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Unsymmetrical Hydride-Bridged A-Frame Complexes of Platinum and Palladium

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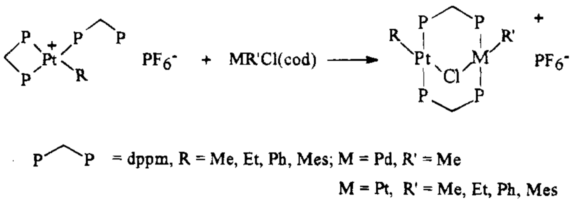
The symmetrical hydride-bridged complexes $[Pt_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ (R = Me, Et, Ph) and $[Pd_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ (R = Me, Ph) have been prepared by $NaBH_4$ reduction of the corresponding chloride-bridged complexes in CH_2Cl_2 solution. The unsymmetrical analogues $[RPt(\mu\text{-}H)(\mu\text{-}dppm)_2MR']PF_6$ (R = Me, Et, Ph; MR′ = PtMe, PtEt, PtPh, PdMe, PdPh) have been generated by consecutive addition to [PtR(dppm-*P*,*P*)(dppm-*P*)]Cl of [PtClR(cod)] or $[Pd_2(\mu\text{-}Cl)_2R_2(AsPh_3)_2]$, $NaBH_4$, and NH_4PF_6. The products have been characterized by microanalysis and by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

There is an extensive chemistry of diplatinum and dipalladium systems bridged by bis(diphenylphosphino)methane (dppm) ligands.[1-3] In particular, A-frame complexes containing a bridging halide or hydride, or one of a range of small molecules, have been studied in some detail. A number of examples of hydride-bridged, A-frame complexes of platinum have been prepared by Puddephatt and co-workers, including $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$, formed by sodium borohydride reduction of $[PtCl_2(dppm)]$,[4] $[Pt_2HMe(\mu\text{-}H)(\mu\text{-}dppm)_2]SbF_6$ and $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$.[5,6] The last was prepared by $NaBH_4$ reduction of either $[Pt_2Me_3(\mu\text{-}dppm)_2]PF_6$ or $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. It has been characterized by an X-ray diffraction study, which revealed a Pt—Pt distance of 2.932(1) Å.[6] The analogous ethyl complex $[Pt_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2]SbF_6$ was obtained by β-elimination of ethene from $[Pt_2Et_3(\mu\text{-}dppm)_2]SbF_6$.[7] These hydride-bridged platinum cations $[Pt_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (R = Me, Et) exhibit considerable thermal stability. The corresponding hydride-bridged palladium system $[Pd_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]BPh_4$ was prepared by treatment of $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ with excess Me_3Al at −78 °C, followed by $NaBPh_4$ and ethanol, but was reported to be stable in solution only below ambient temperature.[8]

We have reported previously a method for the synthesis of unsymmetrical, diplatinum or platinum–palladium chloride-bridged A-frame complexes $[RPt(\mu\text{-}Cl)(\mu\text{-}dppm)_2MR']PF_6$ (R = Me, Et, Ph; MR′ = PtMe, PtEt, PtPh, PdMe) based on the $[PtR(dppm\text{-}PP)(dppm\text{-}P)]PF_6$ precursor (eq 1).[9] In this paper we report the conversion of these, and the symmetrical diplatinum and dipalladium complexes, to thermally stable hydride-bridged species.



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Results and Discussion

We have prepared the symmetrical, hydride-bridged diplatinum complexes $[Pt_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ (R = Me, Et, Ph) by reaction of the corresponding chlorides, generated *in situ* from [PtClR(cod)] and 1 equiv of dppm, with sodium borohydride and NH_4PF_6. As noted previously for the methyl complex,[6] the isolated yield is affected dramatically by the reaction conditions employed. In particular, a long reaction time with excess $NaBH_4$ leads to replacement of one or both of the terminal R groups to produce $[Pt_2RH(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ or $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$. We have found that the reaction may be carried out conveniently in CH_2Cl_2 solution, in which $[Pt_2R_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ is quite soluble but $NaBH_4$ is not. Slow addition of a small amount of methanol allows dissolution of the borohydride, but substantial concentrations are avoided, thus preventing significant amounts of the di- or trihydride from forming. A reaction time of 1 h at 0 °C, using a 4-fold excess of $NaBH_4$, followed by addition of NH_4PF_6, leads to good yields of $[Pt_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$. This is a relatively straightforward method, which avoids the large excess of $NaBH_4$ used previously,[6] and it is quite general (*vide infra*).

