

## Stereochemical pattern of phosphine oxidation by a peroxometallacyclic platinum complex. Evidence of an intramolecular process

Gastone Paiaro <sup>a,\*</sup>, Luciano Pandolfo <sup>a</sup>, Franco Morandini <sup>a</sup>, Silvio Darin Fioretto <sup>b</sup>

<sup>a</sup> Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy

<sup>b</sup> Centro di Studio sui Biopolimeri del C.N.R., Dipartimento di Chimica Organica, Università di Padova, Via Marzolo, 1, 35131 Padova, Italy

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### Abstract

The prochiral peroxometallacyclic ketenyl platinum complex  $[(PPh_3)_2Pt-O-O-C(O)-C=C=O]$  (**1**) reacts with (*S*)-(-)- $\alpha$ -methylbenzylamine to give the diastereomeric amidic derivatives, **2**. One of the two possible diastereomers, **2a**, has been obtained pure and the absolute configuration at the carbon atom  $\sigma$ -bonded to the metal is inferred from its CD spectrum. Compound **2a** has been used to oxidize the chiral racemic phosphine (*RS*)-PPhCyPr using a molar ratio, PPhCyPr **2a** = 2:1. The reaction products contains an enantiomeric excess of (*S*)-(-)-OPPhCyPr whereas unreacted PPhCyPr shows the prevalent (*S*) configuration, indicating that the reaction occurred with asymmetric induction. These findings are rationalized by a mechanism based on the coordination to the metal of PPhCyPr mainly in the (*R*) configuration, followed by an intramolecular oxidation by the peroxide moiety.

**Keywords:** Phosphine oxidation; Stereochemistry; Platinum; Peroxocomplex

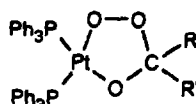
### 1. Introduction

Dioxygen, the most available oxidizing agent, is hardly even used directly to oxidize organic compounds. The interaction of molecular oxygen, in a triplet ground state, with organic molecules, which are in a singlet state, is spin-forbidden, with the consequence that the reaction, although thermodynamically favoured, occurs too slowly to be useful. Consequently, molecular oxygen needs to be activated and one way is to transform it into organic or inorganic peroxides.

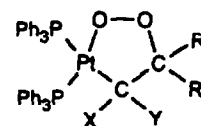
Because of its importance in industrial and natural processes, the interaction of molecular oxygen with transition metals and catalytic or stoichiometric oxidation reactions promoted by peroxometal derivatives have been widely studied and reviewed [1].

Peroxo-cyclic metal compounds of the type  $[(PPh_3)_2PtO_2]$  ( $M = Ni, Pd$  or  $Pt$ ) are catalysts in the oxidation of phosphines [2]. Furthermore, these compounds can react with ketones [3] or activated olefins [4] to form five-membered peroxometallacyclic compounds of the

type shown below and in some cases, these also behave as oxidizing agents.



I



II

As an example, adducts **I** undergo a partial deoxygenation by  $PPh_3$  and/or  $H_2$ , depending on  $R$  and  $R'$  [5], whereas the adducts with olefins having strongly electron withdrawing groups, **II**, are not active under similar conditions [4]. Phosphine oxides are obtained only if the complexes **II** are treated with phosphines more basic than  $PPh_3$ , such as  $PMe_2Ph$  or  $PMePh_2$ , but this reaction is complicated by exchange of phosphines on the metal [4].

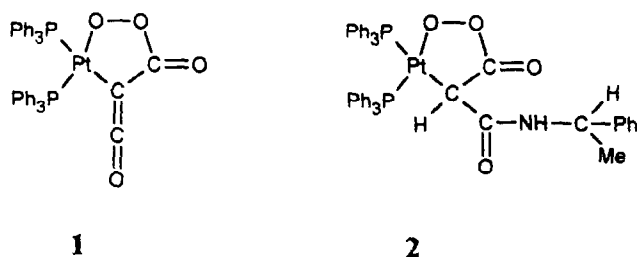
Although there is a large number of studies on the catalytic oxidation of phosphines promoted by  $[(PPh_3)_2MO_2]$  [**2c**], few data have been reported on the oxidation of phosphines by five-membered peroxometallacycles [4].

