DOI: 10.1021/om100602j

ORGANOMETALLICS
Article

Steric Control in the Synthesis of Phosphinous Acid-Coordinated Mono- and Binuclear Platinum(II) Complexes

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Received June 21, 2010

Several phosphinous acid-coordinated platinum complexes were prepared and characterized. In the presence of secondary phosphine oxide (2 equiv), $PtCl_2$(cod) was converted to a series of *cis*/*trans* platinum complexes $PtCl_2[R^1R^2POH]_2$ featuring phosphinous acids (PAs) as ligands (**20**−**29**). A balance between the steric and electronic effects of ligands governs their coordination mode. NMR experiments and density functional theory calculations show that the *anti* conformer for *trans* complexes is favored by intramolecular H···Cl bonding. $PtCl_2[R^1R^2POH]_2$ treated with NEt_3 (1 equiv) gave bimetallic platinum complexes *cis*-$[Pt_2(\mu\text{-}Cl)_2\{(R^1R^2PO)_2H\}_2]$ characterized by ^{31}P NMR and X-ray diffraction. An unusual monometallic platinum complex, *cis*-$[PtCl_2\{(i\text{-}Bu)_2PO\}_2H]^-[HNEt_3]^+$ (**30**), was isolated and characterized as a possible intermediate in the formation of dinuclear species. Silver acetate and triethylamine both reacted with $PtCl_2[(t\text{-}Bu)_2POH]_2$ to yield new bulky Pt(κ^2-acetato)$\{[(t\text{-}Bu)_2PO]_2H\}$ platinum complex **31**. The structure of complexes **20d** (R^1 = Ph, R^2 = Cy), **21** (R^1 = Ph, R^2 = *t*-Bu), **21d** (R^1 = Ph, R^2 = *t*-Bu), **24** (R^1 = R^2 = *t*-Bu), **25** (R^1 = R^2 = Cy), **30** (R^1 = R^2 = *i*-Bu), and **31** (R^1 = R^2 = *t*-Bu) were determined by X-ray diffraction.

1. Introduction

The coordination chemistry of symmetrically (R^1 = R^2) and nonsymmetrically substituted ($R^1 \neq R^2$ = alkyl, aryl)[1] phosphinous acids (PAs) R^1R^2POH toward transition metal salts is of interest due to their applications in metal-catalyzed organic reactions, homogeneous catalysis,[2−12] and asymmetric catalysis using chiral enantiopure secondary phosphine oxides (SPOs).[3]

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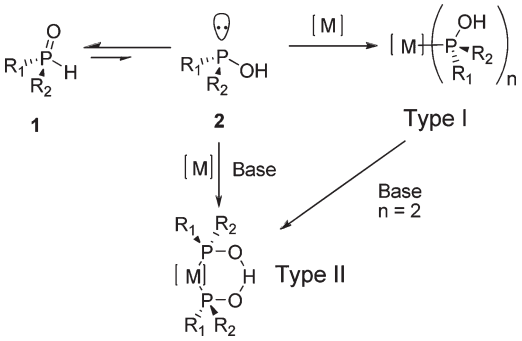
 Published on Web 08/11/2010

Scheme 1. SPOs as *L*-Type Preligands, *L* = PA



In 1968, Chatt and Heaton reported that in solution secondary phosphine oxide **1** is in equilibrium with phosphinous acid **2**. PAs are appropriate to coordinate transition metal complexes through phosphorus P(III) form (Scheme 1);[4] therefore SPOs may be considered as *L*-type preligands (Scheme 1).[3a,i] In the presence of base, type I complexes containing two PA ligands can be converted into type II complexes in which the PA and $R^1R^2PO^-$ are in a *cis* relationship and strongly linked through a hydrogen bond.[1,5] In such events, the PAs act similarly to bidentate ligands. Alternatively, type II complexes have also been prepared by treatment of R_2P-X (X = Cl,[4] R′O,[5,6] or C≡CCF$_3$[7]) with a metal salt in the presence of water.

Palladium complexes containing PA ligands have been widely studied in the past decade. These complexes, now commercially available, are highly efficient catalysts[8] in various cross-coupling reactions (Suzuki,[8d,e] Heck,[8a,f] Kumada,[8b,c] Negishi,[8d] and Stille[8e]), hydroformylation reactions,[2] and asymmetric allylic substitution.[9] Recently, Li reported that POPd complexes[10] (Figure 1) are particularly efficient catalysts in C−C, C−N,[8a,e,f] and C−S[8a,d,e] bond-forming reactions.

In contrast, very little was reported for the synthesis of similar platinum PA complexes.[11] Mononuclear complexes **3** and **4** (Figure 2) are known to catalyze hydrolysis of nitriles to amide compounds[2a,c,12,13] and hydroformylation.[2a,b,14] Recently our group reported the synthesis of dinuclear palladium complexes (PAPd) derived from SPOs and their applications as catalysts in a formal [2+1] cycloaddition between bicyclic alkenes and alkynes.[15] A similar reaction was observed with the mononuclear Pt complex **5**.[16]

Herein, we report a general study on the coordination behavior of PAs to platinum complexes and the synthesis of PA mononuclear (type I, $n = 2$), PA binuclear (type II), and κ^2-acetato PA mononuclear platinum (type II) complexes (see Scheme 1). We show that the formation of these complexes is highly dependent on the steric properties of the PAs.

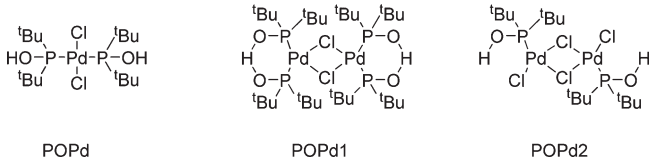


Figure 1. Li's Combiphos catalysts.

The structures of several platinum complexes have been characterized by X-ray analysis.

2. Results and Discussion

2.1. Synthesis of Secondary Phosphine Oxides. Secondary phosphine oxides are valuable intermediates in phosphorus chemistry, especially used as precursors of tertiary phosphine oxides.[17] Several preparative methods of symmetrically substituted SPOs have been developed; for instance, hydrolysis of R_2PY (Y = Cl[18] or NR′$_2$[19]), addition of Grignard reagents to dialkylphosphites,[20] reduction of phosphoryl chlorides,[18a,20a,21] oxidation of secondary phosphines,[22] or reductive cleavage of tertiary phosphine oxides[23] are among the most relevant methods. Most of the syntheses have been described in homogeneous media[24,25] and involved multistep routes. In contrast with these procedures, Li's group reported an interesting synthesis of SPOs based on the cleavage of the P−N bond of polymer-supported aminophosphines.[8f] For our purpose, the following set of SPOs was selected (Figure 3) to prepare several platinum complexes and study their coordination chemistry.

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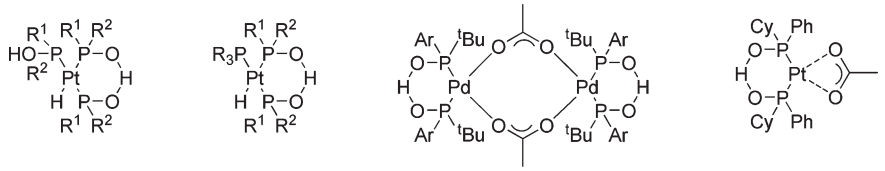


Figure 2. Phosphinous acid platinum and palladium complexes.

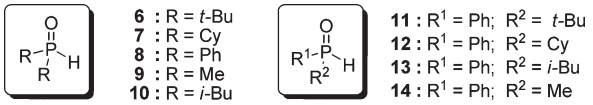
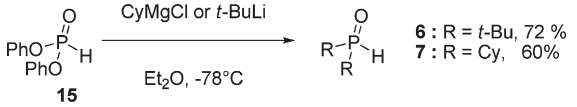
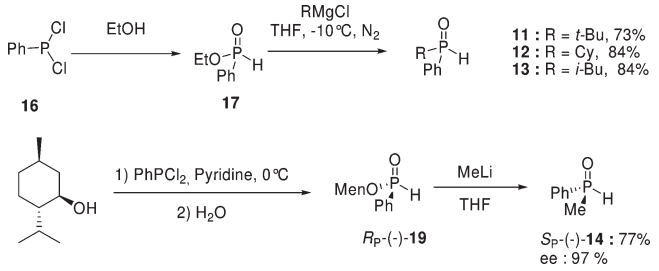


Figure 3. Selected secondary phosphine oxides.

Scheme 2. Synthesis of SPOs 6 and 7



Scheme 3. Synthesis of SPOs 11−14



Di-*tert*-butylphosphine oxide **6**, which is known to be among the best SPO preligands in metal-catalyzed cross-coupling reactions, was readily prepared by addition of *tert*-butyllithium on commercially available diphenylphosphite (Scheme 2).

Dicyclohexylphosphine oxide **7** was prepared similarly from cyclohexylmagnesium chloride. Both **6** and **7** were conveniently purified on deactivated silica (20% H_2O, 80/20 petroleum ether (PE/Et_2O) in 72% and 60% yields, respectively.

Phosphine oxides **8**, **9**, and **10** were obtained by reaction of diethylphosphite with the corresponding Grignard reagent or organolithium compounds according to established procedures.[25a]

Various methodologies are available for the synthesis of racemic SPOs.[26] Nonsymmetrically substituted SPOs R^1R^2-P(O)H **11**−**13** were prepared according to the Emmick[27] procedure from ethylphenylphosphinate **17** (Scheme 3). SPO **14** was obtained by a slight modification procedure from a mixture of (*L*)-menthylphenylphosphinate **19** diastereomers.[28] Furthermore enantiopure diastereomers **19** have been successfully used for the synthesis of enantioenriched SPO.[29]

2.2. Synthesis of Platinum Complexes. Recently, our group reported the synthesis of new monuclear platinum(II) complexes featuring κ^2 carboxylate ligands such as Pt(κ^2-acetato){$[RPhPO]_2H$} and their use as catalysts in the benzylidenecyclopropanation of norbornene derivatives.[16]

These platinum complexes were easily obtained in two steps. First, $PtCl_2$(cod) was treated with 2 equiv of RPhP(O)H in refluxing THF. The ^{31}P NMR spectrum of the crude reaction mixture revealed two sets of signals indicative of *cis* and *trans* complexes $PtCl_2[RPhPOH]_2$ as a mixture of *meso* and *dl* stereoisomers. A *cis*/*trans* mixture of $PtCl_2[RPhPOH]_2$ intermediates (**20**−**23**) obtained after evaporation of the solvent was used in the next step without further purification. Addition of AgOAc (2 equiv) at room temperature to the mixture afforded after purification by chromatography Pt(κ^2-acetato)-{$[RPhPO]_2H$} complexes (Scheme 4).

When $PtCl_2(CH_3CN)_2$ was used as the platinum source with 2 equiv of enantiopure (*R*)-(+)-*tert*-butylphenylphosphine oxide **11**, a single *trans* complex, (+)-**21**, was obtained with partial racemization.[16] Interestingly, when the reaction was carried out with $PtCl_2$(cod) at room temperature for 12 h in CH_2Cl_2, a 1:1 mixture of *cis*- and *trans*-**21** was obtained with almost no racemization.

Following these preliminary results, we have retained $PtCl_2$(cod) for the synthesis of $PtCl_2$ complexes **20** to **28**. These platinum complexes were investigated in order to establish the coordination mode of PA ligands.

2.3. PA Coordination Behavior toward Platinum Salts (^{31}P NMR Study). At the outset, we studied the coordination mode of the PA from racemic preligand **12** on the platinum center. The NMR studies of platinum complexes were performed with $PtCl_2$(cod) because of its higher solubility in most of the solvents in regard to $PtCl_2(CH_3CN)_2$ and $PtCl_2$.