We have also used the above method to prepare the dipalladium complexes $[Pd_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ (R = Me, Ph) in excellent yields. In each case, the chloride-bridged dimer was prepared from $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPh_3)_2]$[10] or $[Pd_2Ph_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (see Experimental Section) and 2 mol equiv of dppm, the arsine serving

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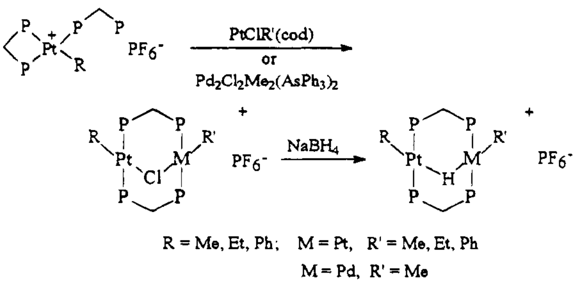
Table 1. ^{1}H NMR Data for the Hydride-Bridged Complexes in Acetone-d_6 Solution[a]

	hydride			dppm				other resonances			
complex	δ(H)	$^2J_{PH}$	$^1J_{PtH}$	δ(CH$_2$)	J_{PH}	$^3J_{PtH}$	Ph	δ(H)	J_{PH}	J_{PtH}	assgnt
MePtH(dppm)$_2$PtMe$^+$	−7.33 q	9	512	5.06 br		32	7.3−7.8	0.16 br		68	Me
EtPtH(dppm)$_2$PtEt$^+$	−7.73 q	9	486	4.96 q	4	39	7.3−7.8	−0.10 t[b]		60	CH$_3$
								0.84 m		70	CH$_2$
PhPtH(dppm)$_2$PtPh$^+$	−9.29 q	9	486	5.04 q	4	38	6.9−7.9	5.9−6.8			Ph
MePdH(dppm)$_2$PdMe$^+$	−7.54 q	15		4.58 br			7.3−7.7	0.07 s			Me
PhPdH(dppm)$_2$PdPh$^+$	−9.11 q	15		4.61 br			7.1−7.5	6.35 m			Ph
								6.55 m			
EtPtH(dppm)$_2$PtMe$^+$	−7.53 q	9	498	5.01 m			7.3−7.8	−0.10 t[c]		69	CH$_3$
								0.09 t	7	67	PtMe
								0.9 m			CH$_2$
PhPtH(dppm)$_2$PtMe$^+$	−8.33 q	9	509	5.05 q	4	38	7.2−7.9	0.20 t	7	69	Me
								6.1−6.6			Ph
PhPtH(dppm)$_2$PtEt$^+$	−8.59 q	9	495	5.00 q	4	35	7.2−7.9	0.05 t[b]		60	CH$_3$
								0.96 q[b]		73	CH$_2$
								6.1−6.6			Ph
MePtH(dppm)$_2$PdMe$^+$	−7.25 q	12	564	4.84 m		42	7.3−7.8	0.09 t	6	65	PtMe
								0.17 t	6		PdMe
EtPtH(dppm)$_2$PdMe$^+$	−7.52 q	12	539	4.80 br		43	7.3−7.9	−0.05 t[b]		56	CH$_3$
								0.84 m			CH$_2$
								0.09 t	6		PdMe
PhPtH(dppm)$_2$PdMe$^+$	−8.38 q	12	536	4.84 q	4	42	7.1−7.8	0.23 t	6		Me
								6.1−6.6			Ph
MePtH(dppm)$_2$PdPh$^+$	−7.94 q	12	557	4.84 br		40	7.2−7.8	0.13 t	6	66	Me
								6.2−6.5			Ph
EtPtH(dppm)$_2$PdPh$^+$	−8.29 q	12	531	4.80 br		44	7.2−7.8	0.11 t[b]		57	CH$_3$
								0.86 q[b]		70	CH$_2$
								6.2−6.4			Ph
PhPtH(dppm)$_2$PdPh$^+$	−9.05 q	11	535	4.70 br		43	7.1−7.8	6.2−6.7			Ph

[a] Chemical shifts are relative to the solvent resonance at 2.04 ppm. Coupling constants are in hertz. q = quintet; t = triplet. [b] $^3J_{HH}$ = 7 Hz. [c] $^3J_{HH}$ = 6 Hz.

