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Synthesis and characterization of bifunctional *trans*-$(Ph_3P)_2Pt(CO_2Me)(X)$ complexes

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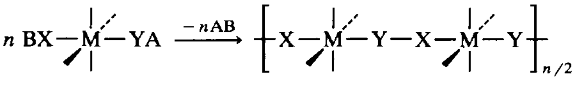
Abstract

A series of *trans*-$(Ph_3P)_2Pt(X)(Y)$ complexes (X = CO_2Me or CO; Y = CO_2Me, CO, OMe, OTf) has been prepared in order to determine the compatibility of electrophilic (CO, CO_2Me) and nucleophilic (OH, OMe) ligands in the same platinum coordination sphere. Dealkoxylation of CO_2Me complexes by trimethylsilyl triflate affords the corresponding cationic carbonyl derivatives, and represents a potentially useful metalloester deprotection method for controlling the formation of dimetalloester linkages. The crystal structure of [*trans*-$(Ph_3P)_2Pt(CO_2Me)(CO)]BF_4$ has been determined, and reveals an unusual distortion of the P–Pt–P angle perpendicular to the square planar coordination geometry. Attempted condensation reactions between *trans*-$(Ph_3P)_2Pt(CO_2Me)(CO)^+$ and *trans*-$(Ph_3P)_2Pt(CO_2Me)(OH)$ did not yield a dimetalloester condensation product, presumably due to the steric bulk of the ancillary Ph_3P ligands.

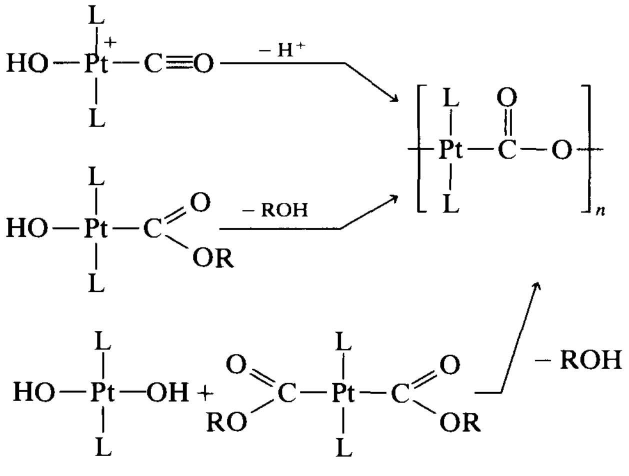
Keywords: Platinum; Metallocarboxylates; Hydroxide; Alkoxide; Carbonyl

1. Introduction

The rational design of organometallic polymers with potentially novel redox and/or conductivity properties is a challenging area of research [1]. In principle, applying known synthetic methodologies for the formation of metal–carbon bonds to bifunctional metal complexes with well-defined coordination geometries should allow one to control the extended structure of the resulting polymer or oligomer. One general scheme for condensation polymerization based on a reactive *trans* monomeric precursor is shown below. Although condensation polymerizations are quite commonly employed in the design of organic polymers, there is presently only a handful of inorganic and organometallic systems which have been developed along these lines [2,3].



One of the major limitations in the application of condensation polymerization to inorganic systems is the lack of suitable bifunctional monomeric precursors. Accordingly, we initiated a program to design new bifunctional precursor systems for study. In an effort to minimize complications, we focused on the synthesis of simple square planar d^8 platinum systems, *trans*-$(Ph_3P)_2Pt(X)(Y)$ (X, Y = OH, CO, CO_2H, or CO_2R). Sterically-demanding triphenylphosphine auxiliary ligands were chosen in order to maintain a *trans* stereochemistry between the condensing ligand functions.



Scheme 1.

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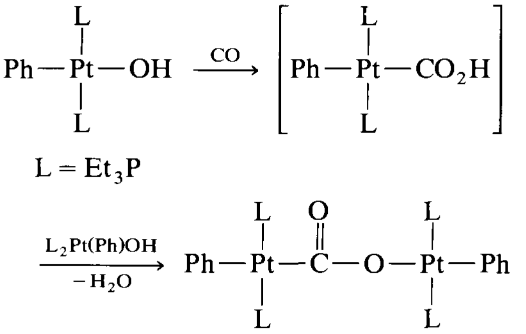
The choice of potentially reactive M–OH, M–CO$^+$ [4], M–CO$_2$H, and M–CO$_2$R ligating groups was guided by analogy with well known organic polyester syntheses (Scheme 1).