A solution of racemic SPO **12** in dry DCM was added to a solution of $PtCl_2$(cod) in DCM at room temperature, and the solution mixture was warmed to 40 °C. The reaction was

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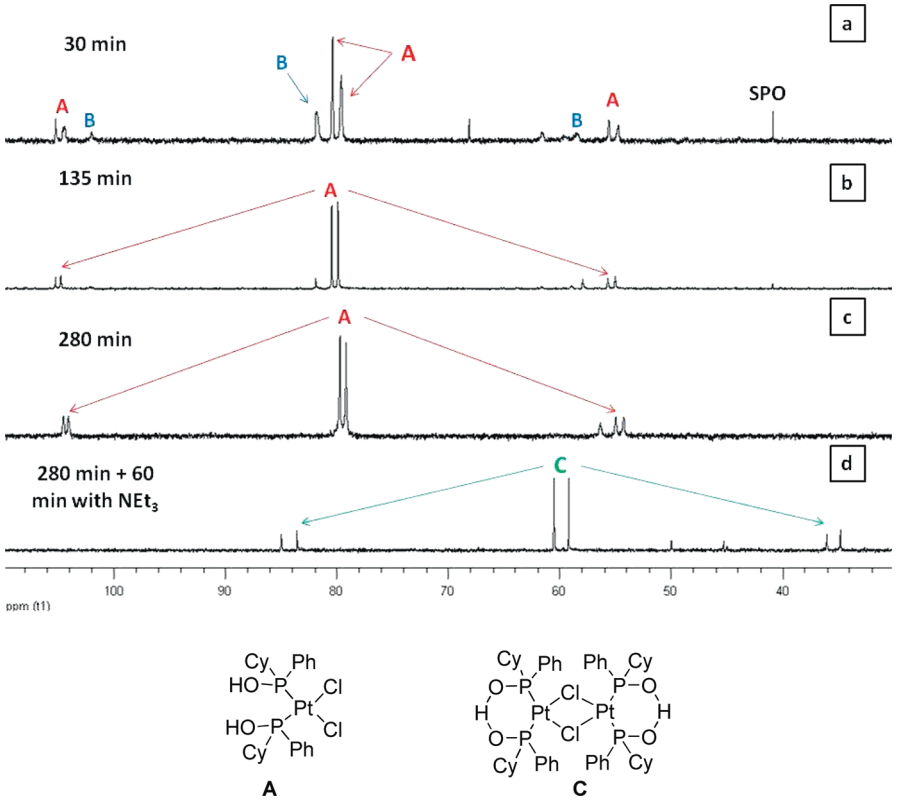
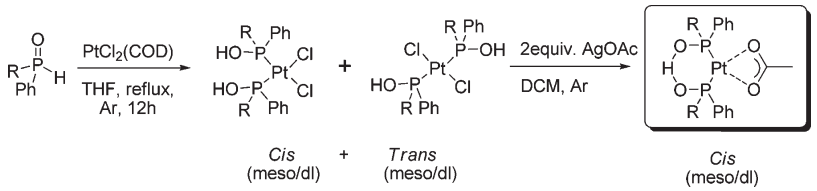


Figure 4. Progress of the reaction between $PtCl_2$(cod) and SPO **12** monitored by $^{31}P\{^1H\}$ NMR ($CDCl_3$).

Scheme 4. Synthesis of (κ^2-Acetato) Platinum Complexes



monitored by ^{31}P NMR using a capillary C_6D_6 as the external lock (Figure 4). All the spectra were obtained at room temperature and recorded after 128 scans, and the chemical shifts were not corrected. The expected $^{31}P\{^1H\}$ NMR spectrum with ^{195}Pt satellites for one diastereomer platinum complex **A** showed a centered signal and a doublet due to the J_{P-Pt}. The direct assignment *cis* and *trans* configurations is based on the *J* values between platinum and phosphorus. The *trans* complexes reveal typical values around 2500 Hz for J_{Pt-P}, whereas *cis* complexes show J_{Pt-P} values around 4000 Hz.[30]

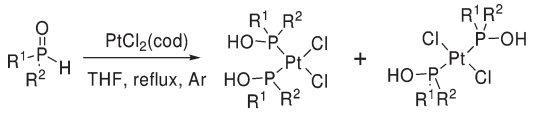
At 30 min, the formation of *cis* complex **A** as the major species was observed around 79−80 ppm as a mixture of *cis-dl* [(R_P*,R_P*)] and *cis-meso* [(R_P*,S_P*)] complexes at δ 79.6 ppm (J_{Pt-P} = 4026 Hz) and 80.4 ppm (J_{Pt-P} = 4024 Hz), respectively (Figure 4a). Uncoordinated SPO **12** (δ 40 ppm) and other platinum species (**B**) were also detected. After 135 min, the spectrum is greatly simplified, and the *cis* complex **A** was observed at 79−80 ppm with traces of both free SPO and complex **B** at δ 81 ppm (J = 3282 Hz) (Figure 4b). After 280 min, we observed a total consumption of SPO and disappearance of **B** to form exclusively the *cis* platinum complex **A** as a 1:1 mixture of *meso*/*dl* diastereomers (Figure 4c).

After 280 min, addition of NEt_3 (1 equiv) as the hydrochloride scavenger afforded a new *cis*-dimeric platinum complex **C** as a mixture of *meso* and *dl* diastereomers located at δ 59.2 and 60.5 with J_{Pt-P} values of 3965 and 3946 Hz, respectively (Figure 4d).

A mixture of SPO **12** and $PtCl_2$(cod) refluxed for 16 h in THF led to the formation of complex *cis*-**20** and dimer *cis*-**20d** in a 1.8:1 ratio. When the same reaction was conducted for 5 days, the *cis* dimer **20d** was formed exclusively. Similar results were observed when the reaction was carried out in DCM or acetonitrile. Consequently the *cis* dimer **20d** appeared to be the thermodynamic compound. It is worthwhile to note that the formation of **20d** occurred even in the absence of NEt_3, but in this case, release of HCl in the reaction media occurred with the formation of minor side phosphorus products.

(30) The structures of complexes were deduced from coupling constants between platinum and phosphorus atoms. For the *cis* isomer, the $^1J_{^{195}Pt-P}$ coupling constant is larger (≈3700 Hz) than that for the *trans* isomer (≈2500 Hz). For a ^{31}P NMR study of tertiary phosphine complexes of platinum(II), see: (a) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133. (b) Cobley, C. J.; Pringle, P. G. *Inorg. Chim. Acta* **1997**, *265*, 107. (c) Pregosin, P. S. ; Kunnz, R. W., P.; Fluck, E.; Kosfeld, R., Eds. *^{31}P and ^{13}C of Transition Metal Complexes*; Springer: New York, 1979. (d) Mather, G. G.; Pidcocok, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095. (e) Crispini, A.; Harisson, K. N.; Orpen, A. G.; Prongle, P. G.; Wheatcroft, J. R. *J. Chem. Soc., Dalton Trans.* **1996**, 1069. (f) Payne, N. C.; Stephan, D. W. *J. Organomet. Chem.* **1981**, *221*, 203.

Scheme 5. Synthesis of Mononuclear Type I *cis*, *trans* Platinum Complexes



non-symmetrical

20: R^1 = Ph; R^2 = Cy
21: R^1 = Ph; R^2 = *t*-Bu
22: R^1 = Ph; R^2 = Me
23: R^1 = Ph; R^2 = *i*-Bu

symmetrical

24: R^1 = R^2 = *t*-Bu
25: R^1 = R^2 = Cy
26: R^1 = R^2 = Ph
27: R^1 = R^2 = Me
28: R^1 = R^2 = *i*-Bu

Table 1. Synthesis of Mononuclear Platinum Complexes

entry	complex	R^1	R^2	time	*cis*/*trans*	yield
1	**24**	*t*-Bu	*t*-Bu	12	0:1[a]	>99
2	**24**	*t*-Bu	*t*-Bu	20	0:1[b]	>99
3	**25**	Cy	Cy	12	0:1	>99
4	**26**	Ph	Ph	12	1:0	>99
5	**27**	Me	Me	12	1:0	[d]
6	**28**	*i*-Bu	*i*-Bu	24	1:0	[d]
7	**20**	Ph	Cy	16	1:0	[d]
8	**21**	Ph	*t*-Bu	12	1.6:1	
9	**21**	Ph	*t*-Bu	24	0:1	>99[c]
10	**22**	Ph	Me	24	1:0	[d]
11	**23**	Ph	*i*-Bu	24	1:0	[d]

[a] *syn*/*anti*: 1:7.7. [b] Only *anti*. [c] 30% yield of *meso*-crystal. [d] Not isolated. 100% conversion was observed in all cases.

2.4. Synthesis of Mononuclear Type I Platinum Complexes. Having identified THF as the optimal solvent, the synthesis of platinum complexes coordinated to symmetrical and nonsymmetrical racemic PAs was undertaken from $PtCl_2$(cod) with SPOs preligands (2 equiv) in refluxing THF for 12−16 h (Scheme 5). The results are reported in Table 1.

SPOs **6** and **7**, with bulky alkyl groups such as *t*-Bu and Cy on the phosphorus atom, allowed the quantitative formation of mononuclear *trans* platinum complexes **24** and **25** exclusively (Table 1 entries 1, 2, and 3). The *trans* configuration for these complexes was easily deduced with ^{31}P NMR spectroscopy ($J_{Pt-P} \approx 2500$ Hz) (Figure 5) and secured by X-ray diffraction analyses (Figures 6 and 7a). Complexes **26** and **27**, with smaller groups on the phosphorus atom, were obtained exclusively in a *cis* configuration according to ^{31}P NMR data ($J_{Pt-P} \approx 4000$ Hz) (see Table 1, entries 4 and 5). These complexes were obtained in high chemical yields but contaminated with trace amounts of unreacted $PtCl_2$(cod) complex. Use of a slight excess of SPO drove the reaction to the formation of platinum complexes containing two and three phosphinous acid ligands. The coordination of the third SPO ligand onto the metal was possible thanks to the smaller size of the alkyl groups bound to the phosphorus atom.[12,14] A SPO with a medium-sized groups (such as *i*-Bu) led exclusively to the formation of *cis* complex **28**.

Phosphines bearing both alkyl and aryl groups at the phosphorus atom afforded generally *cis* complexes.[31] A similar behavior was observed for nonsymmetrical SPOs **12** (Ph, Cy), **13** (*i*-Bu, Ph), and **14** (Ph, Me), providing only *cis* complexes **20**, **23**, and **22**, respectively. In contrast, preligand SPO **11** (Ph, *t*-Bu) did not provide the *cis* complex but favored the exclusive formation of *trans* complex **21**. Indeed in this configuration, nonbonded interactions between the two bulky *t*-Bu groups on the phosphorus atoms are minimized (Figure 7b). The observed configurations of these complexes reflect the delicate balance between the electronic and steric effects. For nonsymmetrical phosphinous acid complexes, the stereochemistry of the product depends on a competition between electronic effects induced by the phenyl group and steric hindrance of the alkyl group. The formation of *cis* complexes is governed by the electronic effects of the substituents, while the predominance of steric effects of substituents led to the *trans* configuration.[31,32]

After 12 h of reaction (Table 1, entry 1), the ^{31}P NMR spectrum of **24** showed two signals with satellites at δ 109.4 and 110.3 ppm (7.7:1 ratio) (Figure 5), corresponding to *anti* (J_{Pt-P} 2409 Hz) and *syn* (J_{Pt-P} 2432 Hz) *trans* complexes, respectively. This assignment is based on NMR data reported by Mastorilli et al.[33] for the platinum complex **29** in equilibrium between *syn*/*anti* conformations (*anti*/*syn* = 1.2) (Scheme 6). These conformers showed a coupling constant of J_{Pt-P} = 2429 Hz for *syn*-**29** and J_{Pt-P} = 2421 Hz for *anti*-**29**.

DFT calculations[34] revealed no significant Gibbs energy difference between the *syn* and *anti* conformers for compound **29**, while for compound **24**, the calculated energy difference of 1.1 kcal·mol^{-1} favors the *anti* conformer.

When the reaction of $PtCl_2$(cod) with *t*-$Bu_2P(O)H$ **6** was refluxed for 20 h in THF, stereoisomer *anti*-*trans* **24** (Table 1 entry 2) was observed exclusively by ^{31}P NMR (Figure 5). Interestingly, a mixture of *syn*/*anti*-**24** after reflux led only to the thermodynamically more stable *anti* isomer. X-ray diffraction analysis showed unambiguously the *anti* conformer platinum complex **24** (Figure 6).

2.4.1. Crystal Structure of Complexes 21, 24, and 25. Suitable crystals were obtained by slow diffusion (hexane/CH_2Cl_2 solution) for complexes **24**, **21**, and **25**, which were characterized by X-ray diffraction analysis.[35] These complexes showed square-planar complexes with a platinum(II) center coordinated with two PA ligands. Unexpectedly, partial crystallization of **21** (as a diastereomeric mixture) allowed isolation of pure crystals for diastereomer (*R**,*S**)-**21** (Figure 7b).

