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Nucleophilic Attack on or Displacement of Coordinated 1,5-Cyclooctadiene. Structures of $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ and $[Pt(dppe)(H_2O)_2][SO_3CF_3]_2$

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The complex $[Pt(cod)(dppe)][ClO_4]_2$ reacts with acetonitrile to give $[Pt(dppe)(CH_3CN)_2]^{2+}$, from which the solvent molecules may be displaced by tertiary phosphines. In contrast, in CH_2Cl_2 solution phosphine attack at the coordinated diene takes place and the crystal structure of $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ (1) has been determined. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.749$ (5) Å, $b = 14.126$ (4) Å, $c = 14.356$ (3) Å, $\alpha = 118.48$ (2)°, $\beta = 94.47$ (2)°, $\gamma = 96.78$ (2)°, $V = 2404.7$ (12) Å^3, and $Z = 2$. Least-squares refinement converged at $R = 0.0616$ and $R_w = 0.0686$ based on 6348 reflections with $F > 4.0\sigma(F)$. In $[Pt(cod)(dppe)][SO_3CF_3]_2$ the diene is slowly displaced by triflate, and $[M(SO_3CF_3)_2(dppe)]$ (M = Pd, Pt) and $[Pt(SO_3CF_3)_2(dppm)]$ have been prepared by reaction of the dichloro complex with $AgSO_3CF_3$. When isolated the dppe complexes contain two water molecules and the crystal structure of the platinum derivative shows that it exists as $[Pt(dppe)(H_2O)_2][SO_3CF_3]_2$ (2) in the solid state. The latter crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.663$ (3) Å, $b = 24.255$ (9) Å, $c = 13.720$ (2) Å, $\beta = 104.36$ (2)°, $V = 3437.6$ (17) Å^3, and $Z = 4$. Least-squares refinement converged at $R = 0.0529$ and $R_w = 0.0454$ based on 3291 reflections with $F > 4.0\sigma(F)$.

Introduction

Platinum and palladium compounds containing weakly bound ligands represent useful precursors to a range of complexes of these two metals. Dichloro compounds such as $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene),[1] $[PdCl_2(cod)]$,[2] and $[MCl_2(PhCN)_2]$[3] are convenient sources of neutral complexes of the type $[MCl_2L_2]$, and cationic species containing weakly bound ligands have been employed as homogeneous catalytic precursors.[4] 1,5-Cyclooctadiene functions as a leaving group in most cases, but in certain instances attack on the coordinated double bond, resulting in an alkylmethyl species, takes place.[5]

In this paper we describe the reactions of $[Pt(cod)(dppe)][ClO_4]_2$ (dppe = 1,2-bis(diphenylphosphino)ethane)[6] with tertiary phosphines, which result in attack on or displacement of the coordinated diene, depending on the reaction conditions. We report the crystal structure of $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ (1), obtained by attack of PPh_3 on the $[Pt(cod)(dppe)]^{2+}$ cation. We also report the preparation of the triflate complexes $[M(SO_3CF_3)_2(dppe)]$ (M = Pd, Pt) and $[Pt(SO_3CF_3)_2(dppm)]$ (dppm = bis(diphenylphosphino)methane), from which the anionic ligands are readily displaced. The crystal structure of the platinum–dppe complex reveals that it exists as $[Pt(H_2O)_2(dppe)][SO_3CF_3]_2$ (2) in the solid state.

Results and Discussion

We have reported previously that the reaction of $[PtCl_2(dppe)]$ with silver perchlorate in acetone solution in the presence of 1,5-cyclooctadiene produces $[Pt(cod)(dppe)][ClO_4]_2$. The latter is only sparingly soluble in CH_2Cl_2, but addition of a few drops of CH_3CN followed by 1 molar equiv of $Ph_2PCH_2CH_2E$ (E = $AsPh_2$, NMe_2) results in displacement of the diene and formation of $[Pt(Ph_2PCH_2CH_2E)(dppe)][ClO_4]_2$.[6]

The diene complex $[Pt(cod)(dppe)][ClO_4]_2$ is sparingly soluble in $CDCl_3$ also (δP 50.7, $^1J(Pt,P) = 3075$ Hz), but addition of a few drops of acetone or acetonitrile causes complete dissolution. In acetone-d_6 the value of $^1J(Pt,P)$ is almost unchanged (δP 53.6, $^1J(Pt,P) = 3034$ Hz), but in CD_3CN solution the spectrum changes dramatically (δP 42.1, $^1J(Pt,P) = 3586$ Hz). In the case of acetone the solubility of $[Pt(cod)(dppe)][ClO_4]_2$ is simply increased, and the small changes in δP and $^1J(Pt,P)$ are due to the change in solvent, but with acetonitrile it is clear that the diene is actually displaced to yield $[Pt(dppe)(CD_3CN)_2]^{2+}$. Addition of $Ph_2PCH_2CH_2E$ (E = $AsPh_2$, NMe_2) to a CH_2Cl_2 solution containing CH_3CN would then result in displacement of the coordinated solvent molecules. Similarly, reaction of a CD_3CN solution of $[Pt(cod)(dppe)][ClO_4]_2$ with 1 molar equiv of triphenylphosphine produces a species that we propose to be $[Pt(dppe)(PPh_3)(CD_3CN)]^{2+}$ (δP_A 20.9 dd, $^1J(Pt,P_A) = 2322$ Hz; δP_B 40.0 dd, $^1J(Pt,P_B) = 3680$ Hz; δP_C 57.9 dd, $^1J(Pt,P_C) = 2274$ Hz; $^2J(P_A,P_B) = 17$ Hz, $^2J(P_A,P_C) = 320$ Hz, $^2J(P_B,P_C) = 6$ Hz), and with a second molar equivalent the $[Pt(dppe)(PPh_3)_2]^{2+}$ cation[7] is formed (eq 1).

