Synthesis and Use of Borane and Platinum(II) Complexes of 3-Diphenylphosphino-1phenylphospholane (LuPhos)

K. Michał Pietrusiewicz,¹ Anna Flis,¹ Viktória Ujj,² Tamás Körtvélyesi,³ László Drahos,⁴ Péter Pongrácz,⁵ László Kollár,⁵ and György Keglevich⁶

¹Department of Organic Chemistry, Faculty of Chemistry, Marie Curie-Sklodowska University, 20614 Lublin, Poland

²Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary

³Department of Physical Chemistry and Material Science, University of Szeged, 6701 Szeged, Hungary

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

⁵Department of Inorganic Chemistry, University of Pécs, H-7624 Pécs, Hungary

⁶Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary

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ABSTRACT: 3-Diphenvlphosphinovl-1-phenvlphospholane 1-oxide (2) obtained by the Michael addition of diphenylphosphine oxide to the double-bond of 1-phenyl-2-phospholene 1-oxide (1) was subjected to double deoxygenation to afford the corresponding bisphosphine (3, LuPhos) that was converted to bis(phosphine borane) **4** and to cis chelate platinum(II) complex 6. A mixed phosphine oxidephosphine borane 5 was also prepared. Stereostructures of the bidentate P-ligand 3 and the ring platinum(II) complex (6) were evaluated by quantum chemical calculations. Complex 6 used as a catalyst

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showed modest activity, but unusual regioselectivity in the hydroformylation of styrene and its 4-substituted analogues. © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:730-736, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20741

INTRODUCTION

Platinum(II) complexes incorporating P(III)-ligands are important catalysts in homogeneous catalytic transformations [1–4].

Complexes including heterocyclic P-ligands form a representative group [5]. Heterocyclic P-ligands occurring in Pt(II) complexes, comprise, among others [6-8], arylphospholes [9,10], phospholenes [11], phospholanes [11,12], phosphinine (phosphorine) derivatives [11,12], phosphepanes [12], as well as 9-phosphabicyclononanes

Correspondence to: G. Keglevich; e-mail: gkeglevich@mail .bme.hu.

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(Phobanes) [13] and 6-phospha-2,4,8-trioxaadamantanes [14].

Among the bidentate heterocyclic P-ligands, DuPhos [15], PennPhos [16], and BIPNOR [17] are well known. In this series, only DuPhos has been applied in platinum complexes [18–20]. 3-Diphenylphosphino-1-phenyl-1,2,3,6-tetrahydrophosphinine and its 1,2,3,4,5,6-hexahydrophosphinine derivative were also described as novel bidentate P-ligands in Pt(II) complexes [21–26] showing unusual regioselectivity as catalysts in the hydroformylation of styrene [27].

In this paper, 3-diphenylphosphino-1-phenylphospholane (LuPhos) [28] is converted to novel borane and Pt(II) complexes useful as protected ligands or catalyst, respectively.

RESULTS AND DISCUSSION

3-Diphenylphosphinoyl-1-phenylphospholane oxide **2** was prepared by the Michael addition of diphenylphosphine oxide to the double-bond of 1-phenyl-2-phospholene 1-oxide (**1**) at 26° C in the presence of NaOMe/MeOH in toluene (Scheme 1). The diastereomer exhibiting the P-phenyl and the P(O)Ph₂ substituents in position *trans* was formed selectively.

Bis(phosphine oxide) **2** was then subjected to double deoxygenation by trichlorosilane in benzene at $0 \rightarrow 25^{\circ}$ C to give bidentate P-ligand LuPhos (**3**). The configurations of the stereogenic centers were preserved during the double deoxygenation. The reaction of LuPhos (**3**) with two equivalents of dimethylsulfide borane afforded bis(phosphine borane) **4** (Scheme 2).

Phosphine boranes may be regarded as precursors of phosphines, because on treatment with secondary amines in an aromatic solvent at around 80°C they undergo deboronation [29].

It was found that without the complete exclusion of air during the deoxygenation of bis(phosphine oxide) **2** and subsequent operations, a 55:45 mixture of bis(phosphine borane) **4** and phosphine borane– phosphine oxide **5** was formed. Compound **5** was



SCHEME 1 Preparation of a bis(phosphine oxide) by Michael addition.



SCHEME 2 Preparation of a bis(phosphine borane) as a protected bidentate P-ligand.

separated from the expected product **4** by column chromatography.



