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Synthesis of Unsymmetrical dppm-Bridged Platinum and Palladium A-Frame Complexes

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Reactions of [PtClR(cod)] (R = Me, Et, Ph) or [PtBr(Mes)(cod)] (Mes = mesityl) with 2 equiv of bis(diphenylphosphino)methane (dppm), followed by treatment with NH_4PF_6 or $TlPF_6$, lead to complexes of the type [PtR(dppm-*P,P'*)(dppm-*P*)]PF_6, **1a–d**, which contain one chelated and one dangling dppm ligand. The symmetrical, dppm-bridged complexes [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]PF_6, **2a–c** (R = Me, Et, Ph), are formed by treatment of [PtClR(cod)] with 1 equiv of dppm, followed by NH_4PF_6, and the unsymmetrical diplatinum A-frame complexes [Pt_2RR'(μ-Cl)(μ-dppm)$_2$]PF_6, **2d–i**, are formed by reactions of **1a–d** with [PtClR'(cod)] (R' = Me, Et, Ph). The reaction of [PtMe(dppm-*P,P'*)(dppm-*P*)]Cl with [PtBrMe(cod)] produces [Pt_2Me_2(μ-Br)(μ-dppm)$_2$]Cl, which illustrates that it is the halide bound to platinum in the cyclooctadiene compound which ultimately occupies the bridging position in the A-frame product. The dipalladium complex [Pd_2Me_2(μ-Cl)(μ-dppm)$_2$]PF_6, **2j**, is prepared from [PdClMe(cod)], dppm, and NH_4PF_6, and the mixed metal complexes [PtPdRMe(μ-Cl)(μ-dppm)$_2$]PF_6, **2k–m** (R = Me, Et, Ph), are obtained by addition of **1a–c** to [PdClMe(cod)].

Introduction

The chemistry of metal complexes containing bridging bis(diphenylphosphino)methane (dppm) or related ligands has developed tremendously over the last 20 years, and a number of reviews of this area have been written.[1-6] In particular, dppm-bridged, A-frame complexes of platinum or palladium, which contain a bridging group such as a halide, hydride, CH_2, CO, S, SO_2, or another metal, have received considerable attention.

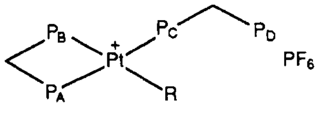
The chloride-bridged A-frame complex [Pt_2Me_2(μ-Cl)(μ-dppm)$_2$]Cl has been prepared by addition of HCl to [$PtMe_2$(dppm)] in benzene.[7] The reaction of [PtClR(cod)] (R = Me, Ph) with 1 equiv of dppm results in a mixture of [PtClR(dppm)] and [Pt_2R_2(μ-Cl)(μ-dppm)$_2$]Cl, whereas when R = COPh, the corresponding A-frame complex is obtained as the sole product.[8] Addition of bromo- or iodomethane to [Pd_2(μ-dppm)$_3$] produces the face-to-face dimers [$Pd_2X_2Me_2$(μ-dppm)$_2$] (X = Br, I), but further treatment with NH_4PF_6 is required to generate the halide-bridged A-frame species.[9] To our knowledge, chloride-bridged, A-frame palladium complexes have not been reported.

The above methods are limited to symmetrical complexes, that is, those containing similar metals and identical organic groups on the two metals. Here we report the synthesis of cationic platinum complexes of the type [PtR(dppm-*P,P'*)(dppm-*P*)]$^+$ (R = Me, Et, Ph, mesityl) and their use in the synthesis of unsymmetrical diplatinum or platinum–palladium A-frames.

Results and Discussion

In contrast to the reactions of [PtClR(cod)] (R = Me, Ph) with dppm, addition of dppm to a solution of [PtBr(Mes)(cod)][10] produces only the chelate complex, [PtBr(Mes)(dppm)] (δ(P) −44.5 (d), ^1J(Pt,P) 1245 Hz, ^2J(P,P) 44 Hz; δ(P) −49.8 (d), ^1J(Pt,P) 3899 Hz). Its ^{31}P NMR parameters are very similar to those reported for the analogous chloride complex.[11] Addition of a second equivalent of dppm produces a new species, which exhibits only broad ^{31}P resonances at ambient temperature. On cooling to −60 °C, however, the signals become sharp and the spectrum may be analyzed in terms of four nonequivalent, closely coupled ^{31}P nuclei, each of which exhibits coupling to ^{195}Pt. Three of the signals are at relatively low frequency and the fourth is deshielded by about 40 ppm. The product is identified as [Pt(Mes)(dppm-*P,P'*)(dppm-*P*)]Br, which contains one chelated and one dangling dppm ligand.

