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Synthesis and Reactions of Cationic Palladium and Platinum Cyclopentadienyl Complexes. Molecular Structure of (η^5-Cyclopentadienyl)[1,2-bis(diphenylphosphino)ethane]platinum(II) Triflate

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The palladium and platinum triflate complexes [M(OTf)$_2$(P–P)] (P–P = dppm, dppe, dppp) react with cyclopentadienylthallium to produce the ionic, η^5-cyclopentadienyl complexes [M(η^5-C$_5$H$_5$)(P–P)]OTf, which are isolated as air-stable solids. They have been characterized by NMR spectroscopy, elemental analysis, and, in the case of [Pt(η^5-C$_5$H$_5$)(dppe)]OTf, X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1$ with a = 9.822(3) Å, b = 12.072(4) Å, c = 13.702(5) Å, β = 110.56(2)°, V = 1521.2(9) Å^3, and Z = 2. Least-squares refinement converged at R = 0.0390 and R_w = 0.0516 based on 3819 reflections with $F > 4.0\sigma(F)$. In CDCl$_3$ solution [Pd(η^5-C$_5$H$_5$)(dppe)]$^+$ reacts with PEt$_3$ to give [PdCl(PEt$_3$)(dppe)]$^+$, but in d_6-acetone displacement of dppe occurs to produce [Pd(η^5-C$_5$H$_5$)(PEt$_3$)$_2$]$^+$. The reaction of the dppm compound with PEt$_3$ gives many products, whereas the reaction of [Pd(η^5-C$_5$H$_5$)(dppp)]$^+$ is very slow. The reactions of [Pt(η^5-C$_5$H$_5$)(P–P)]$^+$ (P–P = dppm, dppp) with PEt$_3$ are also very slow, but with the dppe complex two isomeric products are obtained. These are identified from their NMR spectra as the two possible sp^2-bonded, η^1-cyclopentadienyl complexes [Pt(C$_5$H$_5$)(PEt$_3$)(dppe)]$^+$.

Introduction

Many cyclopentadienyl complexes of palladium and platinum have been reported, although they are relatively few compared with those of the other late transition metals. Most are η^5-bonded, formally 18-electron complexes, and several have been structurally characterized. Most of these are monomeric palladium(II) species,[1-11] including one complex which contains one η^5- and one η^1-cyclopentadienyl ring,[5] but there are also dimeric palladium complexes in which one metal center is coordinated by an η^5 ring,[12,13] and two complexes in which the cyclopentadienyl group functions as a bridging ligand.[14] Only four platinum cyclopentadienyl complexes have been characterized by X-ray diffraction methods,[10,15-17] and only one of these is a monomeric platinum(II) compound.[10]

The η^5-cyclopentadienyl complexes of palladium and platinum undergo a variety of reactions, including η^5 to η^1 rearrangements of the cyclopentadienyl ring. We have made a thorough investigation of the reactions of [M(C$_6$H$_4$-2-N=NC$_6$H$_5$-*C,N*)(η^5-C$_5$H$_4$R)] (M = Pd, Pt; R = H, Me, SiMe$_3$) with tertiary phosphines, which result in conversion to η^1-C$_5$H$_5$ or ionic C$_5$H$_5^-$ species, depending on the reaction conditions.[8,18-21]

We have previously reported the preparation of palladium and platinum complexes containing diphosphine and coordinated triflate ligands.[22,23] In this paper we report the use of these species as precursors to stable, cationic η^5-cyclopentadienyl complexes and their reactions with tertiary phosphines.

Results and Discussion

When [Pt(cod)(dppe)][OTf]$_2$[22] was treated with TlC$_5$H$_5$ in CH$_2$Cl$_2$ solution several products were formed, as

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determined by ^{31}P NMR spectroscopy. A species with parameters consistent with the $[Pt(\eta^5\text{-}C_5H_5)(dppe)]^+$ cation was detected, but it was only a minor component of the mixture. A number of species in the mixture appeared to be derived from cyclopentadienyl attack on the coordinated diene.[24] Since cyclooctadiene is slowly displaced from platinum by the triflate anions,[22] it seems likely that the presence of $[Pt(OTf)_2(dppe)]$ was responsible for the fact that any cyclopentadienyl complex was formed at all. Thus, we decided to investigate the reaction of the triflate complex itself with TlC_5H_5.