$$[Pt(dppe)(CH_3CN)_2]^{2+} + PPh_3 \rightarrow [Pt(dppe)(PPh_3)(CH_3CN)]^{2+}$$

$$[Pt(dppe)(PPh_3)(CH_3CN)]^{2+} + PPh_3 \rightarrow [Pt(dppe)(PPh_3)_2]^{2+} \quad (1)$$

In contrast to the above, reactions of tertiary phosphines with suspensions of $[Pt(cod)(dppe)][ClO_4]_2$ in CH_2Cl_2 result in products derived exclusively from attack of the nucleophile on the coordinated diene. We have generated the complexes $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PR_3)\}(dppe)][ClO_4]_2$ (PR_3 = PPh_3, PEt_3, PBu_3, $Ph_2PCH_2CH_2OCH_3$) in solution and have isolated the PPh_3 and PEt_3 derivatives. We have also determined the crystal structure of $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ (1). The $^{31}P\{^1H\}$ NMR parameters for complexes of the type $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PR_3)\}(dppe)]$-

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Table I. $^{31}P\{^1H\}$ NMR Spectroscopic Parameters for the Complexes $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PR_3)\}(dppe)][ClO_4]_2$ in CD_2Cl_2 Solution[a]

	L			
	PEt_3	PBu_3	PPh_3	PC_2O[b]
δP_A (L)	41.7 dd	37.4 dd	26.1 d	28.8 dd
δP_B (trans to C)	48.1 d	48.0 d	46.2 d	46.7 d
δP_C (cis to C)	45.8 d	46.4 d	47.9 s	47.0 d
$^3J(Pt,P_A)$	214	217	223	207
$^1J(Pt,P_B)$	1577	1580	1617	1585
$^1J(Pt,P_C)$	3917	3910	3892	3922
$^4J(P_A,P_B)$	50	49	53	50
$^4J(P_A,P_C)$	4	5	*c*	5

[a] Chemical shifts are in parts per million relative to external 85% H_3PO_4. Positive shifts represent deshielding. [b] PC_2O = $Ph_2PCH_2CH_2OCH_3$. [c] Unresolved.

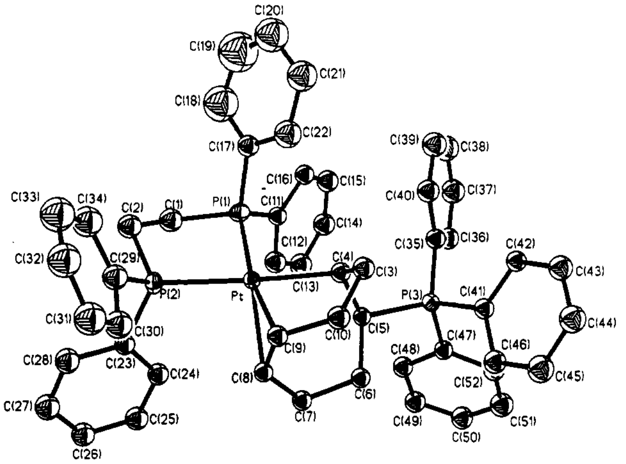

Figure 1. Projection view of the molecular structure of $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)]^{2+}$, the cation of **1**, showing the atom labeling scheme.

$[ClO_4]_2$ are given in Table I. In each case three ^{31}P resonances are observed, the two due to the dppe ligand being significantly downfield of the other.[8] The coupling between the two dppe P atoms is unresolved, but $^4J(P,P)$ values of ca. 5 and 50 Hz are observed between the unique phosphorus atom and the cis and trans P atoms of the dppe ligand, respectively. The small $^1J(Pt,P)$ value for P_A is typical of a P atom lying trans to a strong σ-donor such as an sp^3 carbon, whereas the larger value for P_B is indicative of its being trans to coordinated alkene. The carbon-bound P_C exhibits a $^3J(Pt,P)$ value of ca. 200 Hz. In the case of the potentially bidentate $Ph_2PCH_2CH_2OCH_3$, the ether function remains uncoordinated. Since the $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PR_3)\}(dppe)]^{2+}$ cations are formed from achiral precursors, they should exist in two diastereomeric forms in a 1:1 ratio (vide infra), but the two forms cannot be distinguished by NMR spectroscopy.

The structure of one $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)]^{2+}$ cation is shown in Figure 1. This reveals that the product is the result of exo attack of PPh_3 on the coordinated diene, such that trans 1,2-addition of the phosphine and the platinum to the alkene takes place. As mentioned above, two diastereomers should be formed and, indeed, the centrosymmetric unit cell contains one *R,R* and one *S,S* cation, related by crystallographic $\bar{1}$ symmetry. The C(4)–C(5) separation is 1.517 Å, indicative of a carbon–carbon single bond, and the geometries at C(4) and C(5) are pseudotetrahedral. The coordination sphere of the platinum is approximately square planar, with the remaining alkene moiety lying nearly perpendicular to this plane. The Pt–P distances are 2.256 and 2.341 Å, the longer bond being trans to the sp^3 carbon, and the Pt–C(4) distance of 2.158 Å is typical of an alkyl group lying trans to phosphorus.[9]