Analogous reactions of [PtClR(cod)] (R = Me, Et, Ph) with 2 equiv of dppm produce [PtR(dppm-*P,P'*)(dppm-*P*)]Cl, each of which also exhibits very broad NMR resonances at ambient temperature. Metathesis reactions of all four complexes with $TlPF_6$ produce the hexafluorophosphate salts, [PtR(dppm-*P,P'*)(dppm-*P*)]PF_6 (**1a**, R = Me; **1b**, R = Et; **1c**, R = Ph; **1d**, R = Mes) (Table I).



1a, R = Me; **1b**, R = Et; **1c**, R = Ph; **1d**, R = Mes

These also show broad features in their NMR spectra at

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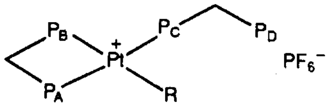
Table I. $^{31}P\{^1H\}$ **NMR Data for Complexes of the Type** $[PtR(dppm\text{-}P,P')(dppm\text{-}P)]PF_6$**, 1a–d**[a]



	1a (R = Me)	1b (R = Et)	1c (R = Ph)	1d[b] (R = Mes)
$\delta(P_A)$	−31.5 (ddd)	−27.4 (ddd)	−34.9 (ddd)	−35.7 (ddd)
$\delta(P_B)$	−32.0 (dd)	−25.9 (dd)	−35.9 (dd)	−33.2 (dd)
$\delta(P_C)$	15.7 (ddd)	19.8 (ddd)	11.9 (ddd)	8.9 (ddd)
$\delta(P_D)$	−28.5 (dd)	−29.1 (dd)	−28.7 (dd)	−30.2 (dd)
$^1J(Pt,P_A)$	2412	2619	2404	2402
$^1J(Pt,P_B)$	1409	1199	1356	1298
$^1J(Pt,P_C)$	2777	2941	2761	2819
$^3J(Pt,P_D)$	106	nr	130	121
$^2J(P_A,P_B)$	41	33	38	34
$^2J(P_A,P_C)$	395	391	391	385
$^2J(P_B,P_C)$	22	22	22	16
$^2J(P_C,P_D)$	97	91	67	44
$^4J(P_A,P_D)$	nr	nr	nr	7

[a] Recorded at −90 °C in CD_2Cl_2 solution. Chemical shifts are in parts per million and are reported relative to external H_3PO_4, positive shifts representing deshielding. Coupling constants are in Hertz. (nr = not resolved). [b] Recorded at −60 °C in $CDCl_3$ solution.

Table II. $^{31}P\{^1H\}$ **NMR Data for Complexes of the Type** $[MM'RR'(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$**, 2a–m**[a]

	$\delta(P)$	$^1J(Pt,P)$	$^3J(Pt,P)$	$^2J(P,P)$	$^4J(P,P)$
2a	14.0	3023	36	32	<2
2b	14.6	3244	45	30	<2
2c	9.1	3027	31		
2d	14.0	3024	nr		
	14.4	3262	nr		
2e	8.3	3049	36	24	8
	13.9	3019	nr		
2f	8.7	3041	42	30	<2
	14.9	3248	40		
2g	6.2	3096	64	18	6
	14.1	3051	54		
2h	7.0	3114			
	15.8	3307			
2i	8.8	3111	55		
	10.7	3097	51		
2j	17.6				
2k	15.1		30	28	10
	16.9	2992			
2l	14.9		39	32	6
	17.1	3215			
2m	11.2	3004		30	7
	15.0		nr		

[a] Recorded at 25 °C in $CDCl_3$ solution. Chemical shifts are in parts per million and are reported relative to external H_3PO_4, positive shifts representing deshielding. Coupling constants are in Hertz.