While it is true that the reactivity modes of L$_n$M–OH and R–OH as well as L$_n$M–CO$_2$R and R–CO$_2$R analogues might be quite distinct despite any rough functional similarities, Bennett et al. [5] (Eqn. (1)) and Strukul et al. [6] have nevertheless reported the condensation of Pt–OH and Pt–CO$_2$H functions to give dimetalloesters.



$$\mathrm{Ph{-}\underset{L}{\overset{L}{Pt}}{-}OH} \xrightarrow{\mathrm{CO}} \left[\mathrm{Ph{-}\underset{L}{\overset{L}{Pt}}{-}CO_2H}\right]$$

$\mathrm{L = Et_3P}$

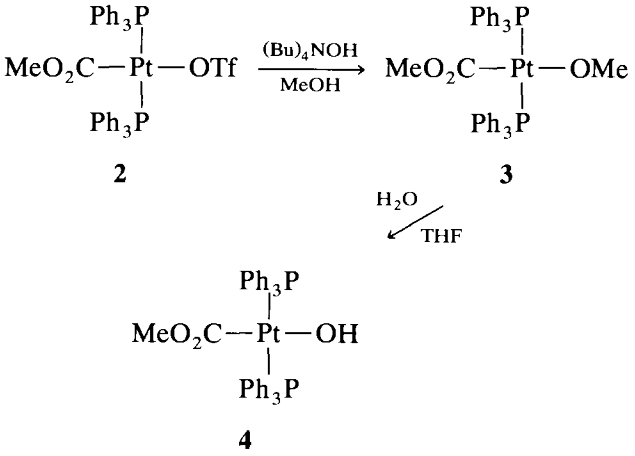
$$\xrightarrow[-\mathrm{H_2O}]{\mathrm{L_2Pt(Ph)OH}} \mathrm{Ph{-}\underset{L}{\overset{L}{Pt}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{L}{\overset{L}{Pt}}{-}Ph} \qquad (1)$$

This type of transformation is exceptional in several respects. First, metallocarboxylic acids are frequently unstable with respect to decarboxylation and hydride formation [5–7]. Second, the chemistry of transition metal hydroxides differs from that of simple protic organic alcohols in that M–OH and not MO–H heterolysis is generally favored, so the actual mechanism of metalloester formation is likely to be different. *Trans* ligand effects may also prove to be an important factor to consider in extending Eqn. (1) to bifunctional systems. Here we report the synthesis and characterization of a number of bifunctional platinum complexes and assess their potential as precursors to organometallic polymeric systems.

2. Results and discussion

2.1. Synthesis of *trans*-$(Ph_3P)_2Pt(CO_2CH_3)X$, (X = OH, OCH$_3$, OTf)

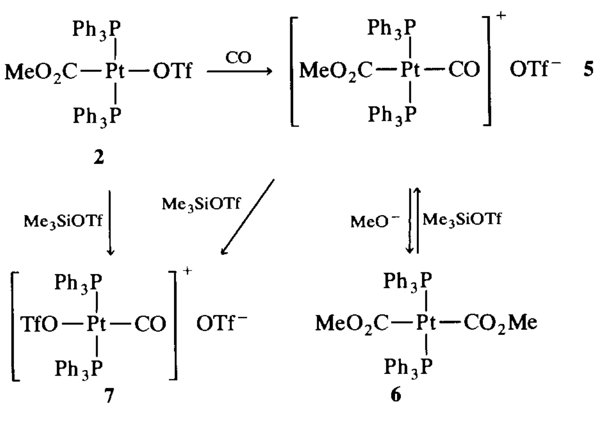
Synthetic routes to all of the platinum systems examined employ the same precursor complex, *trans*-$(Ph_3P)_2Pt(CO_2CH_3)Cl$ (**1**) [8]. Treatment of **1** with AgOTf (OTf = OSO$_2$CF$_3$) in CH$_2$Cl$_2$ afforded the labile triflate complex *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OTf)$ (**2**) in 76% yield. Retention of the metal *trans* stereochemistry was confirmed by ^{31}P and ^{1}H NMR. In particular, the ^{1}H NMR spectrum of **2** shows two separate aromatic regions for the triphenylphosphine protons centered at δ 7.71 and 7.43 which integrate 12 : 18 (*ortho* : (*meta*, *para*)). This distinctive multiplet pattern is common to almost all *trans* complexes examined. The ^{31}P NMR spectrum exhibits a single resonance at δ 24.5 with a $J(^{195}\mathrm{Pt}\text{–}\mathrm{P})$ of 3137 Hz, which is also characteristic of chemically equivalent *trans* phosphines in related systems.



Scheme 2.

