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Synthesis and Structure of Pt(II) Phosphonato-Phosphine Complexes and of a P,O-Stabilized Metal–Metal-Bonded Pt_2Ag_2 Complex

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As part of our interest in the design and reactivity of P,O ligands, and because the insertion chemistry of small molecules into a metal alkyl bond is very dependent on the ancillary ligands, the behavior of Pt–methyl complexes containing the β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$ (abbreviated PPO in the following) toward CO insertion has been explored. New, mononuclear Pt(II) complexes containing one or two PPO ligands, [PtClMe(κ^2-PPO)] (**1**), [Pt{C(O)Me}Cl(κ^2-PPO)] (**2**), [PtMe(CO)(κ^2-PPO)]OTf (**3**·OTf), [PtMe(OTf)(κ^2-PPO)] (**4**), *trans*-[PtClMe(κ^1-PPO)$_2$] (**5**), [PtMe(κ^2-PPO)(κ^1-PPO)]BF_4 (**6**·BF_4), [PtMe(κ^2-PPO)(κ^1-PPO)]OTf (**6**·OTf), and [Pt{C(O)Me}(κ^2-PPO)(κ^1-PPO)]BF_4 (**7**·BF_4) have been prepared and characterized. Hemilability of the ligands is observed in the cations **6** and **7** in which the terminally bound and chelating PPO ligands exchange their role on the NMR time-scale. The acetyl complexes **2** and **7** are stable in solution, but the former deinserts CO upon chloride abstraction. We also demonstrate the ability of PPO to behave as an assembling ligand and to stabilize a heterometallic Pt–Ag metal complex, [PtMe(κ^2-PPO){μ-(η^1-P;η^1-O)PPO)}Ag(OTf)(*Pt–Ag*)]OTf (**8**·OTf), which was obtained by reaction of **5** with AgOTf to generate more reactive, cationic complexes. Whereas the first equivalent of AgOTf abstracted the chloride ligand, the second equivalent added to the cationic complex with formation of a Pt–Ag bond (2.819(1) Å). The complexes **1**, **2**, **4**, **5**·CH_2Cl_2, and (**8**·OTf)$_2$ have been structurally characterized by single-crystal X-ray diffraction. The latter has a dimeric nature in the solid state, with two silver-bound triflates acting as bridging ligands between two Pt–Ag moieties. In addition to the Ag–Pt bond, the Ag^+ cation is stabilized by a dative O → Ag interaction involving one of the PPO ligands.

Introduction

The increasing interest in organometallic and coordination chemistry for functional phosphine ligands whose donor atoms significantly differ in their hard−soft properties has been discussed in recent review articles.[1] In particular, this has stimulated the synthesis of various P,O ligands in which a phosphine moiety is associated with carboxylate, ketone, alcohol, ether, ester, sulfoxide, or phosphine oxide functions. Main motivations include a better understanding of the requirements for selective metal−ligand interactions when competing donors are present and the preparation of metal complexes displaying catalytic properties or hemilability of their coordinated ligands. The latter aspect has direct relevance to delineating the conditions for the occurrence of intramolecular dynamic behavior of functional ligands and its implications in molecular activation and homogeneous catalysis.[1]

We have noted recently that phosphine ligands containing a phosphoryl function, that is, phosphinate, phosphonate, or phosphate, have received relatively little attention[2] in contrast to the phosphine oxide ligands, although it has been structurally proven that their P═O group can coordinate to a metal center via the oxygen atom,[2,3] including in the case of the softer palladium[4] or platinum[5] ions. Such ligands could be used as potential P,O chelates, likely to display hemilabile behavior under suitable conditions, or as assembling ligands in the formation of di- or polymetallic metal complexes. As

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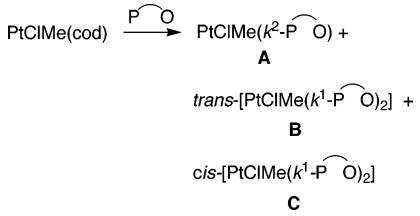
part of our interest in the design and reactivity of P,O ligands,[1d] we have recently reported the synthesis of the first enolphosphato-phosphine ligands, $Ph_2PCH{=}CPh[OP(O)(OR)_2]$ (R = Et, Ph),[2] and of the new β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$,[6] which associate P(III) and P(V) donor centers. They form with Pd(II) complexes seven- or five-membered rings, respectively, and some of them display hemilabile behavior.

In view of the difficulties often encountered in isolating Pd(II) reaction intermediates because of their high reactivity or instability, Pt(II) complexes are often taken as valuable models because their isolation and full characterization is easier. Furthermore, cationic Pt−methyl complexes of an enantiomerically pure chelating P,N ligand have been recently used in asymmetric catalysis.[7] Because the insertion chemistry of small molecules into a metal−alkyl bond is very dependent on the ancillary ligands, we decided to explore the behavior of Pt−methyl complexes containing the β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$[6] (abbreviated PPO in the following) toward CO insertion. We also describe the ability of PPO to behave as an assembling ligand and to stabilize a heterometallic Pt−Ag metal complex obtained in the course of studies aiming at generating more reactive, cationic complexes. The new compounds **1**, **2**, **4**, **5**·CH_2Cl_2, and (**8**·OTf)$_2$ have been structurally characterized by X-ray diffraction.

Results and Discussion

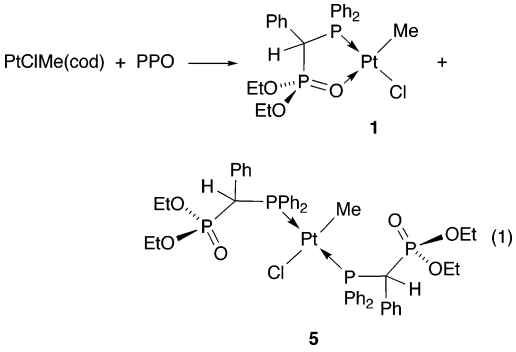
Synthesis of Pt(II) Complexes Containing One PPO Ligand. Earlier studies on the coordination properties of other P,O ligands led us to perform the reaction of the acetamido-derived phosphine ligand $Ph_2PNHC(O)Me$[8] with 1 equiv of [PtClMe(cod)] (cod = 1,5-cyclooctadiene) (Scheme 1). This afforded exclusively product **B** after stirring for 2 h in CH_2Cl_2. The remaining half equivalent of the Pt precursor did not react with **B** to give the desired product **A** when stirring was continued overnight. An analogous reaction with the ketophosphine ligand $Ph_2PCH_2C(O)Ph$[9] yielded

Scheme 1. Possible Reaction Products between [PtClMe(cod)] and a Bifunctional P,O Ligand



again **B** as the main product, but the cis-isomer **C** could also be detected. In both cases, the products have been identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[10] For compounds of type **B**, the Pt-bound methyl group appears as a triplet in the ^1H NMR spectrum due to coupling with two equivalent PPh_2 nuclei, whereas a doublet of doublets was observed for the methyl group of **C** because of the presence of two nonequivalent PPh_2 functions. As is often the case for complexes with two mutually trans phosphorus nuclei, the large $^2J_{P-P}$ coupling leads to the appearance of virtual triplets in the ^1H NMR spectra for the protons α to phosphorus.[11] This was also observed for the NH proton in *trans*-[PtClMe{κ^1-$Ph_2PNHC(O)Me$}$_2$].[10]

To see whether the formation of **A** could become more selective and that of species **B** and **C** avoided, we decided to use the recently synthesized PPO ligand and reacted it with [PtClMe(cod)]. This afforded [PtClMe(κ^2-PPO)] (**1**) as a main product with small amounts of the **B**-type complex **5** (ca. 9:1 ratio), and formation of **C** was not observed (eq 1).



These results show the influence of the phosphine and phosphonato donor functions on the reactivity of their Pt(II) complexes when compared to the P,O donors of $Ph_2PNHC(O)Me$ or $Ph_2PCH_2C(O)Ph$. There is no obvious angular parameter that could explain the greater propensity for ligand

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(10) Selected NMR data for *trans*-[PtClMe{κ^1-$Ph_2PNHC(O)Me$}$_2$], ^1H NMR (300.13 MHz, $CDCl_3$) δ: −0.19 (t, $^3J_{P-H}$ = 7.4 Hz, $^2J_{Pt-P}$ = 80 Hz, $PtCH_3$), 8.81 (virtual t, $|^2J_{P-H} + {}^4J_{P-H}|$ = 20.2 Hz, NH). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$) δ: 48.6 (s, $^1J_{Pt-P}$ = 3210 Hz). Selected NMR data for *trans*-[PtClMe{κ^1-$Ph_2PCH_2C(O)Ph$}$_2$], ^1H NMR (300.13 MHz, $CDCl_3$) δ: −0.13 (t, $^3J_{P-H}$ = 6.8 Hz, $^2J_{Pt-P}$ = 81 Hz, $PtCH_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$) δ: 22.4 (s, $^1J_{Pt-P}$ = 3173 Hz). Selected NMR data for *cis*-[PtClMe{κ^1-$Ph_2PCH_2C(O)Ph$}$_2$], ^1H NMR (300.13 MHz, $CDCl_3$) δ: 0.64 (dd, $^3J_{P-H}$ = 7.5 Hz, $^3J_{P-H}$ = 4.8 Hz, $^2J_{Pt-P}$ = 56 Hz, $PtCH_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$) δ: 11.7 (d, $^2J_{P-P}$ = 13 Hz, $^1J_{Pt-P}$ = 4582 Hz, P trans to Cl), 18.5 (d, $^2J_{P-P}$ = 13 Hz, $^1J_{Pt-P}$ = 1752 Hz, P trans to Me).

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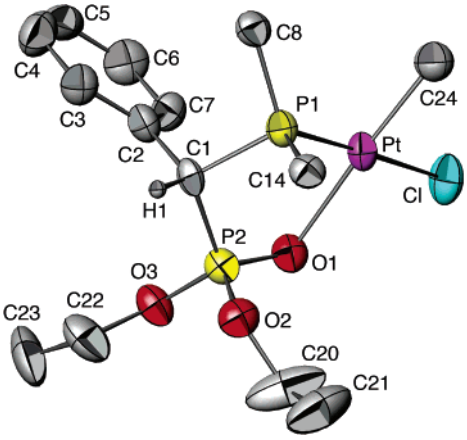
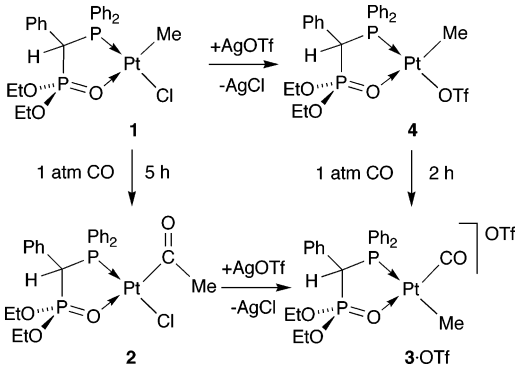


Figure 1. View of the molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms except H1 and the non-ipso aryl carbons of the PPh_2 group have been omitted for clarity.

Scheme 2. Synthesis of Complexes **1**−**4**



chelation in the case of the PPO ligand (such as the PCP or CPO angles as compared to the related angles in the other P,O ligands) so that electronic effects dominate with a greater coordinating ability of the P═O function as compared to the C═O group of the amide or ketone function of the other P,O ligands. In the course of attempts to optimize the reaction conditions, it was found that slow addition of PPO did not influence the product ratio. After addition of a $CDCl_3$ solution of PPO to 1 equiv of solid [PtClMe(cod)], monitoring of the reaction by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed after 10 min the formation of a 1:2 mixture of the kinetically favored **5** and the thermodynamically favored **1**. The proportion of **1** clearly increases with time. We could show in a separate experiment that transfer of the monodentate PPO ligand from the bis-substituted complex **5** to [PtClMe(cod)] is possible and yields the desired product **1**. Indeed, $^{31}P\{^1H\}$ NMR monitoring of the evolution of an equimolar mixture of **5** and [PtClMe(cod)] in $CDCl_3$ showed the progressive formation of the thermodynamic product **1** within 3−4 days. Complex **1** can therefore be obtained from the direct reaction of [PtClMe(cod)] with 1 equiv of PPO or indirectly, from **5** and [PtClMe(cod)]. The X-ray structure of **1** is discussed below (Figure 1).