25 °C. Thus, the broadness is due presumably to exchange of the dppm ligands in the cation, either intra- or intermolecularly, and does not depend on attack by the counterion. ^{31}P NMR data for each of these compounds are presented in Table I. In each case the ^{31}P NMR spectrum is first order and may be analyzed readily. The resonance due to P_A is recognized by its negative chemical shift and its large coupling to P_C, indicating a trans disposition of these two nuclei, and P_C exhibits the high frequency resonance expected of a nonchelated dppm ligand. The relatively small value of $^1J(Pt,P_B)$ (1200–1400 Hz) allows identification of the signal due to P_B, since P_B lies trans to the high trans-influence group R. The value of $\delta(P_D)$ is close to that found for free dppm, as expected for an uncoordinated phosphorus atom, and the very small coupling to platinum is consistent with a three-bond coupling. All the P–P couplings are observed, with the exception of $^4J(P_B,P_D)$ which is too small to be resolved.

Platinum complexes containing dangling dppm ligands have been used in a number of instances to prepare dimetallic species.[12] Reaction of $[PtMe_2(dppm\text{-}P)_2]$ with $[PtClMe(cod)]$, for example, yields $[Pt_2Me_3(\mu\text{-}dppm)_2]Cl$.[13] It seemed likely that addition of a source of a coordinatively unsaturated platinum fragment, such as $[PtClR(cod)]$, to the $[PtR(dppm\text{-}P,P')(dppm\text{-}P)]^+$ cation would also lead to dimeric species. Indeed, reaction of $[Pt(Mes)(dppm\text{-}P,P')(dppm\text{-}P)]Br$ with $[PtBr(Mes)(cod)]$ produces the dimesityl A-frame complex $[Pt_2(Mes)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]Br$ ($\delta(P)$ 9.0, $^1J(Pt,P)$ 3096 Hz, $^3J(Pt,P)$ 54 Hz), which was unavailable from the direct reaction of $[PtBr(Mes)(cod)]$ with dppm (*vide supra*).

The discovery of this stepwise method for the preparation of A-frame complexes suggested that it should be possible to produce such compounds with different organic groups on each metal center by the reaction shown in eq 1. For comparison, and to help in the assignment of NMR

$$[PtR(dppm\text{-}P,P')(dppm\text{-}P)]^+ + [PtClR'(cod)] \rightarrow [Pt_2RR'(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+ + cod \quad (1)$$

resonances, the symmetrical complexes $[Pt_2R_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$ (**2a**, R = Me; **2b**, R = Et; **2c**, R = Ph) were prepared from $[PtClR(cod)]$ and 1 equiv of dppm, followed by addition of NH_4PF_6. Each exhibits a singlet in its ^{31}P NMR spectrum, with complex sets of satellites due to short- and long-range coupling to ^{195}Pt (Table II). The appearance and analysis of these spectra have been discussed previously.[7,8]

Addition of $[PtBrMe(cod)]$ to a solution of $[Pt(Mes)(dppm\text{-}P,P')(dppm\text{-}P)]Br$ results in formation of the unsymmetrical A-frame complex $[Pt_2Me(Mes)(\mu\text{-}Br)(\mu\text{-}dppm)_2]Br$ ($\delta(P)$ 5.2, $^1J(Pt,P)$ 3083 Hz, $^3J(Pt,P)$ 67 Hz; $\delta(P)$ 12.5, $^1J(Pt,P)$ 3020 Hz, $^3J(Pt,P)$ 41 Hz), whereas with $[PtClMe(cod)]$ a mixture of two products is obtained. We assign these as $[Pt_2Me(Mes)(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Br$ ($\delta(P)$ 6.2, $^1J(Pt,P)$ 3108 Hz, $^3J(Pt,P)$ 64 Hz; $\delta(P)$ 14.1, $^1J(Pt,P)$ 3051 Hz, $^3J(Pt,P)$ 54 Hz) and $[Pt_2Me(Mes)(\mu\text{-}Br)(\mu\text{-}dppm)_2]Cl$, the latter having NMR parameters identical to those of $[Pt_2Me(Mes)(\mu\text{-}Br)(\mu\text{-}dppm)_2]Br$. On standing, the signals associated with the latter complex increase in intensity at the expense of those due to the chloride-bridged species. This suggests that $[Pt_2Me(Mes)(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Br$ is the initial product of the reaction but, over time, replacement of the bridging chloride by the softer bromide takes place. In fact, the reaction of $[PtBrMe(cod)]$ with $[PtMe(dppm\text{-}P,P')(dppm\text{-}P)]Cl$ yields a single product, which is identified as $[Pt_2Me_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]Cl$ ($\delta(P)$ 13.1, $^1J(Pt,P)$ 3022 Hz). The chloride-bridged cation is not observed. The absence of any chloride-bridged species in this case indicates that it is the halide which is coordinated to platinum in the cyclooctadiene complex that is incorporated into the bridging position and that dissociation of this halide does not occur during the reaction. Thus we postulate the mechanism shown in Scheme I to account for the product(s) of the reaction.