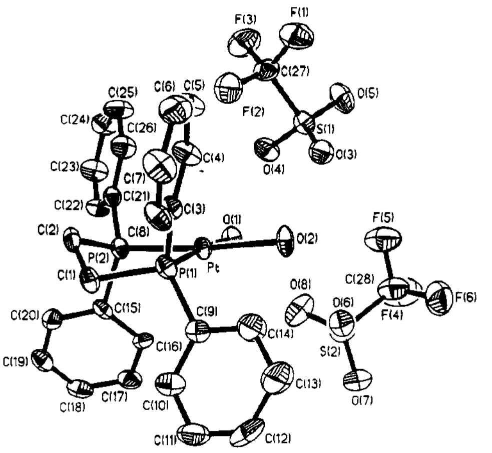

Figure 2. Projection view of the molecular structure of **2**, showing the atom labeling scheme.

Treatment of **1** with excess PPh_3 causes no further reaction. In contrast, addition of a second molar equivalent of PEt_3 to a solution containing $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PEt_3)\}(dppe)]^{2+}$ yields a product of formula $[Pt\{\sigma:\sigma\text{-}C_8H_{12}(PEt_3)_2\}(dppe)]^{2+}$, in which the second PEt_3 molecule has added to the other alkene group. This complex gives rise to an AA′BB′ pattern in its $^{31}P\{^1H\}$ NMR spectrum, which has been analyzed[10] and simulated (see under Experimental Section). Since 1,4- or 1,5-addition to the diene would lead to a species containing a plane or axis of symmetry, respectively, either could account for the ^{31}P NMR data. Similarly, four ^{13}C signals are detected for the C_8 unit, consistent with either structure, and the ^1H NMR spectrum is exceedingly complex. We believe it is most likely that the product is formed by exo attack of the second phosphine. Attempts to isolate $[Pt\{\sigma:\sigma\text{-}C_8H_{12}(PEt_3)_2\}(dppe)][ClO_4]_2$ result in loss of phosphine, and $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PEt_3)\}(dppe)][ClO_4]_2$ is obtained. When **1** is treated with 1 molar equiv of PEt_3, the $[Pt\{\sigma:\eta^2\text{-}C_8H_{12}(PEt_3)\}(dppe)]^{2+}$ cation is formed. Thus displacement of PPh_3 takes place more readily than attack at the second alkene moiety.

In order to avoid the potentially explosive perchlorate salts, we attempted to prepare the corresponding triflate complex $[Pt(cod)(dppe)][SO_3CF_3]_2$. Reaction of $[PtCl_2(dppe)]$ with 2 molar equiv of silver triflate in the presence of 1,5-cyclooctadiene does indeed yield the desired product, but on standing in solution displacement of the diene by the triflate anions occurs. Treatment of $[PtCl_2(dppe)]$ with $AgSO_3CF_3$ alone generates $[Pt(SO_3CF_3)_2(dppe)]$ in good yield. Similar treatment of the corresponding dichloro complexes produces $[Pd(SO_3CF_3)_2(dppe)]$ or $[Pt(SO_3CF_3)_2(dppm)]$. Triflate complexes of the type $[M(SO_3CF_3)_2L_2]$ (M = Pd, Pt) have been reported previously, having been prepared by treatment of the corresponding dichloro compounds with HSO_3CF_3.[11]

When isolated from CH_2Cl_2/Et_2O solution the dppe complexes analyze as $[M(SO_3CF_3)_2(dppe)]\cdot 2H_2O$. Crystals of the platinum complex were obtained from CH_2Cl_2 solution by slow addition of ether, and the structure of the complex was determined by X-ray diffraction. In fact, the

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molecular structure (Figure 2) reveals that the two water molecules are coordinated to platinum in the solid state, giving a complex of the form $[Pt(H_2O)_2(dppe)][SO_3CF_3]_2$ (**2**). Complexes of the type $[Pt(H_2O)_2(PR_3)_2][SO_3CF_3]_2$ have been reported previously,[12] but this represents the first solid-state structural characterization of a platinum complex containing two phosphine ligands and two water molecules. The coordination around platinum is planar, the P–Pt–O angles being slightly greater than 90° and the P–Pt–P and O–Pt–O angles less than 90°. The Pt–P distances are almost identical and are somewhat shorter than those in complexes of the type $[PtCl_2(PR_3)_2]$, reflecting the lower trans influence of water compared to chloride.[13] One noteworthy feature of the structure is the location of the two triflate ions above and below the coordination plane in close proximity to the coordinated water molecules. In one of the triflates the CF_3 group is bent back toward the metal, whereas in the other the CF_3 group is directed away from the rest of the molecule. The O(1)–O(4), O(1)–O(8), O(2)–O(3), and O(2)–O(6) distances all lie within the range 2.61–2.74 Å, which strongly suggests that, for each water molecule, there is hydrogen bonding to one oxygen of each of the triflate ions.[14]

In contrast to the above, reaction of $[PtMe_2\{1,2\text{-}C_6H_4(PMePh)_2\}]$ with HSO_3CF_3 gives $[Pt(SO_3CF_3)_2\{1,2\text{-}C_6H_4(PMePh)_2\}]$. Treatment with ethane-1,2-diol results in displacement of the triflate anions and isolation of the alcohol complex $[Pt(HOCH_2CH_2OH)\{1,2\text{-}C_6H_4(PMePh)_2\}]$. Both complexes have been structurally characterized.[15]

