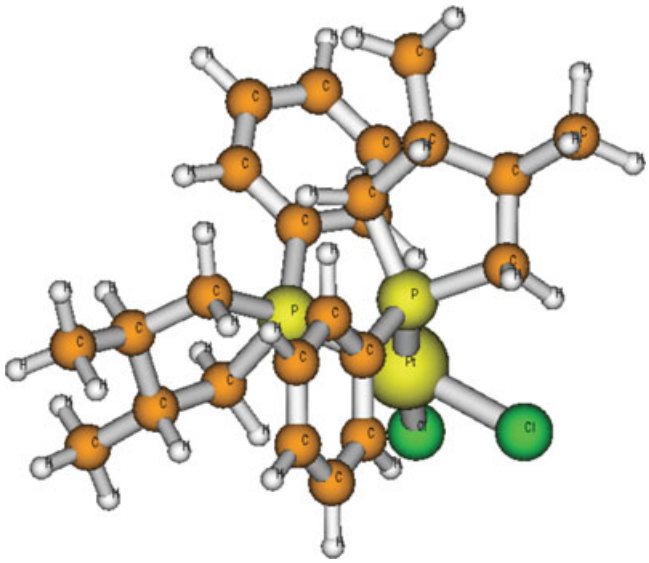


FIGURE 4 Stereostructure of **8b** calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.419, Pt–P1 2.300, P1–C(Ph) 1.837, P1–C2 1.870, C2–C3 1.520, C3–C4 1.548, C4–C5 1.546, C5–P1 1.865, Cl–Pt–P1 86.88, P1–C2–C3 106.03, C2–C3–C4 106.78, C3–C4–C5 106.61, C4–C5–P1 107.02, Cl1–Pt–P1–C(Ph) −84.07, Pt–P1–C2–C3 105.50, P1–C2–C3–C4 39.64, P1–C2–C3–CH_3 165.13.

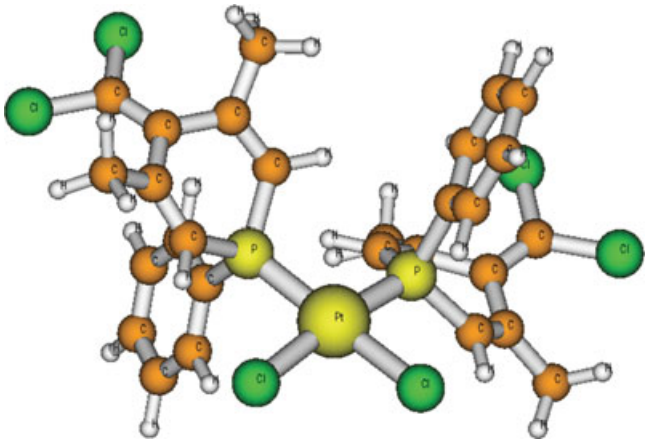


FIGURE 5 Stereostructure of **11** calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.420, Pt–P1 2.303, P1–C(Ph) 1.842, P1–C2 1.814, C2–C3 1.345, C3–C4 1.499, C4–C5 1.499, C5–C6 1.348, C6–P1 1.815, C(Cl2)–C4 1.353, Cl1–Pt–P1 87.74, P1–C2–C3 123.09, C2–C3–C4 119.47, C3–C4–C5 116.07, C4–C5–C6 119.66, C5–C6–P1 123.12, Cl1–Pt–P1–C(Ph) −87.72, Pt–P1–C2–C3 −146.81, P1–C2–C3–C4 −6.00, C2–C3–C4–C5 43.05, P1–C2–C3–CH_3 169.51.