Structural data of various *trans*-Pt(II) dichloride complexes with phosphorus ligands, provided by the Cambridge Structural Database (CSD),[36] were examined in order to

(31) Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, 1974.

(32) Crabtree, R. H. *The Organometallic Chemistry of The Transition Metals*, 4th ed.; Wiley: New York, 2009.

(33) Giannandrea, R.; Mastrorilli, P.; Palma, M.; Fanizzi, F. P.; Englert, U.; Nobile, C. F. *Eur. J. Inorg. Chem.* **2000**, *12*, 2573.

(34) DFT computations were carried out using the B3LYP functional as implemented in Gaussian. The platinum atom was described by a double-ζ basis set (SDD),[34a] and the 6-31G(d,p) basis set[34b−f] was used for the other elements. (a) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss., H. *Mol. Phys.* **1991**, *74*, 1245. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (c) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (f) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(35) The crystallographic data for complexes **21** (CCDC 771346), **24** (CCDC 771340), and **25** (CCDC 771345) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.ac.uk/data\request/cif.

(36) Cambridge Structural Database System, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Redman, J.; Willett, P.; Allen, F. H.; Taylor, R. A Citation Analysis of the Cambridge Crystallographic Data Centre. *J. Appl. Crystallogr.* **2001**, *34*, 375.

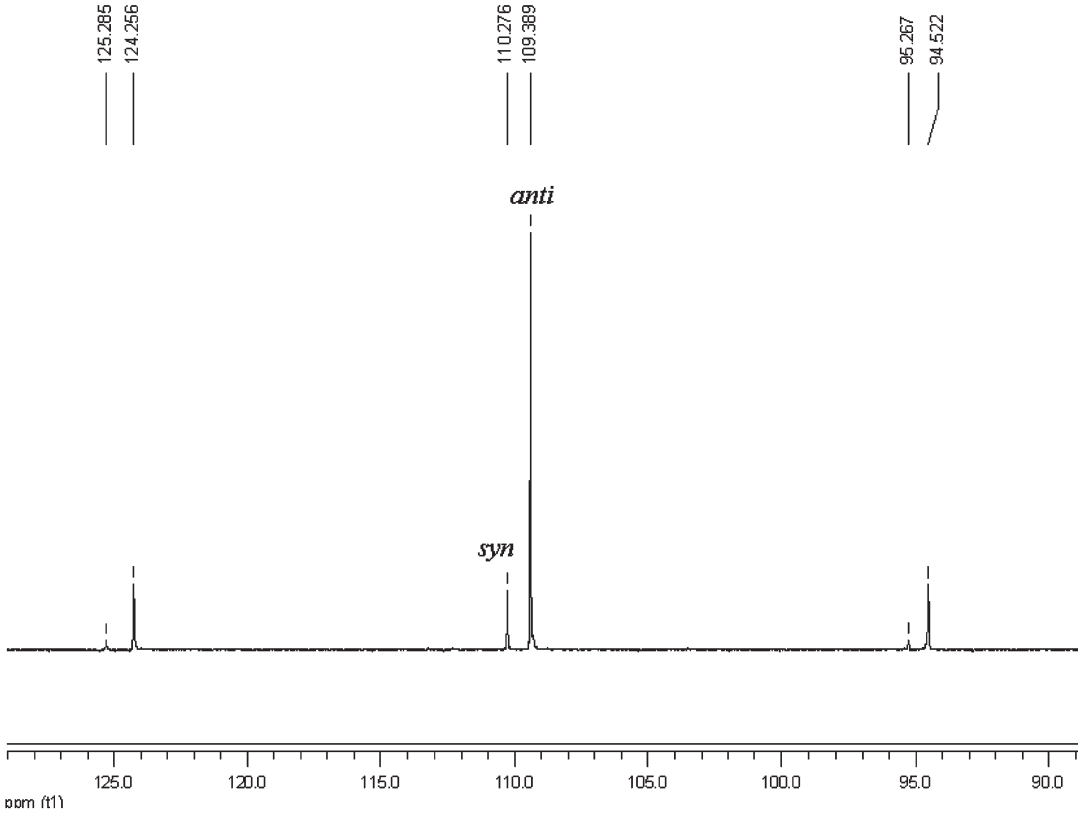


Figure 5. ^{31}P NMR ($CDCl_3$) spectra of **24**. $J_{Pt-Panti}$ = 2409 and $J_{Pt-Psyn}$ = 2432 Hz.

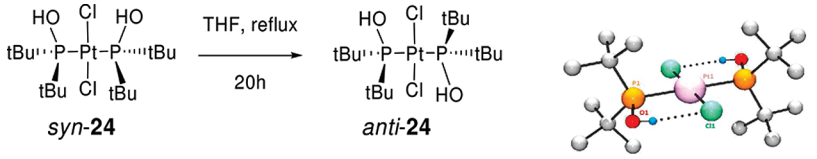
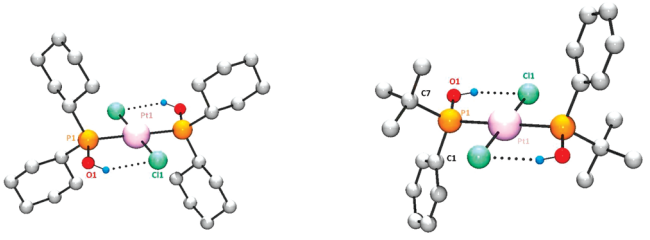


Figure 6. PLUTO representation of the X-ray crystal structure of *anti*-**24**. Most of the hydrogen atoms are omitted for clarity.



(a) Complex **25** (b) complex (R^*_P,S^*_P) **21**

Figure 7. PLUTO representation of the X-ray crystal structure of **25** and (R^*_P,S^*_P)-**21**. Most hydrogen atoms are omitted for clarity.

evaluate and compare standard Pt−P and Pt−Cl bond lengths (Figure 8a and b). The average length of the Pt−Cl bond for complexes **21**, **24**, and **25** (2.308 Å) is in agreement with values for *trans* $PtCl_2L_2$ (L = phosphorus ligand) complexes (average ≈ 2.305 Å, Figure 8a). Similarly the Pt−P bond length average (2.324 Å) is in agreement with the Pt−P average value (2.320 Å, Figure 8b) for *trans* $PtCl_2L_2$. For example, the corresponding values in several complexes containing a *trans* Cl−Pt−Cl are in the range 2.266 to 2.379 Å and 2.25 to 2.42 Å for *trans* P−Pt−P.[33,37] In platinum square-planar complexes Pt−Cl bond lengths are between 2.276(3) and 2.313(2) Å (Table 2).[38] The slightly larger P(1)−Pt−Cl(2) angles in comparison with P(1)−Pt−Cl(1) angles accommodate an intramolecular hydrogen bonding (O−H···Cl) (Table 3). These two hydrogen bonds stabilize the "spiro" structure with two five-membered rings centered on the platinum atom.

The average P−O bond lengths of 1.609 Å for these three complexes are slightly longer in comparison with

Scheme 6. *syn*/*anti* Equilibrium for Complex 29

(37) (a) Croxtall, B.; Fawcett, J.; Hope, E. G.; Stuart, A. M. *J. Chem. Soc., Dalton Trans.* **2002**, *4*, 491. (b) Giannandrea, R.; Mastrorilli, P.; Nobile, C. F. *Inorg. Chim. Acta* **1999**, *284*, 116. (c) Colbran, S. B.; Craig, D. C.; Sembiring, S. B. *Inorg. Chim. Acta* **1990**, *176*, 225. (d) Sembiring, S. B.; Colbran, S. B.; Bishop, R.; Craig, D. C.; Rae, A. D. *Inorg. Chim. Acta* **1995**, *228*, 109. (e) Aljibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, *12*, 2589. (f) Hursthouse, M. B. X-ray CSD IPOPEI from Cambridge database ; Department of Chemistry, University of Cardiff. (g) Coleman, K. S.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C. *Polyhedron* **1995**, *14*, 2107. (h) Gallo, V.; Latronico, M.; Mastrorilli, P.; Nobile, C. F.; Suranna, G. P.; Ciccarella, G.; Englert, U. *Eur. J. Inorg. Chem.* **2005**, *22*, 4607.

(38) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380.

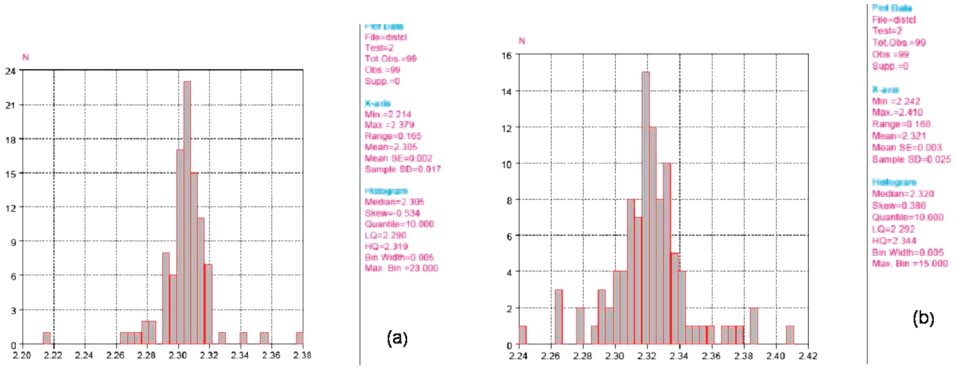


Figure 8. Histograms of Pt−Cl (a) and Pt−P (b) bond length distribution in *trans* $PtCl_2L_2$ complexes (L = phosphorus ligand) provided by CSD.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Compounds *trans*-21, 24, and 25 with Estimated Standard Deviations in Parentheses

bond	*trans*-**21**	*trans*-**24**	*trans*-**25**
Pt1−Cl1	2.3112 (14)	2.3096 (18)	2.3054 (11)
Pt−P1	2.3276 (12)	2.3379 (16)	2.3065 (10)
P1−O1	1.607(4)	1.613(5)	1.608(3)
P1−Pt−Cl1	88.23(5)	88.77(6)	89.28(4)
P1−Pt−Cl2	91.77(5)	91.22(6)	90.72(4)

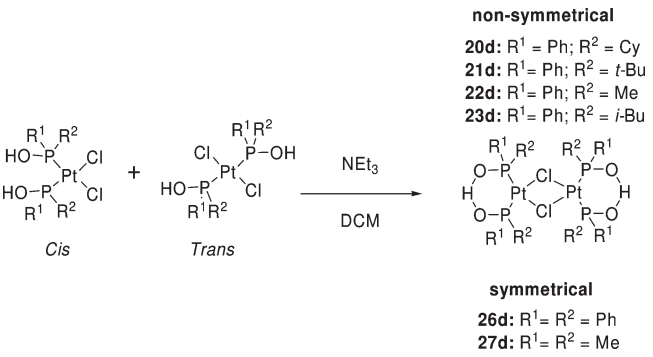
Table 3. Hydrogen Bond Lengths (Å) and Angles (deg) of 21, 24, and 25

complex	D−H···A	D−H	H···A	D···A	D−H···A
21	O1−H···Cl1	0.820	2.227	2.940	145.61
24	O1−H···Cl1	0.821	2.309	3.008	143.41
25	O1−H···Cl1	0.820	2.231	2.944	145.56

corresponding lengths in the *cis*-$[PtCl_2(Ph_2POH)_2]$ monomer complex[39a] and complexes featuring a P−O---H---O−P interaction such as *cis*-$[Pt_2(\mu\text{-}Cl)_2\{(Ph_2PO)_2H\}_2]$ (1.547 Å),[11b] $[Pd_2(\mu\text{-}SCN)_2\{(Ph_2PO)_2H\}_2]$ (1.543 Å),[7] $(Pd(S_2PMe_2)\{(Ph_2PO)_2H)]$ (1.545 Å),[40] $[Mo(CO)_4(Ph_2PO)_2H\}]^-$ (1.562 and 1.581 Å),[41] and $[Mn(CO)_4\{(Ph_2PO)_2H\}]$ (1.551 Å),[42] but fit within the normal range of P−O single bond lengths.[43] For instance, the P−O bond (1.613 Å) of complex **24** is indeed longer compared to the P═O bond (1.4819 Å) of free secondary phosphine oxide ligand **6**.[44]

The most interesting structural feature of *trans* complexes concerns the hydrogen bonding involving P−O−H groups, which account for their stabilization. Previous observations reported by Berry et al.[39a] on the *cis*-$[PtCl_2(Ph_2POH)_2]$THF complex showed an intramolecular hydrogen bond with a chlorine atom (OH---Cl = 2.148 Å) and an intermolecular H-bond involving the oxygen atom of tetrahydrofuran (OH---O = 1.902 Å). For structures **21**, **24**, and **25** two similar intramolecular hydrogen bonds with chlorine atoms (O−H···Cl range 2.94−3.00 Å, Table 3) were observed. These values are in agreement with a wide range of O−H···Cl hydrogen bonds (2.86−3.21 Å) reported by Stout and Jensen.[45]

Scheme 7. Synthesis of Dinuclear Platinum Complexes



2.5. Dinuclear Platinum Type II Chloro-Bridged Complexes. Treatment of a mixture of *cis* and/or *trans* $(PA)_2PtCl_2$ with triethylamine generates cleanly dinuclear complexes **20d**−**23d** and **26d**,**27d** (Scheme 7). ^{31}P NMR of these complexes revealed signals ranging from 53 to 65 ppm (Table 4) characteristic of *cis* dimer platinum structures. Although different diastereomeric complexes[46] could be formed from racemic SPOs, only *meso* and *dl* complexes are observed.