When **2** is redissolved, no ^1H NMR signal due to water is detected, suggesting that it is very broad due to exchange.[16] In CD_2Cl_2 solution a ^{31}P resonance is observed at δP 36.7, $^1J(Pt,P)$ 3980 Hz. In contrast, when 10 μL of water is added to a dichloromethane solution of $[Pt(cod)(dppe)][ClO_4]_2$ a second species is formed (δP 34.0, $^1J(Pt,P)$ 3624 Hz), which we presume to be the diaquo complex $[Pt(dppe)(H_2O)_2]^{2+}$. Thus it appears that when **2** is dissolved the triflate anions compete for the coordination sites at platinum and that triflate exerts a somewhat lower NMR trans influence than water or chloride. As in the case of $[Pt(cod)(dppe)]^{2+}$, the NMR parameters are only marginally affected by changing the solvent to acetone-d_6 (δP 39.3, $^1J(Pt,P) = 3953$ Hz), but the $[Pt(dppe)(CD_3CN)_2]^{2+}$ cation (δP 42.1, $^1J(Pt,P) = 3587$ Hz) is formed when CD_3CN is used. The lack of a coupling constant in the palladium case means that less can be inferred about the nature of $[Pd(SO_3CF_3)_2(dppe)]$ in solution, but the ^{31}P chemical shift changes from 73.7 ppm in $CDCl_3$ solution to 76.7 ppm in acetone-d_6. A CD_2Cl_2 solution of $[Pt(SO_3CF_3)_2(dppm)]$ gives rise to a broad $^{31}P\{^1H\}$ NMR spectrum, the central resonance being at −70.7 ppm, flanked by ^{195}Pt satellites with a coupling of 3490 Hz. Whereas the dppe complexes are obtained as diaquo species, $[Pt(SO_3CF_3)_2(dppm)]$ is isolated from the same solvent mixture in analytically pure form without the incorporation of water.

Displacement of the triflate ions from $[M(SO_3CF_3)_2L_2]$ in solution is readily achieved. Addition of 2 molar equiv of PPh_3 to a CD_2Cl_2 solution of $[Pt(SO_3CF_3)_2(dppe)]$ yields the $[Pt(dppe)(PPh_3)_2]^{2+}$ cation[7] as the sole product. Coordinated iodide is also sufficiently nucleophilic to cause displacement of triflate. Thus, when an acetone solution of an equimolar mixture of $[Pt(SO_3CF_3)_2(dppe)]$ and $[PtI_2(dppe)]$ is allowed to stand at ambient temperature, a single product is obtained, namely, $[Pt_2(\mu\text{-}I)_2(dppe)_2][SO_3CF_3]_2$. The Pt–P coupling constant (3470 Hz) shows a small increase from that found in $[PtI_2(dppe)]$ (δP 48.1, $^1J(Pt,P) = 3377$ Hz), consistent with a slight decrease in NMR trans influence when the iodide becomes a bridging ligand. When $[Pd(SO_3CF_3)_2(dppe)]$ and $[PdI_2(dppe)]$ are allowed to react $[Pd_2(\mu\text{-}I)_2(dppe)_2][SO_3CF_3]_2$ is obtained. When $[Pd(SO_3CF_3)_2(dppe)]$ and $[PtI_2(dppe)]$ are mixed in a 1:1 ratio, the dipalladium, the diplatinum, and the heterometallic complex are produced in an approximately statistical ratio ($[PdPt(\mu\text{-}I)_2(dppe)_2][SO_3CF_3]_2$: δP 52.5, $^1J(Pt,P) = 3487$ Hz; δP 79.6). Analogous results are obtained for neutral palladium and platinum dimers.[17]

The ease of displacement of the triflate ions means that these complexes may be used to prepare a range of neutral and cationic species. In particular, cationic complexes that have been shown to function as homogeneous catalytic precursors (for example, $[Pt(dppe)(CH_3CN)_2]^{2+}$)[4] may be generated in situ; then the stable triflate compound may be regenerated by solvent removal.

Experimental Section

All reactions were carried out under an atmosphere of argon, and the products were worked up in air. NMR spectra were recorded on a Varian XL-300 spectrometer, operating in the FT mode. ^1H and ^{13}C chemical shifts are relative to the residual solvent resonance, and ^{31}P shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. Microanalyses were performed by Atlantic Microlab, Inc, Norcross, GA. The compounds $[PdCl_2(cod)]$, $[PtCl_2(dppe)]$, $[PtCl_2(dppm)]$, and $[Pt(cod)(dppe)][ClO_4]_2$ were prepared by established methods.[2,6,18] $[PdCl_2(dppe)]$ was prepared by displacement of cyclooctadiene from $[PdCl_2(cod)]$. Silver(I) triflate was purchased from Aldrich and used without further purification.

Preparation of $[Pt\{\sigma{:}\eta^2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ (1). To a CH_2Cl_2 solution (200 mL) of $[Pt(cod)(dppe)][ClO_4]_2$ (0.625 g, 0.694 mmol) was added PPh_3 (0.328 g, 1.25 mmol). After it was stirred for 2.5 h the solution was concentrated and ether was added to cause precipitation. After filtration, the white powder was washed with ether and dried in vacuo (0.641 g, 80%). Anal. Calcd for $C_{52}H_{51}Cl_2O_8P_3Pt$: C, 53.7; H, 4.4. Found: C, 53.8; H, 4.4. Crystals suitable for X-ray analysis were grown from CH_2Cl_2/Et_2O solution. $[Pt\{\sigma{:}\eta^2\text{-}C_8H_{12}(PEt_3)\}(dppe)][ClO_4]_2$ was prepared similarly. Anal. Calcd for $C_{40}H_{51}Cl_2O_8P_3Pt$: C, 47.2; H, 5.1. Found: C, 46.5; H, 5.2.