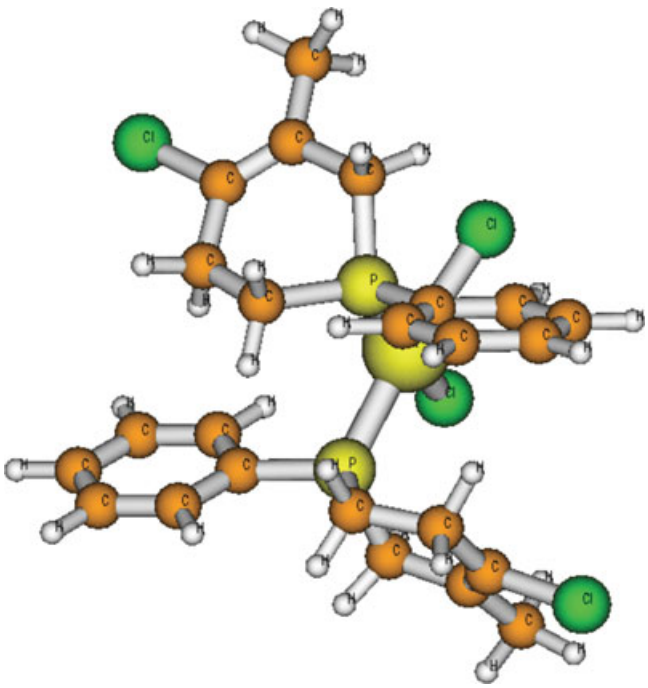
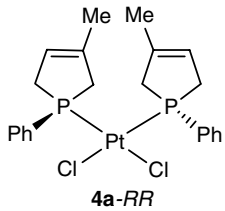


FIGURE 6 Stereostructure of **15** calculated by B3LYP/6-31G(d) (basis set of Pt is LANL2DZ). Selected geometries: Pt–Cl1 2.417, Pt–P1 2.309, P1–C(Ph) 1.833, P1–C2 1.848, C2–C3 1.540, C3–C4 1.511, C4–C5 1.341, C5–C6 1.522, C6–P1 1.848, C5–CH_3 1.506, Cl1–Pt–P1 87.96, P1–C2–C3 110.14, C2–C3–C4 115.38, C3–C4–C5 128.66, C4–C5–C6 121.76, C5–C6–P1 114.07, Cl1–Pt–P1–C(Ph) −91.23, Pt–P1–C6–C5 73.06, P1–C2–C3–C4 −46.64, C2–C3–C4–C5 13.48, P1–C6–C5–CH_3 −153.18.

In the case of the 3-phospholene ligand **2a**, the corresponding *trans*-PtP_2Cl_2 complex was also calculated. In agreement with the observation of Pringle et al. [33], DFT calculations (see below) should that, in the gas phase, the trans complex (**4a**′) is by 3.15 kcal/mol more stable as compared with the cis one. However, in toluene solution (when the relative dielectric constant is 2.38), the cis isomer (**4a**), formed exclusively in synthesis, was found to be by 5.0 kcal/mol more favored as compared with the trans species (**4a**′) according for PMG calculation [34]. This must be due to the effect of solvation that may overcome the electrostatic trans preference [33]. Our experiments showed that in solution, the cis isomer could not be isomerized to the trans form.

On the basis of our earlier experiences, the stereostructures and geometrical data of the platinum complexes may be adequately described by the B3LYP/6-31G(d)-LANL2DZ ECP calculations applied. The calculated data and stereostructure of a related platinum complex [*cis*-bis(ethoxydibenzooxaphosphorino)$PtCl_2$] [22] were well validated by the X-ray measurement carried out later on a suitable single crystal of the methoxy analogue [35]. Another example of validation also confirmed this [16,36].

As the optically active (R_P) form of 3-methyl-1-phenyl-3-phospholene oxide (**1a**-*R*) was available by resolution using TADDOL derivatives [37,38], it was also converted to the corresponding homochiral platinum complex (**4a**-*R,R*). The solubility properties of this species (**4a**-*R,R*) were more unfavorable than those of the racemate of **4a**.



4a-*RR*

In summary, simple cyclic phosphines, such as phospholenes, phospholanes, a 1,4-dihydrophosphinine, and a 1,2,3,6-tetrahydrophosphinine were converted to the corresponding phosphine boranes and platinum complexes that were characterized by spectral data. As regard to the geometry, always the cis platinum complexes were formed selectively. Their stereostructure was elucidated by quantum chemical calculations. The platinum complexes prepared are potential catalysts in

homogeneous catalytic reactions, such as hydrogenations and hydroformylations.