2.5.1. X-ray Crystal Structure of *meso*-[(*R$_P$,*S**$_P$),(*R**$_P$, *S**$_P$)]-20d.** Complex *cis*-**20d** derived from SPO **12** was purified by column chromatography (64%) and obtained as a bright yellow solid (Scheme 7). Upon recrystallization from petroleum ether and diethyl ether, suitable crystals of *meso*-**20d** were obtained for an X-ray analysis (Figure 9).[47] Selected bond lengths and angles are given in Table 5.

The achiral complex is essentially planar and displays an inversion center; the short distance between the two oxygen atoms [O1···O2 (2.373 Å)] suggested a strong and

(39) (a) Berry, D. E.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Can. J. Chem. Soc.* **1985**, *63*, 2949. (b) Han, L. B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259. (c) Van Leeuwen, P.; Roobeek, C. F.; Orpen, A. G. *Organometallics* **1990**, *9*, 2179. (d) Fornies, J.; Gomez, J.; Lalinde, E.; Moreno, M. T. *Inorg. Chim. Acta* **2003**, *347*, 145. (e) Browning, C. S.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1995**, *12*, 2005.

(40) Cornock, M. C.; Gould, R. O.; Jones, L.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, *13*, 1307.

(41) Cotton, F. A.; Falvello, L. R.; Tomas, M.; Gray, G. M.; Kraihanzel, C. S. *Inorg. Chim. Acta* **1984**, *82*, 129.

(42) Fawzi, R.; Hiller, W.; Lorenz, I. P.; Mohyla, J.; Zeiher, C. *J. Organomet. Chem.* **1984**, *262*, C43.

(43) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam. 1974.

(44) Dornhaus, F.; Lerner, H.-W.; Bolte, M. *Acta Crystallogr. Sect. E* **2005**, *61*, o657.

(45) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination, a Practical Guide*, 2nd ed.; MacMillan: New York, 1968; p 303.

(46) Five diastereomeric dimer complexes could be expected from one racemic SPO: (*R**,*R**)(*R**,*R**); (*R**,*R**)(*S**,*S**); (*R**,*R**)(*S**,*R**); (*R**,*S**)(*R**,*S**); (*R**,*S**)(*S**,*R**).

(47) The crystallographic data for complex **20d** (CCDC 771342) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.ac.uk/data\request/cif.

Table 4. NMR Spectral Data of Platinum Complexes

entry	R^1	R^2	*trans*	*cis*	dimer
1	*t*-Bu	*t*-Bu	109.2 (J = 2409 Hz)[a]	no	no
2	Cy	Cy	107.2 (J = 2482 Hz)[a]	no	no
3	Me	Me	no	73.7 (J = 3970 Hz)[b]	54.3 (J = 3884 Hz)[a]
4	Ph	Ph	no	70.9 (J = 4066 Hz)[a]	53.5 (J = 4002 Hz)[c]
5	*i*-Bu	*i*-Bu	no	88.9 (J = 3960 Hz)[c]	no
6	*t*-Bu	Ph	87.8 (J = 2493 Hz)[a]	no	61.4 (J = 3982 Hz)[c]
			87.0 (J = 2491 Hz)[a]		63.1 (J = 3982 Hz)[c]
7[e]	*t*-Bu*	Ph*	87.8 (J = 2492 Hz)[a]	84.9 (J = 4008 Hz)[a]	65.0 (J = 4000 Hz)[a]
8	Cy	Ph	90.9 (J = 2557 Hz)[d]	77.3 (J = 4007 Hz)[c]	58.9 (J = 3961 Hz)[a]
			90.6 (J = 2557 Hz)[d]	74.8 (J = 3984 Hz)[c]	57.5 (J = 3938 Hz)[a]
9	Me	Ph	86.1−85.8 [b]	69.9 (J = 3985 Hz) [b]	51.6 (J = 3939 Hz) [c]
				68.9 (J = 3974 Hz)[b]	50.5 (J = 3919 Hz) [c]
10	*i*-Bu	Ph	no	75.9 (J = 4021 Hz)[c]	55.5 (J = 3953 Hz)[c]
				74.8 (J = 4008 Hz[c]	54.5 (J = 3928 Hz)[c]

[a] $CDCl_3$. [b] ^{31}P NMR of platinum complexes recorded on a reaction mixture using a C_6D_6 capillary as external reference in THF. [c] In DCM. [d] In CH_3CN. [e] Complexes with (*S*)-(−)-*tert*-butylphenylphosphine oxide.

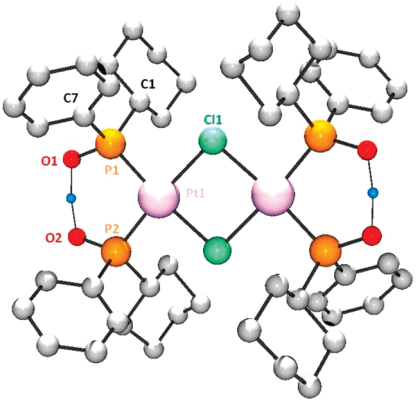


Figure 9. Molecular structure of *meso*-[(R^*_P,S^*_P),(R^*_P,S^*_P)]-**20d** (PLUTO representation). Most of the hydrogen atoms are omitted for clarity.

symmetrical H−O−H bonding.[7] The X-ray structure of the *cis*-[$Pt_2(\mu\text{-}Cl)_2\{(Ph_2PO)_2H\}_2$][11b] complex reported by Bergamini et al. showed intramolecular hydrogen bonds (2.415 Å) comparable to our complex **20d**. To our best knowledge, this X-ray structure provided a rare example of bridged-chlorine nonsymmetrical-PA bis-platinum complexes. They belong to the class of negative-charge-assisted H-bonds [(−)CAHB][48] in which the negative charge spreads out between two oxygen atoms $(O-H\cdots O)^-$. Accordingly, all P−O bonds lengths are of similar values [in the range 1.527(7)−1.549(6) Å][43] and significantly longer compared to P═O distances [1.48−1.50 Å].[49] The Cl(1)−Pt−P(2) and Cl(2)−Pt−P(1) bond angle values of 174.8° and 174.2°, respectively, showed a slight tetrahedral distortion.

The two platinum centers located in square-planar structures are separated by 3.669 Å, and the Pt−Cl bond length average of 2.4335 Å is usual for a chlorine-bridged dinuclear complex without metal−metal interaction.[50] The Pt−P bond length average (2.2295 Å) is consistent with the low *trans* influence of chlorine, and the observed pincer P−O---H---O−P "bidentate" ligand is in accord with analogous structures.[11b,39]

Table 5. Selected Bonds Lengths [Å] and Angles [deg] for *meso*-20d with Estimated Standard Deviations in Parentheses

Pt1−Cl1	2.436(2)	P2−C13	1.839(12)
Pt1−Cl2	2.431(2)	P2−C19	1.812(8)
Pt−P1	2.233(2)	Cl1−Pt1−Cl2	82.16(8)
Pt−P2	2.226(2)	Cl1−Pt1−P1	92.09(8)
P1−O1	1.549(6)	Cl1−Pt1−P2	174.86(8)
P2−O2	1.527(7)	Cl2−Pt1−P1	174.21(8)
P1−C1	1.792(11)	Cl2−Pt1−P2	92.81(8)
P1−C7	1.833(7)	P1−Pt1−P2	92.96(9)
		Hydrogen Bonds	
O1···O2	2.373		

2.5.2. Synthesis and X-ray Crystal Structure of Chiral [(R_P,R_P),(R_P,R_P)]-21d. On mixing $PtCl_2$(cod) and (*S*)-(−)-*tert*-butylphenylphosphine oxide (*S*)-(−)-**11**[51] in dichloromethane at room temperature to prevent racemization, complex **21d** type I was formed as a 1:1 mixture of *cis* and *trans* isomers.[16] It is worth noting that coordination of the chiral *t*-Bu(Ph)POH to the metal proceeds with retention of configuration. On treatment with triethylamine, dinuclear platinum complex [(R_P,R_P),(R_P,R_P)]-**21d** was obtained and purified by column chromatography (50% yield) without loss of configuration on the phosphorus atom. Suitable crystals were obtained for an X-ray analysis (Figure 10).[52] Selected bond lengths and angles are given in Table 6.

This structure is similar to those observed for complex *meso*-**20d** (Figure 9), but in this case complex **21d** has approximate C_2 symmetry and the two O−P−P−O planes are slightly distorted, as observed with two pincer dihedral angle (O1−P1−P2−O2 and O3−P3−P4−O4) values of 9° and −5°, respectively.

A small dissymmetry for this complex induced by different strengths of the two hydrogen bonds was observed. Indeed, the distance O3−O4 (2.189 Å) is shorter compared to the O1−O2 distance (2.227 Å). The distance between the two chlorine atoms (3.085 Å) was found shorter compared to the one observed for complex **20d** (3.198 Å). Bond lengths Pt−Cl (average ≈ 2.4 Å) and Pt−P (average ≈ 2.3 Å) are in accord with chlorine-bridged dinuclear platinum complexes. The

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(50) The Pt−Pt bond length average determined for 66 error-free data from CSD[38] is equal to 2.633 Å.
(51) NMR analyses became easier by monitoring the reaction with enantiopure **11**. For the enantioselective synthesis of SPOs, see ref 28b.
(52) The crystallographic data for complex **21d** (CCDC 771341) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.ac.uk/data\request/cif.

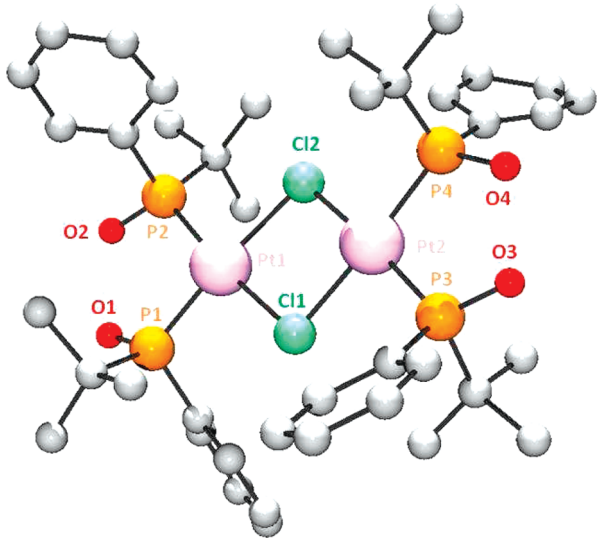

Figure 10. Molecular structure of [(R_P,R_P),(R_P,R_P)]-**21d** (PLUTO representation). All hydrogen atoms are omitted for clarity.