Preparation of $[Pt\{\sigma,\sigma\text{-}C_8H_{12}(PEt_3)_2\}(dppe)][ClO_4]_2$. A NMR tube was loaded with $[Pt(cod)(dppe)][ClO_4]_2$ (ca. 20 mg) and CD_2Cl_2 (0.5 mL) was added. Triethylphosphine (slightly more than 2 equiv) was introduced. The $^{31}P\{^1H\}$ NMR spectrum indicated that the only product was $[Pt\{\sigma,\sigma\text{-}C_8H_{12}(PEt_3)_2\}(dppe)][ClO_4]_2$. $^{31}P\{^1H\}$ NMR: δP_A (PEt_3) 38.8, δP_B (dppe) 44.3, $^3J(Pt,P_A) = 358$, $^1J(Pt,P_B) = 1875$, $J(P_A,P_{A'}) = J(P_A,P_B) = J(P_{A'},P_{B'}) = 0$, $J(P_A,P_{B'}) = J(P_{A'},P_B) = 50$, $J(P_B,P_{B'}) = 3$ Hz. $^{13}C\{^1H\}$ NMR: δC 6.5 d, $^2J(P,C) = 6$ (PCH_2CH_3); 12.0 d, $^1J(P,C) = 44$ (PCH_2CH_3); 12.5 dd, $^1J(Pt,C) = 622$, $^2J(P,C) = 78, 11$; 26.0, $^2J(Pt,C) = 43$; 36.9 d, $^1J(P,C) = 22$ Hz; 30.0–31.5 m (dppe CH_2 carbons; the fourth carbon of the C_8 unit is obscured); 128–135 m (phenyl carbons). Loss of PEt_3 on attempted isolation yielded $[Pt\{\sigma,\eta^2\text{-}C_8H_{12}(PEt_3)\}(dppe)][ClO_4]_2$.

Preparation of $[Pt(H_2O)_2(dppe)][SO_3CF_3]_2$ (2). To a CH_2Cl_2 solution (300 mL) of $[PtCl_2(dppe)]$ (1.03 g, 1.56 mmol) was added $AgSO_3CF_3$ (0.946 g, 3.68 mmol), and the resulting suspension was

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(16) When the sample of $[Pt(dppe)(H_2O)_2][SO_3CF_3]_2$ from which the crystal used in the structural determination was chosen was dissolved in CD_2Cl_2 the sharp peak due to H_2O (or HDO) originally present in the solvent disappeared, suggesting that a rapid exchange process occurs.

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Table II. Crystallographic Data for 1 and 2

	1	**2**
formula	$C_{52}H_{51}Cl_2O_8P_3Pt$	$C_{28}H_{28}F_6O_8P_2PtS_2$
mol wt	1162.83	927.65
color, habit	colorless, prismatic	colorless, rectangular
space group	$P\bar{1}$	$P2_1/n$
a, Å	13.749 (5)	10.663 (3)
b, Å	14.126 (4)	24.255 (9)
c, Å	14.356 (3)	13.720 (2)
α, deg	118.48 (2)	90
β, deg	94.47 (2)	104.36 (2)
γ, deg	96.78 (2)	90
cell vol, Å^3	2404.7 (12)	3437.6 (17)
Z	2	4
D(calcd), Mg/m^3	1.606	1.792
temp, K	298	298
radiatn	graphite monochromated Mo Kα (λ = 0.710 69 Å)	graphite monochromated Mo Kα (λ = 0.710 73 Å)
cryst dimens, mm	0.5 × 0.3 × 0.2	0.4 × 0.3 × 0.3
abs coeff, mm^{-1}	3.210	4.407
2θ range, deg	3.5–55.0	3.5–60.0
scan speed, deg/min	4.0–15.0	4.0–15.0
scan range (ω), deg	0.70 plus Kα separation	0.70 plus Kα separation
independent rflns	8510	10082
obsd rflns ($F > 4.0\sigma(F)$)	6348	3291
absorptn correctn	semiempirical	semiempirical
min/max transmissn	0.63/1.00	0.70/0.99
no. params refined	605	425
R	0.0616	0.0529
R_w	0.0686	0.0454
goodness of fit	1.50	2.57

stirred for 3 h. The AgCl formed and unreacted $AgSO_3CF_3$ were removed by filtration. The pale yellow filtrate was concentrated and ether was added to give the product as a white precipitate, which was washed with ether and dried (1.10 g, 79%). $^{31}P\{^1H\}$ NMR: δP 36.7, ^1J(Pt,P) = 3980 Hz. Anal. Calcd for $C_{28}H_{28}F_6O_8P_2PtS_2$: C, 36.3; H, 3.0. Found: C, 36.4; H, 3.0. Crystals suitable for X-ray analysis were grown from CH_2Cl_2/Et_2O solution.

Preparation of [Pt(SO_3CF_3)$_2$(dppm)]. In a manner similar to that described above, [PtCl_2(dppm)] (0.529 g, 0.814 mmol) and $AgSO_3CF_3$ (0.483 g, 1.88 mmol) yielded the product as a white powder (0.537 g, 76%). $^{31}P\{^1H\}$ NMR: δP −70.7, ^1J(Pt,P) = 3490 Hz. Anal. Calcd for $C_{27}H_{22}F_6O_6P_2PtS_2$: C, 37.0; H, 2.5. Found: C, 36.8; H, 2.5.