\* Corresponding author.

In order to investigate the mechanism of this oxidation using a series of asymmetric reactions, we synthesized a chiral, diastereomerically pure, peroxometallacyclic platinum complex that was used to oxidize an asymmetric phosphine.

## 2. Results and discussion

Previously we reported the synthesis and the reactivity of the five-membered peroxometallacyclic ketenyl adduct **1** obtained by reaction of  $[(PPh_3)_2PtO_2]$  with carbon suboxide,  $C_3O_2$  [6]. This compound has features that prompted us to study the stereochemistry of the oxidation of phosphines by peroxometallacycles.



Compound **1** is reactive towards phosphines, giving the corresponding oxides [6b], and has a prochiral carbon atom  $\sigma$ -bonded to the metal that can be easily transformed into a stereogenic centre by addition of nucleophilic reagents such as water and amines to the olefinic double bond of the ketenyl moiety [6a].

The reaction of **1** with (*S*)-(-)- $\alpha$ -methylbenzylamine gives the amide derivative in the two possible diastereomeric forms. The yields of the two possible diastereomers were determined by  $^1H$  NMR spectra of the crude products, integrating the signals due to the NH protons of the two diastereomers, which were easily discernible. The reaction occurred with asymmetric induction, giving preferentially one of the diastereomers (**2a**) and the ratio between the two possible diastereomers (**2a/2b**) appeared to depend largely on reaction conditions, as shown in some examples reported in Table 1. A similar behaviour has been reported for the addition of (*S*)-(-)- $\alpha$ -methylbenzylamine to phenylmethyl ketene [7].

Crude reaction products were recrystallized from acetonitrile, giving pure diastereomer **2a**, as proved by  $^1H$  NMR spectroscopy. Attempts to obtain crystals

Table 1  
Diastereomeric ratios of **2a** and **2b** obtained under different experimental conditions

Solvent	Temperature ( $^{\circ}C$ )	Ratio <b>2a/2b</b>
$CH_2Cl_2$	-100	5
$(CH_3)_2CO$	-90	3
$CH_3CN$	-30	2.1

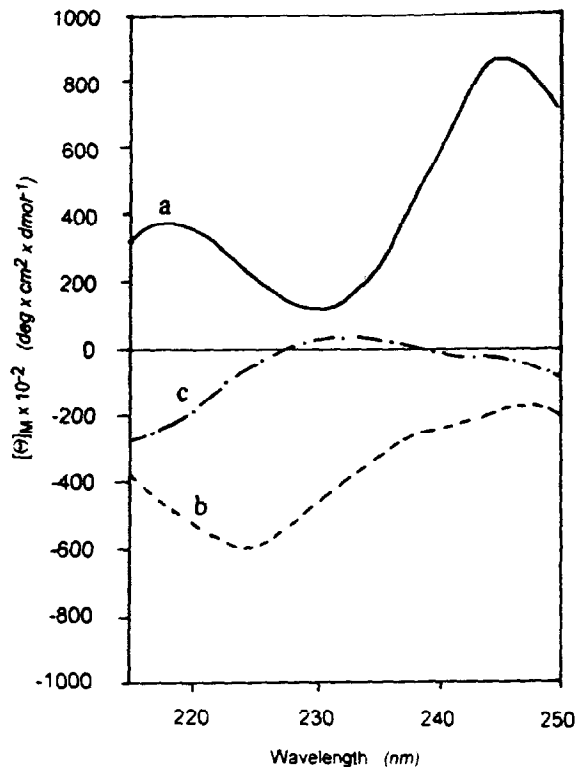
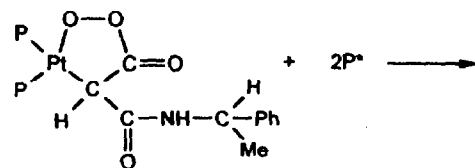


Fig. 1. CD spectra of **2a** (a), **3** (b) and of a mixture of **2a** and **2b** enriched in **2b** (molar ratio ca. 1:2) (c) in  $CH_3CN$ .