CO insertion into the Pt−Me bond of **1** afforded the acetyl complex **2** (Scheme 2), which was fully characterized, including by X-ray diffraction (Figure 2 and see below). The $^{31}P\{^1H\}$ NMR chemical shift is here a poorer indicator of the transformation alkyl→acyl ($\Delta\delta_{P(PPh2)}$ = 2 ppm) when

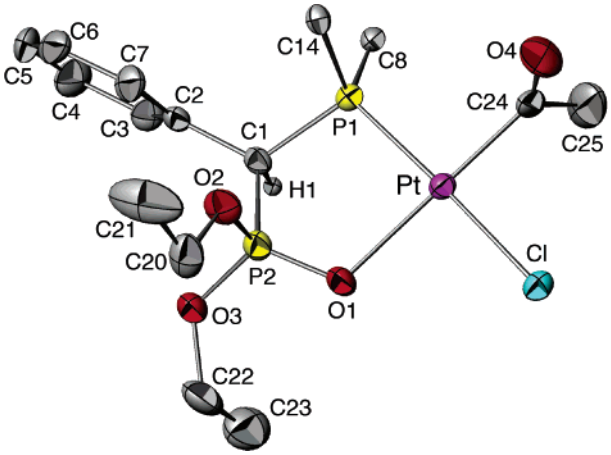


Figure 2. View of the molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms except H1 and the non-ipso aryl carbons of the PPh_2 group have been omitted for clarity.

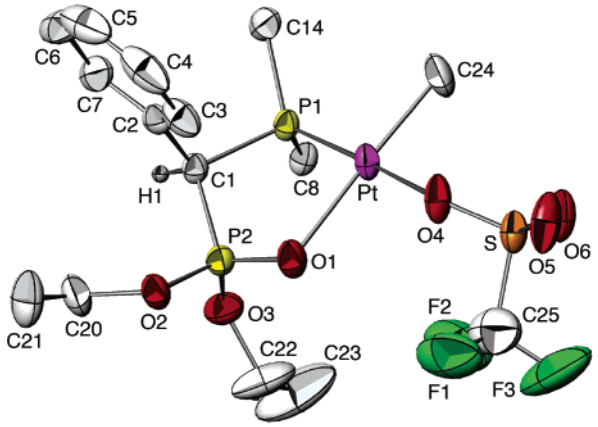


Figure 3. View of the molecular structure of **4** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms except H1 and the non-ipso aryl carbons of the PPh_2 group have been omitted for clarity.

compared to the shifts observed in related neutral or cationic Pd(II) complexes, which amount to 10−15 ppm.[12] However, the Pt−P coupling constant and the $^{195}Pt\{^1H\}$ NMR chemical shifts are very different in the alkyl and acyl complexes: the Pt−P coupling constant increases by 425 Hz, and the $^{195}Pt\{^1H\}$ NMR signal undergoes a downfield shift of ca. 670 ppm when going from **1** to **2**.

Reaction between **2** and 1 equiv of AgOTf (OTf = SO_3CF_3) led to halide abstraction, but the direct metathesis product with a coordinated triflate could not be isolated. Instead, CO deinsertion occurred and [PtMe(CO)(κ^2-PPO)]OTf (**3**·OTf) was isolated in good yield. The latter complex could also be synthesized by first substituting the chloride for triflate in **1**, to obtain **4**, which was fully characterized including by X-ray diffraction (Figure 3 and see below), and then exposing its CH_2Cl_2 solution to a CO atmosphere for 2 h. Because the CO ligand in **3** prefers to avoid being trans to P, the methyl group is now trans to P, in contrast to the situation in **1**, and these observations are in agreement with the thermodynamic preference for high trans-influence ligands to avoid being in mutual trans position.[13] In contrast

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Table 1. Comparison of Selected $^{31}P\{^1H\}$ NMR Data for the PPh_2 Group

	δ/ppm	$^1J_{Pt-P}$/Hz
trans-[PtClMe{κ^1-$Ph_2PNHC(O)Me$}$_2$]	48.6	3210
trans-[PtClMe{κ^1-$Ph_2PCH_2C(O)Ph$}$_2$]	22.4	3173
cis-[PtClMe{κ^1-$Ph_2PCH_2C(O)Ph$}$_2$]		
P trans to Cl	11.7	4582
P trans to Me	18.5	1752
[PtClMe(κ^2-PPO)] (**1**)	14.2[a]	4661
[Pt{C(O)Me}Cl(κ^2-PPO)] (**2**)	12.2[b]	5086
trans-[PtMe(CO)(κ^2-PPO)]$^+$ (**3**)	34.0[b]	1294
[PtMe(OTf)(κ^2-PPO)] (**4**)	9.9[a]	5360
[PtMe(NCMe)(κ^2-PPO)]$^+$	12.9[a]	4828
[PtMe(C_2H_4)(κ^2-PPO)]$^+$	19.4[a]	4335
trans-[PtClMe(κ^1-PPO)$_2$] (**5**)[d]	32.8/32.9	3250/3242
[PtMe(tht)(κ^2-PPO)]$^+$ (**9**)	18.4[b]	4012
cis-[PtMe(CO)(κ^2-dppmS)]$^+$	25.3[a,c]	3336
trans-[PtMe(CO)(κ^2-dppmS)]$^+$	31.2[a,c]	1556

[a] In CD_2Cl_2. [b] In $CDCl_3$. [c] From ref 14. [d] Presence of diastereomers.

to the present study where a carbonyl complex with the *cis*-Me−Pt−PPh_2 arrangement could not be detected, the kinetic product with a *cis*-Me−Pt−PPh_2 arrangement was observed in the related complex [PtMe(CO)(dppmS)]$^+$ which contains a bis(phosphanyl)monosulfide ligand, and its isomerization to the trans structure proceeded only slowly.[14] This behavior reflects the difference in the nature of the O→Pt and S→Pt dative bonds between these complexes. A good indicator for the cis/trans geometry is the value of the $^1J_{Pt-P}$ coupling constant, which was found to be about 1300 Hz for complex **3**·OTf (Table 1). This small value is typical for a PPh_2 moiety trans to an alkyl group. In the $^{13}C\{^1H\}$ NMR spectrum of **3**·OTf, the $^2J_{P-C}$ value for the methyl group bonded to Pt is 74 Hz, whereas it was around 7 Hz for compounds **1** and **4**. The triflate group in **4** can be displaced by MeCN or C_2H_4 to give the corresponding cationic complexes [PtMe(L)(κ^2-PPO)]$^+$ (L = MeCN, C_2H_4) in which the methyl group remains trans to oxygen (^1H and $^{31}P\{^1H\}$ NMR monitoring); no isomerization was observed, which is consistent with these ligands having a weaker trans-influence than a methyl or a CO group. That both MeCN and C_2H_4 are better donors than triflate is consistent with the decrease in the $^1J_{Pt-P}$ coupling constant for the trans phosphine moiety (see Table 1 and Experimental Section).

Reaction of **2** with AgOTf in CH_2Cl_2 under ethylene atmosphere also led to the formation of **3**, so that deinsertion/coordination of CO appears more favorable than coordination of C_2H_4 to the vacant site created by chloride abstraction. Complex **3**·OTf was found to decompose when kept in a $CDCl_3$ solution at room temperature. This is likely to be due to progressive loss of CO, because after approximately 1 week traces of **4** could be detected in the $^{31}P\{^1H\}$ NMR spectrum, but no **1** was found as a reaction product between **3** and the chlorinated solvent.

The molecular structures of compounds **1**, **2,** and **4** have been determined by X-ray diffraction (Figures 1−3, Table 2). In all three complexes, the platinum has a typical square-planar coordination geometry. There are only small variations in the Pt−C_{Me} distance, which is 2.0316(4) Å for **1** and 2.025(5) Å for **4**, but in the acetyl complex **2** the Pt−$C_{(O)Me}$ bond is at 1.973(8) Å slightly shorter. The Pt−C(24)−O(4) plane of the acetyl ligand is oriented almost perpendicular to the metal coordination plane (dihedral angle between the "best planes" of 81(1)°), which is usual for Pt(II)− and Pd(II)−acyl complexes.[15] The Pt−C(24)−O(4) angle of 122.0(7)° is typical for a η^1-coordination mode, in contrast to the smaller angle for a η^2-coordination.[16] The two Pt−Cl distances for **1** and **4** are also in the expected range (2.389(2) Å for **1** and 2.344(2) Å for **4**). A significant difference was found for the angle between the Pt center and the aromatic rings of the phosphine moiety. In the solid-state structure of **2**, one of the two phenyl groups is oriented nearly parallel to the Pt−P_{PPh2} axis (torsion angle Pt−P1−C14−C15: −10.7(7)°) so that the Pt−H15 distance is 2.99(1) Å. This is the shortest Pt−H distance found for these three complexes, and a weak interaction cannot be excluded, although packing effects might also be the reason for this orientation. No further significant intra- or intermolecular interactions were found.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, and **4**

	1	**2**	**4**
Pt−C24	2.0316(4)	1.973(8)	2.025(5)
Pt−Cl	2.389(2)	2.344(2)	
Pt−P1	2.145(2)	2.212(2)	2.156(1)
Pt−O1	2.231(5)	2.263(5)	2.227(3)
Pt−O4			2.127(3)
P2−O1	1.491(5)	1.482(5)	1.496(3)
C24−O4		1.192(9)	
C24−Pt−P1	93.64(6)	92.7(2)	93.4(2)
C24−Pt−O1	176.4 (1)	177.1(3)	176.6(2)
P1−Pt−O1	89.8(1)	88.2(1)	89.96(9)
C24−Pt−Cl	88.92(6)	89.5(2)	
C24−Pt−O4			90.3(2)
O1−Pt−Cl	87.7(1)	89.8(1)	
O1−Pt−O4			86.4(1)
Pt−C24−O4		122.0(7)	

Because cationic Pt(II)−acetyl complexes readily deinsert CO when no strong donor ligand is available to block a potentially vacant coordination site in cis position, we were interested in obtaining a cationic methyl Pt(II) system, anticipated to be more reactive than a neutral complex such as **1** toward CO insertion, and in which the ancillary ligand could provide an intramolecular donor to block the temporarily vacant coordination site after halide abstraction. For this reason, we investigated the synthesis of complexes containing two PPO ligands.

Synthesis of Pt(II) Complexes Containing Two PPO Ligands. The precursor to a series of Pt(II) complexes containing two PPO ligands, [PtClMe(κ^1-PPO)$_2$] (**5**) (Scheme 3), was obtained either by addition of 2 equiv of PPO to [PtClMe(cod)] or of 1 equiv of PPO to **1**. Because of the

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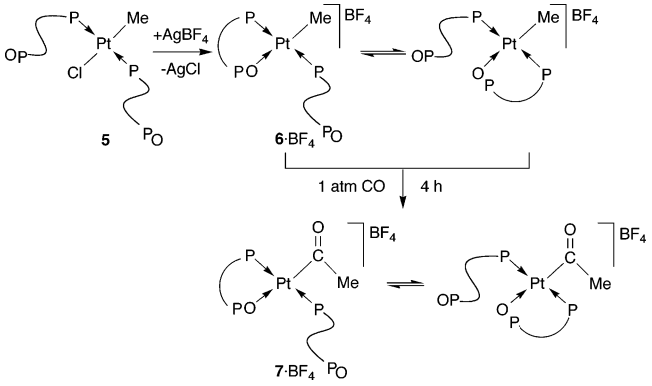
(16) For a review on η^2-acyl coordination, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

Scheme 3. Synthesis of Complexes **5**−**7**



presence of a stereogenic center in the PPO ligand, a mixture of two pairs of diastereomers was obtained that we did not attempt to separate. Consistently, the $^{31}P\{^1H\}$ NMR spectrum contained two very closely spaced singlets for the mutually trans PPh_2 groups, and two singlets for the P═O groups. In contrast to the $^{31}P\{^1H\}$ NMR spectra for compounds **1**−**4**, no $J_{P(O)-P}$ coupling was detected in the case where PPO acts as a monodentate ligand. The trans ligand arrangement in **5** was again established by the appearance of virtual triplets in both the ^1H and the $^{13}C\{^1H\}$ NMR spectra for the signals of the *CH*Ph group α to phosphorus.[11]

The X-ray structure determination of **5** established the bonding parameters in the *RS*/*SR* pair (see Figure 4, Table 3). The two phosphorus atoms are mutually trans with an angle P1−Pt−P3 of 177.42(2)°. The Pt−C_{Me} distance of 2.061(3) Å is slightly longer than that in complexes **1**, **2**, and **4**. Similarly, the Pt−Cl bond of 2.4288(9) Å is slightly longer than that in complexes **1** and **4**.