Preparation of [Pd(SO_3CF_3)$_2$(dppe)]·2H_2O. In a manner similar to that described for the platinum analogue, [PdCl_2(dppe)] (0.507 g, 0.881 mmol) and $AgSO_3CF_3$ (0.616 g, 2.40 mmol) gave the product as a pale yellow powder (0.388 g, 55%). $^{31}P\{^1H\}$ NMR: δP 73.7. Anal. Calcd for $C_{28}H_{28}F_6O_8P_2PdS_2$: C, 40.1; H, 3.4. Found: C, 40.2; H, 3.1.

Preparation of [Pt_2(μ-I)$_2$(dppe)$_2$][SO_3CF_3]$_2$·CH_2Cl_2. To a CH_2Cl_2 solution of [Pt(SO_3CF_3)$_2$(dppe)]·2H_2O (0.051 g, 0.055 mmol) was added [PtI_2(dppe)] (0.047 g, 0.055 mmol). The yellow solution was stirred for 1 h, when it was concentrated and ether was added to give the product as a pale yellow powder (0.080 g, 82%). $^{31}P\{^1H\}$ NMR: δP 54.3, ^1J(Pt,P) = 3470 Hz. ^1H NMR integration revealed that the product contained one CH_2Cl_2 molecule per dimer, which could not be removed by pumping in vacuo. Anal. Calcd for $C_{55}H_{50}Cl_2F_6I_2O_6P_4Pt_2S_2$: C, 36.2; H, 2.8. Found: C, 36.1; H, 2.8.

Preparation of [Pd_2(μ-I)$_2$(dppe)$_2$][SO_3CF_3]$_2$. In a manner similar to that described above, [Pd(SO_3CF_3)$_2$(dppe)]·2H_2O (0.054 g, 0.065 mmol) and [PdI_2(dppe)] (0.049 g, 0.065 mmol) gave the product as a yellow powder (0.095 g, 92%). $^{31}P\{^1H\}$ NMR: δP 77.1. Anal. Calcd for $C_{54}H_{48}F_6I_2O_6P_4Pd_2S_2$: C, 41.5; H, 3.1. Found: C, 41.3; H, 3.1.

X-ray Structure Determinations. Single crystals of the compounds 1 and 2 were mounted on glass fibers in a random orientation. Preliminary examination was carried out with Mo Kα radiation, using a Siemens R3 automated four-circle diffractometer. Final cell parameters and orientation matrices were obtained by least-squares refinement of 25 automatically centered reflections (20° < 2θ < 25°) in each case. Axial photographs of the three axes were taken to confirm cell lengths and the lattice symmetry. ω-Scans of representative reflections indicated acceptable crystal quality.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 1

	x	y	z	U(eq)[a]
Pt	2280 (1)	2873 (1)	2523 (1)	34 (1)
Cl(1)	1757 (3)	8017 (3)	6678 (3)	68 (2)
Cl(2)	3569 (3)	7339 (3)	2609 (4)	93 (3)
P(1)	2252 (2)	1078 (2)	1948 (2)	46 (1)
P(2)	1740 (2)	2315 (2)	721 (2)	46 (1)
P(3)	2349 (2)	3611 (2)	6120 (2)	39 (1)
O(1)	813 (9)	7425 (11)	6479 (12)	140 (9)
O(2)	1772 (14)	8341 (15)	5903 (15)	190 (14)
O(3)	1903 (16)	8920 (13)	7599 (13)	224 (12)
O(4)	2459 (10)	7390 (10)	6504 (15)	174 (11)
O(5)	3827 (13)	8440 (12)	3273 (18)	209 (14)
O(6)	4239 (12)	6706 (13)	2445 (16)	220 (13)
O(7)	2688 (12)	6947 (16)	2037 (18)	235 (15)
O(8)	3236 (35)	7238 (41)	3448 (41)	268 (48)
O(9)	3858 (37)	7498 (35)	1750 (38)	233 (37)
C(1)	1463 (10)	326 (9)	618 (10)	70 (6)
C(2)	1723 (10)	855 (10)	−44 (9)	69 (6)
C(3)	3723 (8)	4240 (9)	4471 (9)	54 (6)
C(4)	2842 (8)	3359 (8)	4162 (8)	44 (5)
C(5)	2005 (8)	3564 (7)	4826 (7)	39 (4)
C(6)	1609 (8)	4617 (8)	5034 (8)	44 (5)
C(7)	1124 (8)	4606 (8)	4043 (8)	43 (5)
C(8)	1739 (8)	4509 (7)	3180 (8)	41 (5)
C(9)	2748 (8)	4720 (8)	3241 (8)	45 (5)
C(10)	3510 (8)	5143 (9)	4207 (9)	53 (5)
C(11)	1681 (8)	504 (8)	2707 (8)	46 (5)
C(12)	739 (9)	700 (10)	2930 (10)	62 (6)
C(13)	250 (10)	224 (12)	3463 (12)	77 (8)
C(14)	702 (12)	−429 (11)	3759 (12)	80 (8)
C(15)	1628 (10)	−601 (10)	3552 (10)	65 (6)
C(16)	2143 (8)	−138 (8)	3032 (9)	50 (5)
C(17)	3450 (9)	691 (9)	1790 (11)	60 (6)
C(18)	3609 (15)	−318 (16)	1055 (20)	177 (14)
C(19)	4513 (18)	−536 (23)	997 (31)	294 (27)
C(20)	5306 (16)	81 (21)	1694 (21)	145 (16)
C(21)	5191 (11)	1057 (15)	2414 (15)	104 (11)
C(22)	4271 (11)	1365 (13)	2466 (13)	87 (8)
C(23)	486 (9)	2482 (8)	452 (8)	51 (5)
C(24)	−163 (9)	2572 (9)	1178 (9)	55 (5)
C(25)	−1126 (9)	2674 (10)	977 (10)	63 (6)
C(26)	−1477 (10)	2672 (10)	65 (13)	73 (7)
C(27)	−854 (11)	2558 (11)	−694 (12)	76 (8)
C(28)	121 (10)	2464 (10)	−501 (10)	67 (6)
C(29)	2473 (9)	2974 (12)	113 (9)	64 (7)
C(30)	2492 (10)	4045 (12)	412 (10)	75 (8)
C(31)	3117 (15)	4563 (16)	50 (14)	114 (11)
C(32)	3765 (18)	4026 (25)	−625 (18)	149 (18)
C(33)	3729 (13)	2934 (24)	−1006 (15)	135 (16)
C(34)	3118 (11)	2373 (16)	−601 (12)	99 (10)
C(35)	2774 (9)	2384 (9)	5955 (8)	50 (5)
C(36)	2238 (10)	1752 (9)	6328 (10)	64 (6)
C(37)	2592 (13)	846 (11)	6253 (13)	87 (9)
C(38)	3431 (15)	546 (13)	5801 (13)	96 (9)
C(39)	3935 (11)	1178 (12)	5449 (11)	78 (8)
C(40)	3621 (9)	2075 (10)	5514 (9)	61 (6)
C(41)	3277 (8)	4795 (8)	7035 (8)	44 (5)
C(42)	4215 (8)	4649 (9)	7352 (8)	50 (5)
C(43)	4921 (9)	5579 (12)	8016 (10)	67 (7)
C(44)	4713 (11)	6590 (13)	8372 (11)	80 (8)
C(45)	3788 (11)	6721 (10)	8082 (11)	78 (7)
C(46)	3069 (8)	5818 (9)	7406 (9)	55 (5)
C(47)	1243 (8)	3715 (9)	6742 (8)	46 (5)
C(48)	324 (8)	3185 (9)	6115 (9)	53 (6)
C(49)	−518 (8)	3265 (11)	6620 (12)	64 (8)
C(50)	−426 (11)	3856 (12)	7712 (14)	75 (9)
C(51)	461 (13)	4370 (12)	8316 (12)	84 (9)
C(52)	1317 (10)	4314 (10)	7850 (10)	66 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2