EXPERIMENTAL

The ^{31}P, ^{13}C, ^{1}H, and ^{11}B NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, 500, and 160.4 MHz, respectively. The couplings are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

Phospholene oxides **1a** and **1b** were prepared as described earlier [26,27]. Phospholane oxides **5a** and **5b** were synthesized by the catalytic hydrogenation of compounds **1a** and **1b** [28,29].

General Procedure for the Hydrogenation Reactions

The hydrogenation of the corresponding phospholene oxides **1a** and **1b** (5.2 mmol) was carried out under 12.5 bar at 60°C in the presence of Pd/C catalyst (0.40 g) in methanol (30 mL).

Compound **5a**: ^{31}P NMR ($CDCl_3$) δ 60.6; δ_P [lit 28] 56.0.

Compound **5b**: ^{31}P NMR ($CDCl_3$) δ 59.1 (for the major isomer); δ_P [lit 29] 59.4.

Dihydrophosphinine oxide **9** and tetrahydrophosphinine oxide **12** were available from earlier studies [30,31].

General Procedure for the Deoxygenation of Phosphine Oxides **1, 5, 9**, *and* **12**

0.50 mL (3.9 mmol) of trichlorosilane and 0.67 mL (8.1 mmol) of pyridine were added to 2.7 mmol of the corresponding phosphine oxides (**1, 5, 9**, and **12**) in 40 mL of degassed toluene, and the mixture was stirred at the boiling point for 2 h under nitrogen. The precipitated material was removed by filtration under nitrogen, and the filtrate was concentrated in vacuum to give the corresponding phosphines (**2, 6, 10**, and **13**) that were characterized as their borane complexes (see below).

General Procedure for the Preparation of Borane Complexes **3, 7**, *and* **14**

To the 20 mL toluene solution of 4.3 mmol of the corresponding phosphine (**2, 6**, and **13**), 6.5 mmol (3.3 mL) of 2 M tetrahydrofuran solution of dimethylsulfide borane at 26°C was added under nitrogen, and the mixture was stirred for 24 h. Then 5 mL of water was added and the mixture was stirred for 5 min. The precipitated boric acid was removed by filtration, and the organic phase was dried (Na_2SO_4). Chromatography (silica gel, 3% methanol in chloroform) of the crude product obtained after evaporation of the volatile components gave **3, 7**, and **14**.

Compound **3a**-*R*: Yield: 91%. ^{31}P NMR ($CDCl_3$) δ 28.4 (broad); δ_P [lit 39] (dmso) 33.3.

Compound **3b**: Yield: 89%. ^{31}P NMR ($CDCl_3$) δ 16.1 (broad); δ_P [lit 29] 21.8.

Compound **7a**: Yield: 89%. ^{31}P NMR ($CDCl_3$) δ 30.6 (broad); δ_P [lit 40] 30.8.

Compound **7b**: Yield: 79%. ^{31}P NMR ($CDCl_3$) δ 28.2 (for the major isomer); δ_P [lit 29] 28.9.

Compound **14**: Yield: 96%. ^{31}P NMR ($CDCl_3$) δ −0.14 (broad); ^{1}H NMR ($CDCl_3$) δ 1.66–1.88 (broad, 3H, BH_3), 1.99 (s, 3H, CH_3), 2.12 (q, $J^1 = 7.1$, $J^2 = 7.2$, 2H, C(3)H_2), 2.55 (q, $J^1 = 12.5$, $J^2 = 16.9$, 1H, C(2)H_aH_b), 2.66 (d, $J = 9.4$, 2H, C(6)H_2), 2.76 (q, $J^1 = 16.6$, $J^2 = 16.3$, 1H, C(2)H_aH_b), 7.44–7.70 (m, 5H, Ar).