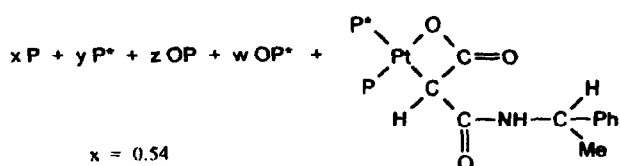
suitable for X-ray structural determination failed. Therefore we tentatively assigned the absolute configuration to **2a** by means of its CD spectrum, by comparison with the CD spectrum obtained for the complex of known configuration  $[(R, R, R)$ -(diop)PtCl{C(H)(Cl)-CO<sub>2</sub>Et}] (**3**) [8]. The UV spectrum of **2a** shows an intense band near 220 nm that can be related to a platinum-carbon  $\sigma$ -bond [9]. In Fig. 1 are the CD spectra of **2a** and **3**; they show bands of opposite sign near 220 nm, that can be related to the chirality of the carbon atom. Assuming that the asymmetric moieties  $\sigma$ -bonded to platinum of **2a** and **3** are similar enough to give rise to comparable effects in the CD spectra [10], and absolute (*S*) configuration may be attributed to the carbon bonded to platinum in **2a**.

This assignment is supported by the CD spectrum of a mixture of **2a** and **2b**, enriched in **2b**, which shows bands of opposite sign to those of pure **2a**.

Owing to our inability to obtain pure diastereomer **2b**, only **2a** was used for the oxidation reaction. The reaction of **2a** with a twofold racemic chiral phosphine PPhCyPr was followed by  $^{31}P$  NMR spectroscopy. The oxidation proceeded slowly and, as time went on, the spectra showed the presence of unreacted PPhCyPr ( $P^*$ ) and the formation of OPPhCyPr ( $OP^*$ ), free  $PPh_3$  ( $P$ ),  $OPPh_3$  ( $OP$ ). Moreover, the original doublets at +22.65 and +11.01 ppm, due to **2a**, were replaced by



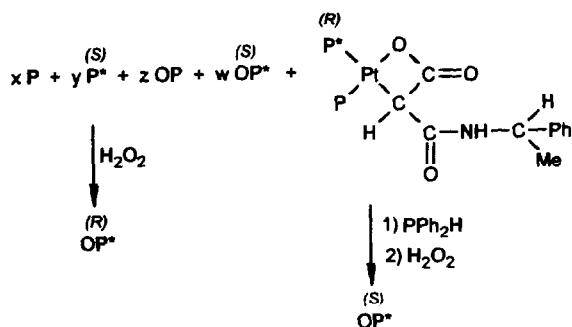
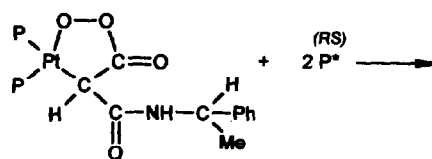
2a



$$\begin{aligned} x &= 0.54 \\ y &= 0.46 \\ z &= 0.29 \\ w &= 0.71 \end{aligned}$$

4

Scheme 1.