Phospholane boranes **4** and **5** were identified by ³¹P, ¹³C, and ¹H NMR, as well as mass spectral data. The ³¹P NMR spectrum of **4** comprised two broad signals, whereas that of **5** showed a broad signal for the ring P and a doublet of 29.9 Hz for the exocyclic P-function. The similar ¹ J_{PC} couplings of ca 34 Hz for C₂ and C₅ of phospholanes **4** and **5** in the ¹³C NMR spectra confirmed the ring phosphine borane moiety.

LuPhos **3** was also reacted with one equivalent of dichlorodibenzonitrile-platinum(II) in benzene at 26°C, to provide *cis* chelate complex **6** (Scheme 3).

The structure of complex **6** was confirmed by ³¹P and ¹H NMR, as well as mass spectral data. In the ³¹P NMR spectrum, the two phosphorus atoms are coupled by a J_{PP} of 14.1 Hz, whereas the two P-signals revealed a J_{P-Pt} of 3409 (P₁) and 3488 (P₂) Hz. It is worthy to mention that the *cis* chelate structure of complex **6** is of novelty. In some respects, analogous platinum complexes incorporating the 3-diphenylphosphino-1-phenyl-1,2,3,6-tetrahydrophsophinine or the 3-diphenylphosphino-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine bidentate P-ligands were described by the authors in previous articles [25,26].



SCHEME 3 Preparation of a novel *cis* chelate platinum complex.

The stereostructures of the Pt(II) complex 6 and its bidentate P-ligand 3 were evaluated by B3LYP/6-31G^{*} calculations, and LANL2DZ calculations for Pt. The best conformation of LuPhos **3** and its Pt(II) complex 6 (Figs. 1 and 2, respectively) suggests that the bidentate P-ligand (3) must undergo a slight rotation around the C(3)-P(Ph)₂ axis before complexation, which can be considered to be a rotation with a low energetic barrier. In the stereostructure of Pt(II) complex of LuPhos (6), there is a weak π -stacking interaction between the two phenyl rings of the PPh₂ moiety, as suggested by the distance of 2.95 Å between the $C_{\alpha'}$ and $C_{\alpha''}$ atoms and by the distance of 3.55 Å between the $C_{\beta'}$ and $C_{\beta''}$ atoms. The $C_{\alpha'}\!-\!$ $C_{\alpha''}$ and $C_{\beta'}-C_{\beta''}$ distances were found to be 3.02 and 3.52 A, respectively, by the PM6-DH2 method. There may be a slight interaction between the C_{β} -H of one of the two Ph₂P phenyl groups and the CH of the corresponding methylene moiety of the hetero ring. According to PM6-DH2 calculations, the best structure has a weak T-shape π -stacking interaction.

inum complexes may be adequately described by the B3LYP/6-31G^{*} – LANL2DZ calculations applied. The calculated data and stereostructure of a related platinum complex [*cis*-bis(ethoxydibenzooxaphosphorino)PtCl₂] [30] were well validated by the X-ray measurement carried out later on a suitable single crystal of the methoxy analogue [31]. Another example of validation also justified the potential of B3LYP/6-31G^{*} calculations in the elucidation of the stereostructures of P-ligands [32,33].

Cis chelate complex **6** was tested as a catalyst precursor in the hydroformylation of styrene and its 4-substituted derivatives. A catalyst formed in situ from **6** and two equivalents of tin(II) chloride was used under standard "oxo-conditions" $[p(CO)=p(H_2) = 45$ bar, $100^{\circ}C]$. As observed generally, in addition to the two types of regioisomers, 1-aryl-propanal (**A**) and 2-aryl-propanal (**B**), substituted ethylbenzene (**C**) was also formed as a hydrogenation by-product (Eq. (1)).

$$\operatorname{ArCH}=\operatorname{CH}_{2} \xrightarrow{\operatorname{CO}/\operatorname{H}_{2}} \frac{\operatorname{ArCH}(\operatorname{CHO})\operatorname{CH}_{3} + \operatorname{ArCH}_{2}\operatorname{CH}_{2}\operatorname{CHO} + \operatorname{ArCH}_{2}\operatorname{CH}_{3}}{\operatorname{\mathbf{A}} \qquad \operatorname{\mathbf{B}} \qquad \operatorname{\mathbf{C}}}$$
$$\operatorname{Ar} = \operatorname{C}_{6}\operatorname{H}_{5}, 4\operatorname{-CH}_{3}\operatorname{-C}_{6}\operatorname{H}_{4}, 4\operatorname{-AcO}\operatorname{-C}_{6}\operatorname{H}_{4}, 4\operatorname{-Cl}\operatorname{-C}_{6}\operatorname{H}_{4} \qquad (1)$$

In complex **6**, the distances between $C_{\beta'}$ and C2, $C_{\beta'}$ and C4, as well as C_{β} and C5 are 4.0, 3.47, and 3.25 Å, respectively. According to PM6-DH2, these data are 4.13, 3.48, and 3.81 Å, respectively. One can see that in the case under discussion, the application of the much simpler semiempirical calculation is also appropriate.