General Procedure for the Preparation Pt-complexes **4, 4a**-*R*, **8, 11**, *and* **15**

To 0.21 mmol of the corresponding phosphine **2, 6, 10**, and **13** in 10 mL of toluene, 0.05 g (0.10 mmol) of dichlorodibenzonitrileplatinum was added under nitrogen. The mixture was stirred at 26°C for 3 h under nitrogen, whereupon the complex gradually precipitated. The solid product was separated by filtration. 5 mL of pentane was added to the mother liquor to promote further precipitation, and the flask was placed in the refrigerator for several hours. The newer crystal fraction was collected by filtration.

Compound **4a**: Yield: 92%. ^{31}P NMR ($CDCl_3$) δ 16.37 ($J_{Pt-P} = 3512$) and 16.44 ($J_{Pt-P} = 3512$) (1:1) for the homo- and heterochiral forms; ^{1}H NMR ($CDCl_3$) δ 1.75 and 1.76 (6H, CH_3), 2.64–2.87 (m, 4H, CH_2), 3.05–3.44 (m, 4H, CH_2), 5.46 (d, $J = 22.3$, CH=), 7.34–8.02 (m, 10H, Ar); FAB, $[M–Cl]^+_{found}$ = 581.0853, $C_{22}H_{26}ClP_2Pt$ requires 581.0825 for the ^{35}Cl and the ^{194} Pt isotopes.

Compound **4a**-*R*: Yield: 95%. ^{31}P NMR ($CDCl_3$) δ 16.9 ($J_{Pt-P} = 3490$); ^{1}H NMR ($CDCl_3$) δ 1.74 (broad, 6H, CH_3), 2.65–2.85 (m, 4H, CH_2), 3.10 (dm, $^2J_{PH}$ = 17.5, 2H, CH_2), 3.40 (dm, $^2J_{PH} = 17.5$, 2H, CH_2), 5.46 (d, $J = 22.3$, 2H, CH=), 7.34–8.02 (m, 10H, Ar).

Compound **4b**: Yield: 90%. ^{31}P NMR ($CDCl_3$) δ 5.8 ($J_{Pt-P} = 3520$); ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 12H, CH_3), 2.65–2.83 (m, 4H, CH_2), 3.18–3.39 (m, 4H, CH_2), 7.30–7.84 (m, 10H, Ar); FAB, $[M–Cl]^+_{found}$ = 609.1142, $C_{24}H_{30}ClP_2Pt$ requires 609.1138 for the ^{35}Cl and the ^{194}Pt isotopes.

Compound **8a**: Yield: 91%. ^{31}P NMR ($CDCl_3$) δ 15.9 ($J_{Pt-P} = 3520$), 16.0 ($J_{Pt-P} = 3520$) (1:1); ^{1}H

NMR ($CDCl_3$) δ 1.01 (broad, d, $^2J_{PH} = 5.6$, 6H, CH_3), 1.34–2.48 (m, 12H, CH_2), 7.29–7.74 (m, 10H, Ar); FAB, $[M–Cl]^+_{found} = 585.1148$, $C_{22}H_{30}ClP_2Pt$ requires 585.1138 for the ^{35}Cl and the ^{194}Pt isotopes.

Compound **8b**: Yield: 81%. ^{31}P NMR ($CDCl_3$) δ 14.5 ($J_{Pt-P} = 3512$); ^1H NMR ($CDCl_3$) δ 0.72 (d, $J_{HH} = 5.6$, 12H, CH_3), 2.04–2.47 (m, 12H, CH_2, CH), 7.35–7.85 (m, 10H, Ar); FAB, $[M–Cl]^+_{found} = 613.1474$, $C_{22}H_{34}ClP_2Pt$ requires 613.1451 for the ^{35}Cl and the ^{194}Pt isotopes.

Compound **11**: Yield: 96%. ^{31}P NMR ($CDCl_3$) δ −25.3 ($J_{Pt-P} = 3602$); ^1H NMR ($CDCl_3$) δ 2.33 (s, 12H, C_3—CH_3), 6.28 (d, $^2J_{PH} = 18.1$, 4H, CH=), 7.21–7.86 (m, 10H, Ar); FAB, $[M–Cl]^+_{found} = 792.9614$, $C_{28}H_{26}Cl_5P_2Pt$ requires 792.9579 for the ^{35}Cl isotopes and for the ^{194}Pt isotope.