Chloride abstraction from **5** using $AgBF_4$ or AgOTf afforded the cationic complex $[PtMe(\kappa^2\text{-PPO})(\kappa^1\text{-PPO})]^+$ **6** in which the two phosphine moieties are still mutually trans and one of the PPO ligand has become a chelate. Variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy established that the phosphonato groups of **6**·OTf are exchanging at room temperature, which leads to only one broad signal in $^{31}P\{^1H\}$ NMR that becomes a triplet at higher temperature (see the variable-temperature $^{31}P\{^1H\}$ NMR spectrum in Figure S-1 and the P,P-COSY spectrum of **6** in Figure S-2 of the Supporting Information). Consistently, for the mixture of diastereomers, each of the two PPh_2 resonances appears as a triplet in the dynamic regime due to coupling with two P═O functions, which appear equivalent on the NMR time-scale. Related observations have been made, for example, in the case of complexes with a dangling η^1-dppm ligand that undergoes an "end over end" P,P exchange at room temperature.[17] The broadening of the P═O resonance at room temperature is also due to the presence of a mixture of diastereomers with very similar chemical shifts. Therefore, the $^{31}P\{^1H\}$ NMR spectrum at low temperature shows not only the signals for coordinated and noncoordinated P═O moieties, but also for the two pairs of diastereomers.

(17) Braunstein, P.; de Méric de Bellefon, C.; Oswald, B.; Ries, M.; Lanfranchi, M.; Tiripicchio, A. *Inorg. Chem.* **1993**, *32*, 1638 and references therein.

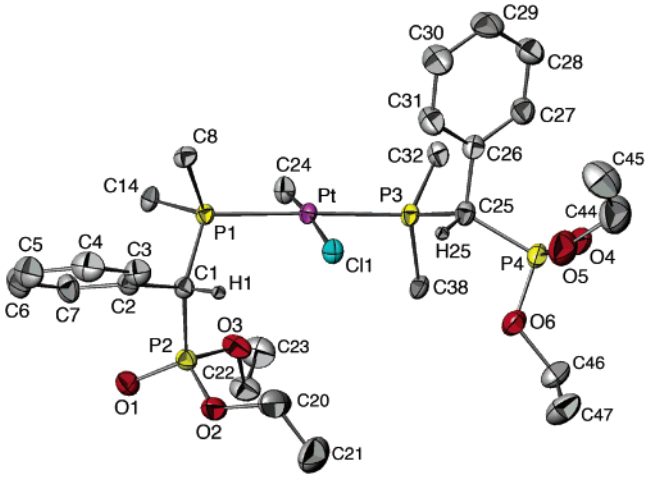


Figure 4. View of the molecular structure of **5** in **5**·CH_2Cl_2 with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms except H1 and H25, the non-ipso aryl carbons of the PPh_2 group and the solvent molecule have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**·CH_2Cl_2 and (**8**·OTf)$_2$

	5	(**8**·OTf)$_2$		(**8**·OTf)$_2$
Pt−C24	2.061(3)	2.033(5)	Pt−O1	2.188(3)
Pt−Cl	2.4288(9)		Pt−Ag	2.819(1)
Pt−P1	2.3009(9)	2.284(1)	Ag−O4	2.234(5)
Pt−P3	2.3092(9)	2.317(1)	Ag−O7	2.261(6)
P2−O1	1.456(3)	1.493(4)	Ag−O8a′	2.471(5)
P4−O4	1.463(2)	1.479(4)	C24−Pt−O1	175.6(2)
C24−Pt−P1	88.35(8)	89.1(2)	P1−Pt−O1	87.7(1)
C24−Pt−P3	89.86(8)	90.2(2)	P3−Pt−O1	92.8(1)
P1−Pt−P3	177.42(2)	175.84(4)	P1−Pt−Ag	89.72(3)
C24−Pt−Cl1	174.19(9)		O1−Pt−Ag	81.5(1)
P1−Pt−Cl	92.73(4)		P3−Pt−Ag	94.44(3)
P3−Pt−Cl	88.86(4)		C24−Pt−Ag	101.5(2)
			P4−O4−Ag	135.6(3)
			O7−Ag−O8a′	103.6(2)
			O4−Ag−O7	136.5(2)
			O4−Ag−O8a′	94.6(2)

Carbonylation of **6**·BF_4 in CH_2Cl_2 at room temperature under CO atmosphere afforded a diastereomeric mixture of the acetyl complex **7**·BF_4. The chemical shifts of the phosphine moieties are more separated than in the case of **6**·BF_4, and the broad P═O resonance is again consistent with a dynamic exchange of the chelating and monodentate PPO ligands. In general, acetyl ligands are less common in cationic than in neutral Pt-complexes, and only eight crystal structures of cationic acetyl Pt-complexes were found in the CSD (CSD version 5.25). Interestingly, complex **7** does not readily decarbonylate because of the presence of two strong phosphorus donors in cis position to the acetyl ligand. Related acetyl−Pd(II) complexes with two mutual trans phosphines have been investigated in alkoxycarbonylation reactions, with the alcoholysis of the Pd−acetyl bond being a key step of the reaction.[18] We were therefore interested in the behavior of **7**·BF_4 when its CH_2Cl_2 solution is exposed to an atmosphere of ethylene for 12 h, but no insertion of C_2H_4 was observed. A possible explanation for the inertness of compound **7**·BF_4 against olefin insertion is that the required

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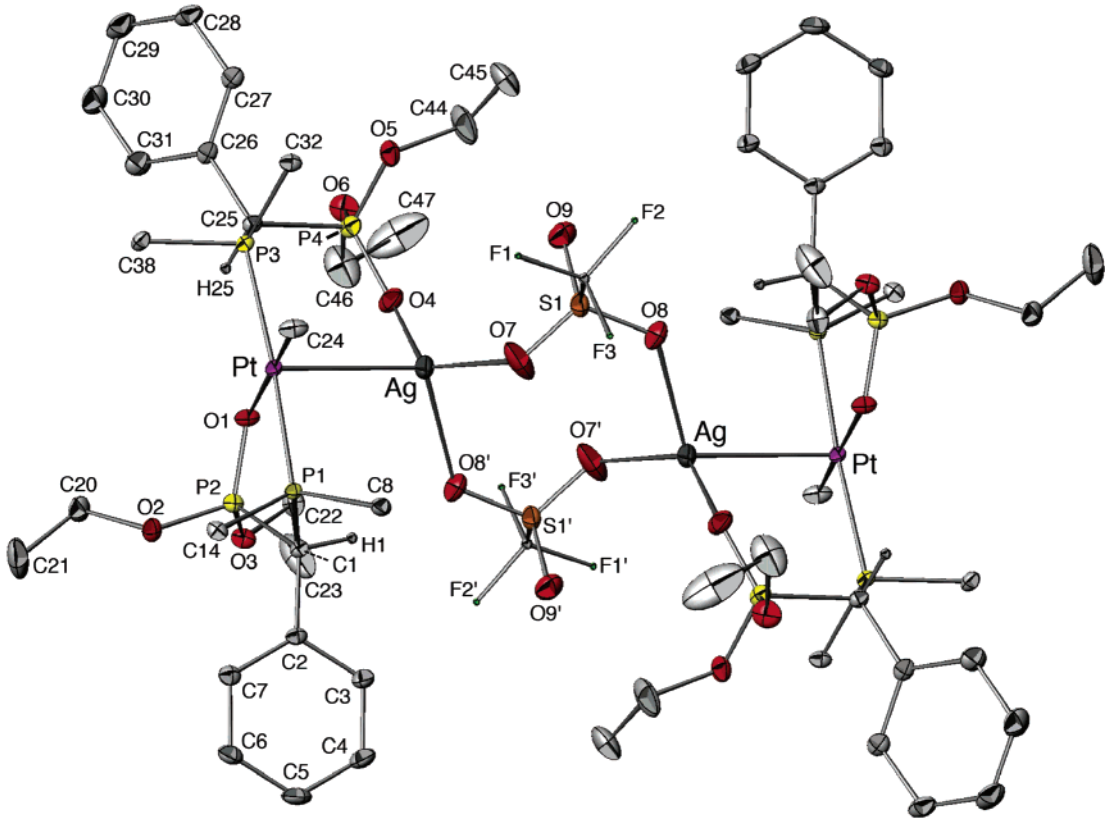
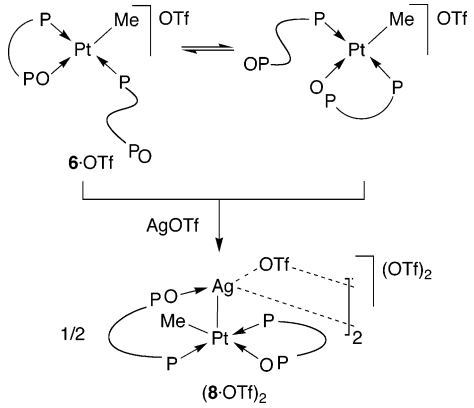


Figure 5. View of the molecular structure of (**8**·OTf)$_2$ with thermal ellipsoids drawn at the 30% probability level except for F1, F2, and F3 which for clarity have been represented with only very small ellipsoids. The hydrogen atoms except H1 and H25, the non-ipso aryl carbons of the PPh_2 group and the noncoordinated counterions have been omitted for clarity.

cis arrangement between the acetyl function and the olefin is not readily accessible. Similar observations have been made for the alcoholysis of related acetylpalladium systems, which only took place in cases where the acetyl and alcohol ligands are mutually cis.[18] There appears to be no precedent for an isolated complex resulting from olefin insertion into a Pt−acetyl bond, and this is not too surprising when considering the lower reactivity of Pt(II) complexes as compared to their Pd(II) analogues which readily catalyze CO/olefin copolymerization,[19] and whose stability is sometimes sufficient to allow isolation of key metallacyclic intermediates.[12a,20]

In one experiment, an excess of AgOTf was used to abstract the chloride ligand from **5**, and we noted a slight change of the signals for the C*H*Ph and *P*Ph$_2$ nuclei in ^{1}H and ^{31}P{^{1}H} NMR spectra, respectively, when compared to the values for **6**, suggesting the formation of a new complex. The reaction was repeated using 2 equiv of AgOTf, and this new complex could then be obtained in quantitative spectroscopic yield (^{31}P{^{1}H} NMR monitoring). It was isolated and fully characterized by X-ray diffraction as the heterodimetallic Pt−Ag complex ([PtMe(κ^2-PPO){μ-(η^1-P;η^1-O)-PPO)}Ag(OTf)(*Pt*−*Ag*)]OTf)$_2$ (**8**·OTf)$_2$ (Figure 5, Table 3, Scheme 4). Although the spectroscopic solution data indicated again the presence of a mixture of diastereomers, the single crystal used for X-ray analysis contained only the *RR*/*SS* diastereomers.

Scheme 4. Synthesis of the Pt−Ag Cationic Complex **8**



The crystal structure determination revealed the existence in the solid state of a centrosymmetric, tetranuclear complex based on two heterodinuclear Pt−Ag moieties linked by triflate bridges. Whereas one of the Pt-bound PPO ligands has remained chelated around the Pt(II) center, the other has turned from dangling to bridging between the platinum and silver centers, forming a six-membered ring, with a dative P═O→Ag$^+$ bond of 2.234(5) Å. Interestingly, a Pt−Ag metal−metal interaction of 2.819(1) Å is present, whose value is similar to the sum of the atomic radii (Pt, 1.295 Å;

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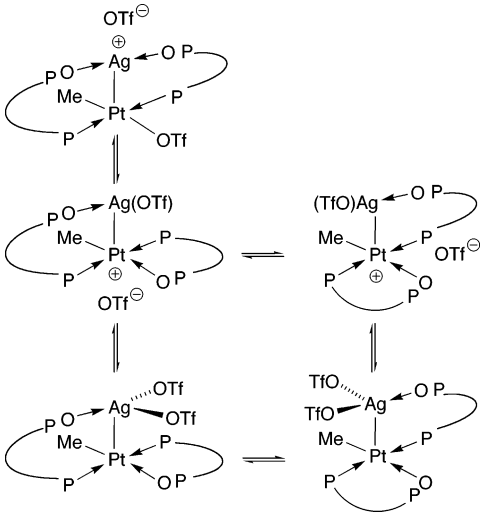
(20) Braunstein, P.; Durand, J.; Knorr, M.; Strohmann, C. *Chem. Commun.* **2001**, 211.

Ag, 1.339 Å), but larger than the sum of the ionic radii (Pt, 0.80 Å; Ag, 1.26 Å).[21] This distance is in the range found for complexes displaying a Pt(II)−Ag(I) interaction: a search in CSD resulted in a median value around 2.8 Å for an upper limit chosen for the Pt−Ag distance of 3.1 Å (CSD version 5.25). Another interesting feature is that in complex (**8**·OTf)$_2$ the Pt−Ag bond is almost perpendicular to the Pt-plane, which allows a better overlap between the filled Pt(II) $5d_{z2}$ and the vacant silver orbitals. This square-based pyramidal geometry around the Pt center is typical for complexes with only one Pt−Ag bond and no bridging ligand covalently bonded to Pt and Ag.[22] Although numerous Pt(II)−Ag(I) complexes involving penta- or hexacoordinated platinum have been reported, there seems to be only one other structurally characterized dinuclear, metal−metal-bonded complex with an oxygen donor bridging ligand,[23] and none involving P═O donors.