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[12] See, for examples: Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1015. Hutton, A. T.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2121.

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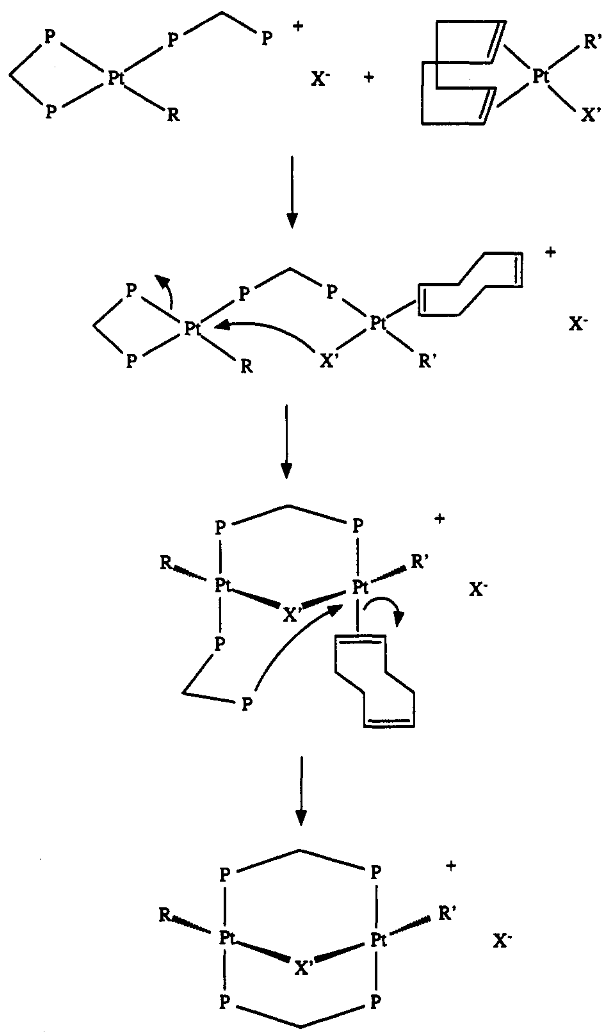
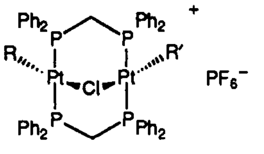
Scheme I



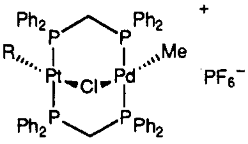
In order to avoid further complications due to the presence of two different halides we used the hexafluorophosphate salts of the [PtR(dppm-*P,P′*)(dppm-*P*)]$^+$ cations to prepare the series of unsymmetrical platinum A-frames, **2d–i**. [PtR(dppm-*P,P′*)(dppm-*P*)]PF$_6$ (R = Me, Et or Ph) and [PtClR′(cod)] were allowed to react in CH$_2$Cl$_2$ solution. Additional NH$_4$PF$_6$ was added, and after the solution was passed down a short alumina column, **2d–f** were obtained as pale yellow solids in good yield. With [Pt(Mes)(dppm-*P,P′*)(dppm-*P*)]PF$_6$ the unsymmetrical complexes **2g–i** were isolated as white solids without chromatographic purification. It may be noted that either of the starting materials may act as the source of a particular organic group in these diplatinum species. Thus, for example, **2f** may be prepared from [PtMe(dppm-*P,P′*)(dppm-*P*)]PF$_6$ and [PtClPh(cod)] or from [PtPh(dppm-*P,P′*)(dppm-*P*)]PF$_6$ and [PtClMe(cod)]. ^{31}P NMR data for complexes **2d–i** are given in Table II.