On addition of TlC_5H_5 to a CH_2Cl_2 solution of $[Pt(OTf)_2(dppe)]$ the originally colorless solution became bright yellow, and $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ was isolated in virtually quantitative yield. The complex has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, by elemental analysis, and by a single-crystal X-ray diffraction study. Its ^{1}H NMR spectrum exhibits a resonance at 5.78 ppm, corresponding to the η^5-cyclopentadienyl group, which appears as a triplet due to coupling with the two equivalent phosphorus nuclei. The relatively small value of J_{PtH} is also indicative of an $\eta^5\text{-}C_5H_5$ moiety.[20] The $^{13}C\{^1H\}$ NMR spectrum exhibits a triplet at δ_C 95.5 (coupling to ^{195}Pt is not resolved), as well as signals due to the dppe ligand. The $^{31}P\{^1H\}$ NMR spectrum shows only one resonance, with a large coupling to ^{195}Pt of 4495 Hz.

Related η^5-cyclopentadienyls of platinum, $[Pt(\eta^5\text{-}C_5H_5)(P\text{-}P)]OTf$ (P-P = dppm, dppp), and palladium, $[Pd(\eta^5\text{-}C_5H_5)(P\text{-}P)]OTf$ (P-P = dppm, dppe, dppp), have been prepared in good yield by similar procedures. These have also been characterized by NMR spectroscopy and by elemental analyses. The platinum complexes are yellow or orange, whereas their palladium analogues are pink or purple. They are all air-stable solids. In each case the ^{1}H NMR signal for the C_5H_5 group appears as a triplet, due to coupling to the two phosphorus atoms. Coupling to ^{195}Pt is resolved in the dppp complex but not in $[Pt(\eta^5\text{-}C_5H_5)dppm)]OTf$. The ^{1}H chemical shifts of the signals due to the cyclopentadienyl groups are dependent on the nature of the diphosphine ligand, rather than the metal. Thus, the C_5H_5 resonances appear around 5.4, 5.8, and 6.1 ppm for the dppp, dppe, and dppm complexes, respectively. In the $^{13}C\{^1H\}$ NMR spectra, the cyclopentadienyl resonances do not exhibit coupling to phosphorus or platinum for the dppm or dppp complexes, but a small J_{PC} value of 2 Hz is resolved for each of the dppe complexes. The ^{13}C shifts do not parallel those found in the ^{1}H NMR spectra, however; in each case the palladium complex appears *ca.* 5 ppm to higher frequency of its platinum analogue. The $^{31}P\{^1H\}$ NMR spectrum of each of the palladium complexes exhibits a single resonance, and the central resonance is flanked by ^{195}Pt satellites for each of the platinum compounds. The ^{31}P chemical shifts show the usual dependence on ring size,[25] and the magnitudes of $^1J_{PtP}$ also vary with the size of the chelate ring.

Table I. Crystallographic Data for $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$

formula	$C_{32}H_{29}F_3O_3P_2PtS$
fw	807.6
color, habit	yellow, cubic
space group	$P2_1$
a, Å	9.822(3)
b, Å	12.072(4)
c, Å	13.702(5)
β, deg	110.56(2)
cell vol, Å^3	1521.2(9)
Z	2
D(calcd), Mg/m^3	1.763
temp, K	298
radiation	graphite monochromated Mo Kα (λ = 0.710 73 Å)
cryst dimens, mm	0.4 × 0.4 × 0.4
abs coeff, mm^{-1}	4.878
2θ range, deg	3.5–60.0
scan speed, deg/min	4.0–15.0
scan range (ω), deg	0.70 plus Kα separation
no. of indep rflns	4217
no. of obsd rflns ($F > 4.0\sigma(F)$)	3819
abs cor	semiempirical
min/max transmissn	0.37/0.97
absolute structure	η = 1.01(5)
no. of params refined	380
R	0.0390
R_w	0.0516
goodness of fit	0.83

Table II. Selected Bond Lengths (Å) and Angles (deg) for $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$