Compound **15**: Yield: 30%. ^{31}P NMR ($CDCl_3$) δ −14.7 ($J_{Pt-P} = 3567$); ^1H NMR ($CDCl_3$) δ 1.55 (s, 6H, CH_3), 1.98–3.24 (m, 12H, CH_2), 7.34–7.65 (m, 10H, Ar).

CALCULATIONS

Stereostructures of selected examples of the platinum complexes were evaluated by the B3LYP/6-31G(d) and in respect of the platinum atom, by the LANL2DZ ECP methods implemented in Gaussian'03 [41]. The force matrices of the optimized structures were found to be positive definite. The most favorable structures of complexes **4a, 4b, 8a, 8b, 11**, and **15** together with the relevant geometrical data are shown in Figs. 1–6, respectively. Semiempirical calculations were performed by the PMG method [34] implemented in MOPAC 2009. 30 structures were analyzed and described by the software MOLDEN [42].

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REFERENCES

[1] Brunner, H.; Zettlmeier, W. Handbook of Enantioselective Catalysis with Transition Metal Compounds; VCH: Weinheim, Germany, 1993.
[2] Botteghi, C.; Marchetti, M.; Paganelli, S. In Transition Metals for Organic Synthesis; Beller, M.; Bolm, C. (Eds.); Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, p. 25.
[3] Mathey, F. In Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain; Mathey, F. (Ed.); Pergamon Press: Amsterdam, the Netherlands, 2001, 753.
[4] Keglevich, G. In Targets in Heterocyclic Systems; Attanasi, O. A.; Spinelli, D. (Eds.); Italian Society of Chemistry, Roma, Italy: 2002; Vol. 6, p. 245.
[5] Csók, Zs.; Keglevich, G.; Petöcz, G.; Kollár, L. Inorg Chem 1999, 38, 831.
[6] Csók, Zs.; Keglevich, G.; Petöcz, G.; Kollár, L. J Organomet Chem 1999, 586, 79.
[7] Baber, R. A.; Haddow, M. F.; Middleton, A. J.; Orpen, A. G.; Pringle, P. G. Organometallics 2007, 26, 713.
[8] Carreira, M.; Charemsuk, M.; Eberhard, M.; Fey, N.; van Ginkel, R.; Hamilton, A.; Mul, W. P.; Orpen, A. G.; Phetmung, H.; Pringle, P. G. J Am Chem Soc 2009, 131, 3078.
[9] Downing, J. H.; Floure, J.; Heslop, K.; Haddow, M. F.; Hopewell, J.; Luisi, M.; Phetmung, H.; Orpen, A. G.; Pringle, P. G.; Pugh, R. I.; Zambrano-Williams, D. Organometallics 2008, 27, 3216.
[10] Clark, T. P.; Landis, C. R. Tetrahedron: Asymmetry 2004, 15, 2123.
[11] Jiang, Q.; Jiang, Y.; Xiao, D.; Cao, P.; Zhang, X. Angew Chem, Int Ed 1998, 37, 1100.
[12] Robin, F.; Mercier, F.; Ricard, L.; Mathey, F.; Spagnol, M. Chem—A Eur J 1997, 3, 1365.
[13] Scriban, C.; Glueck, D. S.; Golen, J. A.; Rheingold, A. L. Organometallics 2007, 26, 1788.
[14] Anderson, B. J.; Glueck, D. S.; DiPasquale, A. G.; Rheingold, A. Organometallics 2008, 27, 4992.
[15] Anderson, B. J.; Guino-o, M. A.; Glueck, D. S.; Golen, J. A.; DiPasquale, A. G.; Liable-Sands, L. M.; Rheingold, A. L. Org Lett 2008, 10, 4425.
[16] Keglevich, G.; Sipos, M.; Szieberth, D.; Nyulászi, L.; Imre, T.; Ludányi, K.; Töke, L. Tetrahedron 2004, 60, 6619.
[17] Keglevich, G.; Sipos, M.; Körtvélyesi, T.; Imre, T.; Töke, L. Tetrahedron Lett 2005, 46, 1655.
[18] Keglevich, G.; Sipos, M.; Szieberth, D.; Petöcz, G.; Kollár, L. J Organomet Chem 2004, 689, 3158.
[19] Keglevich, G.; Sipos, M.; Ujj, V.; Körtvélyesi, T. Lett Org Chem 2005, 2, 608.
[20] Keglevich, G.; Szelke, H.; Kerényi, A.; Imre, T.; Ludányi, K.; Dukai, J.; Nagy, F.; Arányi, P. Heteroatom Chem 2004, 15, 459.
[21] Keglevich, G.; Szelke, H.; Kerényi, A.; Kudar, V.; Hanusz, M.; Simon, K.; Imre, T.; Ludányi, K. Tetrahedron: Asymmetry 2005, 16, 4015.
[22] Keglevich, G.; Kerényi, A.; Mayer, B.; Körtvélyesi, T.; Ludányi, K. Transit Metal Chem 2008, 33, 505.
[23] Keglevich, G.; Szelke, H.; Kerényi, A.; Imre, T. Transit Metal Chem 2006, 31, 306.
[24] Keglevich, G.; Kerényi, A.; Szelke, H.; Ludányi, K.; Körtvélyesi, T. J Organomet Chem 2006, 691, 5038.
[25] Kerényi, A.; Balassa, A.; Körtvélyesi, T.; Ludányi, K.; Keglevich, G. Transit Metal Chem 2008, 33, 459.
[26] Keglevich, G.; Petneházy, I.; Miklós, P.; Almásy, A.; Tóth, G.; Töke, L.; Quin, L. D. J Org Chem 1987, 52, 3983.
[27] Chang, L. L.; Denney, D. Z.; Denney, D. B.; Hsu, Y. F. Phosphorus 1974, 4, 265.
[28] Quin, L. D. The Heterocyclic Chemistry of Phosphorus. Systems Based on the Phosphorus–Carbon Bond; Wiley, New York, 1981; p. 237.
[29] Keglevich, G.; Fekete, M.; Chuluunbaatar, T.; Dobó, A.; Harmat, V.; Töke, L. J Chem Soc, Perkin Trans 1 2000, 4451.