2d, R = Me, R′ = Et; **2e**, R = Me, R′ = Ph; **2f**, R = Et, R′ = Ph;
2g, R = Me, R′ = Mes; **2h**, R = Et, R′ = Mes; **2i**, R = Ph, R′ = Mes

The nonequivalence of the two pairs of phosphorus atoms in each of the complexes **2d–i** results in an AA′BB′ spin system, with additional couplings to ^{195}Pt for those isotopomers containing one or two ^{195}Pt nuclei. The two central resonances appear as five-line multiplets for **2e** and **2g** (Figure 1a), the separation of the outer lines giving N ($J(P_A,P_B) + J(P_A,P_{B'})$) and that of the inner pair of lines giving L ($J(P_A,P_B) - J(P_A,P_{B'})$).[14] For **2f**, **2h**, and **2i** only three lines are resolved, indicating that $J(P_A,P_{B'})$ is close to zero. In the case of **2d** the two ^{31}P chemical shifts are so similar that only one complex multiplet is observed. In general, the resonances due to the phosphorus atoms attached to a phenyl- or mesitylplatinum moiety appear to low frequency of those attached to an alkylplatinum fragment, and the value of ^1J(Pt,P) is about 200 Hz greater when an ethylplatinum moiety is involved.

It is also possible to prepare mixed-metal complexes by the above methodology. This is illustrated by the reactions of [PtR(dppm-*P,P′*)(dppm-*P*)]PF$_6$ (R = Me, Et, Ph) with [PdClMe(cod)] to produce the platinum–palladium A-frames, **2k–m**. The ^{31}P NMR parameters for **2k–m** are presented in Table II. In each case the ^{31}P{^{1}H} NMR spectrum consists of two five-line multiplets, one of which exhibits a short-range coupling to ^{195}Pt of *ca.* 3000 Hz, whereas the other displays a three-bond coupling to platinum of *ca.* 30 Hz (Figure 1a).



2k, R = Me; **2l**, R = Et; **2m**, R = Ph

For comparison, we carried out the reaction of [PdClMe(cod)] with 1 equiv of dppm. This generates the symmetrical A-frame complex [Pd$_2$Me$_2$(μ-Cl)(μ-dppm)$_2$]Cl, which exhibits a single ^{31}P NMR resonance at 17.6 ppm. Treatment with NH$_4$PF$_6$ yields [Pd$_2$Me$_2$(μ-Cl)(μ-dppm)$_2$]PF$_6$, **2j**, for which the chemical shift is identical, indicating that the chloride complex does exist in solution in the ionic form. The complex [Pd$_2$Me$_2$Cl$_2$(μ-dppm)$_2$] has been characterized previously in the solid state by X-ray diffraction and has been shown to adopt a face-to-face structure.[15] The ^{31}P chemical shift reported for this complex in solution, however, is identical to that observed here, indicating that it, in fact, adopts the ionic, A-frame structure in solution. Reaction of [PdClMe(cod)] with 2 equiv of dppm does not lead to a palladium complex of type **1**. Thus, it is only possible to prepare the mixed-metal complexes by one route, namely, by reaction of the [PtR(dppm-*P,P′*)(dppm-*P*)]$^+$ cation with [PdClMe(cod)]. The lack of suitable organopalladium precursors also limits the number of platinum–palladium species that may be produced.

Experimental Section

All reactions were carried out under an atmosphere of argon. The complexes [PtClR(cod)] (R = Me, Et, Ph),[16] [PtBrMes(cod)],[10] and [PdClMe(cod)][17] were prepared as described