	Bond Lengths		
Pt–P(1)	2.239(3)	Pt–P(2)	2.230(3)
Pt–C(27)	2.313(23)	Pt–C(28)	2.238(13)
Pt–C(29)	2.308(20)	Pt–C(30)	2.286(25)
Pt–C(31)	2.343(17)	Pt(1)–C(1)	1.840(10)
P(1)–C(3)	1.826(11)	P(1)–C(9)	1.814(9)
P(2)–C(2)	1.828(9)	P(2)–C(15)	1.820(9)
P(2)–C(21)	1.804(12)	C(27)–C(28)	1.303(25)
C(27)–C(31)	1.281(35)	C(28)–C(29)	1.396(34)
C(29)–C(30)	1.371(35)	C(30)–C(31)	1.346(43)
	Bond Angles		
P(1)–Pt–P(2)	86.4(1)	Pt–P(1)–C(1)	108.4(3)
Pt–P(1)–C(3)	119.1(3)	Pt–P(1)–C(9)	112.9(3)
Pt–P(2)–C(2)	107.3(4)	Pt–P(2)–C(15)	116.5(3)
Pt–P(2)–C(21)	114.8(3)	P(1)–C(1)–C(2)	108.3(7)
P(2)–C(2)–C(1)	108.1(6)	C(28)–C(27)–C(31)	113.4(21)
C(27)–C(28)–C(29)	107.0(18)	C(28)–C(29)–C(30)	103.1(20)
C(29)–C(30)–C(31)	110.3(27)	C(27)–C(31)–C(30)	105.8(20)

Yellow, cubic crystals of $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ were obtained by slow diffusion of ether into a dichloromethane solution of the complex, and a crystal was chosen for an X-ray diffraction study. Crystallographic data are given in Table I, and selected bond lengths and angles are presented in Table II. The molecular structure of the complex is shown in Figure 1. The cyclopentadienyl ring is bound in an η^5 fashion, and the two phosphorus atoms of the diphosphine ligand complete the coordination about platinum. There are no short contacts between the cation and the triflate counterion. The carbon atoms of the cyclopentadienyl ring exhibit considerable thermal motion, principally within the plane of the ring, and as a result, the precision of the bond lengths and angles within the ring is low. The ring is slightly tilted, and there is considerable variation in the Pt–C distances, the Pt–C(28) distance being shorter than the others. The tilting brings C(28) to a position that is almost trans to P(1); the P(1)–Pt–C(28) angle approaches linearity (168.9(5)°). The Pt–P bond lengths differ slightly, the longer distance being that to P(1).

The palladium analogue of this complex was unexpectedly obtained from the reaction of $[Zr(\eta^5\text{-}C_5H_5)_2Cl(CH_2CH_2Bu^t)]$ with $[PdCl_2(dppe)]$ in the presence of silver triflate.[9] The structure of $[Pd(\eta^5\text{-}C_5H_5)(dppe)]OTf$ is virtually identical with that of the platinum complex; both complexes belong to the same space group, and the cell dimensions are very similar. The palladium complex also exhibits a tilting of the cyclopentadienyl ring and two

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(24) When a few drops of acetonitrile were added prior to TlC_5H_5 introduction $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ was isolated, but only in low yield.

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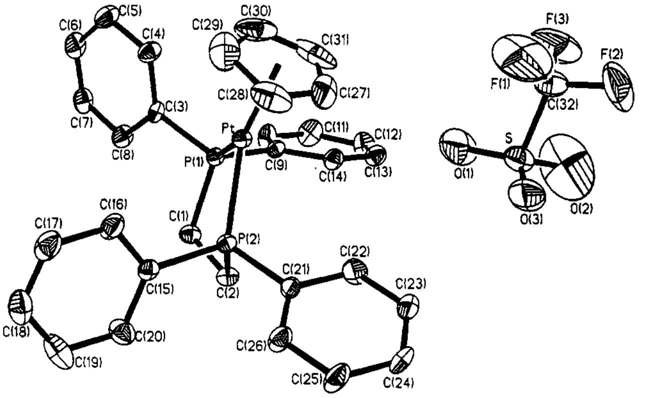

Figure 1. Projection view of [Pt(η^5-C_5H_5)(dppe)]OTf showing the atom-numbering scheme.

different Pd–P distances, the latter being more noticeable than in the platinum case.

We have observed previously that nucleophilic attack on the 18-electron center in [M(C_6H_4-2-N=NC_6H_5-*C,N*)(η^5-C_5H_5)] (M = Pd, Pt) resulted in rearrangement of the five-membered ring to the η^1 bonding mode.[8,19–21] We anticipated that these cationic palladium and platinum cyclopentadienyl complexes might react similarly. Thus, we decided to investigate their reactions with a number of phosphorus ligands. No reaction occurred when [Pd(η^5-C_5H_5)(dppe)]OTf or [Pt(η^5-C_5H_5)(dppe)]OTf was treated with PPh_3 in $CDCl_3$ solution. Presumably this phosphine is insufficiently nucleophilic and/or too bulky to attack the metal center. A reaction did take place, however, when PEt_3 was added to a solution of each of the complexes. It was found that both the rate of the reaction and the nature of the product were dependent on the metal, the diphosphine, and the solvent.