as a convenient leaving group. Reduction of [Pd_2R_2(μ-Cl(μ-dppm)$_2$]Cl with sodium borohydride, followed by addition of NH_4PF_6, generated the hydride-bridged species. This method represents a much simpler approach to the synthesis of [Pd_2Me_2(μ-H)(μ-dppm)$_2$]PF_6 than that employed by Stille and co-workers.[8] In contrast to their finding with the tetraphenylborate salt, we find this complex, as well as its phenyl analogue, to be quite stable in CH_2Cl_2 or acetone solution at ambient temperature.

We have extended this approach to the preparation of unsymmetrical diplatinum or platinum−palladium species. In each case the chloride-bridged intermediate [RPt(μ-Cl)(μ-dppm)$_2$MR′]Cl was generated *in situ* from [PtR(dppm-*P*,*P*)(dppm-*P*)]PF_6 (R = Me, Et, Ph) and [PtClR(cod)] (R = Me, Et, Ph) or [Pd_2R_2(μ-Cl)$_2$($AsPh_3$)$_2$] (R = Me, Ph). Further treatment with $NaBH_4$ (4 equiv), followed by NH_4PF_6, gave the hydride-bridged products in good to excellent yields as air-stable, white or yellow solids (eq 2).



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The complexes [RPt(μ-H)(μ-dppm)$_2$MR′]PF_6 have been characterized by elemental analysis and by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. In each case, the ^{1}H NMR spectrum exhibits a resonance due to the bridging hydride between −7.25 and −9.29 ppm (Table 1). The signal appears as a quintet due to coupling to the four P atoms (although there are two pairs of nonequivalent P atoms in the unsymmetrical complexes, the $^2J_{PH}$ couplings are identical). Where R and R′ are methyl or ethyl, the resonance is observed between −7.25 and −7.73 ppm; when one phenyl substituent is involved, the signal is shifted to lower frequency (−8.33 to −8.59 ppm), and in the diphenyl derivatives the resonance appears at still lower frequency (−9.03 to −9.29 ppm). Thus, the effect of replacing each alkyl group by a phenyl group appears to be approximately additive. The hydrides show couplings to ^{195}Pt of around 500 Hz in the diplatinum species, the values being slightly higher in the mixed platinum−palladium complexes. The methylene groups of the bridging dppm ligands appear as a single, usually broad, resonance (with observable ^{195}Pt satellites in most of the platinum-containing species), indicating that inversion of the A-frame structure is rapid on the NMR time scale at ambient temperature. This has been observed previously for hydride-bridged diplatinum compounds.[11] Resonances due to the organic substituents are unremarkable.

The ^{31}P{^{1}H} NMR spectrum of [Pd_2Me_2(μ-H)(μ-dppm)$_2$]PF_6 consists of a singlet,[8] as does its phenyl analogue, whereas the symmetrical diplatinum species exhibit a single central resonance with two sets of ^{195}Pt satellites, from which the J_{PP} couplings may be extracted (Table 2).[4,6,12] The unsymmetrical complexes give rise to two central resonances in their ^{31}P{^{1}H} NMR spectra (Figure 1). With the exception of [MePt(μ-H)(μ-dppm)$_2$PtEt]PF_6, for which there is considerable overlap of the central resonances, two J_{PP} values may be obtained. The

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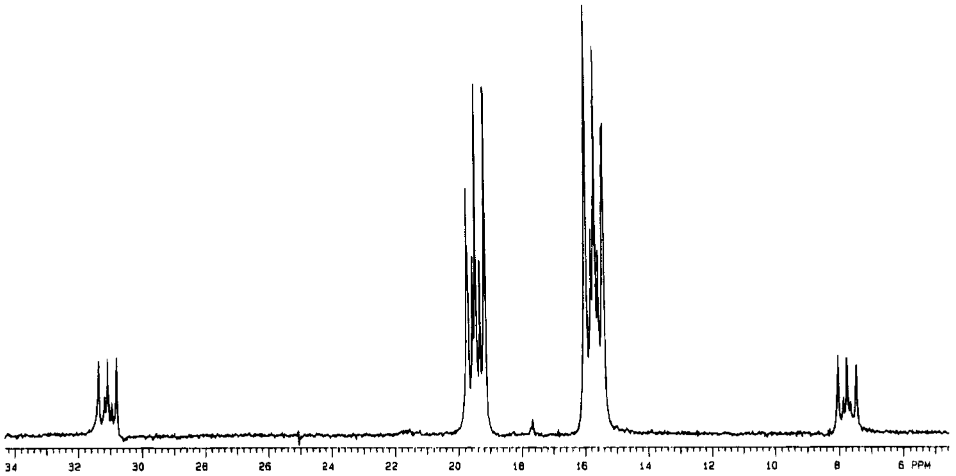