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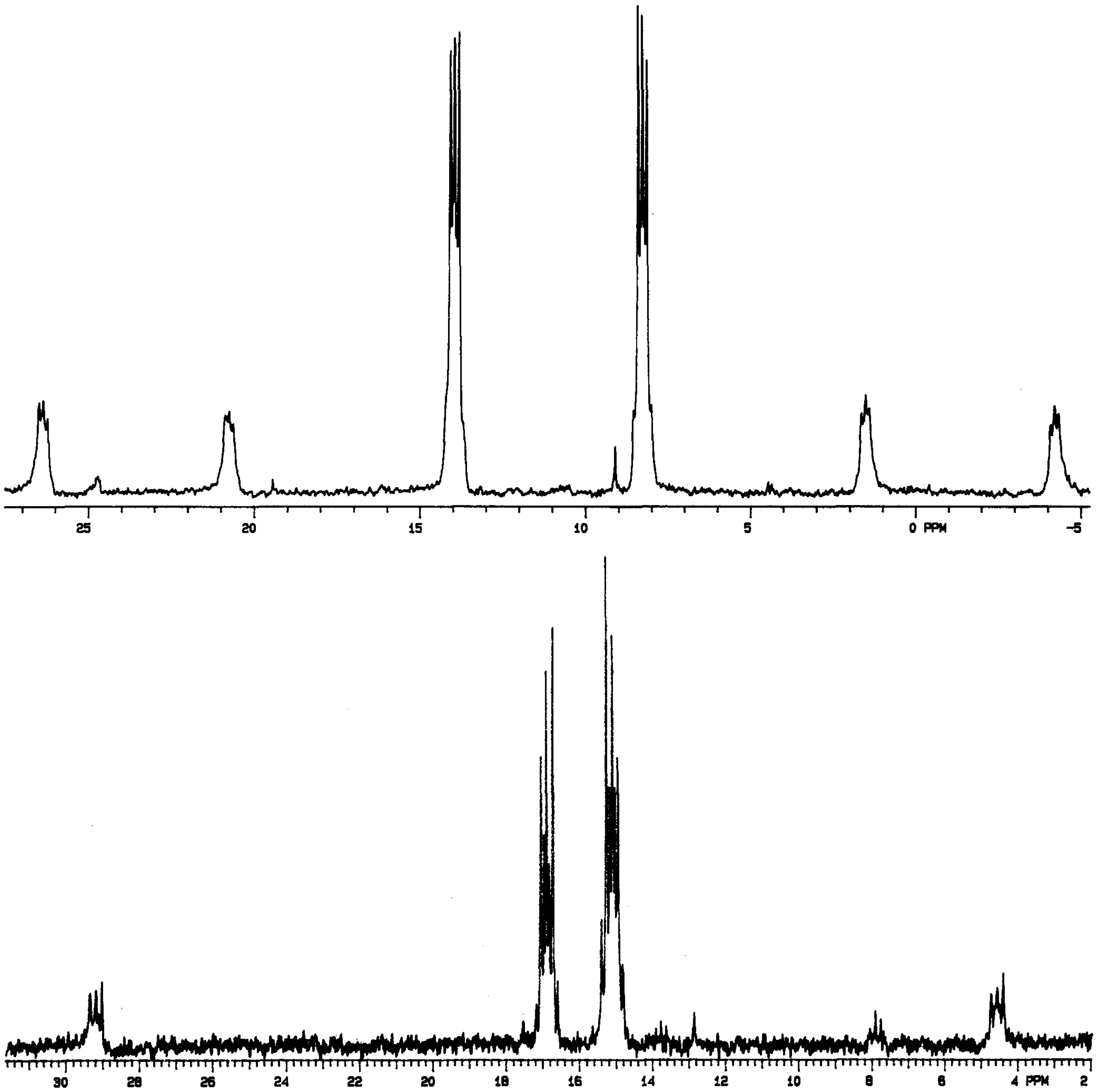

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (a, top) $[Pt_2MePh(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$, **2e**, and (b, bottom) $[PdPtMe_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$, **2k**, in $CDCl_3$ solution.

previously. NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H 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 [PtMe(dppm-*P,P'*)(dppm-*P*)]PF$_6$, 1a. [PtClMe(cod)] (0.10 g, 0.29 mmol) and dppm (0.22 g, 0.58 mmol) were placed in a 100-mL flask and transferred to the drybox. Dry CH_2Cl_2 (40 mL) was introduced, and the mixture was stirred for 10 min before NH_4PF_6 (0.050 g, 0.31 mmol) was added. The mixture was stirred for 12 h and then filtered. The filtrate was evaporated to dryness, leaving the product as a white solid (0.25 g, 79%). Anal. Calcd for $C_{51}H_{47}F_6P_5Pt$: C, 54.50; H, 4.22. Found: C, 54.64; H, 4.31.

Preparation of [PtEt(dppm-*P,P'*)(dppm-*P*)]PF$_6$, 1b. This complex was prepared as above from [PtClEt(cod)] (0.14 g, 0.39 mmol), dppm (0.30 g, 0.77 mmol), and NH_4PF_6 (0.071 g, 0.44 mmol) and obtained as a white solid (0.37 g, 85%). Anal. Calcd for $C_{52}H_{49}F_6P_5Pt$: C, 54.89; H, 4.34. Found: C, 54.66; H, 4.43.

Preparation of [PtPh(dppm-*P,P'*)(dppm-*P*)]PF$_6$, 1c. This complex was prepared analogously from [PtClPh(cod)] (0.17 g, 0.41 mmol), dppm (0.31 g, 0.81 mmol), and NH_4PF_6 (0.071 g, 0.43 mmol) and isolated as a white solid (0.33 g, 69%). Anal. Calcd for $C_{56}H_{49}F_6P_5Pt$: C, 56.71; H, 4.16. Found: C, 56.43; H, 4.17.