	x	y	z	U(eq)[a]
Pt	993 (1)	1738 (1)	1127 (1)	45 (1)
S(1)	1870 (4)	727 (2)	3947 (3)	66 (2)
S(2)	5262 (5)	1408 (2)	1786 (3)	75 (2)
P(1)	−318 (4)	1624 (1)	−391 (3)	51 (1)
P(2)	−47 (3)	2521 (1)	1204 (3)	46 (1)
F(1)	−108 (10)	95 (4)	3835 (8)	122 (6)
F(2)	−551 (9)	849 (5)	3047 (8)	119 (5)
F(3)	−177 (11)	831 (5)	4643 (8)	135 (6)
F(4)	6756 (11)	1106 (6)	3487 (8)	168 (7)
F(5)	4915 (10)	714 (5)	3119 (8)	135 (6)
F(6)	6342 (13)	459 (6)	2392 (9)	158 (8)
O(1)	2308 (8)	1903 (3)	2524 (6)	56 (4)
O(2)	1924 (8)	960 (3)	1137 (6)	64 (4)
O(3)	2003 (10)	524 (4)	2997 (8)	85 (5)
O(4)	1994 (10)	1321 (4)	4046 (7)	79 (5)
O(5)	2524 (11)	434 (4)	4826 (8)	103 (5)
O(6)	4358 (10)	1092 (4)	1040 (7)	75 (4)
O(7)	6382 (10)	1600 (4)	1481 (7)	91 (5)
O(8)	4684 (10)	1818 (5)	2291 (9)	111 (6)
C(1)	−1268 (13)	2255 (5)	−706 (10)	56 (6)
C(2)	−1580 (12)	2476 (5)	251 (10)	55 (6)
C(3)	−1464 (13)	1071 (5)	−466 (10)	51 (6)
C(4)	−1694 (16)	833 (6)	376 (11)	74 (7)
C(5)	−2644 (19)	434 (7)	299 (13)	90 (9)
C(6)	−3313 (17)	258 (7)	−618 (17)	91 (9)
C(7)	−3107 (17)	481 (7)	−1474 (13)	86 (8)
C(8)	−2181 (15)	891 (6)	−1406 (10)	66 (7)
C(9)	541 (13)	1491 (6)	−1354 (9)	53 (6)
C(10)	719 (15)	1894 (6)	−2009 (13)	79 (8)
C(11)	1321 (18)	1787 (9)	−2757 (14)	100 (10)
C(12)	1780 (16)	1283 (11)	−2854 (14)	95 (10)
C(13)	1593 (21)	859 (8)	−2237 (17)	122 (12)
C(14)	991 (18)	966 (7)	−1476 (13)	91 (9)
C(15)	823 (15)	3133 (4)	948 (9)	50 (6)
C(16)	2191 (15)	3112 (5)	1080 (10)	57 (7)
C(17)	2818 (14)	3578 (7)	955 (11)	67 (7)
C(18)	2180 (18)	4076 (7)	755 (11)	74 (8)
C(19)	884 (18)	4099 (6)	640 (11)	68 (7)
C(20)	182 (13)	3628 (6)	746 (10)	60 (6)
C(21)	−345 (12)	2616 (5)	2436 (9)	47 (6)
C(22)	82 (14)	3085 (6)	2991 (11)	61 (6)
C(23)	−139 (17)	3135 (6)	3949 (13)	83 (8)
C(24)	−746 (18)	2726 (8)	4327 (11)	86 (9)
C(25)	−1210 (18)	2266 (7)	3765 (14)	90 (9)
C(26)	−976 (15)	2211 (6)	2824 (12)	73 (7)
C(27)	174 (16)	624 (8)	3879 (14)	76 (8)
C(28)	5904 (21)	918 (10)	2776 (15)	98 (10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths			
Pt–P(1)	2.256 (3)	Pt–P(2)	2.341 (3)
Pt–C(4)	2.158 (11)	Pt–C(8)	2.285 (10)
Pt–C(9)	2.285 (10)	P(1)–C(1)	1.850 (13)
P(1)–C(11)	1.812 (14)	P(1)–C(17)	1.793 (13)
P(2)–C(2)	1.813 (13)	P(2)–C(23)	1.805 (13)
P(2)–C(29)	1.826 (16)	P(3)–C(5)	1.849 (12)
P(3)–C(35)	1.808 (13)	P(3)–C(41)	1.815 (9)
P(3)–C(47)	1.808 (12)	C(1)–C(2)	1.502 (23)
C(3)–C(4)	1.499 (15)	C(3)–C(10)	1.545 (21)
C(4)–C(5)	1.517 (15)	C(5)–C(6)	1.546 (16)
C(6)–C(7)	1.516 (17)	C(7)–C(8)	1.516 (17)
C(8)–C(9)	1.371 (15)	C(9)–C(10)	1.488 (15)
Bond Angles			
P(1)–Pt–P(2)	85.2 (1)	P(1)–Pt–C(4)	93.6 (3)
P(2)–Pt–C(4)	177.3 (3)	P(1)–Pt–C(8)	159.2 (3)
P(1)–Pt–C(9)	164.6 (3)	P(2)–Pt–C(8)	95.0 (3)
P(2)–Pt–C(9)	102.0 (3)	C(4)–Pt–C(8)	87.0 (4)
C(4)–Pt–C(9)	78.5 (4)	Pt–C(4)–C(3)	104.9 (9)
Pt–C(4)–C(5)	110.4 (7)	P(3)–C(5)–C(4)	112.8 (8)
P(3)–C(5)–C(6)	109.3 (6)		