Addition of 1 equiv of PEt_3 to a suspension of [Pd(η^5-C_5H_5)(dppe)]OTf in $CDCl_3$ resulted in a slow reaction and eventual formation of a clear solution. $^{31}P\{^1H\}$ NMR analysis of the resulting solution indicated that the major species formed contained three nonequivalent phosphorus atoms, as expected for [Pd(η^1-C_5H_5)(PEt_3)(dppe)]$^+$. The ^1H NMR spectrum, however, revealed the presence of a significant amount of cyclopentadiene (δ_H 6.57 (m, 2H), 6.46 (m, 2H), 2.98 (m, 2H)), indicating that the cyclopentadienyl group had been cleaved from the metal. The major phosphorus-containing product was identified as the [PdCl(PEt_3)(dppe)]$^+$ cation, by comparison of its NMR parameters with those of a sample prepared from [$PdCl_2$(dppe)] and PEt_3. The chloropalladium cation must have been formed by reaction with the chlorinated solvent. Since a deuterated solvent was used, the cyclopentadiene was likely to have been C_5H_5D, in fact, where the deuterium was randomly distributed throughout the molecule. This is to be expected, since 1,5-sigmatropic hydrogen shifts occur readily in cyclopentadienes at ambient temperature. The analogous reaction of [Pd(η^5-C_5H_5)(dppe)]OTf with PBu_3 gave [PdCl(PBu_3)(dppe)]$^+$ (δ_P 11.0 (dd, $^2J_{PP}$ = 407, 19 Hz), 60.5 (dd, $^2J_{PP}$ = 407, 10 Hz), 63.7 (dd, $^2J_{PP}$ = 19, 10 Hz)).[23] The reaction of [Pd(η^5-C_5H_5)(dppm)]OTf with PEt_3 produced a large number of products, including the [PdCl(PEt_3)(dppm)]$^+$ cation, whereas the reaction of the dppp complex was very slow, the only observable product being [PdCl(PEt_3)(dppp)]$^+$.

Since the palladium compounds reacted with the chlorinated solvent, the corresponding reactions were performed in d_6-acetone solution. Surprisingly, [Pd(η^5-C_5H_5)(dppe)]OTf underwent displacement of the diphosphine ligand to produce [Pd(η^5-C_5H_5)(PEt_3)$_2$]$^+$ (δ_H 6.04 (t, J_{PH} = 2 Hz); δ_P 36.8). With 1 equiv of PEt_3 half of the starting complex remained, but when a second equivalent was added, the reaction went to completion. The reaction of [Pd(η^5-C_5H_5)(dppm)]OTf again produced a large number of species, whereas no reaction took place with the dppp complex.

The reactions of the platinum cyclopentadienyl complexes with PEt_3 were investigated also. The reactions of [Pt(η^5-C_5H_5)(dppm)]OTf and [Pt(η^5-C_5H_5)(dppp)]OTf in $CDCl_3$ or d_6-acetone solution were extremely slow, no new resonances being observed in their $^{31}P\{^1H\}$ NMR spectra even after 7 days. The reaction of [Pt(η^5-C_5H_5)(dppe)]OTf with PEt_3 in either solvent was also slow at ambient temperature, but ^{31}P resonances for a new species were apparent after 24 h. On standing, a second, very similar set of resonances appeared in the $^{31}P\{^1H\}$ NMR spectrum, and both sets grew in steadily over several days at ambient temperature (see Experimental Section).[26] It is clear that the two sets of resonances were due to two very closely related complexes, each exhibiting three doublets of doublets, with ^{195}Pt satellites. In each case, the low-frequency resonance may be assigned to the triethylphosphine, the two signals at higher frequency being associated with the two nonequivalent phosphorus atoms of the dppe ligand. The $^1J_{PtP}$ value of 1760–1770 Hz for one of the dppe P atoms indicates that it lies trans to a ligand of high trans influence, probably a σ-carbon ligand, but not the expected η^1-cyclopentadienyl. Values of $^1J_{PtP}$ for tertiary phosphines lying trans to η^1-C_5H_5 groups are found to be around 2500 Hz.[27,28]