Our initial attempts to synthesize *trans*-$(Ph_3P)_2$-$Pt(CO_2CH_3)(OH)$ (**4**) by the addition of water to **2** were unsuccessful and resulted in a mixture of uncharacterized platinum products. Delivery of hydroxide by the addition of NaOH/H$_2$O gave a similar negative result. Instead, **4** was successfully prepared via an indirect route from the corresponding methoxide derivative, *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OCH_3)$ (**3**). Treatment of **2** with tetrabutylammonium hydroxide in methanol gave **3** in 93% yield (Scheme 2). The ^{1}H NMR spectrum of the methoxide complex exhibits two singlets at δ 2.27 and 2.43; the presence of $^3J(^{195}\mathrm{Pt}\text{–}\mathrm{H})$ satellites with a coupling of 21.5 Hz for the 2.43 singlet confirmed the assignment of this resonance to the platinum-bound methoxide group. Infrared data (ν(CO) = 1622 cm^{-1}) further confirmed the retention of a *trans* CO$_2$CH$_3$ group in **3**.

Slow addition of water to a stirred solution of *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OCH_3)$ in THF results in clean conversion to *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OH)$ (**4**). The key to the synthesis of **4** from **3** seems to be avoiding acid- or base-catalyzed hydrolysis of the spectator CO$_2$CH$_3$ ligand in aqueous media (*note*: direct OH$^-$ delivery by H$_2$O addition to **2** generates the strong acid HOTf stoichiometrically). Stirring **4** in methanol at 20°C quantitatively and cleanly produces **3** after several minutes, showing that the conversion of **3** to **4** is reversible. Despite the presence of both hydrolyzable ester and potentially labile OH$^-$ functions, *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OH)$ is surprisingly stable both in solution and in the solid state at ambient temperature. **4** is soluble in aromatic hydrocarbons, acetone, dichloromethane and chloroform, although in chlorinated solvents the chloro complex **1** slowly forms over the course of several days at ambient temperature. This type of chlorination reaction has also been ob-



Scheme 3.

served previously for (dppe)Pt(C_6H_9)(OH) [9a] and is due presumably to the highly basic nature of the Pt–OH compounds. The IR spectrum of **4** is consistent with the above formulation, with bands observed at 3618 (ν(OH)) and 1636 cm^{-1} (ν(CO$_2$CH$_3$)). The OH resonance in the ^{1}H NMR spectrum is quite distinctive and appears as a broad singlet at −2.18 ppm without resolved ^{195}Pt satellites, within the range (−2 to −4 ppm) reported for other known Pt-OH complexes [9].

2.2. Synthesis of trans-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(X) (X = CO, CO$_2$CH$_3$)

Both the direct carbonylation of **2** and the addition of silver triflate to the chloro complex **1** under an atmosphere of carbon monoxide in CH$_2$Cl$_2$ at ambient temperature gave *trans*-[(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO)]OTf (**5**) in high yield (Scheme 3). The BF$_4^-$ salt of **5** has been prepared previously by Beck via an independent route [10]. From **5** the metallodiester complex *trans*-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)$_2$ (**6**) was prepared in 50% yield by the addition of sodium methoxide in methanol.

Cationic platinum carbonyl complexes may also be prepared via dealkoxylation of metalloesters. Thus, treatment of the platinum triflate **2** with trimethylsilyl triflate gave *trans*-[(Ph$_3$P)$_2$Pt(OTf)(CO)]OTf, (**7**) in moderate yield. The IR spectrum of **7** exhibits a single ν(CO) band at 2150 cm^{-1}, somewhat higher than the value of 2116 cm^{-1} observed for carbonyl **5**. Similarly, the reaction of **5** with trimethylsilyl triflate gave **7** in 43% yield. Presumably the unstable initial product in the reaction of **5** with Me$_3$SiOTf is the dicarbonyl dication, [*trans*-(Ph$_3$P)$_2$Pt(CO)$_2$](OTf)$_2$.

Although platinum hydroxide, metalloester and carbonyl compounds have been successfully prepared, a corresponding carboxylic acid derivative such as *trans*-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO$_2$H) was not obtained. Exposure of the hydroxo complex **4** to an atmosphere of carbon monoxide in an attempt to insert carbon monoxide into the Pt-OH bond produced a large number of uncharacterized compounds.