Preparation of [PtMes(dppm-*P,P'*)(dppm-*P*)]PF$_6$, 1d. This compound was prepared from [PtBr(Mes)(cod)] (0.22 g, 0.43 mmol), dppm (0.33 g, 0.86 mmol), and $TlPF_6$ (0.17 g, 0.50 mmol) and obtained as a white solid (0.50 g, 95%). Anal. Calcd for $C_{59}H_{55}F_6P_5Pt$: C, 57.70; H, 4.51. Found: C, 57.45; H, 4.66.

Preparation of [Pt$_2$Me$_3$(μ-Cl)(μ-dppm)$_2$]PF$_6$, 2a.[7] To a CH_2Cl_2 solution (15 mL) of [PtClMe(cod)] (0.18 g, 0.50 mmol) and dppm (0.19 g, 0.50 mmol) was added NH_4PF_6 (0.16 g, 1.0 mmol), and the mixture was stirred for 3 h. The solvent was removed, and the residue was washed repeatedly with pentane to remove cyclooctadiene and then redissolved in CH_2Cl_2. The solution was passed through a short alumina column and then evaporated to dryness. The residue was washed with pentane and dried *in vacuo*, leaving the product as a pale yellow solid (0.31 g, 91%).

Anal. Calcd for $C_{52}H_{50}ClF_6P_5Pt_2$: C, 45.61; H, 3.68. Found: C, 46.35; H, 3.80.

Preparation of [Pt_2Et_2(μ-Cl)(μ-dppm)$_2$]PF_6, 2b. This was prepared as above from [PtClEt(cod)] (0.18 g, 0.50 mmol), dppm (0.19 g, 0.50 mmol), and NH_4PF_6 (0.16 g, 1.0 mmol) and obtained as a yellow powder (0.20 g, 57%). Anal. Calcd for $C_{54}H_{54}ClF_6P_5Pt_2$: C, 46.41; H, 3.90. Found: C, 46.96; H, 4.06.

Preparation of [Pt_2Ph_2(μ-Cl)(μ-dppm)$_2$]PF_6, 2c.[8] This was prepared as above from [PtClPh(cod)] (0.21 g, 0.50 mmol), dppm (0.19 g, 0.50 mmol), and NH_4PF_6 (0.25 g, 1.5 mmol), after stirring overnight, and isolated as a white powder (0.37 g, 99%). Anal. Calcd for $C_{62}H_{54}ClF_6P_5Pt_2$: C, 49.86; H, 3.64. Found: C, 50.34; H, 3.73.

Preparation of [Pt_2MeEt(μ-Cl)(μ-dppm)$_2$]PF_6, 2d. A CH_2Cl_2 solution (15 mL) of [PtClEt(cod)] (0.074 g, 0.20 mmol) was added dropwise to [PtMe(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.23 g, 0.20 mmol) in CH_2Cl_2 (2 mL). NH_4PF_6 (0.098 g, 0.60 mmol) was then added, and the mixture was stirred for 4 h. The solvent was evaporated, and the residue was washed with pentane, redissolved in CH_2Cl_2, and passed through a short alumina column. The resulting solution was evaporated, and the residue was washed with pentane, leaving the product as a pale yellow powder (0.20 g, 77%). Anal. Calcd for $C_{53}H_{52}ClF_6P_5Pt_2$: C, 46.01; H, 3.79. Found: C, 46.24; H, 3.92.

Preparation of [Pt_2MePh(μ-Cl)(μ-dppm)$_2$]PF_6, 2e. This complex was prepared as above from [PtMe(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.23 g, 0.20 mmol), [PtClPh(cod)] (0.083 g, 0.20 mmol), and NH_4PF_6 (0.094 g, 0.58 mmol) and obtained as a light yellow powder (0.17 g, 59%). Anal. Calcd for $C_{57}H_{52}ClF_6P_5Pt_2$: C, 47.82; H, 3.66. Found: C, 48.39; H, 3.95.

Preparation of [Pt_2EtPh(μ-Cl)(μ-dppm)$_2$]PF_6, 2f. This species was generated as above from [PtEt(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.23 g, 0.20 mmol), [PtClPh(cod)] (0.083 g, 0.20 mmol), and NH_4PF_6 (0.098 g, 0.60 mmol) and isolated as a pale yellow solid (0.20 g, 69%). Anal. Calcd for $C_{58}H_{54}ClF_6P_5Pt_2$: C, 48.19; H, 3.77. Found: C, 48.44; H, 4.06.