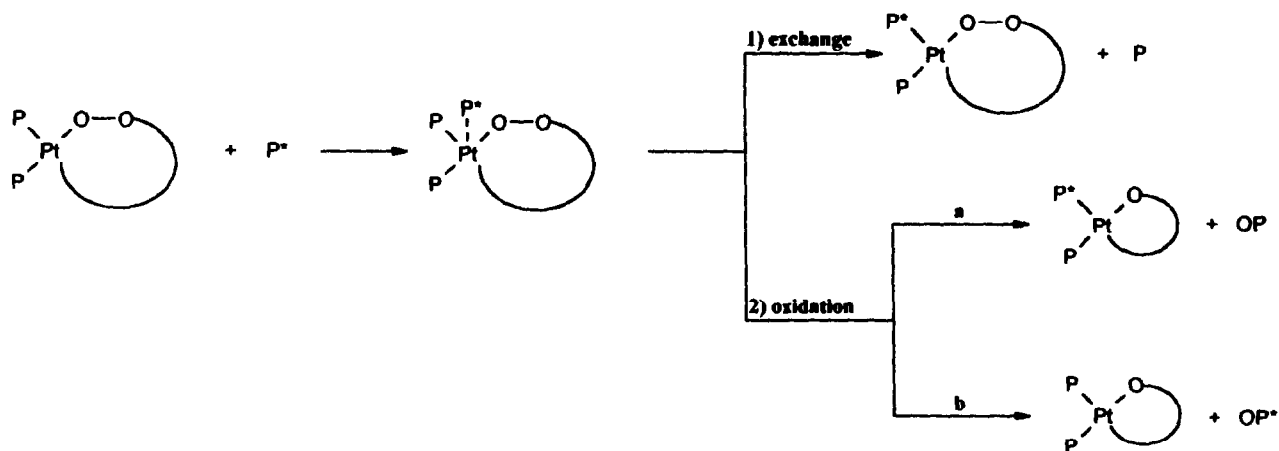


Scheme 2.

a very complex pattern, between about +19 and about +5 ppm, due to a mixture of deoxidized platinum complexes containing both phosphines, which were not further characterized. These findings show that the exchange reaction between phosphines (P and P\*) and the oxidation occurred competitively, as summarized in Scheme 1. In this scheme, 4 represents the mixture of unidentified deoxidized platinum complexes containing both P\* and P. To these complexes we assign the four-membered oxametallacyclic structure sketched in Scheme 1, likewise the structure of the related compound  $[(PPh_3)_2Pt-O-C(O)-C(H)COOH]$ , obtained by deoxygenation of 1 with  $PPh_3$  in the presence of water [6b].

The values of  $x$ ,  $y$ ,  $z$  and  $w$  (Scheme 1) were obtained by integration of the corresponding signals of the final  $^{31}P$  NMR spectrum (see Section 3).

Separation of the reaction products was achieved by evaporation of the solvent followed by extraction and chromatography. Three fractions were obtained, the first containing OP and Pt complexes 4, the second P and P\*, and the third OP\*. The optical activity of the fraction containing OP\* ( $[\alpha]_D = -1.55$ ) compared with available literature data [11] [ $(S)(-)-OP^*$ ,  $[\alpha]_D = -3.7$ ] shows that the oxidation reaction proceeded in a stereospecific way, obtaining an e.e. of  $(S)(-)-OP^*$ . These results might be confirmed by determination of the configuration of unreacted P\* contained in the second fraction, that showed a negative optical activity, but neither the value nor the sign of  $[\alpha]_D$  of P\* are given in the literature. To overcome this, we oxidized the fraction containing free P\* with  $H_2O_2$ , obtaining an excess of  $(R)(+)-OP^*$ , indicating that unreacted P\* had a predominant  $(S)$  configuration [12].



Scheme 3.

The determination of the configuration of P\* bonded to platinum in **4** further corroborated these findings. Addition of an excess of PPh<sub>2</sub>H to the fraction containing platinum complexes **4** led to a mixture of free phosphines (P, PPh<sub>2</sub>H and P\*) that were oxidized with H<sub>2</sub>O<sub>2</sub>. A mixture of phosphine oxides with a polarimetric negative sign was obtained, indicating that OP\*, the sole chiral oxide present in the mixture, had a prevalent (*S*) configuration and consequently that P\* bonded to platinum had an (*R*) configuration [12].

The results are summarized in Scheme 2, where (*R*) and (*S*) indicate the configuration of the prevalent enantiomers.

These findings indicate: (i) that the exchange reaction on platinum between P\* and P is important even in presence of the oxidation reaction; and (ii) that the coordination of P\* and the oxidation occur with asymmetric induction. Therefore, we propose a mechanism involving coordination of P\* with asymmetric induction and formation of an intermediate pentacoordinate platinum complex, which undergoes either phosphine exchange (Route 1) or phosphine oxidation (Route 2a, b) (Scheme 3).

Complex **2a** is stable both in the solid state and in solution in various organic solvents. On the other hand the addition of free phosphine, including triphenylphosphine promotes the deoxygenation of the peroxometallacyclic complex and the formation of the corresponding phosphine oxide. Therefore, the coordination of the added free phosphine to form a pentacoordinate 18-electron platinum(II) intermediate seems to be necessary to promote intramolecular attack of the nucleophilic oxygen moiety on the coordinated electrophilic phosphines, facilitating the oxidation reaction and giving rise to OP (Route 2a) or OP\* (Route 2b).