The ^1H NMR spectra did not contain the anticipated singlet for a fluxional η^1-C_5H_5 ring either. Instead, the first species exhibited broad resonances at 6.4 (2 overlapping signals) and 6.1 ppm, which were found from a ^1H–^1H correlation (COSY) experiment to couple to each other and to a resonance at 2.1 ppm. As the ^{31}P signals associated with the second species increased in intensity, new signals appeared in the ^1H NMR spectrum at 6.2, 6.0, and 5.8 ppm, which were found to couple to a resonance at δ_H 2.3. It appears that the cyclopentadienyl ring had undergone a hydrogen atom shift to produce an sp^2-bonded ring. This could exist as two isomers, where the CH_2 group is either α or β to the position of metalation, which would account for the observation of two very similar sets of ^{31}P NMR resonances. Supporting evidence for such structures was obtained from $^{13}C\{^1H\}$ NMR spectroscopy. When a mixture of the two isomers in d_6-acetone solution was analyzed by $^{13}C\{^1H\}$ NMR spectroscopy, two resonances which could be assigned to methylene carbons were observed at 44.1 ppm (d, J_{PC} = 8 Hz, J_{PtC} = 63 Hz) and 48.7 ppm (d, J_{PC} = 7 Hz, J_{PtC} = 54 Hz). The complexity of the aromatic region (128–136 ppm), however, precluded identification of the other resonances due to the five-membered ring carbons, which were apparently obscured by those arising from the dppe phenyl carbons, with the exception of a signal at 140.1 ppm (d, J_{PC} = 6 Hz, J_{PtC} = 46 Hz).

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(26) In $CDCl_3$ solution, resonances due to a very small amount of [PtCl(PEt_3)(dppe)]$^+$ (δ_P 16.7 (dd, $^1J_{PtP}$ = 2310 Hz, $^2J_{PP}$ = 368, 17 Hz), 43.3 (dd, $^1J_{PtP}$ = 3520 Hz, $^2J_{PP}$ = 17, 6 Hz), 53.0 (dd, $^1J_{PtP}$ = 2260 Hz, $^2J_{PP}$ = 368, 6 Hz) are also present (<5% at ambient temperature), which increase in intensity if the solution is heated.

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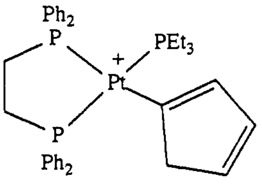
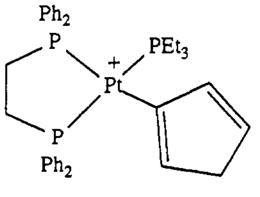
We have previously reported the rearrangement of (η^1-cyclopentadienyl)platinum species to two sp^2-bonded isomers in [Pt(C_6H_4-2-N=NC_6H_5-*C,N*)(η^1-C_5H_5)(PEt_3)$_2$].[21] It is likely that a 1,5-sigmatropic shift is involved, analogous to that found in cyclopentadiene itself. Thus, we assign structure **A**, which requires a single hydrogen shift from the η^1-cyclopentadienyl bonding mode, to the complex which was formed initially. Structure **B** would then correspond to the second species. Since **A** diminished in intensity but did not disappear on standing for several days, it is evident that an equilibrium between forms **A** and **B** is established. A similar situation was found to prevail in the case of the sp^2-bonded cyclopentadienyl complex [Pt(C_6H_4-2-N=NC_6H_5-*C,N*)(sp^2-C_5H_5)(PEt_3)$_2$].[21] Attempts to isolate the sp^2-bonded complexes [Pt(sp^2-C_5H_5)(PEt_3)(dppe)]OTf were unsuccessful. In chlorinated solvents conversion to [PtCl(PEt_3)(dppe)]$^+$ occurs on standing, and intractable oils were obtained from acetone solution. The lack of solubility in less polar solvents precluded efforts to crystallize the products from other media.



A



B

Addition of 1 equiv of dppe to a $CDCl_3$ solution of [Pt(η^5-C_5H_5)(dppe)]OTf produced a thick, white precipitate, and no resonances could be detected in the ^{31}P NMR spectrum. When this reaction was performed in d_6-acetone, resonances due to the [Pt(η^5-C_5H_5)(dppe)]$^+$ cation, free dppe (−11.7 ppm) and the platinum(0) complex [Pt(dppe)$_2$] (δ_P 30.9 ($^1J_{PtP}$ = 3726 Hz))[29] were observed after 18 h. Formation of the last species was quite unexpected, but it could be envisaged as taking place by reductive coupling of the cyclopentadienyl and triflate groups.

In summary, the reactions of [Pd(η^5-C_5H_5)(P–P)]OTf with PEt_3 show a strong dependence on the nature of the diphosphine, being quite indiscriminate when dppm is involved and exceedingly slow in the case of dppp. For platinum, only the dppe complex reacts fast enough for any products to be observed. In no case is an η^5 to η^1 rearrangement of the five-membered ring observed, but the reaction of [Pt(η^5-C_5H_5)(dppe)]OTf with PEt_3 produces two isomers of [Pt(sp^2-C_5H_5)(PEt_3)(dppe)]$^+$, in which a hydrogen atom shift has occurred and the cyclopentadienyl group is bonded to platinum by means of an sp^2 carbon. Although formation of the latter is likely to proceed via an η^1-cyclopentadienyl intermediate, the reaction is so slow at ambient temperature that the intermediate would be impossible to detect.