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $[MePt(\mu\text{-}H)(\mu\text{-}dppm)_2PdPh]^+$ recorded for an acetone-d_6 solution at ambient temperature.

diplatinum species exhibit one-bond and three-bond Pt–P couplings, but the $^3J_{PtP}$ values are too small to be observed in the platinum–palladium complexes. As in the case of the chloride-bridged complexes,[9] the resonances due to P atoms coordinated to palladium appear at slightly higher frequencies than those attached to platinum, and the signals associated with phenylplatinum or -palladium centers are observed at lower frequencies than those due to their alkyl analogues. The $^1J_{PtP}$ values associated with ethylplatinum fragments are consistently *ca.* 200 Hz larger than those found for methyl- or phenylplatinum moieties. In the case of $[PhPt(\mu\text{-}H)(\mu\text{-}dppm)_2PdPh]^+$ the two ^{31}P resonances are coincident, appearing at 15.3 ppm, shifted only slightly from that in the corresponding diplatinum species and with an almost identical $^1J_{PtP}$ coupling constant. The $^{195}Pt\{^1H\}$ NMR spectrum, however, consists of a simple 1:2:1 triplet, whereas that of the diplatinum derivative also exhibits a platinum–platinum coupling of *ca.* 420 Hz.

Table 2. $^{31}P\{^1H\}$ NMR Data for the Hydride-Bridged Complexes in Acetone-d_6 Solution[a]

complex	$\delta(P)$	$^1J_{PtP}$	$^3J_{PtP}$	J_{PP}
$MePtH(dppm)_2PtMe^+$	18.2	2850	42	51, 15
$EtPtH(dppm)_2PtEt^+$	19.2	3047	35	49, 12
$PhPtH(dppm)_2PtPh^+$ [d]	14.0	2857	24	50, 11
$MePdH(dppm)_2PdMe^+$	23.4			
$PhPdH(dppm)_2PdPh^+$	17.6			
$EtPtH(dppm)_2PtMe^+$	18.2	*ca.* 2870	*b*	*b*
	18.8	*ca.* 3070	*b*	*b*
$PhPtH(dppm)_2PtMe^+$	14.0	2858	24	45, 16
	18.1	2844	21	
$PhPtH(dppm)_2PtEt^+$	13.4	2866	26	47, 14
	19.5	3033	31	
$MePtH(dppm)_2PdMe^+$	19.1	2841		50, 16
	21.6		*c*	
$EtPtH(dppm)_2PdMe^+$	19.5	3023		52, 14
	21.7		*c*	
$PhPtH(dppm)_2PdMe^+$	14.8	2852		53, 14
	21.4		*c*	
$MePtH(dppm)_2PdPh^+$	19.4	2835		48, 20
	15.6		*c*	
$EtPtH(dppm)_2PdPh^+$	20.1	3017		47, 18
	15.4		*c*	
$PhPtH(dppm)_2PdPh^+$ [e]	15.3	2847		48, 18
	15.3		*c*	

[a] Chemical shifts are relative to external H_3PO_4. Coupling constants are in hertz. [b] Not resolved. [c] Not observed. [d] $\delta(Pt)$ −3060 t, $^1J_{PtP}$ 2850 Hz, $^2J_{PtPt}$ 420 Hz (^{195}Pt shifts are relative to external K_2PtCl_4 in D_2O). [e] $\delta(Pt)$ −3237 t, $^1J_{PtP}$ 2840 Hz.

This work provides a simple method for the preparation of a series of thermally and air stable hydride-bridged bimetallic complexes of platinum and palladium. Further studies of the structures and reactions of these complexes are in progress.