The bridging triflate anions interact with the silver cations at distances of 2.261(6) and 2.471(5) Å, representing the formally covalent and dative bonds, respectively. To the best of our knowledge, there are only 10 other cases where a Ag−OTf bond is shorter or equal to 2.26 Å (CSD version 5.25).[24] The other two triflate anions do not interact with the cationic complex. It is difficult to say whether the solid-state structure is fully retained in solution, in particular if heterodi- or tetranuclear complexes are present and/or in equilibrium. Breaking of the dimeric structure could result from coordination of the second triflate in solution. A sharp singlet was observed in $^{19}F\{^1H\}$ NMR, which could result from fast exchange on the NMR time-scale between coordinated and uncoordinated triflates or to magnetic equivalence due to coordination of both triflates to Ag^+ in a heterodinuclear structure. The broad $^{31}P\{^1H\}$ NMR resonance observed at room temperature for the P═O nuclei is consistent with a chemical exchange involving these nuclei. At least two possibilities can be envisaged (Scheme 5): migration of the Pt-bound P═O donor to silver with triflate migration from silver to platinum or a mutual, intramolecular exchange between the Pt- and Ag-bonded ligands. Unfortunately, the low-temperature $^{31}P\{^1H\}$ NMR spectra of **8**·OTf were too complicated to be readily interpreted. Low-temperature $^{195}Pt\{^1H\}$ NMR measurements showed an increasing broadening of the signal down to 183 K, preventing detection of J(Pt−Ag) coupling. Therefore, the dynamic exchanges sketched in Scheme 5 remain speculative.

Scheme 5. Possible Intramolecular Rearrangements of Monomeric **8**·OTf in Solution



Recently, dimetallic Pt/Ag systems have been employed in the hydroarylation of unactivated arenes and olefins under mild conditions.[25] These systems are not monomolecular but consist of a mixture of a Pt(II)−Cl complex and AgX (X = BF_4, OTf), and investigations showed that the role of the silver salts clearly extended beyond simple chloride abstraction. In the alkoxycarbonylation reaction with acetyl−Pd(II) complexes,[18] the intermediates in the precatalyst activation by chloride abstraction were found to contain Pd−Ag−Cl moieties. This is in agreement with our own recent studies on the reactivity of various halide abstractors, which surprisingly led to the isolation and structural characterization of an unprecedented Cl−Pt−Tl complex.[26]

Attempts to prepare dimetallic Pt−Tl or Pt−Au complexes related to **8** were unfortunately not successful. In contrast to the reaction with a second equivalent AgOTf, no reaction was observed between complex **6**, prepared from **5** and $TlPF_6$, and a second equivalent of $TlPF_6$. After mixing the compounds in an NMR tube using $CDCl_3$ as solvent, $TlPF_6$ remained undissolved even after 1 day and no change was observed in the $^{31}P\{^1H\}$ NMR spectrum. The reaction between **6**·BF_4 and [Au(BF_4)(tht)] (tht = tetrahydrothiophene) in CH_2Cl_2 at −60 °C also did not lead to the formation of a dimetallic compound, but rather to some decomposition of the gold precursor and formation of the mononuclear complex [PtMe(tht)(κ^2-PPO)]BF_4 (**9**·BF_4), which was also synthesized directly (see Experimental Section). According to the values of the ^1J(Pt−P) coupling constant of 4012 Hz, the PPh_2 group in this complex must be cis to the methyl ligand. The remaining Au precursor was complexed by two PPO ligands to yield [Au(κ^1-PPO)$_2$]BF_4 (**10**·BF_4), whose direct synthesis was carried out for comparison by a one-pot synthesis from [AuCl(tht)] and PPO (see Experimental

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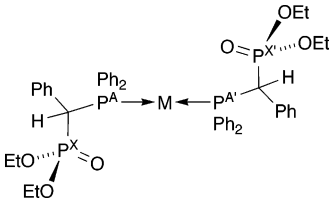
Section). Similar to compound **5**, **10**·BF_4 was obtained as a mixture of two pairs of diastereomers, but its $^{31}P\{^1H\}$ NMR spectrum contains two closely spaced triplets for the mutually trans PPh_2 groups, and two triplets for the P═O groups. Attempts were made to simulate the spectrum of this AA′XX′ spin system (A = A′ = P; X = X′ = P(O)) by using the program Win-Daisy.[27] Assuming very small, not detectable $J_{AX'}$ and $J_{A'X}$ coupling constants, a large coupling constant for the mutually trans PPh_2 nuclei was obtained ($J_{AA'} = 772$ Hz) and a small intra-ligand coupling constant ($J_{AX} = J_{A'X'} = 18$ Hz). The pattern of the signals changes to two singlets for the related Pt(II) complex **5**, because in this case the intra-ligand coupling constant ($J_{AX} = J_{A'X'}$) was also too small to be detected.



Conclusion

We have shown that the β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$ (abbreviated PPO) can display hemilabile behavior in Pt(II) alkyl or acyl complexes when two such functional ligands show a trans-arrangement of their phosphine functions. The carbonylation of the methyl complex **6**·OTf under 1 atm of CO leads to Pt(II) acetyl complex **7**, which is stable toward decarbonylation. As shown by the reactions of **5** and 2 equiv of Ag^+ or of **6**·OTf with 1 equiv of Ag^+, the Pt(II) center is sufficiently electron-rich to form a dimetallic Pt−Ag complex, (**8**·OTf)$_2$, whose crystal structure revealed the dimeric nature in the solid state, with two silver-bound triflates acting as bridging ligands. In addition to the Ag−Pt bond, the Ag^+ cation is stabilized by a dative O→Ag interaction involving one of the PPO ligands of **6**·OTf, which has turned from terminal to bridging ligand. In the context of reactivity studies, it is important to note that typical chloride abstractors, such as Ag^+, can compete with the hard donor end of difunctional ligands and interfere with their hemilabile behavior.

The study of the interactions between square-planar Pt(II) complexes and cationic Ag(I) complexes is relevant to the activation or properties of homogeneous catalysts involving these metals,[18,25] and it is clear that typical chloride abstractors, such as Ag^+, do not always merely behave in this way.

Experimental Section

General Procedures. All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.47, 282.40, and 121.49 MHz, respectively, using TMS, $CFCl_3$, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. Alternatively, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance 500 and 400 instruments at 500.13 and 202.46 MHz or 400.13 and 161.98 MHz, respectively. The $^{195}Pt\{^1H\}$ NMR spectra were recorded on the Bruker Avance 400 at 86.02 MHz using H_6PtCl_6 in D_2O as external standard. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by ^1H,^1H-COSY and ^1H,^{13}C-HMQC experiments. IR spectra in the range of 4000−400 cm^{-1} were recorded as KBr pellets on a FT-IR IFS66 Bruker spectrometer. Elemental C, H, and N analyses were performed by the "Service de microanalyses", Université Louis Pasteur, Strasbourg and at the "Chemisches Laboratorium" of the Universität Freiburg.

When BF_4^- was used as a counterion, the $^{19}F\{^1H\}$ spectra provided the appropriate signal with the pattern typical for B^{10}−F^{19} and B^{11}−F^{19} shifts.[28] The following compounds were synthesized according to literature procedures: [PtClMe(cod)],[29] [(diphenylphosphinophenyl)methyl]phosphonic acid diethyl ester (PPO),[6] and [AuCl(tht)].[30] Other chemicals were commercially available and used as received. All yields given are based on Pt.

Preparation and Spectroscopic Data for [PtClMe(κ^2-PPO)] (1). Solid [PtClMe(cod)] (0.34 g, 0.96 mmol) and PPO (0.40 g, 0.97 mmol) were dissolved in CH_2Cl_2 (25 mL), and the resulting solution was stirred for approximately 3 h at room temperature. The volatiles were then removed in vacuo (to remove liberated COD), and the residue was redissolved in CH_2Cl_2. This sequence was repeated until complete conversion has occurred (7 days). The crude product was obtained as a colorless powder, which was washed with diethyl ether (10 mL) followed by pentane (20 mL) and dried again in vacuo to afford **1** (0.59 g, 0.90 mmol, 94%). Suitable single crystals for X-ray analysis were obtained at room temperature by slow diffusion of pentane into a solution in CH_2Cl_2. IR: 1173 s cm^{-1} ($\nu_{P=O}$). ^1H NMR (CD_2Cl_2) δ: 0.74 (d, 3H, $^3J_{P-H} = 3.6$ Hz, $^2J_{Pt-H} = 88$ Hz, $PtCH_3$), 1.08 (dt, 3H, $^3J_{H-H} = 7.0$ Hz, $^4J_{P-H} = 0.8$ Hz, $POCH_2CH_3$), 1.10 (dt, 3H, $^3J_{H-H} = 7.0$ Hz, $^4J_{P-H} = 0.7$ Hz, $POCH_2CH_3$), 3.90−4.30 (overlapping m, 4H, $P(OCH_2CH_3)_2$), 4.32 (dd, 1H, $^2J_{P-H} = 21.1$ and 13.1 Hz, C*H*Ph), 7.10−7.60 (m, 13H, aryl-CH), 7.85−7.95 (m, 2H, aryl-CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: −24.4 (d, $^2J_{P-C} = 6.9$ Hz, $^1J_{Pt-C} = 742$ Hz, $PtCH_3$), 16.0 (d, $^3J_{P-C} = 6.6$ Hz, $POCH_2CH_3$), 16.1 (d, $^3J_{P-C} = 5.9$ Hz, $POCH_2CH_3$), 44.6 (dd, $^1J_{P-C} = 140.1$ and 21.4 Hz, *C*HPh), 65.0/66.4 (2 d, $^2J_{P-C} = 7.4$ Hz, $P(OCH_2CH_3)_2$), 123.9 (d, $^1J_{P-C} = 60.9$ Hz, $^3J_{P(O)-C} = 4.2$ Hz, *ipso*-aryls, PPh_2), 127.8−128.8 (m, aryl-CH), 129.8 (t, $^2J_{P-C} = 5.8$ Hz, *ipso*-aryl, CH*Ph*), 130.4/130.5 (2 d, $^3J_{P-C} = 8.1$ Hz, *m*-aryls, PPh_2), 131.8/132.1 (2 d, $^4J_{P-C} = 2.7$ Hz, *p*-aryls, PPh_2), 133.6 (d, $^2J_{P-C} = 11.3$ Hz, $^3J_{Pt-C} = 35$ Hz, *o*-aryl, PPh_2), 136.2 (d, $^2J_{P-C} = 12.2$ Hz, $^3J_{Pt-C} = 48$ Hz, *o*-aryl, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 14.2 (d, $^{2+3}J_{P-P} = 36$ Hz, $^1J_{Pt-P} = 4661$ Hz, PPh_2), 42.6 (d, $^{2+3}J_{P-P} = 36$ Hz, $^{2+3}J_{Pt-P} = 78$ Hz, P(O)). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2) δ: −4132 ($^1J_{P-Pt} = 4634$ Hz, $^{2+3}J_{P-Pt} = 77$ Hz). Anal. Calcd for $C_{24}H_{29}ClO_3P_2Pt$ (657.97): C, 43.81; H, 4.44. Found: C, 43.49; H, 4.27.