Preparation of [Pt_2MeMes(μ-Cl)(μ-dppm)$_2$]PF_6, 2g. To a flask containing [Pt(Mes)(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.076 g, 0.062 mmol) and [PtClMe(cod)] (0.022 g, 0.063 mmol) was added dry CH_2Cl_2 (25 mL) by syringe. After stirring for 1 h, the solution was reduced in volume and pentane was added to precipitate the product as a white solid (0.081 g, 89%). Anal. Calcd for $C_{60}H_{58}ClF_6P_5Pt_2$: C, 48.90; H, 3.97. Found: C, 48.91; H, 3.99.

Preparation of [Pt_2EtMes(μ-Cl)(μ-dppm)$_2$]PF_6, 2h. This complex was prepared similarly from [Pt(Mes)(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.082 g, 0.067 mmol) and [PtClEt(cod)] (0.025 g, 0.067 mmol) and obtained as a white solid (0.079 g, 79%). Anal. Calcd for $C_{61}H_{60}ClF_6P_5Pt_2$: C, 49.25; H, 4.07. Found: C, 49.29; H, 4.12.

Preparation of [Pt_2PhMes(μ-Cl)(μ-dppm)$_2$]PF_6, 2i. This complex was generated as above from [Pt(Mes)(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.060 g, 0.049 mmol) and [PtClPh(cod)] (0.021 g, 0.051 mmol) and isolated as a white solid (0.055 g, 72%). Anal. Calcd for $C_{65}H_{60}ClF_6P_5Pt_2$: C, 50.84; H, 3.94. Found: C, 50.26; H, 4.01.

Preparation of [Pd_2Me_2(μ-Cl)(μ-dppm)$_2$]PF_6, 2j. This complex was prepared in a manner similar to its platinum analogue from [PdClMe(cod)] (0.13 g, 0.50 mmol), dppm (0.19 g, 0.49 mmol), and NH_4PF_6 (0.16 g, 1.0 mmol) and obtained as a white powder (0.28 g, 87%). Anal. Calcd for $C_{52}H_{50}ClF_6P_5Pd_2$: C, 52.39; H, 4.23. Found: C, 51.89; H, 4.25.

Preparation of [$PdPtMe_2$(μ-Cl)(μ-dppm)$_2$]PF_6, 2k. A CH_2Cl_2 solution (15 mL) of [PdClMe(cod)] (0.053 g, 0.20 mmol) was added dropwise to [PtMe(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.23 g, 0.20 mmol) in CH_2Cl_2 (2 mL), followed by NH_4PF_6 (0.098 g, 0.60 mmol). The mixture was then stirred for 4 h. After solvent removal, the residue was washed with pentane and then redissolved in CH_2Cl_2. The CH_2Cl_2 solution was passed down a short alumina column and then evaporated to dryness. The resulting solid was washed again with pentane and dried *in vacuo*, leaving the product as a pale pink solid (0.20 g, 86%). Anal. Calcd for $C_{52}H_{50}ClF_6P_5$PdPt: C, 48.76; H, 3.94. Found: C, 48.85; H, 3.95.

Preparation of [PdPtMeEt(μ-Cl)(μ-dppm)$_2$]PF_6, 2l. This complex was prepared as above from [PtEt(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.23 g, 0.20 mmol), [PdClMe(cod)] (0.053 g, 0.20 mmol), and NH_4PF_6 (0.098 g, 0.60 mmol) and isolated as a pale yellow powder (0.21 g, 81%). Anal. Calcd for $C_{53}H_{52}ClF_6P_5$PdPt: C, 49.16; H, 4.05. Found: C, 49.52; H, 4.17.

Preparation of [PdPtMePh(μ-Cl)(μ-dppm)$_2$]PF_6, 2m. This compound was prepared as above from [PtPh(dppm-*P,P'*)(dppm-*P*)]PF_6 (0.24 g, 0.20 mmol), [PdClMe(cod)] (0.053 g, 0.20 mmol), and NH_4PF_6 (0.098 g, 0.60 mmol) and obtained as a light yellow solid (0.20 g, 75%). Anal. Calcd for $C_{57}H_{52}ClF_6P_5$PdPt: C, 50.98; H, 3.90. Found: C, 51.28; H, 4.14.

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