2.3. Crystal structure of [trans-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO)]BF

Complexes of the general form *trans*-(Ph$_3$P)$_2$-Pt(CO$_2$CH$_3$)X provide a useful comparison of the relative *trans* influences of CO$_2$Me ligands with a range of *trans* functional groups. Accordingly, the structure of the carbonyl cation (as its BF$_4^-$ salt, **5a**) was crystallographically determined. A representative view of **5a** is presented in Fig. 1. Atomic coordinates and selected bond distances and angles are given in Tables 1 and 2. Compared to the large majority of reported four-coordinate platinum(II) structures, which exhibit nearly ideal square planar coordination geometries, the geometry about the platinum in **5a** is significantly distorted. A 180° angle between the triphenylphosphine groups is not expected owing to the different steric influences of adjacent CO$_2$Me and CO ligands; however, the observed P–Pt–P angle distortion of 167.5(1)° is in a direction perpendicular to the plane defined by Pt, P(1), P(2), C(1), and C(3), not toward either the carbonyl or methoxycarbonyl ligands as might be expected [11]. A closely-related structure, *trans*-(Ph$_3$P)$_2$Pt-(CO)(COCO$_2$Me)$^+$ [13], does not show a similar distortion. There does not appear to be any obvious electronic or crystal-packing reason for the decreased P–Pt–P angle observed for **5a**. The Pt–P bond lengths found for **5a** (2.335(2), 2.343(2) Å) are slightly longer than typical values reported for neutral *trans*-(Ph$_3$P)$_2$Pt(X)(Y) complexes [11] and are essentially identical to values reported for *trans*-(Ph$_3$P)$_2$Pt-(CO)(COCO$_2$Me)$^+$. The methoxycarbonyl Pt–C(1)

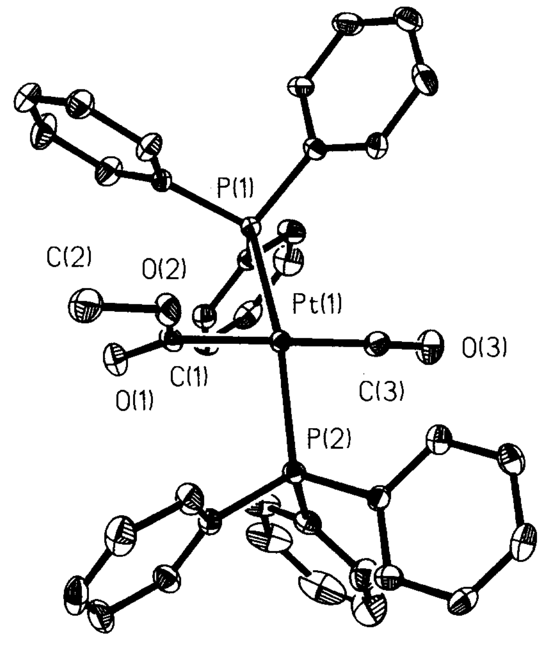


Fig. 1. ORTEP view of *trans*-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO)$^+$ (**5a**) (30% probability ellipsoids).

bond length, 2.038(7) Å, is somewhat shorter than the corresponding ethoxycarbonyl bond length reported for vinyl-substituted *trans*-$(Ph_3P)_2Pt(C(Me)=CH_2)(COCO_2Et)$ (2.092(6) Å) [14], and is much longer than value of 1.945 Å reported for the chloro complex *trans*-$(Ph_3P)_2Pt(CO_2Me)Cl$ [15].

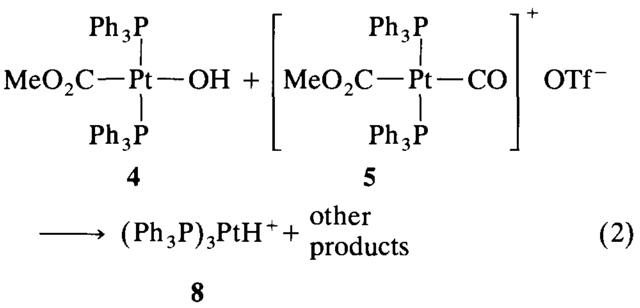
Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients for *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(CO)^+$ (**5a**)