Preparation and Spectroscopic Data for [Pt{C(O)Me}Cl(κ^2-PPO)] (2). A solution of [PtClMe(κ^2-PPO)] (**1**) (0.30 g, 0.46 mmol) in CH_2Cl_2 (25 mL) was placed under CO (1 atm) and stirred for 5 h at room temperature. Removing all volatiles in vacuo and purification of the product by recrystallization from CH_2Cl_2/pentane (2/1) at 5 °C yielded **2** as a pale green solid (0.28 g, 0.41 mmol, 89%), mostly as single crystals suitable for X-ray structure analysis. IR: 1662 s (ν_{CO}), 1175 m cm^{-1} ($\nu_{P=O}$). ^1H NMR ($CDCl_3$) δ: 1.08

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(dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.8 Hz, $POCH_2CH_3$), 1.11 (dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.6 Hz, $POCH_2CH_3$), 2.08 (s, 3H, $C(O)CH_3$), 3.90−4.20 (overlapping m, 4H, $POCH_2CH_3$), 4.30 (dd, 1H, $^2J_{P-H}$ = 22.3 and 13.5 Hz, *CH*Ph), 7.00−7.20 (m, 7H, aryl-CH), 7.25−7.55 (m, 6H, aryl-CH), 7.85−7.95 (m, 2H, aryl-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.9 (d, $^3J_{P-C}$ = 6.9 Hz, $POCH_2CH_3$), 16.0 (d, $^3J_{P-C}$ = 6.2 Hz, $POCH_2CH_3$), 41.2 (d, $^3J_{P-C}$ = 4.2 Hz, $C(O)CH_3$), 44.7 (dd, $^1J_{P-C}$ = 138.4 and 20.1 Hz, *C*HPh), 64.7/66.0 (2 d, $^2J_{P-C}$ = 7.6 Hz, $P(OCH_2CH_3)_2$), 123.5 (dd, $^1J_{P-C}$ = 61.6 Hz, $^3J_{P(O)-C}$ = 3.5 Hz, *ipso*-aryls, PPh_2), 127.3−129.8 (m, aryls and *ipso*-aryl), 130.2/130.3 (2 d, $^3J_{P-C}$ = 8.3 Hz, *m*-aryls, PPh_2), 131.5/132.1 (2 d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryls, PPh_2), 133.0 (d, $^2J_{P-C}$ = 11.1 Hz, *o*-aryl, PPh_2), 136.1 (d, $^2J_{P-C}$ = 12.5 Hz, *o*-aryl, PPh_2), 190.1 (d, $^2J_{P-C}$ = 5.2 Hz, *C*(O)CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 12.2 (d, $^{2+3}J_{P-P}$ = 35 Hz, $^1J_{Pt-P}$ = 5086 Hz, PPh_2), 39.9 (d, $^{2+3}J_{P-P}$ = 35 Hz, $^{2+3}J_{Pt-P}$ = 51 Hz, P(O)). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −3457 (dd, $^1J_{P-Pt}$ = 5066 Hz, $^{2+3}J_{P-Pt}$ = 50 Hz). Anal. Calcd for $C_{25}H_{29}ClO_4P_2Pt$ (685.98): C, 43.77; H, 4.26. Found: C, 43.76; H, 4.291.

Preparation and Spectroscopic Data for [PtMe(CO)(κ²-PPO)]-OTf (3·OTf). Solid [Pt{C(O)Me}Cl(κ²-PPO)] (**2**) (0.16 g, 0.23 mmol) was dissolved in CH_2Cl_2 (20 mL), and solid AgOTf (0.06 g, 0.23 mmol) was added in one portion. A white precipitate formed immediately, and the mixture was stirred at room temperature for 1.5 h. Celite (0.5 g) was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as an off-white powder (0.15 g, 0.19 mmol, 83%). IR: 2093 m (ν_{CO}), 1166 s cm^{-1} ($\nu_{P=O}$). ^1H NMR ($CDCl_3$) δ: 1.08 (dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.9 Hz, $POCH_2CH_3$), 1.10 (dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 1.1 Hz, $POCH_2CH_3$), 1.43 (dd, 3H, $^3J_{P-H}$ = 7.4 Hz, $^4J_{P(O)-H}$ = 0.5 Hz, $^2J_{Pt-H}$ = 48 Hz, $PtCH_3$), 4.12/4.24 (2 dq, 4H, $^2J_{P-H}$ = 7.2 Hz, $^3J_{H-H}$ = 7.1 Hz, $P(OCH_2CH_3)_2$), 5.85 (dd, 1H, $^2J_{P-H}$ = 19.4 and 13.7 Hz, $^{3+4}J_{Pt-H}$ = 8 Hz, *CH*Ph), 7.05−7.70 (m, 13H, aryl-CH), 8.00−8.15 (m, 2H, aryl-CH). ^1H NMR (CD_2Cl_2) selected data δ: 5.32 (dd, 1H, $^2J_{P-H}$ = 13.4 and 20.4 Hz, $^{3+4}J_{Pt-H}$ = 8 Hz, *CH*Ph). $^1H\{^{31}P\}$ NMR ($CDCl_3$) selected data δ: 1.08/1.10 (2 t, 2 × 3H, $^3J_{H-H}$ = 7.1 Hz, $P(OCH_2CH_3)_2$), 1.43 (s, 3H, $^2J_{Pt-H}$ = 48 Hz, $PtCH_3$), 4.12/4.24 (2 q, $^3J_{H-H}$ = 7.1 Hz, 4H, $P(OCH_2CH_3)_2$), 5.85 (br s, 1H, *CH*Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 4.9 (dd, $^2J_{P-C}$ = 74.0 Hz, $^3J_{P(O)-C}$ = 4.7 Hz, $PtCH_3$), 15.6/15.7 (2 d, $^3J_{P-C}$ = 6.8 Hz, $P(OCH_2CH_3)_2$), 36.9 (dd, $^1J_{P-C}$ = 130.4 and 13.8 Hz, *C*HPh), 67.6 (d, $^2J_{P-C}$ = 7.8 Hz, $POCH_2CH_3$), 68.2 (d, $^2J_{P-C}$ = 7.7 Hz, $POCH_2CH_3$), 120.9 (br q, $^1J_{F-C}$ = 318.9 Hz, CF_3), 124.4 (dd, $^1J_{P-C}$ = 49.8 Hz, $^3J_{P(O)-C}$ = 7.0 Hz, *ipso*-aryl, PPh_2), 125.2 (dd, $^1J_{P-C}$ = 49.8 Hz, $^3J_{P(O)-C}$ = 4.8 Hz, *ipso*-aryl, PPh_2), 127.1 (t, $^2J_{P-C}$ = 5.7 Hz, *ipso*-aryl, CH*Ph*), 128.5−129.3/129.8−130.1 (2 m, aryls), 130.6/130.7 (2 d, $^3J_{P-C}$ = 7.7 Hz, *m*-aryls, PPh_2), 132.7 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl, PPh_2), 132.9 (d, $^4J_{P-C}$ = 2.3 Hz, *p*-aryl, PPh_2), 133.8 (d, $^2J_{P-C}$ = 12.6 Hz, $^3J_{Pt-C}$ = 12 Hz, *o*-aryl, PPh_2), 135.1 (d, $^2J_{P-C}$ = 13.1 Hz, $^3J_{Pt-C}$ = 14 Hz, *o*-aryl, PPh_2), 158.9 (dd, $^2J_{P-C}$ = 7.5 Hz, $^3J_{P(O)-C}$ = 3.3 Hz, C═O). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −78.5 (s, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 34.0 (d, $^{2+3}J_{P-P}$ = 74 Hz, $^1J_{Pt-P}$ = 1294 Hz, PPh_2), 59.3 (d, $^{2+3}J_{P-P}$ = 74 Hz, $^{2+3}J_{Pt-P}$ = 47 Hz, P(O)). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −4111 (br d, $^1J_{P-Pt}$ = 1297 Hz). Anal. Calcd for $C_{26}H_{29}F_3O_7P_2PtS$ (799.60): C, 39.06; H, 3.66. Found: C, 38.69; H, 4.04.

Alternatively, the product can be synthesized in quantitative spectroscopic yield by stirring a solution of **4** for 2 h under CO (1 atm) (NMR tube experiment).

Preparation and Spectroscopic Data for [PtMe(OTf)(κ²-PPO)] (4). Solid [PtClMe(κ²-PPO)] (**1**) (0.26 g, 0.40 mmol) was dissolved in CH_2Cl_2 (30 mL), and solid AgOTf (0.11 g, 0.43 mmol) was added in one portion. A white precipitate formed immediately, and the mixture was stirred at room temperature for 2 h. Celite (0.5 g) was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as an off-white powder (0.26 g, 0.34 mmol, 85%). Suitable single crystals for X-ray analysis were obtained from a solution in CH_2Cl_2/toluene (3/1) by slowly removing the solvents under reduced pressure. IR: 1171 s cm^{-1} ($\nu_{P=O}$). ^1H NMR (CD_2Cl_2) δ: 0.78 (d, 3H, $^3J_{P-H}$ = 1.2 Hz, $^2J_{Pt-H}$ = 77 Hz, $PtCH_3$), 1.14 (dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.6 Hz, $POCH_2CH_3$), 1.17 (dt, 3H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.5 Hz, $POCH_2CH_3$), 4.05−4.25 (overlapping m, 4H, $P(OCH_2CH_3)_2$), 4.59 (dd, 1H, $^2J_{P-H}$ = 22.7 and 14.3 Hz, *CH*Ph), 7.05−7.30 (m, 7H, aryl-CH), 7.40−7.52 (m, 3H, aryl-CH), 7.55−7.65 (m, 3H, aryl-CH), 7.80−7.95 (m, 2H, aryl-CH). ^1H NMR (500.13 MHz, CD_2Cl_2) selected data δ: 0.76 (d, 3H, $^3J_{P-H}$ = 1.1 Hz, $^2J_{Pt-H}$ = 78 Hz, $PtCH_3$), 4.54 (dd, 1H, $^2J_{P-H}$ = 22.7 and 14.2 Hz, *CH*Ph). $^1H\{^{31}P\}$ NMR (500.13 MHz, CD_2Cl_2) selected data δ: 0.76 (s, 3H, $^2J_{Pt-H}$ = 78 Hz, $PtCH_3$), 4.54 (br s, 1 H, *CH*Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: −20.3 (d, $^2J_{P-C}$ = 6.7 Hz, $^1J_{Pt-C}$ = 727 Hz, $PtCH_3$), 16.0 (d, $^3J_{P-C}$ = 6.4 Hz, $POCH_2CH_3$), 16.1 (d, $^3J_{P-C}$ = 6.2 Hz, $POCH_2CH_3$), 44.0 (dd, $^1J_{P-C}$ = 140.2 and 26.0 Hz, *C*HPh), 66.0 (d, $^2J_{P-C}$ = 7.5 Hz, $POCH_2CH_3$), 66.8 (d, $^2J_{P-C}$ = 7.8 Hz, $POCH_2CH_3$), 120.6 (br q, $^1J_{F-C}$ = 316.5 Hz, CF_3), 122.8 (dd, $^1J_{P-C}$ = 68.8 Hz, $^3J_{P(O)-C}$ = 2.7 Hz, *ipso*-aryl, PPh_2), 126.6 (dd, $^1J_{P-C}$ = 66.6 Hz, $^3J_{P-C}$ = 4.8 Hz, *ipso*-aryl, PPh_2), 128.2−129.7 (m, aryls and *ipso*-aryl), 130.5 (d, $^3J_{P-C}$ = 7.8 Hz, *m*-aryls, PPh_2), 130.6 (d, $^3J_{P-C}$ = 7.9 Hz, *m*-aryls, PPh_2), 132.5 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl, PPh_2), 132.9 (d, $^4J_{P-C}$ = 2.5 Hz, *p*-aryl, PPh_2), 133.3 (d, $^2J_{P-C}$ = 11.1 Hz, $^3J_{Pt-C}$ = 38 Hz, *o*-aryl, PPh_2), 136.2 (d, $^2J_{P-C}$ = 11.9 Hz, $^3J_{Pt-C}$ = 56 Hz, *o*-aryl, PPh_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ: −78.3 (s, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 9.9 (d, $^{2+3}J_{P-P}$ = 27 Hz, $^1J_{Pt-P}$ = 5360 Hz, PPh_2), 41.0 (d, $^{2+3}J_{P-P}$ = 27 Hz, $^{2+3}J_{Pt-P}$ = 120 Hz, P(O)). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2) δ: −4258 (br d, $^1J_{P-Pt}$ = 5363 Hz). Anal. Calcd for $C_{25}H_{29}F_3O_6P_2PtS$ (771.60): C, 38.92; H, 3.79; S, 4.16. Found: C, 38.85; H, 3.57; S, 3.67.