Experimental Section

All reactions were carried out under an atmosphere of argon. Complexes of the type $[PtR(dppm\text{-}P,P)(dppm\text{-}P)]PF_6$ (R = Me, Et, Ph) and $[PtClR(cod)]$ (R = Me, Et, Ph) were prepared as described previously. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Preparation of $[Pd_2Me_2(\mu\text{-}Cl)_2(AsPh_3)_2]$. $[Pd_2Cl_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (0.387 g, 0.400 mmol) was suspended in CH_2Cl_2 (25 mL), and Me_4Sn (0.150 mL, 1.08 mmol) was added dropwise. The solid gradually dissolved, and after 2 h a clear yellow solution was obtained. The solvent was evaporated, and the resulting solid was washed with several portions of pentane and dried *in vacuo*. The product was obtained as a yellow powder (0.353 g, 94%) and was identified by comparison with an authentic sample.[10]

Preparation of $[Pd_2Ph_2(\mu\text{-}Cl)_2(AsPh_3)_2]$. $[Pd_2Cl_2(\mu\text{-}Cl)_2(AsPh_3)_2]$ (0.484 g, 0.500 mmol) and Ph_4Sn (0.427 g, 1.00 mmol) were suspended in a mixture of THF (50 mL) and CH_2Cl_2 (25 mL). After the suspension was stirred at ambient temperature for 2 h, a dark solution and a white precipitate were present. The solvents were evaporated, and the resulting solid was washed with THF (2 × 25 mL) and then with several portions of pentane. The resulting white solid was dried *in vacuo* (0.360 g, 69%). Anal. Found: C, 54.84; H, 3.90. Calcd for $C_{48}H_{40}As_2Cl_2Pd_2$: C, 54.89; H, 3.84.

Preparation of $[Pd_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. $[Pd_2(\mu\text{-}Cl)_2Me_2(AsPh_3)_2]$ (0.185 g, 0.200 mmol) and dppm (0.154 g, 0.400 mmol) were dissolved in CH_2Cl_2 (15 mL), and NH_4PF_6 (0.0978 g, 0.600 mmol) was added. Methanol (2 mL) was introduced, and the mixture was stirred for 1 h. The solvents were removed, and the solid was washed with pentane and then redissolved in CH_2Cl_2. This solution was passed through a Hyflo Supercel column (5 × 1 cm) and then evaporated to dryness. After washing with pentane and ether, the product was obtained as a pale yellow powder (0.210 g, 88%). Anal. Found: C, 51.89; H, 4.25. Calcd for $C_{52}H_{50}ClF_6P_5Pd_2$: C, 52.39; H, 4.23.

Preparation of $[Pd_2Ph_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]PF_6$. This complex was prepared similarly from $[Pd_2(\mu\text{-}Cl)_2Ph_2(AsPh_3)_2]$ (0.105 g, 0.100 mmol), dppm (0.077 g, 0.200 mmol), and NH_4PF_6 (0.065 g, 0.399 mmol) and obtained as a yellow powder

(0.120 g, 91%). Anal. Found: C, 56.40; H, 4.17. Calcd for $C_{62}H_{54}ClF_6P_5Pd_2$: C, 56.58; H, 4.14, $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 11.0.

Preparation of [MePt(μ-Cl)(μ-dppm)$_2$PdPh]PF$_6$. [$Pd_2(\mu$-$Cl)_2Ph_2(AsPh_3)_2$] (0.105 g, 0.100 mmol) was suspended in CH_2Cl_2 (5 mL). [PtMe(dppm-*P,P*)(dppm-*P*)]PF_6 (0.225 g, 0.200 mmol) in CH_2Cl_2 (15 mL) was added dropwise, followed by NH_4PF_6 (0.0652 g, 0.400 mmol) and methanol (2 mL). After 1 h the solvents were removed, and the resulting solid was washed with pentane. The solid was redissolved in CH_2Cl_2, and the solution was passed through a column of Hyflo Supercel, eluting with CH_2Cl_2. The solution was evaporated to dryness and washed with pentane, leaving the product as a pale yellow solid (0.262 g, 96%). Anal. Found: C, 51.07; H, 3.96. Calcd for $C_{57}H_{52}ClF_6P_5PdPt$: C, 50.98; H, 3.90. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 16.9, $^1J_{PtP} = 2985$ Hz, $\delta(P)$ 8.0, $^3J_{PtP} = 22$ Hz, $J_{PP} = 26$, 13 Hz.