	x	y	z	U_{eq} [a]
Pt(1)	2967(1)	413(1)	975(1)	34(1)
P(1)	2646(2)	−1435(1)	1166(1)	35(1)
P(2)	2870(2)	2283(2)	734(1)	38(1)
O(1)	1826(5)	−76(5)	−101(2)	61(2)
O(2)	3660(5)	−120(5)	−39(2)	58(2)
O(3)	3121(5)	961(5)	2195(3)	76(3)
C(1)	2709(6)	29(6)	164(3)	41(3)
C(2)	3573(9)	−386(8)	−617(3)	78(4)
C(3)	3101(7)	756(6)	1752(3)	50(3)
C(16)	3391(7)	−2572(6)	330(3)	52(3)
C(15)	3354(7)	−3331(7)	−89(3)	61(3)
C(14)	2420(8)	−3923(7)	−243(4)	66(4)
C(13)	1523(8)	−3758(8)	21(4)	82(4)
C(12)	1545(6)	−3007(7)	437(3)	60(3)
C(11)	2479(6)	−2398(5)	596(3)	38(2)
C(26)	1241(7)	−1750(7)	1965(3)	56(3)
C(25)	241(8)	−1610(8)	2159(4)	72(4)
C(24)	−630(7)	−1098(7)	1853(4)	66(4)
C(23)	−525(7)	−734(7)	1331(4)	61(3)
C(22)	451(6)	−881(6)	1130(3)	49(3)
C(21)	1344(6)	−1381(5)	1443(3)	41(3)
C(36)	3449(7)	−3211(6)	1797(3)	54(3)
C(35)	4233(8)	−3787(7)	2153(4)	68(4)
C(34)	5232(8)	−3312(8)	2332(3)	65(4)
C(33)	5457(7)	−2260(8)	2177(3)	65(4)
C(32)	4679(6)	−1665(7)	1835(3)	50(3)
C(31)	3647(5)	−2137(6)	1648(3)	38(2)
C(46)	4942(6)	2683(6)	1328(3)	47(3)
C(45)	5852(7)	3332(7)	1515(3)	53(3)
C(44)	5863(7)	4415(7)	1357(3)	60(3)
C(43)	5015(7)	4843(6)	1008(4)	58(3)
C(42)	4115(7)	4192(6)	809(3)	54(3)
C(41)	4073(6)	3117(6)	973(3)	41(3)
C(56)	741(7)	2230(8)	977(4)	78(4)
C(55)	−168(9)	2604(11)	1198(6)	105(6)
C(54)	−100(12)	3576(13)	1492(5)	116(7)
C(53)	846(11)	4152(12)	1567(5)	109(6)
C(52)	1765(8)	3793(8)	1341(4)	74(4)
C(51)	1711(6)	2825(6)	1041(3)	47(3)
C(66)	3434(7)	2414(7)	−304(3)	56(3)
C(65)	3279(9)	2654(8)	−853(4)	76(4)
C(64)	2319(10)	3112(8)	−1094(4)	79(4)
C(63)	1493(9)	3342(8)	−787(4)	77(4)
C(62)	1627(7)	3095(6)	−231(3)	55(3)
C(61)	2599(6)	2623(6)	6(3)	44(3)
B	6579(9)	681(9)	2377(4)	67(4)
F(1)	7030(5)	1693(5)	2501(3)	102(3)
F(2)	7019(7)	−75(6)	2710(3)	155(4)
F(3)	6684(13)	400(9)	1874(3)	225(8)
F(4)	5506(6)	743(6)	2339(6)	193(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.4. Results of attempted condensations

All attempts to synthesize dimeric or polymeric materials from *trans*-$(Ph_3P)_2Pt(X)(Y)$ compounds by a simple "one step" condensation have failed owing to redistribution of the triphenylphosphine ancillary ligands. The initial reaction surveyed was between equimolar amounts of carbonyl cation **5** and the basic hydroxo complex **4**. The course of the reaction appears to be solvent dependent. When the reaction was conducted in benzene, the known tris(triphenylphosphine) platinum hydride cation **8** was obtained as the main isolable product along with a number of additional uncharacterized compounds (Eqn. (2)).



$$\underset{\mathbf{4}}{MeO_2C-\overset{\displaystyle Ph_3P}{\underset{\displaystyle Ph_3P}{Pt}}-OH} + \underset{\mathbf{5}}{\left[MeO_2C-\overset{\displaystyle Ph_3P}{\underset{\displaystyle Ph_3P}{Pt}}-CO\right]^+} OTf^- \longrightarrow \underset{\mathbf{8}}{(Ph_3P)_3PtH^+} + \begin{matrix}\text{other}\\ \text{products}\end{matrix} \qquad (2)$$

In contrast, changing from benzene to dichloromethane as a solvent produced *trans*-$(Ph_3P)_2Pt(CO_2CH_3)_2$ and $(Ph_3P)_3Pt(CO_2CH_3)^+$ (**9**) as the major identifiable components. Complex **9** has been previously reported by Beck as the product in the reaction of **5a** with free triphenylphosphine [10]. In light of this observation, the observed products from the reaction of **4** and **5** may derive may derive from an initial dissociation of Ph_3P from **4** prior to the desired coupling reaction. In all attempted condensations no residual carbonyl cation **5** was observed in the reaction products.