As regards the ligand LuPhos (**3**), the distance between the $C_{\alpha'}$ and $C_{\alpha''}$ atoms is 2.89 Å (2.93 Å by PM6-DH2), whereas that between the $C_{\beta'}$ and $C_{\beta''}$ atoms is 3.58 Å (3.72 Å by PM6-DH2). The two phenyl rings are almost perpendicular to each other. The distances between $C_{\beta'}$ and C2, $C_{\beta''}$ and C4, as well as C_{β} and C5 are 3.49, 3.75, and 3.38 Å, respectively (and by PM6-DH2 are 3.40, 3.59, and 3.32 Å, respectively).

As the geometries of the best (lowest energy) optimized structures of complex **6** and bidentate P-ligand **3** show, the DFT and PM6-DH2 calculations gave similar geometrical parameters (see the geometries listed in Fig. 2), meaning that, in this particular case, the use of the PM6 semiempirical method is adequate.

On the basis of our earlier experiences, the stereostructures and geometrical data of the plat-

Because at 50°C the conversion of styrene was only 3%, the further experiments were carried out at 100°C (Table 1). Compared to the most widely used PtCl₂(diphosphine) catalyst precursors applied in the hydroformylation of styrene (where diphosphine = achiral dppp and dppp [34], chiral chiraphos [35] and diop analogues [36]; for further examples see [2,4]), the catalyst containing bidentate *P*-ligand **3** has shown lower activity, that is, the conversions obtained after a reaction time of 24 h fell in the range of 18%-20% using the above substrates. Chemoselectivities toward the formyl products were in a narrow range of 79%-85%, which fit well the results obtained with ligands of related structure [8]. The 4-substituent has shown a slight influence on chemoselectivity. 4-Acetoxystyrene provided slightly lower aldehyde selectivity than the corresponding 4-methyl- and 4-chlorostyrene analogues (Table 1, entries 2, 3, 6, 7). Unlike the most conventional platinum-containing catalysts, the use of the above system led to the predominance of the branched aldehyde (A) over the linear one (**B**). Styrene has shown a regioselectivity of 58% toward the branched aldehyde, which was slightly decreased upon 4-substitution (Table 1, entries 2, 3, 6, 7). Under standard conditions, less



FIGURE 1 Perspective view of bidentate P-ligand **3** obtained by B3LYP/6-31G* calculations (in parenthesis: the best geometry can be seen obtained by the PM6-DH2 method). Selected bond lengths (Å) and angles (°) are as follows: P–C(Ph) 1.855, 1.858 (1.878,1.879), P1–C(Ph), 1.860 (1.882), P1–C2 1.900 (1.925), C2–C3 1.547 (1.527), C3–C4 1.545 (1.542), C4–C5 1.541 (1.527), C5-P1 1.895 (1.916), P1-C2-C3 107.52 (106.05), C2-C3-C4 106.23 (111.31), C3-C4-C5 108.79 (111.89), C4-C5-P1 108.16 (104.75), P1-C2-C3-C4 38.46 (23.99), C2-C3-C4-C5–45.09 (–37.99), C3-C4-C5-P1 30.96 (31.43), C_β (Ph)-C_α (Ph)-P-C3-17.80, 72.58 (–7.52, 83.99).