In-Situ Reaction between [PtMe(OTf)(κ²-PPO)] (4) and NCMe. Solid [PtMe(OTf)(κ²-PPO)] (**4**) (0.03 g, 0.04 mmol) was dissolved in NCMe (5 mL). After the mixture was stirred for 30 min, the solvent was removed in vacuo and the residue was redissolved in CD_2Cl_2 (0.5 mL). NMR data for [PtMe(NCMe)(κ²-PPO)]OTf, ^1H NMR (CD_2Cl_2) δ: 0.70 (d, 3H, $^3J_{P-H}$ = 2.9 Hz, $^2J_{Pt-H}$ = 82 Hz, $PtCH_3$), 1.09 (t, 3H, $^3J_{H-H}$ = 7.0 Hz, $POCH_2CH_3$), 1.10 (dt, 3H, $^3J_{H-H}$ = 7.0 Hz, $^4J_{P-H}$ = 0.7 Hz, $POCH_2CH_3$), 2.53 (s, 3H, $NCCH_3$), 3.95−4.20 (m, 4H, $P(OCH_2CH_3)_2$), 4.49 (dd, 1H, $^2J_{P-H}$ = 20.9 and 14.1 Hz, *CH*Ph), 7.10−7.30 (m, 7H, aryl-CH), 7.30−7.45 (m, 3H, aryl-CH), 7.55−7.65 (m, 3H, aryl-CH), 7.85−8.00 (m, 2H, aryl-CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: −23.7 (d, $^2J_{P-C}$ = 6.9 Hz, $^1J_{Pt-C}$ = 700 Hz, $PtCH_3$), 3.8 (s, $NCCH_3$), 15.9/16.0 (2 d, $^3J_{P-C}$ = 6.2 Hz, $P(OCH_2CH_3)_2$), 43.0 (dd, $^1J_{P-C}$ = 138.4 and 24.2 Hz, *C*HPh), 65.9/67.1 (2 d, $^2J_{P-C}$ = 7.6 Hz, $P(OCH_2CH_3)_2$), 121.3 (br q, $^1J_{F-C}$ = 320.8 Hz, CF_3), 121.0−126.5 (m, *ipso*-aryls and CH_3CN), 128.3 (t, $^2J_{P-C}$ = 5.5 Hz, *ipso*-aryl, CH*Ph*), 128.5−129.9 (m, aryls), 130.5/130.6 (2 d, $^3J_{P-C}$ = 7.6 Hz, *m*-aryls, PPh_2), 132.8/133.0 (2 d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryls, PPh_2), 133.8 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 39 Hz, *o*-aryl, PPh_2), 136.0 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 51 Hz, *o*-aryl, PPh_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ: = −79.1 (s, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 12.9 (d, $^{2+3}J_{P-P}$ = 33 Hz, $^1J_{Pt-P}$ = 4828 Hz, PPh_2), 44.5 (d, $^{2+3}J_{P-P}$ = 33 Hz, $^{2+3}J_{Pt-P}$ = 108 Hz, P(O)). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2) δ: −4365 (br d, $^1J_{P-Pt}$ = 4837 Hz).

In-Situ Reaction between [PtMe(OTf)(κ²-PPO)] (4) and C_2H_4. Solid [PtMe(OTf)(κ²-PPO)] (**4**) (0.03 g, 0.04 mmol) was dissolved

in CD_2Cl_2 (0.5 mL) and exposed to C_2H_4 (1 atm) for 1 h. Selected NMR data for [PtMe(C_2H_4)(κ^2-PPO)]OTf, ^{1}H NMR (CD_2Cl_2) δ: 0.70 (d, 3H, $^3J_{P-H}$ = 3.8 Hz, $^2J_{Pt-H}$ = 83 Hz, $PtCH_3$), 1.09 (br t, 3H, $^2J_{H-H}$ = 6.5 Hz, $POCH_2CH_3$), 1.11 (br t, 3H, $^2J_{H-H}$ = 6.8 Hz, $POCH_2CH_3$), 3.95−4.20 (m, 4H, $P(OCH_2CH_3)_2$), 4.89 (dd, 1H, $^2J_{P-H}$ = 20.8 and 14.4 Hz, C*H*Ph), 5.39 (s, free and coordinated ethylene), 7.05−7.35 (m, 9H, aryl-CH), 7.45−7.55 (m, 1H, aryl-CH), 7.55−7.70 (m, 3H, aryl-CH), 7.85−8.00 (m, 2H, aryl-CH). ^{19}F{^{1}H} NMR (CD_2Cl_2) δ: −79.0 (s, CF_3). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 19.4 (d, $^{2+3}J_{P-P}$ = 40 Hz, $^1J_{Pt-P}$ = 4335 Hz, PPh_2), 46.2 (d, $^{2+3}J_{P-P}$ = 40 Hz, $^{2+3}J_{Pt-P}$ = 73 Hz, P(O)).

Preparation and Spectroscopic Data for *trans*-[PtClMe(κ^1-PPO)$_2$] (5). Solid [PtClMe(cod)] (0.35 g, 1.00 mmol) and PPO (0.83 g, 2.01 mmol) were dissolved in CH_2Cl_2 (25 mL), and the resulting solution was stirred for 3 h at room temperature. Removing all volatiles in vacuo, washing the residue with a mixture of diethyl ether/pentane (1/5, 25 mL) followed by pentane (20 mL), and drying in vacuo afforded **5** as a colorless powder (1.01 g, 0.94 mmol, 94%). A mixture of diastereomers was obtained, and suitable single crystals for X-ray analysis were obtained from a solution in CH_2Cl_2/pentane (2/1) by slowly removing the solvents under reduced pressure for the CH_2Cl_2 adduct of the *RS*,*SR* diastereomer. IR: 1249 s cm^{-1} ($\nu_{P=O}$). ^{1}H NMR ($CDCl_3$) δ: −0.43/−0.39 (2 t, 2 × 3H, $^3J_{P-H}$ = 6.6 Hz, $^2J_{Pt-H}$ = 77 Hz, 2 $PtCH_3$), 0.85 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$), 0.91/0.94 (2 t, 2 × 6H, $^3J_{H-H}$ = 7.2 Hz, 2 $P(OCH_2CH_3)_2$), 1.08 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$), 3.55−4.15 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 6.20 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 26.6 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 12.6 Hz, 2 C*H*Ph), 6.22 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 24.2 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 12.2 Hz, 2 C*H*Ph), 6.95−7.35 (m, 44H, aryl-CH), 7.50−7.55/7.60−7.65 (2 m, 2 × 4H, aryl-CH), 7.90−7.95/8.05−8.10 (2 m, 2 × 4H, aryl-CH). ^{1}H NMR (500.13 MHz, CD_2Cl_2) δ: −0.46 (t, 3H, $^3J_{P-H}$ = 6.6 Hz, $^2J_{Pt-H}$ = 80 Hz, $PtCH_3$), −0.44 (t, 3H, $^3J_{P-H}$ = 6.5 Hz, $^2J_{Pt-H}$ = 80 Hz, $PtCH_3$), 0.95 (dt, 6H, $^3J_{H-H}$ = 7.0 Hz, $^4J_{P-H}$ = 0.5 Hz, $P(OCH_2CH_3)_2$), 1.01 (dt, 6H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{P-H}$ = 0.7 Hz, $P(OCH_2CH_3)_2$), 1.03/1.14 (2 t, 2 × 6H, $^3J_{H-H}$ = 7.1 Hz, 2 $P(OCH_2CH_3)_2$), 3.65−4.15 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 6.13 (d of virtual t, 2 × 2H, $^2J_{P(O)-H}$ = 25.9 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 11.2 Hz, 4 C*H*Ph), 7.05−7.10 (m, 8H, aryl-CH), 7.15−7.20 (m, 16H, aryl-CH), 7.25−7.35 (m, 8H, aryl-CH), 7.35−7.45 (m, 12H, aryl-CH), 7.50−7.55/7.60−7.65 (2 m, 2 × 4H, aryl-CH), 7.90−7.95/8.05−8.10 (2 m, 2 × 4H, aryl-CH). ^{1}H-{^{31}P} NMR (500.13 MHz, CD_2Cl_2) selected data δ: −0.46/−0.45 (2 s, 2 × 3H, $^2J_{Pt-H}$ = 81 Hz, $PtCH_3$), 0.95/1.01/1.03/1.14 (4 t, 4 × 6H, $^3J_{H-H}$ = 7.0 Hz, 4 $P(OCH_2CH_3)_2$), 6.13 (br s, 2 × 2H, 4 C*H*Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: −10.8/−10.1 (2 t, $^2J_{P-C}$ = 5.3 Hz, $PtCH_3$), 15.4/15.5/15.6/15.9 (4 d, $^3J_{P-C}$ = 5.6 Hz, 4 $P(OCH_2CH_3)_2$), 39.2 (d of virtual t, $^1J_{P(O)-C}$ = 133.4 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 15.6 Hz, 2 *C*HPh), 40.4 (d of virtual t, $^1J_{P(O)-C}$ = 132.8 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 17.4 Hz, 2 *C*HPh), 61.3/61.7/62.2/62.4 (4 d, $^2J_{P-C}$ = 6.8 Hz, 4 $P(OCH_2CH_3)_2$), 126.4−128.0 (m, aryls), 129.4 (d, J_{P-C} = 13.0 Hz, aryl-CH, PPh_2), 130.0 (d, J_{P-C} = 15.5 Hz, aryl-CH, PPh_2), 131.7 (br s, *p*-aryls, PPh_2), 133.4 (dd, $^2J_{P-C}$ = 40.3 and 21.1 Hz, *ipso*-aryls, CH*Ph*), 133.9/134.2 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 11.4 Hz, *o*-aryls, PPh_2), 136.4/136.7 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 13.6 Hz, *o*-aryls, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 23.1 (s, $^3J_{Pt-P}$ = 45 Hz, P(O)), 23.5 (s, $^3J_{Pt-P}$ = 82 Hz, P(O)), 32.8 (s, $^1J_{Pt-P}$ = 3250 Hz, PPh_2), 32.9 (s, $^1J_{Pt-P}$ = 3242 Hz, PPh_2). ^{195}Pt-{^{1}H} NMR ($CDCl_3$) δ: −4582 (tt, $^1J_{P-Pt}$ = 3239 Hz, $^3J_{P-Pt}$ = 82 Hz), −4580 (tt, $^1J_{P-Pt}$ = 3237 Hz, $^3J_{P-Pt}$ = 44 Hz). Anal. Calcd for $C_{47}H_{55}ClO_6P_4Pt$ (1070.38): C, 52.74; H, 5.18. Found: C, 52.47; H, 5.27.

Alternatively, the product can be synthesized in quantitative spectroscopic yield by addition of 1 equiv of PPO to a solution of **1** in CD_2Cl_2 and stirring for 2.5 days (NMR tube experiment).

Preparation and Spectroscopic Data for [PtMe(κ^2-PPO)(κ^1-PPO)]BF$_4$ (6·BF$_4$). Solid [PtClMe(κ^2-PPO)$_2$] (**5**) (0.58 g, 0.54 mmol) was dissolved in CH_2Cl_2 (30 mL), and $AgBF_4$ (0.11 g, 0.57 mmol) was added in one portion. A white precipitate formed immediately, and the mixture was stirred at room temperature for 1 h. Celite (0.5 g) was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as a mixture of diastereomers in the form of an off-white powder (0.53 g, 0.47 mmol, 87%). IR: 1250 m ($\nu_{P=O}$), 1162 s cm^{-1} ($\nu_{P=O}$, coord.). ^{1}H NMR ($CDCl_3$) δ: 0.30/0.32 (2 t, 2 × 3H, $^3J_{P-H}$ = 6.6 Hz, $^2J_{Pt-H}$ = 88 Hz, 2 $PtCH_3$), 1.00/1.01 (2 dt, 2 × 6H, $^3J_{H-H}$ = 7.0 Hz, $^4J_{P-H}$ = 0.6 Hz, 2 $P(OCH_2CH_3)_2$), 1.06/1.08 (2 t, 2 × 6H, $^3J_{H-H}$ = 7.0 Hz, 2 $P(OCH_2CH_3)_2$), 3.70−4.10 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 4.93 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 22.5 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.8 Hz, 2 C*H*Ph), 4.95 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 22.6 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 11.0 Hz, 2 C*H*Ph), 7.10−7.35 (m, 28H, aryl-CH), 7.40−7.55 (m, 16H, aryl-CH), 7.55−7.65 (m, 8H, aryl-CH), 7.85−7.95 (m, 8H, aryl-CH). ^{19}F{^{1}H} NMR ($CDCl_3$) δ: −152.7 (s, BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 29.4 (t, J_{P-P} = 19 Hz, $^1J_{Pt-P}$ = 3174 Hz, PPh_2), 29.6 (t, J_{P-P} = 20 Hz, $^1J_{Pt-P}$ = 3180 Hz, PPh_2), 35.5 (br, P(O)). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4386 (br t, $^1J_{P-Pt}$ = 3157 Hz), −4392 (br t, $^1J_{P-Pt}$ = 3180 Hz). Anal. Calcd for $C_{47}H_{55}BF_4O_6P_4Pt$ (1121.73): C, 50.33; H, 4.94. Found: C, 50.29; H, 5.22.