Table VI. Selected Bond Lengths (Å) and Angles (deg) for 2

Bond Lengths			
Pt–P(1)	2.219 (3)	Pt–P(2)	2.214 (4)
Pt–O(1)	2.114 (7)	Pt–O(2)	2.131 (8)
P(1)–C(1)	1.827 (13)	P(2)–C(2)	1.826 (12)
C(1)–C(2)	1.529 (20)		
Bond Angles			
P(1)–Pt–P(2)	86.9 (1)	P(1)–Pt–O(1)	175.3 (2)
P(1)–Pt–O(2)	94.6 (2)	P(2)–Pt–O(1)	91.2 (2)
P(2)–Pt–O(2)	175.6 (3)		
Nonbonded Distances			
O(1)–O(4)	2.61	O(1)–O(8)	2.64
O(2)–O(3)	2.74	O(2)–O(6)	2.65

Data were collected using the θ–2θ scan technique, and the intensities of three standard reflections were measured every 50 reflections. As no significant variation in intensities of the standard reflections was observed during data collection, no decay correction was applied. In each case, an empirical absorption correction was applied to the data, using 9 psi curves for reflections with $83° < \chi < 89°$.

Data reduction and structure solution was achieved using the SHELXTL PLUS structure solution software package.[19] The structures were solved by Patterson methods in the space groups $P\bar{1}$ and $P2_1/n$ and were refined successfully in the above space groups. The remaining non-hydrogen atoms and noncoordinating anions were located from subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing the function $w(F_o - F_c)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Hydrogen atoms were included in their idealized calculated positions and were held fixed.

The final difference Fourier maps had maximum electron densities of 2.01 and 1.76 e/Å^3 for 1 and 2, respectively, which were close to the platinum atoms. Least-squares planes calculated for the phenyl rings and planar fragments showed very small deviations from planarity. Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table II. Figures 1 and 2 show the projection views and atom labeling schemes for 1 and 2, respectively. Refined positional parameters for the non-hydrogen atoms are listed in Tables III and IV, and selected bond distances and bond angles are presented in Tables V and VI respectively for compounds 1 and 2. All calculations were performed on a VAX Station II GPX computer using SHELXTL PLUS software.

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Supplementary Material Available: Tables of bond lengths (Tables S1 and S6), bond angles (Tables S2 and S7), anisotropic displacement coefficients for non-hydrogen atoms (Tables S3 and S8), and calculated hydrogen atom coordinates and isotropic displacement coefficients (Tables S4 and S9) and structure determination summaries for 1 and 2 (15 pages); tables of observed and calculated structure factors for 1 and 2 (Tables S5 and S10) (67 pages). Ordering information is given on any current masthead page.

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(19) Sheldrick, G. M. Siemens Analytical X-ray Division, Madison, WI, 1989.