FIGURE 2 Perspective view of platinum(II) complex **6** obtained by B3LYP/6-31G* calculations (in parenthesis: the best geometry can be seen obtained by the PM6-DH2 method). Selected bond lengths (Å) and angles (°) are as follows: Pt-Cl, 2.418, 2.401 (2.358, 2.354), Pt-P 2.303 (2.290), Pt-P1 2.282 (2.278), P-C(Ph) 1.837, 1.836 (1.845, 1.842), P1-C(Ph), 1.817 (1.831), P1-C2 1.857 (1.907), C2-C3 1.544 (1.528), C3-C4 1.561 (1.546), C4-C5 1.561 (1.536), C5-P1 1.862 (1.903), CI-Pt-Cl 90.72 (81.85), CI-Pt-P1 92.98 (97.78), CI-Pt-P 91.99 (95.88), Pt-P1-C(Ph) 104.53 (127.45), Pt-P-C(Ph) 114.04, 120.08 (110.53, 117.67), P1-C2-C3 98.34 (97.34), C2-C3-C4 106.02 (108.52), C3-C4-C5 110.25 (112.19), C4-C5-P1 104.15 (103.07), CI-Pt-P1-C(Ph) -22.29 (-14.66), CI-Pt-P1-C2-152.40 (-146.14), Pt-P1-C2-C3-61.13 (-65.78), P1-C2-C3-C4-52.77 (-50.28), C2-C3-C4-C5 33.06 (40.04), C3-C4-C5-P1 3.43 (-6.64), C_β(Ph)-C_α(Ph)-P1-Pt 61.75 (40.16), C_β(Ph)-C_α(Ph)-P-Pt 29.85, -4.11 (12.16, -4.39).

Entry	Substrate (Ar)	Тетр. (° С)	Reaction Time (h)	Conversion (%)	R _c ^b (%)	R _{br} c (%)
1	C ₆ H ₅	50	70	3	n.d. ^e	66
2	C ₆ H ₅	100	24	20	80	58
3	$4-CH_3-C_6H_4$	100	24	20	85	58
4 ^{<i>d</i>}	4-CH ₃ -C ₆ H ₄	100	24	29	95	49
5 ^d	$4-CH_3-C_6H_4$	100	72	48	94	55
6	4-Cl-C ₆ H ₄	100	24	18	85	55
7	4-AcO-Č ₆ H ₄	100	24	18	79	52

TABLE 1 Hydroformylation of Styrene and Its 4-Substituted Derivatives in the Presence of In Situ Catalysts Formed from PtCl₂(3) Complex 6 and Tin(II) Chloride^a

^aReaction conditions: Pt/SnCl₂/styrene = 1:2:100, p(CO) = p(H₂) = 45 bar, 1 mmol of substrate, solvent: 8 mL of toluene.

^bChemoselectivity towards aldehydes (A, B). [(moles of A + moles of B)/(moles of A + moles of B + moles of C) × 100].

^cRegioselectivity towards branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) \times 100].

 ${}^{d}p(\breve{CO}) = 45 \text{ bar}, p(H_2) = 22 \text{ bar}.$

Not determined.

regioselective hydroformylation was observed with 4-acetoxy-styrene (Table 1, entry 7).

The change of the partial pressures, that is, keeping p(CO) at 45 bar and decreasing $p(H_2)$ to 22 bar, resulted in a substantial increase in chemoselectivity and a slight decrease in the regioselectivity using 4-methyl-styrene as the substrate (Table 1, entries 3 and 4). After a prolonged reaction time (at p(CO) = 45 bar and $p(H_2) = 22$ bar), the regioselectivity somewhat increased (Table 1, entry 5).

In conclusion, 3-diphenylphosphinoyl-1-phenylphospholane 1-oxide was prepared and used in the synthesis of a bis(phosphine borane) complex, a mixed phosphine borane–phosphine oxide, and a *cis* chelate platinum(II) complex. The stereostructures of the bidentate P-ligand LuPhos and its ring Pt(II) complex were evaluated by quantum chemical calculations. It is noteworthy that the PM6 and PM6-DH2 semiempirical calculations also describe the Pt(II) complex adequately. The *cis* chelate ring complex used as a catalyst showed moderate activity and the prevalence of the branched regioisomer in the hydroformylation of substituted styrenes.

EXPERIMENTAL

General (Instruments)

The ³¹P, ¹³C, ¹H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. The couplings are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument. Elemental analysis was performed on a PERKIN ELMER HCN 2400 analyzer at the Faculty of Chemistry, Maria Curie-Sklodowska University.

trans-3-Diphenylphosphinoyl-1phenylphospholane 1-oxide (**2-trans**)

A solution of sodium methoxide (0.61 g, 11.4 mmol) in 4 mL of methanol was added dropwise at 26°C to a magnetically stirred mixture of 1-phenylphosphol-2-ene 1-oxide [37] (2.0 g, 11.4 mmol) and diphenylphosphine oxide (2.3 g, 11.4 mmol) dissolved in 20 mL of dry toluene. After 0.5 h of additional stirring at room temperature, ³¹P NMR monitoring of the reaction mixture indicated 85% conversion and formation of a single adduct. The mixture was then concentrated and the residue was dissolved in 50 mL of chloroform, washed with 2×10 mL of water, and dried (MgSO₄). After removal of the solvent, the resulting solid was crystallized from toluene to afford 2.6 g (61%) of diastereomerically pure product **2-trans** as white crystals. Mp 209–210°C.