Table 6. Selected Bonds Lengths [Å] and Angles [deg] for Compound [(R_P,R_P),(R_P,R_P)]-21d with Estimated Standard Deviations in Parentheses

Pt1−Cl1	2.443(5)	P3−O3	1.598(4)
Pt1−Cl2	2.424(2)	P4−O4	1.663(6)
Pt2−Cl1	2.403(5)	Cl1−Pt1−Cl2	78.67(10)
Pt2−Cl2	2.285(2)	Cl1−Pt2−Cl2	82.27(10)
Pt1−P1	2.237(8)	Cl1−Pt1−P2	173.7(9)
Pt1−P2	2.283(5)	Cl1−Pt2−P3	92.17(10)
Pt2−P3	2.281(5)	Cl2−Pt1−P1	172.9(9)
Pt2−P4	2.245(2)	Cl2−Pt1−P4	94.10(11)
P1−O1	1.539(6)	P1−Pt1−P2	92.04(8)
P2−O2	1.499(4)	P3−Pt2−P4	92.37(9)
Hydrogen Bonds			
O1···O2	2.227	O3···O4	2.189

Cl(1)−Pt1−P(2) and Cl(2)−Pt1−P(1) bond angle values of 173.7° and 172.9° respectively (Table 6), showed a slightly tetrahedral distortion.

2.6. Preparation and X-ray Crystal Structure of Platinum Complex 30. Attempts to prepare complex **28d** from **28** according to the established procedure as described for complex **21d** proved to be unsuccessful; instead the new *cis* complex **30** (δ 63.9 ppm, J_{Pt-P} = 3974 Hz) was obtained in 51% yield after purification on column chromatography (Scheme 8). The structure of **30** resolved by X-ray analysis showed unusual features.[53]

Complex **30** (Figure 11) consists of a slightly distorted square-planar structure centered on a platinum atom (Cl−Pt−P angle ≈ 176°, Table 7). The Pt−C1 bond length average of 2.394(3) Å is slightly elongated compared to several complexes containing a *trans* Cl−Pt−P fragment (typical values ranging from 2.333 to 2.366 Å). In contrast, the Pt−P bond length average of 2.222 Å is shorter compared with those in *cis*-$PtCl_2L_2$ complexes (typical values ranging from 2.241 to 2.262 Å).[54] The P−O bond length average (1.54 Å) fits with the usual value range in complexes featuring a P−O···H···O−P[7,11b,40−43] pincer and for complex **20d** (Table 5).

An interesting feature of the X-ray structure of **30** is the association of the *cis* complex with the triethylammonium ion through hydrogen bonding (see packing in Figure 12). Henderson et al. reported an X-ray structure of platinum thiosalicylate $[(PPh_3)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ that revealed hydrogen bonding between the NH proton and the carbonyl group of the thiosalicylate ligand.[55] In solution, the ^{1}H NMR spectrum of complex **30** revealed resonances due to the dissociated triethylammonium cation.

It is now established that C−H···O bonds determine crystal packing especially if stronger hydrogen bonding is not observed.[56,57]

In complex **30**, the two ions are bound by three different hydrogen bonds: NH···Cl,[58] CH···O, and CH···Cl. The cell unit (see packing in Figure 12) is composed of four *cis* complexes and four $[NHEt_3]^+$ in which the $[NHEt_3]^+$ ion interacts with three different Pt complexes. The first *cis* complex binds to the triethylammonium ion with two CH···O−P hydrogen bonds, the second one with a C−H···Cl−Pt hydrogen bond, and the third one with a N−H···Cl−Pt hydrogen bond interaction. The two chlorine atoms of the first complex are involved in two intermolecular hydrogen bonds with two different $[NHEt_3]^+$.

Orpen et al. reported different types of M−Cl···H hydrogen bonds for neutral and ionic chlorine, classified as "short" (≤2.52 Å), intermediate (2.52−2.95 Å), and long interactions (2.95−3.15 Å) (values based on the sum of van der Waals radii for H and Cl: 1.20 + 1.75 = 2.95 Å).[59] The C−H···Cl−M bond interactions are well established and importantly represent connections in supramolecular chemistry.[59,60] The Pt−Cl···H−N distance between the proton of $[NHEt_3]^+$ and the chlorine atom (2.299 Å) highlights intermolecular bond interactions as "strong" hydrogen bonds.

The shortness of the NH···Cl−Pt bond in complex **30** (Table 7) presumably derives in part from the large negative charge on the chlorine atom in this partially ionic bond involving the cationic nitrogen. This ionic bond character, in agreement with the longer Pt−Cl(1) length observed (2.398 Å) compared with Pt−Cl(2) (2.390 Å), suggested that the chlorine atom is involved in a weaker CH···Cl bond. Moreover, the distance between nitrogen and chlorine atoms (3.179 Å) is in agreement with typical distances N···Cl (2.91−3.52 Å).[61]

The CH···Cl hydrogen bond is generally weak due to the poor acidity of the hydrogen in saturated carbon atoms. Usually, strong hydrogen bonding has been reported when chloride ions

(53) The crystallographic data for complexes **30** (CCDC 771343) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.ac.uk/data\request/cif.

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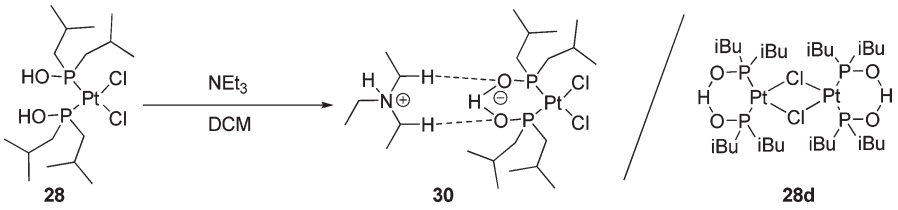
Scheme 8. Synthesis of *cis* Platinum Complex 30



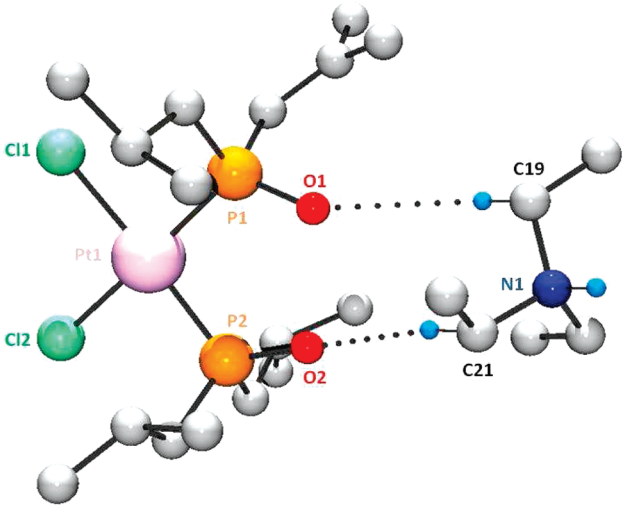


Figure 11. Molecular structure of complex **30** (PLUTO representation). Most hydrogen atoms are omitted for clarity.

are involved rather than covalently bonded chlorine.[62] The distance of 3.685 Å between C(17)···Cl in complex **30** is typical of such interactions.[60,63] Intermolecular interactions of chlorine bonded to a metal atom[62b,63a] with a saturated carbon such as C···Cl−Pt (3.582−3.852 Å)[64] and C···Cl−Pd (3.523−3.783 Å)[65] have been reported.

The third kind of hydrogen bond, which involved a C−H---O interaction,[61,66] is well established.[62a,67] These interactions are not restricted to small molecules but have also been reported for biological systems such as proteins,[68] nucleic acids,[69] and carbohydrates.[70] Moreover,

Table 7. Selected Bonds Lengths [Å] and Angles [deg] for Complex 30 with Estimated Standard Deviations in Parentheses

Pt1−Cl1	2.398(3)	N1−C17	1.473(17)
Pt1−Cl2	2.390(3)	N1−C19	1.493(17)
Pt−P1	2.222(3)	N1−C21	1.485(17)
Pt−P2	2.222(2)	Cl1−Pt1−Cl2	88.99(11)
P1−O1	1.542(8)	Cl1−Pt1−P1	89.02(11)
P2−O2	1.553(8)	Cl1−Pt1−P2	176.96(11)
P1−C1	1.798(18)	Cl2−Pt1−P1	176.35(11)
P1−C5	1.818(14)	Cl2−Pt1−P2	87.97(11)
P2−C9	1.813(15)	P1−Pt1−P2	94.01(11)
P2−C13	1.816(15)	Pt1−P1−O1	116.9(3)
		Pt1−P2−O2	116.6(3)

Hydrogen Bonds

D−H···A	D−H	H···A	D···A	D−H···A
C19−H···O1	0.970	2.718	3.515	139.83
C21−H···O2	0.972	2.517	3.476	169.28
C17−H···Cl2[a]	0.971	2.790	3.685	153.75
N1−H···Cl1[a]	0.910	2.299	3.179	167.77
O1···O2			2.396	

[a] Chlorine from a second molecule of the Pt complex.

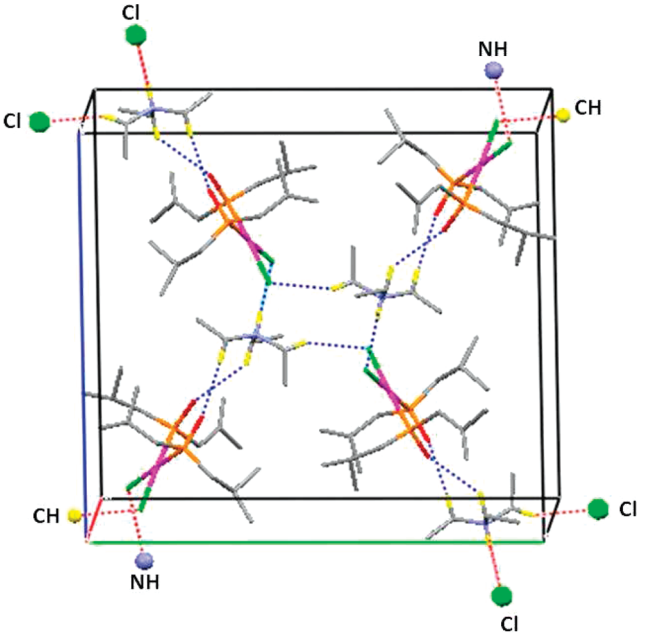


Figure 12. View of packing for complex **30** and some bonding interactions in the crystal structure. Only hydrogen atoms involved in H bonding are represented, in yellow.

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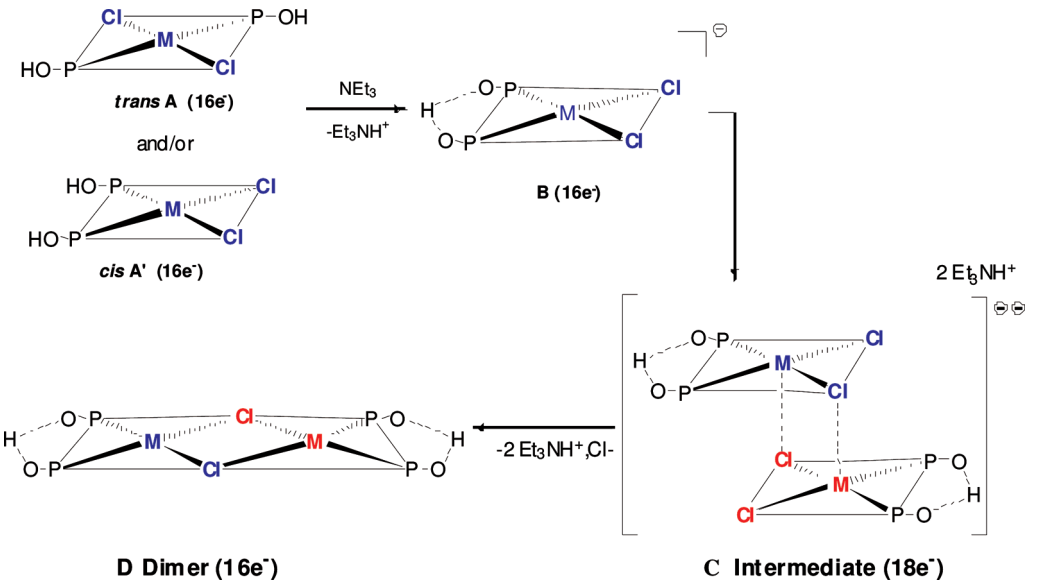
Scheme 9. Proposed Pathway for the Formation of Dimer D[a]



[a] Substituents at phosphorus atoms are omitted for clarity.

these interactions can persist in liquid phase.[71] The intermolecular CH···O distance average (3.495 Å) found in structure **30** fits in the range of such interactions.[65a,72]

2.7. Proposed Mechanism of the Dimer Formation. The formation of the binuclear chloro-bridged complex **D** might be explained by an associative/dissociative mechanism (Scheme 9). This may involve an 18*e* dimer bridged intermediate **C** followed by loss of a chloride anion to afford the neutral 16*e* chloro-bridged product **D**.