Experimental Section

All reactions were carried out under an atmosphere of argon, and the products were worked up in air, unless otherwise stated. The complexes [M(H_2O)$_2$(dppe)][OTf]$_2$, and [M(OTf)$_2$(dppm)] and [M(OTf)$_2$(dppp)] (M = Pd, Pt), were prepared as described previously.[22,23] NMR spectra were recorded on a Varian XL-300 spectrometer, operating in the FT mode. They were recorded in $CDCl_3$ unless stated otherwise. ^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.

Preparation of [Pd(η^5-C_5H_5)(dppe)]OTf. To a CH_2Cl_2 solution of [Pd(H_2O)$_2$(dppe)][OTf]$_2$ (0.12 g, 0.14 mmol) was added TlC_5H_5 (0.046 g, 0.17 mmol). The mixture was stirred for 2 h and then filtered to remove TlCl and unreacted TlC_5H_5. The filtrate was concentrated, and ether was added to precipitate the product as a fluffy, purple solid (0.086 g, 86%). Anal. Calcd for $C_{32}H_{29}F_3O_3P_2PdS$: C, 53.46; H, 4.07. Found: C, 53.20; H, 4.09. ^1H NMR: δ_H 2.67 (d, J_{PH} = 22 Hz, CH_2), 5.81 (t, J_{PH} = 2 Hz, C_5H_5), 7.45–7.65 (C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C 28.9 (t, J_{PC} = 25 Hz, CH_2), 99.8 (t, J_{PC} = 2 Hz, C_5H_5), 129.6 (t, J_{PC} = 7 Hz), 132.3 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: δ_P 71.5.

Preparation of [Pt(η^5-C_5H_5)(dppe)]OTf. To a CH_2Cl_2 solution of [Pt(H_2O)$_2$(dppe)][OTf]$_2$ (0.36 g, 0.39 mmol) was added TlC_5H_5 (0.11 g, 0.41 mmol). After 2 h the solution was filtered and ether was added to precipitate the product as a yellow powder (0.31 g, 99%). Anal. Calcd for $C_{32}H_{29}F_3O_3P_2PtS$: C, 47.59; H, 3.62. Found: C, 47.53; H, 3.65. ^1H NMR (CD_2Cl_2): δ_H 2.50 (d, J_{PH} = 18 Hz, J_{PtH} = 40 Hz, CH_2), 5.78 (t, J_{PH} = 1.5 Hz, J_{PtH} = 12 Hz, C_5H_5), 5.78–5.85 (C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ_C 29.5 (dd, J_{PC} = 47, 6 Hz, CH_2), 95.5 (d, J_{PC} = 2 Hz, C_5H_5), 129.7 (m), 132.8 (m, C_6H_5). $^{31}P\{^1H\}$ NMR: δ_P 41.8 ($^1J_{PtP}$ = 4495 Hz). $^{195}Pt\{^1H\}$ NMR: δ_{Pt} −4881 (relative to K_2PtCl_4 in D_2O solution) ($^1J_{PtP}$ = 4496 Hz). Crystals suitable for X-ray diffraction study were grown from CH_2Cl_2/Et_2O solution.

Preparation of [Pd(η^5-C_5H_5)(dppm)]OTf. [Pd(OTf)$_2$(dppm)] (0.15 g, 0.19 mmol) and TlC_5H_5 (0.060 g, 0.23 mmol) were placed in a round-bottomed flask, and CH_2Cl_2 (100 mL) was introduced. The contents of the flask were stirred for 3 h and then filtered. Addition of ether to the filtrate gave the product as a pink powder (0.12 g, 90%). Anal. Calcd for $C_{31}H_{27}F_3O_3P_2PdS$: C, 52.82; H, 3.86. Found: C, 52.89; H, 3.87. ^1H NMR: δ_H 4.71 (t, J_{PH} = 10 Hz, CH_2), 6.09 (t, J_{PH} = 2.5 Hz, C_5H_5), 7.4–7.8 (C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C 40.6 (t, J_{PC} = 31 Hz, CH_2), 97.6 (C_5H_5), 129.5 (t, J_{PC} = 6 Hz), 132.3, 132.5 (C_6H_5). $^{31}P\{^1H\}$ NMR: δ_P −29.4.