3. Summary

We have been successful in preparing a range of stable, bifunctional platinum complexes which serve as models for metallopolyester syntheses. Although our initial attempt to take advantage of Bennett's condensation methodology was unsuccessful using the described systems, the basic underlying concepts remain valid. The preparation of a stable and potentially amphoteric complex *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(OH)$ is particularly significant in this regard. Dealkoxylations of L_nM-CO_2R ligand systems under mild conditions to generate the corresponding reactive carbonyl cations I_nM-CO^+ reported here also constitute a potentially useful deprotection scheme for controlling stepwise oligomerizations. The nature of the ancillary phosphine ligand appears to be critical. After initiating our studies a number of years ago, a full account of Bennett's work [5] appeared in the literature which indicated that the choice of ancillary phosphine was critical to the success of Pt–OH and Pt–CO_2R condensations. In hindsight it appears reasonable that developing bifunctional systems based on a less bulky and more basic *trans*-$(Et_3P)_2Pt(X)(Y)$ framework may lead to extended linear organometallic structures.

4. Experimental section

4.1. General procedures

All manipulations were conducted under an atmosphere of purified nitrogen using Schlenk, high vacuum and/or glovebox techniques. Dry oxygen-free solvents were purified by vacuum distillation from sodium/benzophenone (diethyl ether, petroleum ether, and hexane) or P_2O_5 (CH_2Cl_2). Deuterated solvents used in NMR experiments were dried over activated 3 Å molecular sieves. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100 or Perkin-Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL JNM-FX270 or GSX-400 instrument. ^{31}P spectra were referenced to a 85% H_3PO_4 external standard. *trans*-$(Ph_3P)_2Pt(CO_2CH_3)Cl$ was prepared following literature procedures [8].

4.2. *trans-$(Ph_3P)_2Pt(CO_2CH_3)(OTf)$ (2)*

A solution of *trans*-$(Ph_3P)_2Pt(CO_2CH_3)Cl$ (2.21 g, 2.71 mmol) and AgOTf (0.754 g, 2.93 mmol) in 25 ml of dichloromethane was stirred for 8 h at ambient temperature. The reaction mixture was then filtered and the volatiles were removed under vacuum. The filtrate residue was taken up in a minimal amount of dichloromethane and 25 ml of diethyl ether was added to precipitate **2** as a white solid. The yield of **2** after drying was 1.90 g (76%). Anal. Calcd. for $C_{39}H_{33}F_3O_5P_2PtS$: C, 50.49; H, 3.59; S, 3.46. Found: C, 50.12; H, 3.48; S, 3.45%. IR (cm^{-1}): 1656s, 1325s, 1233m, 1209s, 1099s, 1016s, 748m, 692m. ^1H NMR ($CDCl_3$, 269.7 MHz, 22°C): δ 2.29 (s, 3H, CO_2CH_3), 7.43 (m, 18H, *meta*, *para*-C_6H_5), 7.71 (m, 12H, *ortho*-C_6H_5). ^{31}P NMR (CD_3NO_2, 109.1 MHz, 22°C): δ 24.5 (s, $J(^{195}Pt–P) = 3137$ Hz).

4.3. *trans-$(Ph_3P)_2Pt(CO_2CH_3)(OCH_3)$ (3)*

To a slurry of **2** (1.21 g, 1.30 mmol) in 50 ml of methanol at −78°C was added a 1.00 M solution of tetrabutylammonium hydroxide (1.43 ml, 1.43 mmol) in methanol. The reaction mixture was allowed to warm slowly to ambient temperature and was stirred for an additional 6 h. The methanol was removed under vacuum and the residue was taken up in dichloromethane and filtered. The volume of the filtrate was reduced to ca. 5 ml and 20 ml of diethyl ether was added. The resulting white precipitate **3** was filtered and washed several times with methanol and dried under vacuum. Yield of **3**: 0.910 g (86%). Anal. Calcd. for $C_{39}H_{36}O_3P_2Pt$: C, 57.85; H, 4.48. Found: C, 57.20; H, 4.36%. IR (cm^{-1}): 1622s, 1184m, 1099s, 1051s, 744m, 694s. ^1H NMR ($CDCl_3$, 269.7 MHz, 22°C): δ 2.27 (s, 3H, CO_2CH_3), 2.43 (s, 3H, $^3J(^{195}Pt–H) = 22$ Hz, OCH_3), 7.37 (m, 18H, *meta*, *para*-C_6H_5), 7.78 (m, 12H, *ortho*-C_6H_5). ^{31}P NMR ($CDCl_3$, 109.1 MHz, 22°C): δ 14.4 (s, $J(^{195}Pt–P) = 3253$ Hz).