As shown previously, the stereochemistry of the initial complex depends on the bulkiness of attached groups on the phosphorus atom. Bulky substituents such as *t*-Bu groups at the phosphorus atom gave the stable thermodynamic *trans* complex **A**, unreactive toward triethylamine. Less bulky groups such as Me gave *cis* complexes **A′**, prone to form complex **B** in the presence of base. Small and bulky groups at the phosphorus atom, such as Ph/*t*-Bu and Ph/Cy, gave either *cis* and *trans* complexes **A′** and **A**. This suggested a *trans* to *cis* isomerization prior to the formation of complex **B**. Then **B** might evolve to dimer **D** through intermediate **C** stabilized by halogen−metal bond interactions. Surprisingly, a bulkier group such as *i*-Bu at the phosphorus atom compared to a small group such as Me did not allow the formation of complex **D**. Indeed, treatment of **A** with NEt_3 afforded only an unusual complex, **30**. In this case, apical coordination sites at the metal center would be less accessible due to the steric hindrance of the *i*-Bu groups (Figure 13).

In summary, the course of the reaction highly depended on the steric hindrance at the phosphorus atom. Less bulky groups such as Me, *i*-Pr, Cy, or Ph drive the reaction to the dimer probably through "intermediate **C**". Indeed, moderately bulky groups (*i*-Bu) allow the reaction to give *cis* complex **B**, which upon treatment with triethylamine remains intact. This ruled out an unstable 14*e* intermediate by dissociation of a chloride ligand and subsequent dimerization to form **D**.

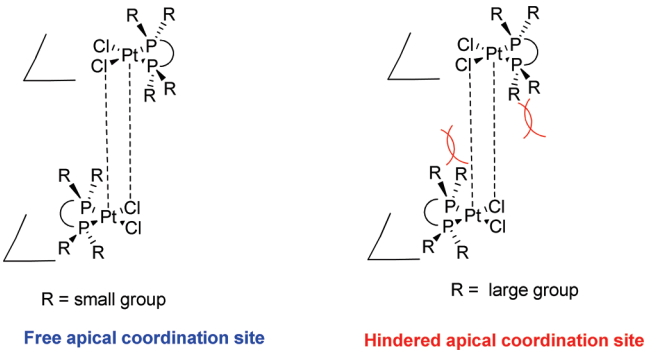


Figure 13. Intermediate **C** platinum complexes.

2.8. Synthesis of Complex Pt(κ^2-acetato){[(*t*-Bu)$_2$PO]$_2$H}, 31. Previously we reported the synthesis of a new class of platinum complexes, Pt(κ^2-acetato){[RPhPO]$_2$H}, featuring the unusual κ^2-acetato ligand with interesting catalytic applications.[16] We wished to extend this class of complexes to the bulky SPO (*t*-Bu)$_2$P(O)H **6** with the aim of accessing more promising catalysts.

Treatment of **24** with silver acetate in dry dichloromethane as described for the synthesis of complex **5** did not provide the desired κ^2-(acetato) platinum complex, instead *trans* $PtCl_2$ complex **24** was totally recovered (Scheme 10). A similar behavior was observed with treatment of complex *trans*-**24** with NEt_3.

Treatment of $PtCl_2$ with 2 equiv of (*t*-Bu)$_2$P(O)H **6** in refluxing DCM for 20 h led to a mixture of various platinum complexes (see spectrum in Figure 14a). ^{31}P NMR of the crude mixture (**a**) showed the presence of *cis* (101.7 ppm, J_{Pt-P} = 3952 Hz) and *trans* complexes **24** in a 15:1 molar

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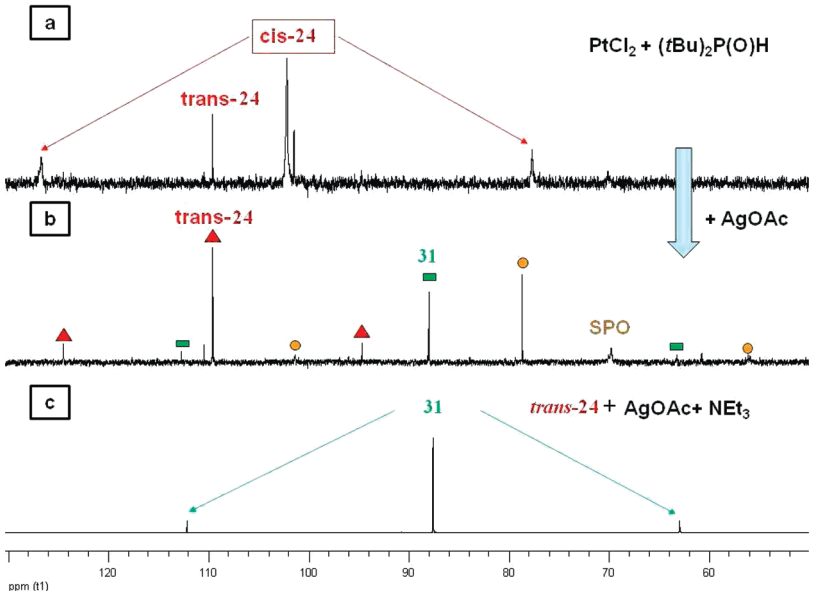
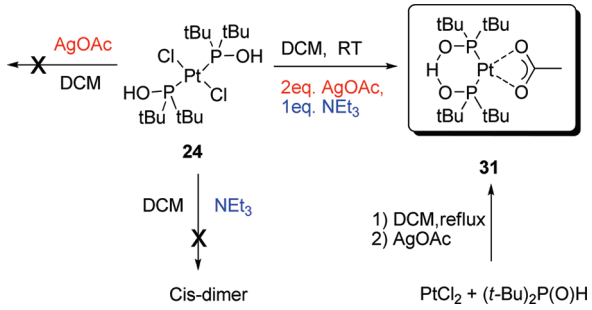


Figure 14. ^{31}P NMR spectra of platinum species derived from platinum and $(t\text{-Bu})_2$P(O)H .

Scheme 10. Synthesis of (κ^2-Acetato) Platinum Complex 31



ratio, respectively. Previously we have shown that preparation of only the *trans* complex was achieved from $PtCl_2$(cod) in THF solution. Addition of AgOAc (2 equiv) to the crude mixture afforded a brown-yellow solution. The ^{31}P NMR spectrum (Figure 14b) showed a complex mixture containing *trans* complex **24** and two new *cis* complexes at δ 87.9 (J_{Pt-P} = 3992 Hz) and 78.6 (J_{Pt-P} = 3665 Hz) in a 1.35:1:1.9 ratio, respectively.[73] One of these complexes proved to be the desired κ^2-acetato complex **31** (see below). Trace amounts of *cis* complex **24** and uncoordinated SPO **6** were also detected. *Trans* complex **24**, observed when the reaction is over, arises presumably from *cis* to *trans* isomerization induced by a small amount of free SPO.[74] Attempted separations of products by column chromatography on silica or Fluorisil were unsuccessful.

At this stage, a protocol to the *cis* configuration that required inducing the formation of the desired κ^2-acetato platinum complex **31** was achieved. Treatment of *trans* complex **24** with both AgOAc (2 equiv) and NEt_3 (1 equiv) in DCM at room temperature for 12 h afforded straightforwardly κ^2-acetato complex **31** (Scheme 10 and Figure 14c) with complete conversion. Purification by column chromatography on silica afforded **31** (90%) as a red-orange solid. ^{1}H NMR

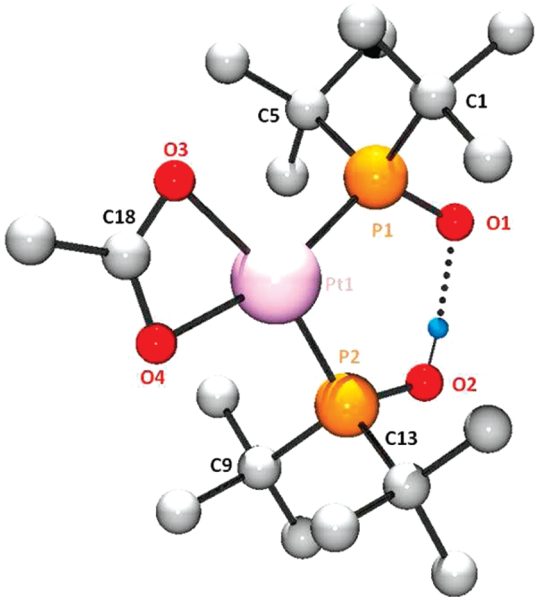


Figure 15. Molecular structure of **31** (PLUTO representation).

confirmed the presence of the acetato group with a singlet at δ 1.95 ppm. High-resolution mass spectrometry data [$C_{19}H_{40}O_4P_2Pt$ (M + H)$^+$: 578.2124] supported the monomeric structure for complex **31**. ^{31}P NMR revealed that *cis* complex **31** (87.5 ppm, J = 3988 Hz) (Figure 14c) was also observed as a byproduct when the reaction was conducted with $PtCl_2$ (Figure 14b).

2.9. X-ray Structure of Complex Pt(κ^2-acetato){[(*t*-Bu)$_2$-PO]$_2$H} 31. X-ray analysis showed unambiguously the monomeric form of **31** and an acetate group in κ^2-coordination mode (Figure 15).[75] The complex is essentially planar with an approximate C_2 symmetry; the short distance between the two oxygen atoms [O1···O2 (2.399 Å)] suggested a strong and symmetrical O−H−O bonding. We previously reported

(73) The first *cis* species is complex **31**, and the second one might be an intermediate such as [{$(R_1R_2PO)_2H$}PtCl(η^1-OAc)].

(74) (a) Louw, W. J. *Inorg. Chem.* **1977**, *16*, 2147. (b) Roulet, R.; Barbey, C. *Helv. Chim. Acta* **1973**, *56*, 2179.

(75) The crystallographic data for complexes **31** (CCDC 771344) have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.ac.uk/data \request/cif. We observed a cocrystallization between two molecules of **31** having slightly different bond lengths; see Supporting Information.

Table 8. Selected Bonds Lengths [Å] and Angles [deg] for Compound 31 with Estimated Standard Deviations in Parentheses

Pt1−O3	2.170(3)	O3−C17	1.256(17)
Pt1−O4	2.168(3)	O4−C17	1.275(17)
Pt−P1	2.241(3)	C17−C18	1.485(17)
Pt−P2	2.237(2)	O3−Pt1−O4	60.10(11)
P1−O1	1.543(8)	O3−C17−O4	118.19(11)
P2−O2	1.540(8)	P1−Pt1−P2	93.32(11)
P1−C1	1.857(18)	Pt1−P1−O1	116.97(3)
P1−C5	1.876(14)	Pt1−P2−O2	116.75(3)
P2−C9	1.884(15)	P1−Pt1−P2	93.32(11)
P2−C13	1.858(15)		

Hydrogen Bonds

D−H···A	D−H	H···A	D···A	D−H···A
C3−H···O3	0.961	2.463	3.300	145.46
C7−H···O3	0.961	2.587	3.396	141.84
C12−H···O4	0.960	2.430	3.335	156.74
C16−H···O4	0.961	2.797	3.262	110.65
O1···O2			2.399	

the X-ray structure of Pt(κ^2-acetato)$\{(t\text{-BuPhPO})_2H\}_2$, which showed intramolecular hydrogen bonds O−H···O (2.391 Å) comparable to complex **31** (Table 8).[16a] To the best of our knowledge this X-ray structure provided the first example of a κ^2-acetato platinum complex with a highly electron-rich bulky phosphinous acid ligand.[76] Indeed, structurally defined (κ^2-acetato)platinum(II) complexes have been described in two reports.[16,77] Usually, these κ^2-acetato complexes are extremely uncommon due to their propensity to form dimeric carboxylate-bridged complexes. Accordingly, P−O bond lengths (average ≈ 1.541 Å) are in agreement with single P−O bonds values. The C−O bond length of an acetato ligand (average ≈ 1.27 Å), between single (1.43 Å) and double C−O bond (1.22 Å) length, is in full agreement with a partial double-bond character (Figure 15).