Preparation of [Pt(η^5-C_5H_5)(dppm)]OTf. A CH_2Cl_2 solution containing [Pt(OTf)$_2$(dppm)] (0.091 g, 0.10 mmol) and TlC_5H_5 (0.029 g, 0.10 mmol) was stirred for 2 h and then filtered. Ether addition gave the product as a yellow powder (0.071 g, 90%). Anal. Calcd for $C_{31}H_{27}F_3O_3P_2PtS$: C, 46.91; H, 3.43. Found: C, 46.89; H, 3.41. ^1H NMR (CD_2Cl_2): δ_H 4.88 (t, J_{PH} = 11.5 Hz, J_{PtH} = 74 Hz, CH_2), 6.11 (t, J_{PH} = 2 Hz, J_{PtH} unresolved, C_5H_5), 7.45–7.80 (C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ_C 46.3 (t, J_{PC} = 37 Hz, CH_2), 93.2 (C_5H_5), 129.9 (m), 132.5 (m), 133.1 (C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ_P −52.6 $^1J_{PtP}$ = 3863 Hz.)

Preparation of [Pd(η^5-C_5H_5)(dppp)]OTf·0.5CH_2Cl_2. TlC_5H_5 (0.090 g, 0.33 mmol) was added to a CH_2Cl_2 solution (40 mL) of [Pd(OTf)$_2$(dppp)] (0.18 g, 0.22 mmol). After 2 h the mixture was filtered and ether was added to the filtrate, giving the product as purple crystals (0.13 g, 83%). Anal. Calcd for $C_{33.5}H_{32}ClF_3O_3P_2PdS$: C, 51.88; H, 4.16. Found: C, 51.90; H, 4.16. ^1H NMR: δ_H 2.00 (br), 2.82 (br, CH_2), 5.41 (t, J_{PH} = 2 Hz, C_5H_5), 7.35–7.65 (C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C 19.0, 25.0 (CH_2), 101.2 (C_5H_5), 129.1 (t, J_{PC} = 5 Hz), 131.5, 132.3 (t, J_{PC} = 5 Hz, C_6H_5). $^{31}P\{^1H\}$ NMR: δ_P 16.0.

Preparation of [Pt(η^5-C_5H_5)(dppp)]OTf·CH_2Cl_2. To a CH_2Cl_2 solution (150 mL) of [Pt(OTf)$_2$(dppp)] (1.3 g, 1.4 mmol) was added TlC_5H_5 (1.4 g, 5.2 mmol). After 3 h the mixture was filtered, and addition of pentane resulted in precipitation of the product as an orange-brown powder (1.0 g, 75%). Anal. Calcd for $C_{34}H_{33}Cl_2F_3O_3P_2PtS$: C, 45.04; H, 3.67. Found: C, 45.07; H, 3.84. ^1H NMR: δ_H 2.09 (br), 2.91 (br, J_{PtH} = 54 Hz, CH_2), 5.36 (t, J_{PH} = 1.5 Hz, J_{PtH} = 11 Hz, C_5H_5), 7.35–7.60 (C_6H_5). $^{13}C\{^1H\}$ NMR: δ_C 18.8 (CH_2), 24.9 (t, J_{PC} = 23 Hz, CH_2P), 96.7 (C_5H_5), 128.9 (t, J_{PC} = 6 Hz), 131.7, 132.4 (t, J_{PC} = 5 Hz, C_6H_5). $^{31}P\{^1H\}$ NMR: δ_P −13.4 ($^1J_{PtP}$ = 4251 Hz).

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(29) Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107.

$[Pt(\eta^5\text{-}C_5H_5)(PEt_3)_2]OTf$ was prepared similarly and characterized in solution. ^1H NMR: δ_H 1.03 (m, CH_3), 1.87 (m, CH_2), 5.80 (t, J_{PH} = 1.5 Hz, J_{PtH} = 9 Hz, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ_C 8.5 (CH_3), 21.0 (t, J_{PC} = 19 Hz, CH_2), 95.3 (C_5H_5). $^{31}P\{^1H\}$ NMR: δ_P 4.5 ($^1J_{PtP}$ = 4382 Hz).