4.4. *trans-$(Ph_3P)_2Pt(CO_2CH_3)(OH)$ (4)*

To a solution of **3** (0.910 g, 1.12 mmol) in 50 ml of tetrahydrofuran was added 1.0 ml of degassed water. After stirring for 6 h at ambient temperature, the

Table 2
Selected bond lengths (Å) and angles (°) for *trans*-$(Ph_3P)_2Pt(CO_2CH_3)(CO)^+$ (**5a**)

Bond distances					
Pt(1)–P(1)	2.335(2)	Pt(1)–P(2)	2.343(2)	Pt(1)–C(1)	2.038(7)
Pt(1)–C(3)	1.945(8)	P(1)–C(11)	1.817(7)	P(1)–C(21)	1.819(8)
P(1)–C(31)	1.799(7)	P(2)–C(41)	1.817(7)	P(2)–C(51)	1.821(8)
P(2)–C(61)	1.828(7)	O(1)–C(1)	1.189(9)	O(2)–C(1)	1.340(10)
O(2)–C(2)	1.453(10)	O(3)–C(3)	1.120(10)		
Bond angles					
P(1)–Pt(1)–P(2)	167.5(1)		P(1)–Pt(1)–C(1)	88.3(2)	
P(2)–Pt(1)–C(1)	88.6(2)		P(1)–Pt(1)–C(3)	90.0(2)	
P(2)–Pt(1)–C(3)	92.2(2)		C(1)–Pt(1)–C(3)	175.8(3)	
Pt(1)–P(1)–C(11)	117.7(2)		Pt(1)–P(1)–C(21)	102.8(2)	
Pt(1)–P(1)–C(31)	118.0(2)		Pt(1)–P(2)–C(41)	116.5(2)	
Pt(1)–P(2)–C(51)	105.0(3)		Pt(1)–P(2)–C(61)	117.7(2)	
Pt(1)–C(1)–O(1)	124.8(6)		Pt(1)–C(1)–O(2)	111.8(5)	
Pt(1)–C(3)–O(3)	176.5(7)		C(1)–O(2)–C(2)	116.5(6)	
O(1)–C(1)–O(2)	123.3(7)				

resulting clear yellow solution was filtered and the volatiles were removed under vacuum. The filtrate residue was taken up in a minimal amount of tetrahydrofuran and 50 ml of diethyl ether was added to precipitate **4** (0.550 g, 62%). Anal. Calcd. for $C_{38}H_{34}O_3P_2Pt$: C, 57.36; H, 4.31. Found: C, 56.43; H, 4.10%. (*note*: repeated analyses of spectroscopically pure **4** were consistently low in carbon). IR (cm^{-1}): 3618w, 1636s, 1098s, 1043s, 746m, 695s. ^1H NMR ($CDCl_3$, 269.7 MHz, 22°C): δ −2.18 (s, 1H, OH), 2.40 (s, 3H, CO_2CH_3), 7.38 (m, 18H, *meta*, *para*-C_6H_5), 7.75 (m, 12H, *ortho*-C_6H_5). ^{31}P NMR ($CDCl_3$, 109.1 MHz, 22°C): δ 19.2 (s, $J(^{195}Pt\text{–}P = 3165$ Hz).

4.5 trans-[(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO)](OTf) (5)

A mixture of *trans*-$(Ph_3P)_2Pt(CO_2CH_3)Cl$ (1.36 g, 1.67 mmol) and AgOTf (0.464 g, 1.83 mmol) in 25 ml dichloromethane was stirred at ambient temperature under an atmosphere of carbon monoxide. After 8 h the reaction mixture was filtered and the volatiles were removed under vacuum. After extraction of the filtrate residue with CH_2Cl_2 and precipitation with from CH_2Cl_2/Et_2O, 1.30 g of **5** (81%) were obtained. Anal. Calcd. for $C_{40}H_{33}F_3O_6P_2PtS$: C, 50.27; H, 3.48; S, 3.35. Found C, 50.03; H, 3.38; S, 3.24%. IR (cm^{-1}): 2116s, 1685m, 1657w, 1265s, 1152m, 1094m, 1032m. ^1H NMR ($CDCl_3$, 269.7 MHz, 22°C): δ 2.42 (s, 3H, CO_2CH_3), 7.57 (m, 30H, C_6H_5). ^{31}P NMR (CD_3NO_2, 109.1 MHz, 22°C): δ 14.4 (s, $J(^{195}Pt\text{–}P) = 2600$ Hz).