Preparation and Spectroscopic Data for [PtMe(κ^2-PPO)(κ^1-PPO)]OTf (6·OTf). This product was synthesized from **5** by addition of 1 equiv of solid AgOTf to a solution of **5** in CH_2Cl_2 and stirring for 1 h. The workup was similar to that for **6**·BF_4, and the product was isolated in 85% yield. The ratio of diastereomers (as determined by ^{1}H NMR resonance of the Pt−Me group) was 2:1 directly after the reaction, but 1:1 after 2 days. ^{1}H NMR (CD_2Cl_2) δ: 0.35 (t, 3H, $^3J_{P-H}$ = 6.7 Hz, $^2J_{Pt-H}$ = 89 Hz, $PtCH_3$, diastereomer 1), 0.36 (t, 3H, $^3J_{P-H}$ = 6.7 Hz, $^2J_{Pt-H}$ = 89 Hz, $PtCH_3$, diastereomer 2), 1.01 (dt, 6H, $^2J_{P-H}$ = 0.7 Hz, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 1), 1.02 (dt, 6H, $^2J_{P-H}$ = 0.5 Hz, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 2), 1.06 (dt, 6H, $^2J_{P-H}$ = 0.7 Hz, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 1), 1.08 (dt, 6H, $^2J_{P-H}$ = 0.5 Hz, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 2), 3.70−4.10 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 4.71 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 22.7 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.7 Hz, 2 C*H*Ph, diastereomer 2), 4.72 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 22.9 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.7 Hz, 2 C*H*Ph, diastereomer 1), 7.20−7.40 (m, 28H, aryl-CH), 7.45−7.60 (m, 24H, aryl-CH), 7.80−7.90 (m, 8H, aryl-CH). ^{1}H{^{31}P} NMR (CD_2Cl_2) selected data δ: 0.35 (s, 3H, $^2J_{Pt-H}$ = 89 Hz, $PtCH_3$, diastereomer 1), 0.36 (s, 3H, $^2J_{Pt-H}$ = 89 Hz, $PtCH_3$, diastereomer 2), 1.01 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 1), 1.02 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, 2 $POCH_2CH_3$, diastereomer 2), 4.71 (br s, 2 × 2H, 4 C*H*Ph). ^{13}C-{^{1}H} NMR (CD_2Cl_2) δ: −20.6/−20.2 (2 t, $^2J_{P-C}$ = 5.2 Hz, $^1J_{Pt-C}$ = 717 Hz, 2 $PtCH_3$), 16.0/16.1/16.1/16.2 (4 d, $^3J_{P-C}$ = 6.2 Hz, 4 $P(OCH_2CH_3)_2$), 42.2/42.3 (2 d virtual t, $^1J_{P(O)-C}$ = 136.3 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 16.6 Hz, 4 *C*HPh), 64.4/64.5 (2 d, $^2J_{P-C}$ = 6.9 Hz, 4 $POCH_2CH_3$), 65.3/65.4 (2 d, $^2J_{P-C}$ = 7.6 Hz, 4 $POCH_2CH_3$), 121.4 (br q, $^1J_{F-C}$ = 321.1 Hz, CF_3), 124.5−125.7/126.3−127.5 (2 br m, *ipso*-aryls, PPh_2), 128.5−129.5 (2 m, aryls), 130.1−130.6 (m, *ipso*-aryls, *C*HPh), 131.3−131.6/132.1−132.4 (2 m, aryls, PPh_2), 134.7/134.9 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 14.1 Hz, *o*-aryls, PPh_2), 135.6/135.7 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 13.9 Hz, *o*-aryls, PPh_2). ^{19}F{^{1}H} NMR (CD_2Cl_2) δ: −79.2 (s, CF_3). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 29.0 (t, J_{P-P} = 20 Hz, $^1J_{Pt-P}$ = 3175 Hz, PPh_2, diastereomer 2), 29.3 (t,

J_{P-P} = 19 Hz, $^1J_{Pt-P}$ = 3194 Hz, PPh_2, diastereomer 1), 34.9 (br, P(O)). $^{31}P\{^1H\}$ NMR (161.98 MHz, $C_2D_2Cl_4$, 383 K) δ: 29.7 (t, J_{P-P} = 18.3 Hz, $^1J_{Pt-P} \approx$ 3200 Hz, PPh_2), 29.8 (t, J_{P-P} = 17.6 Hz, $^1J_{Pt-P} \approx$ 3200 Hz, PPh_2), 34.3 (t, J_{P-P} = 17.2 Hz, P(O)), 34.4 (t, J_{P-P} = 18.4 Hz, P(O)). $^{31}P\{^1H\}$ NMR (202.46 MHz, CD_2Cl_2, 187 K) δ: 20.0 (s, P(O), noncoord.), 21.6 (s, P(O), noncoord.), spin system ABMX (A = B = P, M = P(O), X = Pt), 24.1 (dd, $^2J_{A-B} \approx$ 415 Hz, $^2J_{A-M}$ = 45 Hz, $^1J_{A-X} \approx$ 3000 Hz, PPh_2, chelated ligand, diastereomer 2), 24.4 (dd, $^2J_{A-B} \approx$ 430 Hz, $^2J_{A-M}$ = 47 Hz, $^1J_{A-X} \approx$ 3150 Hz, PPh_2, chelated ligand, diastereomer 1), 31.1 (d, $^2J_{A-B}$ = 422 Hz, $^2J_{B-M} \approx$ 0 Hz, $^1J_{B-X} \approx$ 3240 Hz, 2 PPh_2, nonchelated ligand), 48.0 (br, P(O), coord., diastereomer 2), 49.6 (br, P(O), coord., diastereomer 1). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ = −4388 (br t, $^1J_{P-Pt}$ = 3171 Hz), −4394 (br t, $^1J_{P-Pt}$ = 3175 Hz).

Preparation and Spectroscopic Data for [Pt{C(O)Me}(κ^2-PPO)(κ^1-PPO)]BF_4 (7·BF_4). A solution of [PtMe(κ^2-PPO)(κ^1-PPO)]BF_4 (**6**·BF_4) (0.34 g, 0.30 mmol) in CH_2Cl_2 (25 mL) was placed under CO (1 atm) and stirred for 4 h at room temperature. Removing all volatiles in vacuo and purification by precipitation with pentane yielded a mixture of diastereomers **7**·BF_4 as a white solid (0.31 g, 0.27 mmol, 90%). IR: 1658 s (ν_{CO}), 1250 s ($\nu_{P=O}$, noncoord.), 1163 s cm^{-1} ($\nu_{P=O}$, coord.). ^1H NMR ($CDCl_3$) δ: = 0.95/1.00 (2 dt, 2 × 6H, $^2J_{P-H}$ = 0.7 Hz, $^3J_{H-H}$ = 7.1 Hz, 2 $P(OCH_2CH_3)_2$), 1.09 (s, 3H, $C(O)CH_3$), 1.10/1.11 (2 t, 2 × 6H, $^3J_{H-H}$ = 7.1 Hz, 2 $P(OCH_2CH_3)_2$), 1.36 (s, 3H, $C(O)CH_3$), 3.50−3.90 (overlapping m, 8H, 4 $P(OCH_2CH_3)_2$), 4.95 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 25.1 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 12.8 Hz, 2 C*H*Ph), 5.01 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 24.0 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 12.3 Hz, 2 C*H*Ph), 7.10−7.55 (m, 44H, aryl-CH), 7.60−7.80 (m, 8H, aryl-CH), 7.85−8.00 (m, 8H, aryl-CH). $^1H\{^{31}P\}$ NMR ($CDCl_3$) selected data δ: 4.95/5.01 (2 br s, 4H, 4 C*H*Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.7/15.8/15.9/16.0 (4 d, $^3J_{P-C}$ = 6.5 Hz, 4 $P(OCH_2CH_3)_2$), 41.6/41.7 (2 d of virtual t, $^1J_{P(O)-C}$ = 134.0 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 17.3 Hz, 4 *C*HPh), 41.6 (t, $^3J_{P-C}$ = 5.8 Hz, $C(O)CH_3$), 41.9 (t, $^3J_{P-C}$ = 5.6 Hz, $C(O)CH_3$), 64.1/64.3/64.4/64.6 (4 d, $^2J_{P-C}$ = 7.6 Hz, 4 $P(OCH_2CH_3)_2$), 125.0−126.1 (m, *ipso*-aryls, PPh_2), 127.7−129.0 (m, aryls), 129.2−129.6 (m, *ipso*-aryls, *C*HPh), 130.9−132.1 (m, aryls), 134.6/134.9/135.1/135.6 (4 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 13.8 Hz, *o*-aryls, PPh_2), 196.1 (t, $^2J_{P-C}$ = 5.3 Hz, *C*(O)CH_3), 196.9 (t, $^2J_{P-C}$ = 5.1 Hz, *C*(O)CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −152.4 (s, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 25.4 (t, J_{P-P} = 16 Hz, $^1J_{Pt-P}$ = 3638 Hz, PPh_2), 26.0 (t, J_{P-P} = 17 Hz, $^1J_{Pt-P}$ = 3624 Hz, PPh_2), 33.3 (br, P(O)). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −3662 (br t, $^1J_{P-Pt}$ = 3630 Hz), −3674 (br t, $^1J_{P-Pt}$ = 3620 Hz). Anal. Calcd for $C_{48}H_{55}BF_4O_7P_4Pt$ (1149.74): C, 50.14; H, 4.82. Found: C, 49.89; H, 5.18.

Preparation and Spectroscopic Data for [PtMe(κ^2-PPO){μ-(η^1-*P*;η^1-*O*)PPO}Ag(OTf)(*Pt*−*Ag*)]OTf (8·OTf). Solid [PtClMe(κ^2-PPO)$_2$] (**5**) (0.35 g, 0.33 mmol) was dissolved in CH_2Cl_2 (30 mL), and solid AgOTf (0.17 g, 0.66 mmol) was added in one portion. A white precipitate was formed immediately, and the mixture was stirred at room temperature for 2 h. Celite (0.5 g) was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as an off-white powder (0.43 g, 0.30 mmol, 91%). This mixture of diastereomers was redissolved in CH_2Cl_2/toluene (3/1), and slow removal of the solvents under reduced pressure afforded suitable single crystals for X-ray analysis of the *RR*,*SS* diastereomer. IR: 1262 s cm^{-1} ($\nu_{P=O}$, coord. to Pt). ^1H NMR (CD_2Cl_2) δ: 0.50/0.54 (2 t, 2 × 3H, $^3J_{P-H}$ = 6.6 Hz, $^2J_{Pt-H}$ = 87 Hz, 2 $PtCH_3$), 1.01/1.02/1.08/1.16 (4 t, 4 × 6H, $^3J_{H-H}$ = 7.0 Hz, 4 $P(OCH_2CH_3)_2$), 3.80−4.20 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 4.84 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 23.6 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 11.4 Hz, 2 C*H*Ph), 4.99 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 24.7 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 11.8 Hz, 2 C*H*Ph), 7.15−7.30 (m, 20H, aryl-CH), 7.35−7.45 (m, 8H, aryl-CH), 7.50−7.60 (m, 24H, aryl-CH), 7.75−7.90 (m, 8H, aryl-CH). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, select.) δ: 0.49/0.52 (2 s, 2 × 3 H, $^2J_{Pt-H}$ = 87 Hz, 2 $PtCH_3$), 4.82/4.97 (2 br s, 2 × 2H, 4 C*H*Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: −20.3 (t, $^2J_{P-C}$ = 5.2 Hz, $PtCH_3$), −19.3 (t, $^2J_{P-C}$ = 4.8 Hz, $PtCH_3$), 15.9/16.0/16.1/16.2 (4 d, $^3J_{P-C}$ = 6.2 Hz, 4 $P(OCH_2CH_3)_2$), 41.8/42.0 (2 d of virtual t, $^1J_{P(O)-C}$ = 135.6 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 16.6 Hz, 4 *C*HPh), 64.9/65.2/65.3/65.4 (4 d, $^2J_{P-C}$ = 7.6 Hz, 4 $P(OCH_2CH_3)_2$), 121.2 (q, $^1J_{F-C}$ = 320.4 Hz, CF_3), 123.5−127.0 (m, *ipso*-aryls, PPh_2), 128.7−130.2 (m, aryls and *ipso*-aryl), 131.2−131.6/132.1−132.8 (2 m, aryls), 134.0/134.5 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 12.4 Hz, *o*-aryls, PPh_2), 135.8/136.2 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 13.8 Hz, *o*-aryls, PPh_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ: −78.7 (s, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 27.8 (t, J_{P-P} = 19 Hz, $^1J_{Pt-P}$ = 3036 Hz, PPh_2), 28.9 (t, J_{P-P} = 18 Hz, $^1J_{Pt-P}$ = 3066 Hz, PPh_2), 34.3 (br, P(O)). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2) δ: −4299 (br t, $^1J_{P-Pt} \approx$ 2990 Hz), −4301 (br t, $^1J_{P-Pt} \approx$ 3050 Hz). Anal. Calcd for $C_{49}H_{55}AgF_6O_{12}P_4PtS_2$ (1440.93): C, 40.84; H, 3.85; S, 4.45. Found: C, 40.92; H, 3.64; S, 4.14.

Alternatively, the product can be synthesized in quantitative spectroscopic yield ($^{31}P\{^1H\}$ NMR) by addition of 1 equiv of AgOTf to a CH_2Cl_2 solution of **6**·OTf and stirring for 2 h.