³¹P NMR (CDCl₃) δ : 31.7 (d, J = 45.7), 58.8 (d, J = 45.7); ¹³C NMR (CDCl₃) δ : 24.7 (J =5.3, C₄), 28.9 (dd, $J_1 = 68.7$, $J_2 = 10.0$, C₂),^a 29.9 $(dd, J_1 = 65.1, J_2 = 2.5, C_5)$,^a 38.3 $(dd, J_1 =$ 72.4, $J_2 = 9.2$, C_3), 129.29 (J = 11.6, C_{γ}),^b 129.31 $(J = 11.6, C_{\gamma'})^{\text{b}}$ 129.34 $(J = 11.5, C_{\gamma''})^{\text{b}}$ 130.2 (J =9.6, C_{β}),^c 131.3 (dd, $J_1 = 97.8$, $J_2 = 1.4$, $C_{\alpha'}$), 131.4 $(J = 9.0, C_{\beta'})$, ° 131.6 $(J = 9.0, C_{\beta''})$, ° 131.8 (J = 98.4, J) $C_{\alpha''}$), 132.5 (J = 2.8, C_{δ}),^d 132.6 (J = 2.7, $C_{\delta'}$),^d 132.7 $(J = 2.6, C_{\delta^{*}})^{d}$ 134.1 $(J = 91.1, C_{\alpha})$, where α, β , γ , and δ and the one and two prime symbols mean the corresponding aromatic carbon atoms,^{a-d} tentative assignment; ¹H NMR (CDCl₃)δ: 1.97–2.43 (m, 6H, CH₂), 2.73–2.87 (m, 1H, CH), 7.43–7.82 (m, 15H, ArH); Elemental analysis for $C_{22}H_{22}O_2P_2$ (%) calcd: C 69.46, H 5.83, found: C 69.52, H 5.82.

3-Diphenylphosphinborano-1phenylphospholane 1-borane **4**

The solution of 50 mg (0.13 mmol) of 1-phenyl-3-diphenylphosphinoyl-phospholane 1-oxide (**2**) in 4 mL of benzene was degassed and after cooling to 0°C, 0.30 mL (3.0 mmol) of trichlorosilane was added. The mixture was stirred at 0°C for 3 h and then at 25°C for 2 h under nitrogen to afford bis(phosphine) **3** that was immediately reacted further. 0.26 mL of 2 M dimethyl sulfide borane in tetrahydrofuran (0.52 mmol) was added and the solution was stirred at 25° C for 24 h under nitrogen. Then the mixture was treated with 1 mL of water and stirred for 10 min. The precipitated boric acid was removed by filtration and the organic phase dried (Na₂SO₄). 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 28.5 mg (57%) of **4**.

³¹P NMR (CDCl₃) δ : 22.7 (P₂, broad), 34.1 (P₁, broad); ¹³C NMR (CDCl₃) δ : 26.4 (²*J* = 11.1, ¹*J* = 35.4, C₂), 28.1 (³*J* = 1.9, ¹*J* = 33.3, C₅), 28.4 (*J* = 4.5, C₄), 36.7 (*J* = 34.4, C₃), 127.7 (*J* = 54.5, C_{α'}),^A 127.8 (*J* = 53.9, C_{α'}),^A 129.07 (*J* = 9.8, C_{γ'}),^B 129.11 (*J* = 9.9, C_{γ'}),^B 129.15 (*J* = 9.6, C_γ), 130.3 (*J* = 45.5, C_α), 131.1 (*J* = 9.1, C_β), 131.5 (*J* = 2.5, C_δ), 131.72 (*J* = 2.1, C_{δ'}),^C 131.74 (*J* = 2.0, C_{δ''}),^C 132.5 (*J* = 8.9, C_{β'}),^D 132.6 (*J* = 8.9, C_{β''}),^{A-D} may be reversed; ¹H NMR (CDCl₃) δ : 3.01 (m, H, CH), 7.41–7.60 (m, 9H, Ar), 7.61–7.82 (m, 6H, Ar); HRMS, [M + Na]⁺_{found} = 399.1760, C₂₂H₂₈B₂NaP₂ requires 399.1750.