3. Conclusion

Various SPO preligands with substituents of tunable bulkiness have been prepared for coordination mode investigations. The balance between steric and electronic factors determines the coordination mode of mono- and dinuclear platinum complexes. Bulky and electron-rich SPOs reacted with platinum salts to form *trans* complexes. In contrast, less hindered PA ligands coordinate to the metal in a *cis* fashion. In between these frontiers, mixtures of *cis* and *trans* complexes are obtained. Dinuclear chloro-bridged complexes were observed after treatment of *cis* mononuclear complexes with NEt_3. An associative/dissociative-type mechanism has been proposed on the basis of isolation of intermediate **30**. Rare monomeric κ^2-acetato platinum(II) complex **31** with symmetrical bulky SPO preligands is being tested as a catalyst in cycloaddition reactions in our laboratories.

4. Experimental Section

4.1. General Procedures. All solvents were purified by standard procedures. THF and Et_2O were predried over 4 Å molecular sieves and distilled from sodium/benzophenone. Toluene was distilled from sodium and stored over 4 Å molecular sieves. CH_2Cl_2 and CH_3CN were distilled from CaH_2. Light petroleum ether refers to the fraction distilled at bp 40−60 °C. Thin-layer chromatography was carried out on Merck silica gel 60 F254 and visualized under ultraviolet light (254 and 366 nm), or through spraying with 5% phosphomolybdic acid in EtOH, or by placing in iodine vapor. Flash chromatography was performed with Merck silica gel 60 (230−400 mesh).

Physical and Analytical Measurements. Melting points were determined in a capillary tube with a Metler LP61 apparatus. IR spectra were recorded on an IRTF Perking-Elmer 1700X spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker Advance DPX spectrometers operating at 200 and 300 MHz for ^1H. ^{13}C and ^{31}P nuclei were observed with ^1H decoupling. Phosphoric acid (85%) was used as external reference for ^{31}P NMR spectra. Chemical shifts (δ) of ^1H and ^{13}C spectra are reported in ppm relative to $CHCl_3$ (δ = 7.26 for ^1H and δ = 77.0 for ^{13}C). *J* values are given in Hz.

High-resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ-ORBITRAP. Elemental analyses were performed in the Elemental Microanalysis department of the Faculté de Saint Jérôme.

4.2. Synthesis and Characterization. 4.2.1. Secondary Phosphine Oxide. (±)-Di-*tert*-butylphosphine Oxide (6). A solution of diphenylphosphite (0.4 mL, 2.13 mmol) in dry Et_2O (5 mL) was added dropwise to a 1.7 M solution of *t*-BuLi in pentane (4 mL, 6.8 mmol) in dry Et_2O (20 mL) at −40 °C. The resulting mixture was stirred for 1 h at −40 °C and for 21 h at room temperature. HCl (1 N, 7 mL) was added to the brown solution cooled to 0 °C, and the solution mixture was stirred for 15 min. Et_2O (15 mL) was added, and the mixture was stirred at 0 °C for an additional 5 min. The aqueous layer was acidified with 1 N HCl (20 mL) and extracted with DCM (2 × 20 mL) and $CHCl_3$ (20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. Purification by column chromatography (Et_2O/MeOH, 97:3) on deactivated silica gel (20:80 H_2O/silica) afforded the desired product contaminated with trace amounts of water. A DCM solution of the product was stirred over molecular sieves. Upon evaporation of the solvent, 242 mg (70%) of **6** was obtained as a white solid. NMR data are in agreement with reported data.[44] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 67.5.

(±)-Dicyclohexylphosphine Oxide (7). A solution of cyclohexyl chloride (6.4 g, 54.2 mmol) in THF (40 mL) was added dropwise to a suspension of Mg (1.31 g, 54.2 mmol) previously activated with dibromoethane (1%) in THF (3 mL). The resulting mixture was stirred for 3 h at reflux. Then a solution of diphenylphosphite (2.539 g, 10.8 mmol) in THF (10 mL) was added dropwise to the Grignard solution (54.2 mmol) at −10 °C. The resulting mixture was stirred for 1 h at −10 °C and for 24 h at room temperature. The resulting brown solution cooled to 0 °C was quenched by addition of 1 N HCl (20 mL) and after 15 min diluted with Et_2O (30 mL). The aqueous layer was acidified with 1 N HCl (20 mL) and extracted with Et_2O (2 × 30 mL) and EtOAc (20 mL). The combined organic phases were washed with 10% aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated under vacuum. Purification by column chromatography (Et_2O/MeOH, 97:3) on deactivated silica gel (20:80 H_2O/silica) afforded the desired product contaminated with trace amounts of water. A DCM solution of the product was stirred over molecular sieves. Upon evaporation of the solvent 1.74 g (78%) of **7** was obtained as a white solid. NMR data are in agreement with reported data.[20e,78] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 50.6 ppm.

(±)-Dimethylphosphine Oxide (9). This was prepared according to a published procedure.[25] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 23.4.

(±)-Diisobutylphosphine Oxide (10). A solution of diphenylphosphite (2 g, 8.54 mmol) in THF (20 mL) was added dropwise

(76) Interestingly, there are only two records for the structural motif M[(*t*-Bu)$_2$PO]$_2$H: (a) Mononuclear palladium complex see: Leoni, P.; Marchetti, F.; Pasquali, M. *J. Organomet. Chem.* **1993**, *451*, C25–C27. (b) Dinuclear palladium complex: see ref [9]d. (c) A new bulky monocular Pd complex has recently been reported (see ref [16c]).

(77) Moret, M. E.; Keller, S. F.; Slootweg, J. C.; Chen, P. *Inorg. Chem.* **2009**, *48*, 6972.

(78) Meciarova, M.; Toma, S.; Loupy, A.; Horvath, B. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2008**, *183*, 21.

to a 2 M solution of *i*-BuMgCl in THF (29.16 mmol, 15 mL) cooled at −10 °C. The resulting mixture was stirred for 1 h at −10 °C, warmed to rt, and stirred for 21 h at room temperature. The resulting brown solution was cooled to 0 °C, quenched by addition of 1 N HCl (15 mL), and after 15 min diluted with Et_2O (30 mL). The aqueous layer was diluted with 1 N HCl (20 mL) and extracted with DCM (2 × 30 mL). The combined organic phases were washed with 10% aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated under vacuum to give a colorless oil. Purification by column chromatography (Et_2O/MeOH, 97:3) on deactivated silica gel (20:80 H_2O/silica) afforded the desired product contaminated with trace amounts of water. A DCM solution of the crude product was stirred over molecular sieves. Upon evaporation of the solvent 690 mg (50%) of **10** was obtained as a colorless oil. NMR data are in agreement with reported data.[79] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 31.5.

(±)-*tert*-Butylphenylphosphine Oxide (11). This was prepared according to a published procedure.[15a] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 48.7.

(±)-Cyclohexylphenylphosphine Oxide (12). A solution of cyclohexyl chloride (3.2 g, 27 mmol) in THF (20 mL) was added dropwise to a suspension of Mg (activated with few drop of dibromoethane) (1.4 g, 27 mmol) in THF (5 mL). The resulting mixture was stirred for 3 h at reflux and cooled to −10 °C, and a solution of ethyl phenylphosphinate (2 g, 11.8 mmol) in THF (5 mL) was added dropwise. The mixture was stirred for 1 h at room temperature; then water (5 mL) and 1 N HCl (10 mL) were added successively to the solution at 0 °C. Et_2O (15 mL) was added, and the aqueous phase was extracted with Et_2O (2 × 20 mL) and AcOEt (2 × 20 mL). The combined organic phases were washed with 10% aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under vacuum to give 2.06 g (84%) of **12** as a colorless oil. NMR data are in agreement with reported data.[15a] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 37.6.

(±)-Methylphenylphosphine Oxide (13). This was synthesized following a published procedure.[51b] $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 21.3.

(±)-Isobutylphenylphosphine Oxide (14). A solution of ethyl phenylphosphinate (2 g, 11.8 mmol) in THF (20 mL) was added dropwise to a cooled (−10 °C) 2 M solution of *i*-BuMgCl (3.2 g, 27 mmol) in THF (20 mL). The resulting mixture was stirred for 12 h at rt, cooled to 0 °C, and quenched by addition of water (5 mL) and 1 N HCl (10 mL). The mixture was diluted with Et_2O (15 mL), and the aqueous phase was extracted with Et_2O (2 × 20 mL) and AcOEt (2 × 20 mL). The combined organic phases were washed with 10% aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under vacuum to afford 1.49 g (71%) of **14** as a colorless oil. ^1H NMR (d_6-acetone, 200 MHz): δ 1.01 (d, J_{H-P} = 6.7 Hz, 3H), 1.06 (d, J_{H-P} = 6.6 Hz, 3H), 1.83−1.94 (m, 2H), 1.98−2.17 (overlap with solvent pick, m, 1H), 6.36 (dd, J = 2.8 J_{H-P} = 4.1 Hz, 0.5H), 7.52−7.56 (m, 3H), 7.69−7.80 (m, 2H), 8.66 (t, J_{H-P} = 3.6 Hz, 0.5H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 21.8.

4.2.2. Platinum Complexes. Dichlorobis[(±)-*tert*-butylphenylphosphinous acid]$_2$platinum(II) (21). A solution of $PtCl_2$(cod) (102 mg, 0.274 mmol) and (±)-*tert*-butylphenylphosphine oxide (100 mg, 0.548 mmol) was stirred under refluxing THF (15 mL). After 24 h, the yellow solution was filtered over Celite and concentrated under reduced pressure to afford quantitatively **21** as a yellow powder. The ^{31}P NMR spectrum shows two singlets at δ = 87.7 and 87.1, in a 1:1.1 *meso*/*dl* ratio. Mp: 227−230 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.20 (d, J_{H-P} = 8.1 Hz, 4.5H), 1.24 (d, J_{H-P} = 8.1 Hz, 4.5H) this look like a triplet 9H, 7.45−7.48 (m, 3H), 7.97−8.06 (m,2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 27.5 (CH_3×6), 28.1 (CH_3×6) 39.8 (2×C, J_{C-P} = 26 Hz), 40−4 (2×C, J_{C-P} = 18 Hz), 128.8 (t, J_{C-P} = 5.2 Hz, CH×8), 129.1 (4×C, J_{C-P} = 12 Hz), 129.9 (d, J_{C-P} = 40 Hz, C×2), 130.0 (d, J_{C-P} = 46 Hz, C×2), 131.0 (s, 2×CH), 131.1 (s, 2×CH), 132.1 (t, J_{C-P} = 4.7 Hz, CH×2), 132.8 (t, J_{C-P} = 5.0 Hz, CH×2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 87.8 (s + d, J_{P-Pt} = 2495 Hz), 87.1 (s + d, J_{P-Pt} = 2490 Hz) ppm. IR ν_{max} (KBr): 3401(br, P−OH) 2945, 2897, 2866, 1474, 1459, 1435, 1365, 1186, 1101(P−O), 1014, 904,809, 746, 694, and 608 cm^{-1}. LRMS: *m*/*z* calcd for $C_{20}H_{34}NO_2P_2Cl_2Pt$ $(M + NH_4)^+$ 648.1071, found 648.1072. Anal. Calcd for $C_{20}H_{30}O_2P_2Cl_2P_2$: C 38.11, H 4.80. Found: C 38.03, H 4.93.

Complex (R_P*,S_P*)-**21** crystallized from CH_2Cl_2 (51 mg, 30% yield), and the single-crystal X-ray analysis revealed the *trans meso* structure. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 87.8 (s + d, J = 2494 Hz). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.20 (d, J_{H-P} = 8.1 Hz, 4.5H), 1.24 (d, J_{H-P} = 8.1 Hz, 4.5H), 7.45−7.48 (m, 3H), 7.97−8.06 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 26.38, 26.41, 26.45 (CH_3×3), 39.8 (2×C, d, J_{C-P} = 25 Hz), 128.8 (t, J_{C-P} = 5.2 Hz, CH×2), 130.1 (d, J_{C-P} = 45 Hz, C×2), 131.6 (s, CH), 132.7 (t, J_{C-P} = 6.2 Hz, CH×2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 87.8 (s + d, J_{P-Pt} = 2493 Hz) ppm.