4.6. trans-(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)$_2$ (6)

A mixture of **5** (1.420 g, 1.486 mmol) and $NaOCH_3$ (0.088 g, 1.63 mmol) in 30 ml of dichloromethane was stirred for 8 h at ambient temperature. Filtration and precipitation from CH_2Cl_2/Et_2O afforded analytically pure **6** (0.765 g, 61%). Anal. Calcd. for $C_{40}H_{36}O_4P_2Pt$: C, 57.35; H, 4.33. Found: C, 57.04; H, 4.35%. IR (cm^{-1}): 1633, 1098, 1029, 754. ^1H NMR ($CDCl_3$, 269.7 MHz, 22°C) δ 2.29 (s, 6H, CO_2CH_3), 7.43 (m, 18H, *meta*, *para*-C_6H_5) 7.71 (m, 12H, *ortho*-C_6H_5). ^{31}P NMR (CD_3NO_2, 109.1 MHz, 22°C) δ 24.5 (s, $J(^{195}Pt\text{–}P) = 3136$ Hz).

4.7. trans-[(Ph$_3$P)$_2$Pt(CO)(OTf)](OTf) (7)

Procedure A: To a solution of **5** (0.530 g, 0.554 mmol) in 15 ml of dichloromethane at −78°C was slowly added Me_3SiOTf (0.193 g, 0.868 mmol) via syringe. The reaction mixture was allowed to warm to ambient temperature over a period of one hour. Workup from CH_2Cl_2/ether as described previously gave 0.244 g (43%) of colorless **7**.

Procedure B: To a 10 ml dichloromethane solution of **2** (0.144 g, 0.155 mmol) at −78°C was slowly added Me_3SiOTf (0.037 g, 0.17 mmol). The reaction was allowed to warm to ambient temperature while stirring over a period of 2 h. After the volatiles were removed under vacuum, the residue was extracted with CH_2Cl_2 and filtered. Work up from CH_2Cl_2/ether yielded 97 mg (59%) of colorless analytically pure **7**. Anal. Calcd. for $C_{39}H_{30}F_6O_7P_2PtS_2$: C, 44.79; H, 2.89. Found: C, 44.80; H, 2.74%. IR (cm^{-1}): 2150vs, 1271vs, 1103s, 1028s. ^{31}P NMR (CD_2Cl_2, 109.1 MHz, 22°C): δ 22.1 (s, $J(^{195}Pt\text{–}P) = 1926$ Hz).

4.8. X-ray structure of trans-[(Ph$_3$P)$_2$Pt(CO$_2$CH$_3$)(CO)][BF$_4$] (5a)

X-ray data were collected on a Nicolet R3m/V automated diffractometer system with a dedicated MicroVAX II computer system. The radiation used was Mo Kα monochromatized by a highly-ordered graphite crystal. All computations used the SHELXTL PLUS (Version 3.4) program library (Siemens Corp., Madison, WI).

A sample of **5a** for X-ray analysis was prepared analogously to **5** using $AgBF_4$ instead of AgOTf. A colorless prism (0.30 × 0.30 0.50 mm) of **5a** was grown from dichloromethane at 0°C and was mounted in a glass capillary under nitrogen. Monoclinic unit cell dimensions were derived from a least-squares fit of 21 random reflections ($20° \le 2\theta \le 30°$). Data were collected using the $2\theta\text{–}\theta$ scan technique with a variable scan rate of 4.0 to 15.0 deg/min. A statistical analysis of the total data set indicated that the space group was $P2_1/n$. Two standard reflections monitored after every 50 data collected showed no systematic variation; the R for merging 540 redundant data was 0.019. Data were empirically corrected for absorption using XABS [16].

The structure of **5a** was solved using the SHELXTL PLUS Patterson interpretation program, which revealed most of the nonhydrogen atoms on the initial E map. All remaining nonhydrogen atoms were located in subsequent difference fourier maps and were refined anisotropically. Aryl hydrogen atom positions were added in ideal calculated positions with d(C–H) = 0.96 Å and refined with isotropic thermal parameters fixed to 1.2 times the isotropic equivalent of the attached carbon atom. Methyl hydrogens were refined as a rigid group with a common fixed isotropic thermal parameter. No close contacts between the BF_4 anion and the cationic complex were found. In the final refinement all shift/esd ratios were less than 0.015 with no unusually high variable correlations. The final R indices for $I > 2\sigma(I)$ were $R = 0.031$ and $R_w = 0.038$, with a Goodness-of-Fit of 0.93. The final Fourier difference map showed peaks of 0.79 and −0.75 $e^-/Å^3$ associated with the heavy platinum atom. Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

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