Reactions of $[PdCl_2L_2]$ with PEt_3. Approximately 10 mg of the appropriate complex was suspended in $CDCl_3$, and 1 equiv of PEt_3 was introduced by syringe. The complex dissolved immediately, giving a near-colorless solution. The $^{31}P\{^1H\}$ NMR spectrum was recorded after about 1 h. $[PdCl(PEt_3)(dppm)]Cl$ (−60 °C): δ_P −52.0 (dd, $^2J_{PP}$ = 446, 86 Hz), −31.3 (d, $^2J_{PP}$ = 86 Hz), 24.2 (d, $^2J_{PP}$ = 446 Hz) (the resonance at −52.0 ppm is very broad at ambient temperature). $[PdCl(PEt_3)(dppe)]Cl$ (20 °C): δ_P 18.8 (dd, $^2J_{PP}$ = 404, 20 Hz), 60.6 (dd, $^2J_{PP}$ = 404, 10 Hz), 64.0 (dd, $^2J_{PP}$ = 20, 10 Hz). $[PdCl(PEt_3)(dppp)]Cl$ (20 °C): δ_P −0.7 (dd, $^2J_{PP}$ = 422, 37 Hz), 11.7 (dd, $^2J_{PP}$ = 37, 10 Hz), 19.9 (dd, $^2J_{PP}$ = 422, 10 Hz).

Reaction of $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ with PEt_3. To a d_6-acetone solution of $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ was added PEt_3 and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Resonances due to isomer **A** were observed after 24 h. After the mixture stood at ambient temperature for several days, new resonances due to isomer **B** were also detected. ^1H NMR: δ_H 2.1 (br, 2H), 6.1 (br, 1H), 6.4 (br, 2H), isomer **A**; δ_H 2.3 (br, 2H), 5.8 (br, 1H), 6.0 (br, 1H), 6.2 (br, 1H), isomer **B**. $^{31}P\{^1H\}$ NMR (d_6-acetone): δ_P 12.2 (dd, $^1J_{PtP}$ = 2598 Hz, $^2J_{PP}$ = 365, 18 Hz), 46.6 (dd, $^1J_{PtP}$ = 1766 Hz, $^2J_{PP}$ = 18, 5 Hz), 47.7 (dd, $^1J_{PtP}$ = 2482 Hz, $^2J_{PP}$ = 365, 5 Hz), isomer **A**; δ_P 12.3 (dd, $^1J_{PtP}$ = 2594 Hz, $^2J_{PP}$ = 357, 19 Hz), 47.0 (dd, $^1J_{PtP}$ = 1768 Hz, $^2J_{PP}$ = 19, 5 Hz), 49.3 (dd, $^1J_{PtP}$ = 2486 Hz, $^2J_{PP}$ = 357, 5 Hz), isomer **B**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 11.1 (dd, $^1J_{PtP}$ = 2604 Hz, $^2J_{PP}$ = 367, 18 Hz), 45.7 (dd, $^1J_{PtP}$ = 1762 Hz, $^2J_{PP}$ = 18, 5 Hz), 46.5 (dd, $^1J_{PtP}$ = 2513 Hz, $^2J_{PP}$ = 367, 5 Hz), isomer **A**; δ_P = 11.3 (dd, $^1J_{PtP}$ = 2600 Hz, $^2J_{PP}$ = 359, 18 Hz), 46.0 (dd, $^1J_{PtP}$ = 1763 Hz, $^2J_{PP}$ = 18, 5 Hz), 48.2 (dd, $^1J_{PtP}$ = 2505 Hz, $^2J_{PP}$ = 359, 5 Hz), isomer **B**.

X-ray Structure Determination. A single crystal of $[Pt(\eta^5\text{-}C_5H_5)(dppe)]OTf$ was mounted on a glass fiber in 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 ($20° < 2\theta < 25°$). 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.

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. An empirical absorption correction was applied to the data using 9 ψ curves for reflections with $83° < \chi < 89°$.

Data reduction and structure solution were achieved using the SHELXTL PLUS structure solution software package.[30] The structure was solved by Patterson methods in the space group $P2_1$ and was refined successfully in this space group. 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 map had a maximum electron density of 1.63 e/Å^3, which was close to the platinum atom. Least-squares planes calculated for the phenyl and cyclopentadienyl rings showed very small deviations from planarity. Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table I. Figure 1 shows the projection view and atom-labeling scheme. Selected bond distances and bond angles are presented in Table II. All calculations were performed on a VAX Station II GPX computer using SHELXTL PLUS software.

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Supplementary Material Available: Bond lengths and bond angles (Tables S1 and S2), anisotropic displacement coefficients for non-hydrogen atoms (Table S3), and calculated hydrogen atom coordinates and isotropic displacement coefficients (Table S4) (4 pages). Ordering information is given on any current masthead page.

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[30] Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1989.