[(R_P,R_P)(R_P,R_P)]-[(μ-Cl)Pt(*tert*-butylphenylphosphinito)(*tert*-butylphosphinous)]$_2$ (21d). A solution of $PtCl_2$(cod) (60 mg, 0.16 mmol) and (*S*)-(−)-*tert*-butylphenylphosphane oxide **12** (58 mg, 0.32 mmol) in DCM (3 mL) was stirred overnight at room temperature. NEt_3 (0.16 mmol, 23 μL) was added to the yellow solution, and the resulting mixture was stirred for 6 h at rt and then concentrated under vacuum. Upon purification by chromatography (PE/Et_2O, 1:1) over a pad of Celite and silica gel, 40 mg (53%) of the title compound was obtained as a white solid. Crystals suitable for X-ray analysis were obtained from PE/Et_2O (1:1). Mp: 257−259 °C. $[\alpha]_D$ = −148 (*c* 0.1, $CHCl_3$) at rt. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.01 (d, J_{H-P} = 16 Hz, 36H), 7.32−7.35 (m, 12H), 7.42−7.79 (m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 26.8 (s, CH_3), 39.1 (dd, $J_{C\text{-}195Pt}$ = 4.3 Hz J_{C-P} = 55.6 Hz, C), 127.7 (t, J_{C-P} = 5.4 Hz, CH), 130.4 (s, CH), 131.8 (t, J_{C-P} = 4.8 Hz, CH), 135.0 (dd, J_{C-P} = 3.5 Hz J_{C-P} = 71 Hz, C) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 58.7 (J_{P-Pt} = 3934 Hz), 60.2 (J_{P-Pt} = 3955 Hz). IR ν_{max} (KBr): 3058(w), 2957(m), 2943(m), 2924(w), 2896(w), 2863(w), 1474(m), 1459(m), 1436(m), 1392(w), 1365(w), 1308(w), 1259(w), 1184(m), 1098(s), 1036(P−O, s), 775(s), 742(s), 694(s) cm^{-1}. HRMS: *m*/*z* calcd for $C_{20}H_{30}O_2P_2ClPt$ $(M + H)^+$ 595.1048, found 595.1049.

[(μ-Cl)Pt(±)(cyclohexylphenylphosphinito)(cyclohexyphenyphosphinous)]$_2$ (20d). A solution of $PtCl_2$(cod) (176 mg, 0.47 mmol) and cyclohexylphenylphosphane oxide **12** (200 mg, 0.96 mmol) in DCM (10 mL) was heated at 40 °C for 4 h. NEt_3 (0.47 mmol, 67 μL) was added to the yellow solution, and the resulting mixture was stirred for 6 h at rt then concentrated under vacuum. Upon purification by chromatography (PE/Et_2O, 1:1) over a pad of Celite and silica gel, 195 mg (65%) of the title compound was obtained as a white solid as a 1:1 mixture of *meso* and *dl* isomers. Mp: 161−164 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.75−2.26 (m, 44H), 7.18−7.30 (m, overlap with solvent peak), 7.42−7.52 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 25.9−26.1 (m, CH_2), 26.8 (s, CH_2), 26.9 (s, CH_2), 27.2−27.8 (m, CH_2), 28.6−28.8 (m, CH_2), 39.7−41.6 (m, CH), 128.7−129.1 (m, CH), 130.7−131.0 (m, CH), 131.2−131.9 (m, CH), 135.2−136.8 (m, C) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6, 81 MHz): δ 58.7 (J_{P-Pt} = 3934 Hz), 60.2 (J_{P-Pt} = 3955 Hz). IR ν_{max} (KBr) 3445(P−OH, br), 2929(s), 2848(s), 1482(w), 1447(m), 1435(m), 1291(w), 1261(m), 1174(w), 1104(s), 1072(m), 1043(s), 1025(P−O, s), 915(w), 887(w), 801(s), 726(m), 693(s) cm^{-1}. HRMS: *m*/*z* calcd for $C_{24}H_{33}O_2P_2ClPt$ $(M - H)^-$ 647.1362, found 647.1363. Anal. Calcd for $C_{48}H_{66}O_4P_4Cl_2Pt_2$: C 44.62, H 5.15. Found: C 44.31, H 5.74.

Recrystallization of complex **20d** (PE/Et_2O, 1:1) gave suitable microcrystals for X-ray analysis, which revealed a *cis meso* dimeric structure, (R*$_P$,S*$_P$)(S*$_P$,R*$_P$)-**20d**. However, the minute quantities of microcrystals did not allowed a full characterization.

Dichlorobis[di-*tert*-butylphosphinous acid]$_2$platinum(II) (24). A solution of $PtCl_2$(cod) (115 mg, 0.308 mmol) and (±)-di-*tert*-butylphosphine oxide (100 mg, 0.612 mmol) was stirred under refluxing THF (15 mL). After 16 h, the yellow solution was filtered through a short pad of Celite and concentrated

(79) Klaui, W.; Song, C. E. *Inorg. Chem.* **1989**, *28*, 3845.

under vacuum to afford quantitatively **24** as a yellow powder. Complex **24** was crystallized by slow evaporation in CH_2Cl_2, and the X-ray analysis of the monocrystal revealed the *trans* configuration structure. Mp: 205−208 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.37 (d, J_{H-P} = 7.4 Hz, 18H), 1.41 (d, J_{H-P} = 7.3 Hz, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ major 28.7 (t, J_{C-P} = $J_{C\text{-}195Pt}$ = 2.7 Hz, CH_3), minor 28.9 (t, J_{C-P} = $J_{C\text{-}195Pt}$ = 2.7 Hz, CH_3), major 39.6−40.0 (m, C), minor 41.9−42.1 (m, C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 109.4 (s + d, J_{P-Pt} = 2410 Hz). IR ν_{max} (KBr): 3221 (P−OH, br), 2967, 2948, 1473, 1389, 1368, 1143 (P−O,s), 1022, 864, 811, 636 cm^{-1}. LRMS: *m*/*z* calcd for $C_{16}H_{37}O_2P_2Cl_2Pt$ $(M - H)^-$ 589.1284, found 589.1287. Anal. Calcd for $C_{16}H_{38}O_2P_2Cl_2Pt_2$: C 32.55, H 6.49. Found: C 32.71, H 6.43.

Dichlorobis[dicyclohexylphosphinous acid]$_2$platinum(II) (25). A solution of $PtCl_2$(cod) (87 mg, 0.233 mmol) and (±)-dicyclohexylphosphine oxide (100 mg, 0.467 mmol) was stirred under refluxing THF (15 mL). After 24 h, the yellow solution was filtered through a short pad of Celite and concentrated under vacuum to afford quantitatively **25** as a yellow powder. Complex **25** crystallized from a CH_2Cl_2 solution, and the X-ray analysis of the monocrystal revealed the *trans* configuration structure. Mp: 154−156 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.25−2.16 (m, 46H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ 26.2−26.8 (m); 35.9−36.7 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 107.2 (s + d, J_{P-Pt} = 2485 Hz). IR ν_{max} (KBr): 3258 (br, P−OH), 2927, 2852, 1447, 1273, 1162 (P−O), 1111, 1005, 891, 885, 863 cm^{-1}. LRMS: *m*/*z* calcd for $C_{24}H_{46}O_2P_2Cl_2Pt$ $(M - H)^-$ 693.1914, found 693.1908. Anal. Calcd for $C_{24}H_{46}O_2P_2Cl_2Pt$: C 41.50, H 6.68. Found: C 41.48, H 6.85. Due to the presence of the cyclohexyl group within the structure, probably responsible for dynamic conformational processes, ^{1}H and ^{13}C NMR spectra exhibit very broad signals and are uninformative for the structure assignment.

Dichlorobis[dimethylphosphinous acid]$_2$platinum(II) (27). A solution of $PtCl_2$(cod) (120 mg, 0.32 mmol) and (±)-dimethylphosphine oxide (50 mg, 0.64 mmol) was stirred under refluxing THF (10 mL) for 22 h. The light yellow solution was filtered through a short pad of Celite and concentrated under vacuum to afford quantitatively **27** as a yellowish powder. The ^{31}P NMR spectrum showed one singlet at δ = 76.7 assigned to the *cis* isomer. ^{1}H NMR (THF-d_8, 200 MHz): δ 2.03 (m, 12H). $^{31}P\{^1H\}$ NMR (THF-d_8, 81 MHz): δ 74.7 (s+d, J_{P-Pt}=3911 Hz). LRMS: *m*/*z* calcd for $C_4H_{13}O_2P_2Cl_2Pt$ $(M - H)^-$ 420.9401, found 420.9398.

Dichloro[(di-isobutylphosphinito)(di-isobutylphosphinous)]-platinum(II), Triethylammonium Salts (30). A solution of $PtCl_2$-(cod) (90 mg, 0.242 mmol) and di-isobutylphosphane oxide **10** (80 mg, 0.493 mmol) in DCM (5 mL) was stirred under reflux for 22 h. NEt_3 (0.242 mmol, 35 μL) was added to the yellow solution, and the resulting mixture was stirred for 4 h at rt and then concentrated under vacuum. Upon purification by chromatography (PE/Et_2O, 1:1) over a pad of Celite and silca gel, 84 mg (51%) of the title compound was obtained as a yellowish solid. Mp: 105−110 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 63.9 (J_{P-Pt} = 3974 Hz). IR ν_{max} (KBr): 3426 (P−OH, br), 2954(s), 2926(s), 2969(m), 1735(w), 1725(w), 1464(m), 1401(w), 1381(w), 1366(w), 1262(w), 1165(w), 1089(s), 1078(s), 1025(P−O, s), 848(w), 812(w), and 754(w) cm^{-1}. HRMS: *m*/*z* calcd for $C_{16}H_{37}O_2P_2ClPt$ $[M + H]^+ - [(HNEt_3)^+ - (Cl)^-]$ 554.1599, found 555.1657; $[HNEt_3]^+$ was also observed at 102.1. When the sample was passed in negative mode, $C_{16}H_{37}O_2P_2Cl_2Pt$ (589.1284) was observed. Anal. Calcd for $C_{22}H_{53}NO_2P_2Cl_2Pt$: C 38.21, H 7.72. Found: C 38.51, H 7.53.

In solution this compound was unstable, affording after a few hours a mixture of two complexes: ammonium-free **30** and a minor, unidentified complex (^{31}P NMR δ 66.8 ppm (J_{P-Pt} = 3927 Hz), ^{13}C NMR spectra exhibit too many signals and are uninformative for structural assignment).

κ^2-Acetato{[di-*tert*-butylphosphinito][di-*tert*-butylphosphinous acid]}platinum(II) (31). NEt_3 (85 μL, 0.616 mmol) and AgOAc (205 mg, 1.23 mmol) were successively added to a solution of complex **24** (426 mg, 0.616 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 20 h. The solid residues were filtered over Celite, and the filtrate was concentrated under vacuum. Flash chromatography over silica gel (light petroleum/Et_2O, 1:1) afforded 305 mg (85%) of Pt complex **31** as an orange powder. The formation of a single *cis* complex, Pt(κ^2-acetato){[(*t*-Bu)$_2$PO]$_2$H}, was confirmed by $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 87.6 (d; $J_{195Pt-P}$ = 3990 Hz). Mp: 186−188 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.33 (d, J_{H-P} = 14.4 Hz, 36H), 1.93 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ 26.5 (CH_3), 28.6, 28.8, and 28.9 ($CH_3\times12$), 39.4, 39.5, 39.9, 40.3, and 40.4 ($CH\times4$), 192.4 (C=O). IR (KBr): 2949, 2899, 2869, 1582, 1474, 1466, 1389, 1368, 1333, 1185, 1033, 1019, 993, 944, 898, 813, 689, 631 cm^{-1}. HRMS: *m*/*z* calcd for $C_{19}H_{40}O_4P_2Pt$ $(M + H)^+$ 578.2117, found 578.2124; calcd for $C_{16}H_{37}O_2P_2Pt$ $(M - CH_3COO)^+$ 518.1909, found 518.1913.

Acknowledgment. We are grateful to CNRS and ANR project "SPOs preligands" (Contract No. BLAN07-1_190839) for financial support. We thank Dr. Michel Giorgi (Université P. Cézanne, Marseille) for his kind assistance with X-ray analyses of complexes described in this publication.

Supporting Information Available: Experimental procedures and characterization data of all new compounds. Tables of crystallographic data in cif format. Table of DFT calculations and histograms of **8a** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.