3-Diphenylphosphinoyl-1-phenylphospholane 1 borane **5**

In the case that the above series of reaction $(2 \rightarrow$ $3 \rightarrow 4$) was carried out without careful exclusion of air, a 55%–45% mixture of 4 and 5 was obtained. The phosphine borane-phosphine oxide (5) was separated by column chromatography (silica gel, 3%) methanol in chloroform) in 43% yield. ³¹P NMR (CDCl₃) δ : 30.8 ($J = 29.9, P_2$), 35.2 (P₁, broad); ¹³C NMR (CDCl₃) δ : 26.4 (²J = 12.6, ¹J = 35.5, C₂), 26.7 $({}^{3}J = 1.2, {}^{1}J = 34.0, C_{5}), 27.0 (C_{4}), 40.5 (J = 71.2),$ C₃), 128.88 (J = 11.6, C_{γ'}),^A 128.93 (J = 11.6, C_{γ''}),^A 129.1 $(J = 9.6, C_{\gamma})$, 130.5 $(J = 45.4, C_{\alpha})$, 130.9 (J =8.9, C_{β}), 131.0 (J = 8.9, $C_{\beta'}$),^B 131.1 (J = 8.9, $C_{\beta''}$),^B 131.4 ($J = 2.4, C_{\delta}$), 132.2 ($J = 2.8, C_{\delta'}, C_{\delta''}$), ^{A,B} may be reversed; ¹H NMR (CDCl₃) δ: 2.91 (m, H, CH), 7.41–7.61 (m, 9H, Ar), 7.61–7.72 (m, 2H, Ar), 7.72– 7.83 (m, 4H, Ar); HRMS, $[M + Na]_{found}^+ = 401.1378$, C₂₂H₂₅BONaP₂ requires 401.1371.

The Platinum Complex of 3-Diphenylphosphino-1-phenylphospholane (**6**)

57 mg (0.15 mmol) 1-phenyl-3-diphenylphosphinoyl-phospholane 1-oxide (2) was double deoxygenated using 0.35 mL (3.5 mmol) of trichlorosilane as described above for the $2 \rightarrow 3$ transformation. The solution of bis(phosphine) **3** so obtained was reacted with 71 mg (0.15 mmol) of dichlorodibenzonitrile platinum(II) and the mixture was stirred at room temperature for 24 h under nitrogen. The precipitated material was removed by the filtration to afford 80 mg (87%) of **6**.

³¹P NMR (CDCl₃) δ: 27.58 (J_{Pt-P} =3488, J_{P-P} =14.1, P₂), 33.37 (J_{Pt-P} =3409, J_{P-P} =14.1, P₁); ¹H NMR (CDCl₃) δ: 1.69–1.97 (m, 6H, CH₂), 2.20–2.28 (m, 1H, CH), 7.43–7.61 (m, ArH, 15H). HRMS, [M–Cl]⁺_{found}=577.0508, C₂₂H₂₂P₂³⁵Cl¹⁹⁴Pt requires 577.0512.

Hydroformylation Experiments

A solution of 6.2 mg (0.01 mmol) of $PtCl_2(3)$ and 3.8 mg (0.02 mmol) of tin(II) chloride in 8 mL toluene containing 0.115 mL (1 mmol) of styrene was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 90 bar total pressure (CO/H₂ = 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.

The hydroformylation experiments with the substituted styrenes were carried out following the same procedure.

Quantum Chemical Calculations

The structures in the conformational analysis of the ligand molecule were calculated by the semiempirical quantum chemical methods PM6 [38], PM6-DH2 (PM6 Hamiltonian with the correction for H-bonds and dispersion interactions) [39] and implemented in MOPAC2009 [40] and DFT (density functional theory) with B3LYP/6-31G* functionals implemented in Gaussian '03 [41]. The structure of the Pt complex was obtained by the same methods, but Pt was handled by LANL2DZ effective core potentials. The transition state of the inversion around the P-atom in the ring was also calculated by the methods mentioned above. The force constants in the minima are positive and one and only one force constant has a negative value in the transition state. The gradient norm of the semiempirical calculations was less than 0.1 kcal/mol/R A. In the DFT calculations the criteria were the default. The geometries were evaluated by MOLDEN [42].

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