With regard to the assignment of the absolute configuration of compound **2a**, to the best of our knowledge, this is the first attempt to determine the configuration of a carbon atom  $\sigma$ -bonded to Pt using CD measurements. This technique has been used largely to assign the absolute configuration of several  $\pi$ -bonded olefin–platinum complexes [10b] and we propose to extend this method to assign the absolute configuration of a  $\sigma$ -bonded carbon atom. Obviously only a large number of other data will allow us to determine if this is possible. Work on this is in progress in our laboratory.

### 3. Experimental section

All reactions and manipulations were carried out under an atmosphere of dry argon with standard Schlenk, vacuum line, or spectrum/cannula tech-

niques. Glassware was over-dried prior to use. Solvents were purified, dried, and distilled before use. Compound **1** was synthesized as previously reported, [6] (*R, S*)-PPhCyPr was prepared following literature methods, [13] (*S*)-(-)- $\alpha$ -methylbenzylamine was purchased from EGA Chemie and used without further purification. Compound **3** [8] was kindly provided by Professor P. Bergamini.

IR spectra were obtained on a Perkin-Elmer 597 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AM 400 and <sup>31</sup>P{<sup>1</sup>H} NMR spectra on a Jeol FX 90 Q instrument and chemical shifts are quoted in  $\delta$  relative to internal TMS and to external 85% H<sub>3</sub>PO<sub>4</sub>, respectively. UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Optical activities were measured on a Perkin-Elmer 171 polarimeter and CD spectra were recorded on a Jasco J-600 apparatus. Elemental analyses were provided by the Microanalysis Laboratory of the CIMA Department of the University of Padova.

#### 3.1. Synthesis of [(PPh<sub>3</sub>)<sub>2</sub>Pt-O-C(O)-C(H)-CONH{C(H)(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>}] (**2a, b**)

Compound **1** and (*S*)-(-)- $\alpha$ -methylbenzylamine were allowed to react in various solvents at different temperatures, obtaining different diastereomeric ratios **2a**:**2b**, as reported in Table 1. In a typical reaction, to a cool solution of the amine in the chosen solvent was added an equimolecular amount of **1** with stirring. A rapid reaction, monitored by IR spectroscopy took place and after 10–15 min the solvent was removed under vacuum, giving a nearly quantitative yield of the mixture of the two diastereomers. Repeated recrystallizations of crude product, containing both diastereomers from CH<sub>3</sub>CN, gave white-yellow needles of pure diastereomer **2a**, as shown by <sup>1</sup>H NMR determination. We were unable to obtain pure diastereomer **2b**.

**2a**: m.p. 132–134°C (from CH<sub>3</sub>CN); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +60 (0.75, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Found: C, 58.75, H, 4.53, N, 1.54, C<sub>47</sub>H<sub>41</sub>O<sub>4</sub>NP<sub>2</sub>Pt calcd.: C, 59.81, H, 4.45, N, 1.52% UV (CH<sub>3</sub>CN)  $\lambda_{max}$  215 nm. IR (Nujol):  $\nu$ (NH) 3310, (C=O) 1700–1640 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, SiMe<sub>4</sub>):  $\delta$  8.11 (1H, d, *J*(HH) = 6.7 Hz, N–H); 7.51–7.21 (35 H, compl. patt., C<sub>6</sub>H<sub>5</sub>); 5.10 (1H dq, *J*(HH) = 6.8 Hz, *J*(HH) = 6.7 Hz, N–C–H); 2.59 (1H, s, *J*(PtH) = 10.8 Hz, Pt–C–H), 1.71 (3H, d, *J*(HH) = 6.8 Hz, CH<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  22.65 (d, *J*(PP) = 17.1 Hz, *J*(PtP) = 2216.8 Hz, P–Pt); 11.01 (d, *J*(PP) = 17.1 Hz, *J*(PtP) = 3720.6 Hz, P–Pt).