[30] Keglevich, G.; Szöllösy, Á.; Töke, L.; Fülöp, V.; Kálmán, A. J Org Chem 1990, 55, 6361.
[31] Keglevich, G.; Böcskei, Zs.; Újszászy, K.; Töke, L. Synthesis 1997, 1391.
[32] Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. J Am Chem Soc 1984, 106, 7021.
[33] Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. Chem Commun 2003, 278.
[34] Stewart, J. J. P. J. Mol. Mod. 2007, 13, 1173.
[35] Holzbauer, T.; Keglevich, G.; Kerényi, A.; Czugler, M. Acta Cryst E 2009, 65, m347.
[36] Czugler, M.; Körtvélyesi, T.; Fábián, L.; Sipos, M.; Keglevich, G. Cryst Eng Commun 2007, 9, 561.
[37] Novák, T.; Schindler, J.; Ujj, V.; Czugler, M.; Fogassy, E.; Keglevich, G. Tetrahedron: Asymmetry 2006, 17, 2599.
[38] Novák, T.; Ujj, V.; Schindler, J.; Czugler, M.; Kubinyi, M.; Mayer, Zs. A.; Fogassy, E.; Keglevich, G. Tetrahedron: Asymmetry 2007, 18, 2965.
[39] Keglevich, G.; Újszászy, K.; Szöllösy, Á.; Ludányi, K.; Töke, L. J Organomet Chem 1996, 516, 139.
[40] Keglevich, G.; Fekete, M.; Chuluunbaatar, T.; Dobó, A.; Böcskei, Zs.; Töke, L. Synth Commun 2000, 30, 4221.
[41] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh, PA, 2003.
[42] Schaftenaar, G.; Noordik, J. H. J. Comput-Aided Mol. Design 2000, 14, 123.