Reaction between [Au(BF_4)(tht)] and 6·BF_4. Solid [AuCl(tht)] (0.10 g, 0.31 mmol) in CH_2Cl_2 (10 mL) was cooled to −60 °C, and $AgBF_4$ (0.06 g, 0.31 mmol) was added in one portion. The mixture was stirred for 2 h at −60 °C, and then the precipitate was allowed to settle. The filtered solution of [Au(BF_4)(tht)] was added via cannula to a solution of [PtMe(κ^2-PPO)(κ^1-PPO)]BF_4 (**6**·BF_4) (0.33 g, 0.29 mmol) in CH_2Cl_2 (10 mL) at −60 °C. The mixture was stirred for 3 h while kept at this temperature. Removing the solvent in vacuo was followed by extraction of the residue at −60 °C with CH_2Cl_2. NMR spectra showed the existence of a mixture of [PtMe(tht)(κ^2-PPO)]BF_4 (**9**·BF_4) and [Au(κ^1-PPO)$_2$]BF_4 (**10**·BF_4). A crystalline powder of one diastereomer of **10**·BF_4 with 0.5 equiv of CH_2Cl_2 could be obtained by repeated crystallization at 5 °C from a solution in CH_2Cl_2 layered with pentane. IR: 1248 s cm^{-1} ($\nu_{P=O}$, noncoord.). ^1H NMR ($CDCl_3$) δ: 0.87 (t, 6H, $^3J_{H-H}$ = 7.1 Hz, 2 $POCH_2CH_3$), 0.90 (dt, 6H, $^3J_{P-H}$ = 1.6 Hz, $^3J_{H-H}$ = 7.1 Hz, 2 $POCH_2CH_3$), 3.60−3.95 (overlapping m, 8H, 2 $P(OCH_2CH_3)_2$), 5.03 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 20.9 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.4 Hz, 2 C*H*Ph), 5.30 (s, 1H, CH_2Cl_2), 7.10−7.20/7.35−7.45 (2 m, 2 × 7H, aryl-CH), 7.55−7.65/7.70−7.75/7.85−7.95/8.15−8.25 (4 m, 4 × 4H, aryl-CH). $^1H\{^{31}P\}$ NMR ($CDCl_3$) selected data δ: 0.87/0.90 (2 t, 2 × 6H, $^3J_{H-H}$ = 7.1 Hz, 2 $P(OCH_2CH_3)_2$), 5.03 (s, 2H, 2 C*H*Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.8/15.9 (2 d, $^3J_{P-C}$ = 6.2 Hz, 2 $P(OCH_2CH_3)_2$), 43.5 (d of virtual t, $^1J_{P(O)-C}$ = 134.9 Hz, $|^1J_{P-C} + {}^3J_{P-C}|$ = 11.8 Hz, 2 *C*HPh), 53.4 (CH_2Cl_2), 62.5/64.3 (2 d, $^2J_{P-C}$ = 7.7 Hz, 2 $P(OCH_2CH_3)_2$), 126.2−130.1 (m, aryls), 131.1−131.5 (m, aryls), 132.3/132.7 (2 s, *p*-aryls, PPh_2), 134.5/135.2 (2 virtual t, $|^2J_{P-C} + {}^4J_{P-C}|$ = 16.0 Hz, *o*-aryls, PPh_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −152.9 (s, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 21.0 (t, J_{P-P} = 9.0 Hz, P(O)), 50.6 (t, J_{P-P} = 9.0 Hz, PPh_2). Anal. Calcd for $C_{46}H_{52}AuBF_4O_6P_4$·0.5CH_2Cl_2 (1151.05): C, 48.52; H, 4.64. Found: C, 48.12; H, 4.79.

Preparation and Spectroscopic Data for [PtMe(tht)(κ^2-PPO)]-BF_4 (9·BF_4). Solid [PtClMe(cod)] (0.15 g, 0.48 mmol) and PPO (0.17 g, 0.48 mmol) were dissolved in CH_2Cl_2 (20 mL), and then THT (ca. 0.5 mL) and solid $AgBF_4$ (0.10 g, 0.51 mmol) were added. A white precipitate formed immediately, and the mixture was stirred at room temperature for 2 h. Celite (0.5 g) was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as a

Table 4. Selected Crystallographic Data for Complexes **1**, **2**, **4**, **5**·CH_2Cl_2, and (**8**·$OTf)_2$

	1	2	4	**5**·CH_2Cl_2	(**8**·$OTf)_2$
formula	$C_{24}H_{29}ClO_3P_2Pt$	$C_{25}H_{29}ClO_4P_2Pt$	$C_{25}H_{29}F_3O_6P_2PtS$	$C_{47}H_{55}ClO_6P_4Pt$, CH_2Cl_2	$C_{98}H_{110}Ag_2F_{12}O_{24}P_8Pt_2S_4$
fw	657.95	685.96	771.57	1155.26	2881.78
cryst system	orthorhombic	orthorhombic	monoclinic	triclinic	triclinic
space group	*Aba*2	$P2_12_12_1$	*C*2/*c*	*P*-1	*P*-1
a (Å)	32.453(5)	11.8980(3)	16.876(2)	11.260(5)	13.550(5)
b (Å)	17.774(2)	13.3110(3)	10.482(1)	13.878(5)	14.827(5)
c (Å)	8.834(1)	16.5850(4)	33.257(5)	16.347(5)	15.009(5)
α (deg)				90.352(5)	90.958(5)
β (deg)			90.87(5)	102.141(5)	109.643(5)
γ (deg)				101.173(5)	94.520(5)
V (Å^3)	5096(1)	2626.6 (1)	5882(1)	2447(2)	2828(2)
Z	8	4	8	2	1
crystal size (mm^3)	0.10 × 0.08 × 0.06	0.12 × 0.10 × 0.08	0.12 × 0.10 × 0.08	0.10 × 0.10 × 0.10	0.13 × 0.10 × 0.08
color	colorless	pale green	off-white	colorless	colorless
D_{calc} (g cm^{-3})	1.715	1.735	1.742	1.568	1.692
μ (mm^{-1})	5.760	5.594	5.006	3.208	3.081
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
F(000)	2576	1344	3024	1164	1432
Θ limits (deg)	0.997/30.04	0.998/27.47	0.972/30.01	0.988/30.06	0.996/30.04
no. of data measured	3940	5751	8340	14 307	16 464
no. of data ($I > 2\sigma(I)$)	2551	5139	6467	12 766	13 584
no. of parameters	271	292	337	559	658
flack param.		−0.006(8)			
R	0.0318	0.0347	0.0401	0.0322	0.0499
R_w	0.0755	0.0815	0.1057	0.0811	0.1381
GOF	0.871	0.871	1.133	0.990	1.124
max/min res. dens. (e Å^{-3})	1.484/−1.047	0.848/−1.183	3.513/−2.028	2.254/−2.085	1.829/−1.848

colorless powder (0.35 g, 0.44 mmol, 92%). IR: 1163 s cm^{-1} ($\nu_{P=O}$). ^{1}H NMR ($CDCl_3$) δ: 0.53 (d, 3H, $^3J_{P-H}$ = 3.8 Hz, $^2J_{Pt-H}$ = 71 Hz, $PtCH_3$), 1.06/1.08 (2 t, 6H, $^3J_{H-H}$ = 7.0 Hz, $P(OCH_2CH_3)_2$), 2.08 (br s, 4H, SCH_2CH_2), 3.13 (br s, 4H, SCH_2CH_2), 4.00−4.20 (m, 4H, $P(OCH_2CH_3)_2$), 4.85 (dd, 1H, $^2J_{P-H}$ = 21.0 and 13.9 Hz, $^{3+4}J_{Pt-H}$ = 23 Hz, C*H*Ph), 7.05−7.25 (m, 7H, aryl-CH), 7.30−7.45 (m, 3H, aryl-CH), 7.50−7.60 (m, 3H, aryl-CH), 7.90−8.00 (m, 2H, aryl-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: −23.2 (br s, $^1J_{Pt-C}$ = 718 Hz, $PtCH_3$), 15.8/15.9 (2 d, $^3J_{P-C}$ = 6.2 Hz, $P(OCH_2CH_3)_2$), 28.0 (s, tht), 30.8 (s, tht), 41.8 (dd, $^1J_{P-C}$ = 137.7 and 20.1 Hz, *C*HPh), 65.7/66.3 (2 d, $^2J_{P-C}$ = 7.6 Hz, $P(OCH_2CH_3)_2$), 121.9−125.8 (m, *ipso*-aryls), 128.1−129.5 (m, aryls), 130.4/130.5 (2 d, $^3J_{P-C}$ = 8.3 Hz, *m*-aryls, PPh_2), 132.1/132.5 (2 d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryls, PPh_2), 133.6 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 31 Hz, *o*-aryl, PPh_2), 135.9 (d, $^2J_{P-C}$ = 12.4 Hz, $^3J_{Pt-C}$ = 42 Hz, *o*-aryl, PPh_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −153.5 (s, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 18.4 (d, $^{2+3}J_{P-P}$ = 36 Hz, $^1J_{Pt-P}$ = 4012 Hz, PPh_2), 45.9 (d, $^{2+3}J_{P-P}$ = 36 Hz, $^{2+3}J_{Pt-P}$ = 63 Hz, P(O)). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ: −4342 (dd, $^1J_{P-Pt}$ = 4000 Hz, $^{2+3}J_{P-Pt}$ = 66 Hz). Anal. Calcd for $C_{28}H_{37}BF_4O_3P_2PtS$ (797.50): C, 42.17; H, 4.68. Found: C, 42.34; H, 4.91.

Preparation and Spectroscopic Data for [Au(κ^1-PPO)$_2$]BF$_4$ (10·BF$_4$). Solid [AuCl(tht)] (0.10 g, 0.31 mmol) and PPO (0.26 g, 0.63 mmol) were dissolved in CH_2Cl_2 (10 mL), and $AgBF_4$ (0.06 g, 0.31 mmol) was added in one portion. The mixture was stirred for 2 h at room temperature, and then the precipitate was allowed to settle. Filtration and removal of the volatiles afforded a colorless powder, which was found to be a diastereomeric mixture of the product (0.31 g, 0.28 mmol, 90%). The following spectroscopic assignments are consistent with the data obtained for one of the diastereomers of **10**·BF_4 (see above). IR: 1248 s cm^{-1} ($\nu_{P=O}$). ^{1}H NMR ($CDCl_3$) δ: 0.84−0.94 (m, 2 × 6H, 4 $P(OCH_2CH_3)_2$), 3.60−3.95 (overlapping m, 2 × 8H, 4 $P(OCH_2CH_3)_2$), 5.01 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 20.7 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.3 Hz, 2 C*H*Ph), 5.03 (d of virtual t, 2H, $^2J_{P(O)-H}$ = 20.9 Hz, $|^2J_{P-H} + {}^4J_{P-H}|$ = 10.4 Hz, 2 C*H*Ph), 7.00−8.40 (overlapping m, 2 × 30H, aryl-CH). $^1H\{^{31}P\}$ NMR ($CDCl_3$) selected data δ: 5.01/5.03 (2 s, 2 × 2H, 2 × 2 C*H*Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.7/15.8 (2 d, $^3J_{P-C}$ = 6.8 Hz, 4 $P(OCH_2CH_3)_2$), 42.5−44.7 (overlapping m, 4 *C*HPh), 62.5/62.6 (2 d, $^2J_{P-C}$ = 7.4 Hz, 2 $P(OCH_2CH_3)_2$), 64.3 (d, $^2J_{P-C}$ = 7.4 Hz, 2 $P(OCH_2CH_3)_2$), 126.0−136.0 (overlapping m, aryls). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ: −152.9 (s, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 21.0 (t, J_{P-P} = 9.0 Hz, P(O)), 21.1 (t, J_{P-P} = 9.7 Hz, P(O)), 50.2 (t, J_{P-P} = 9.7 Hz, PPh_2), 50.6 (t, J_{P-P} = 9.0 Hz, PPh_2).

X-ray Collection and Structure Determinations. The diffraction data were collected on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, λ = 0.71070 Å; ϕ scan). The relevant data were summarized in Table 4. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in ϕ angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software. The absorption was corrected empirically (with Sortav) for compounds **1**, **2**, **4**, **5**·CH_2Cl_2, and (**8**·$OTf)_2$.[31] All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were included in their calculated positions and refined with a riding model in SHELXL97.[32]

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Supporting Information Available: Crystallographic information files (CIF), variable-temperature $^{31}P\{^{1}H\}$ NMR and P,P-COSY spectra of compound **6**, and ORTEP plots for complexes **1**, **2**, **4**, **5**·CH_2Cl_2, and (**8**·$OTf)_2$. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic material can also be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk), deposition numbers CCDC 252485−252489.

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