#### 3.2. Oxidation of the racemic phosphine PPhCyPr and determination of the configuration of products

The diastereomer **2a** (0.930 g, 0.98 mmol) was dissolved in 10 ml of CHCl<sub>3</sub> and 0.460 g of (*R, S*)-PPhCyPr

(1.96 mmol) dissolved in 4 ml of  $\text{CHCl}_3$  were added. A similar solution in  $\text{CdCl}_2$  was used to follow the course of the reaction by  $^{31}\text{P}$  NMR spectroscopy. The solutions were kept at  $25^\circ\text{C}$  and the oxidation was followed by means of the integration of the signals due to  $\text{OPPh}_3$  and  $\text{OPPhCyPr}$ . After 100 h these signals stopped increasing and the values obtained from the integration of the signals due to P ( $-5.38$  ppm),  $\text{P}^*$  ( $-11.70$  ppm), OP ( $+29.08$  ppm) and  $\text{OP}^*$  ( $+43.01$  ppm) were used to calculate  $x$ ,  $y$ ,  $z$ , and  $w$  (see Scheme 1), assuming that  $(x + y + z + w) = 2$ . The solution was evaporated to dryness and the residual solid was extracted with hexane. The solution, containing only  $\text{PPh}_3$ ,  $\text{PPhCyPr}$ , and  $\text{OPPhCyPr}$ , ( $^{31}\text{P}$  NMR) was chromatographed on  $\text{SiO}_2$  (hexane/ $\text{CH}_2\text{Cl}_2$  1:1) and the eluate showed the presence of only  $\text{PPh}_3$  and  $\text{PPhCyPr}$  in 1:1.3 ratio ( $^{31}\text{P}$  NMR). Silica containing  $\text{OPPhCyPr}$  was continuously extracted with boiling ethyl acetate for 4 h and the resulting solution was evaporated to dryness giving 0.105 g of a white solid recognized as  $\text{OPPhCyPr}$  by its  $^{31}\text{P}$  NMR spectrum in  $\text{CDCl}_3$ . The specific rotation of this solid in  $\text{C}_6\text{H}_6$  was  $[\alpha]_{\text{D}} = -1.55$ , corresponding to an excess of the enantiomer (*S*)-(-)- $\text{OPPhCyPr}$  [11]. The solution containing  $\text{PPh}_3$  and  $\text{PPhCyPr}$  was evaporated under vacuum to give 0.277 g of a gluey solid with a negative optical rotation. It was dissolved in hexane, the solution shaken with 30%  $\text{H}_2\text{O}_2$  for 2 h and the mixture was evaporated to dryness under vacuum. The  $^{31}\text{P}$  NMR spectrum of the residual solid in  $\text{CDCl}_3$  indicated the presence of only  $\text{OPPh}_3$  and  $\text{OPPhCyPr}$ . The solid dissolved in  $\text{C}_6\text{H}_6$  showed a positive optical rotation, typical of the (*R*)- $\text{OPPhCyPr}$  [11] enantiomer, indicating that the predominant configuration of unreacted  $\text{PPhCyPr}$  was (*S*) [12].

The solid containing  $\text{OPPh}_3$  and the mixture of deoxidized platinum complexes **4** was dissolved in 10 ml of  $\text{CH}_2\text{Cl}_2$  and an excess of  $\text{PPh}_2\text{H}$  was added. The solution became red and after 30 min the solvent was removed under vacuum. The residual solid was extracted with pentane and the solution which contained only  $\text{PPh}_3$ ,  $\text{PPh}_2\text{H}$  and  $\text{PPhCyPr}$  ( $^1\text{H}$  and  $^{31}\text{P}$  NMR), was shaken with 30%  $\text{H}_2\text{O}_2$  for 2 h. The mixture was evaporated to dryness under vacuum and the  $^{31}\text{P}$  NMR spectrum of the residual solid in  $\text{CDCl}_3$  showed the presence of  $\text{OPPh}_3$ ,  $\text{OPPh}_2\text{H}$  and  $\text{OPPhCyPr}$ . Polarimetric measurements in  $\text{C}_6\text{H}_6$  revealed a negative

optical rotation, due to (*S*)- $\text{OPPhCyPr}$ , [11] indicating that the predominant configuration of  $\text{PPhCyPr}$  bonded to Pt was (*R*) [12].

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