[EtPt(μ-Cl)(μ-dppm)$_2$PdPh]PF_6 was prepared similarly and isolated as a yellow powder in 99% yield. Anal. Found: C, 51.74; H, 4.09. Calcd for $C_{58}H_{54}ClF_6P_5PdPt$: C, 51.34; H, 4.01. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 17.6, $^1J_{PtP} = 3218$ Hz, $\delta(P)$ 8.3, $^3J_{PtP} = 33$ Hz, $J_{PP} = 28$, 10 Hz.

[PhPt(μ-Cl)(μ-dppm)$_2$PdPh]PF_6 was prepared similarly and isolated as a yellow powder in 96% yield. Anal. Found: C, 53.41; H, 3.98. Calcd for $C_{62}H_{54}ClF_6P_5PdPt$: C, 53.01; H, 3.87. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 11.9, $^1J_{PtP} = 2996$ Hz, $\delta(P)$ 8.8, $^3J_{PtP} = 32$ Hz, $JP_P = 26$, 10 Hz.

Preparation of [$Pt_2Ph_2(\mu$-H)(μ-dppm)$_2$]PF$_6$. [PtClPh(cod)] (0.208 g, 0.501 mmol) and dppm (0.192 g, 0.500 mmol) were dissolved in CH_2Cl_2 (15 mL). After 1 h the reaction mixture was cooled to 0 °C, and $NaBH_4$ (0.0379 g, 1.00 mmol) was added. Methanol (2 mL) was introduced very slowly, and the solution changed from yellow to dark brown. After 1 h at 0 °C, NH_4PF_6 (0.163 g, 1.00 mmol) was added and the mixture was stirred for a further 15 min. The solvents were removed, and the solid was washed with pentane and redissolved in CH_2Cl_2. The CH_2Cl_2 solution was passed down a Hyflo Supercel column and then evaporated. After washing with benzene, pentane, and ethanol, the product was obtained as a golden-yellow solid (0.312 g, 93%). Anal. Found: C, 50.92; H, 3.82. Calcd for $C_{62}H_{55}F_6P_5Pt_2$: C, 51.04; H, 3.80.

[$Pt_2Me_2(\mu$-H)(μ-dppm)$_2$]PF_6[6] was prepared similarly and obtained as a white powder in 75% yield. Anal. Found: C, 46.67; H, 3.93. Calcd for $C_{52}H_{51}F_6P_5Pt_2$: C, 46.79; H, 3.85.

[$Pt_2Et_2(\mu$-H)(μ-dppm)$_2$]PF_6[7] was prepared similarly and obtained as a golden-yellow powder in 88% yield. Anal. Found: C, 47.70; H, 4.10. Calcd for $C_{54}H_{55}F_6P_5Pt_2$: C, 47.59; H, 4.07.

Preparation of [$Pd_2Me_2(\mu$-H)(μ-dppm)$_2$]PF$_6$. [$Pd_2Me_2(\mu$-$Cl)_2(AsPh_3)_2$] (0.185 g, 0.200 mmol) and dppm (0.154 g, 0.400 mmol) were dissolved in CH_2Cl_2 (15 mL) and allowed to react for 1 h at ambient temperature. The solution was cooled to 0 °C, and $NaBH_4$ (0.0303 g, 0.802 mmol) was added. Methanol (2 mL) was added dropwise, and the solution changed from pale yellow to dark brown. After 1 h, NH_4PF_6 (0.130 g, 0.800 mmol) was introduced, and the mixture was stirred for a further 15 min. The solvents were removed, and the solid was washed with pentane and redissolved in CH_2Cl_2. The CH_2Cl_2 solution was passed down a Hyflo Supercel column and then evaporated. After washing with benzene, pentane, and ethanol, the product was obtained as a white solid (0.201 g, 86%). Anal. Found: C, 53.43; H, 4.41. Calcd for $C_{52}H_{51}F_6P_5Pd_2$: C, 53.96; H, 4.44.

[$Pd_2Ph_2(\mu$-H)(μ-dppm)$_2$]PF_6 was prepared similarly and obtained as a white powder in 70% yield. Anal. Found: C, 58.17; H, 4.37. Calcd for $C_{62}H_{55}F_6P_5Pd_2$: C, 58.10; H, 4.33.

Preparation of [PhPt(μ-H)(μ-dppm)$_2$PtEt]PF$_6$. [PtEt(dppm-*P,P*)(dppm-*P*)]PF_6 (0.228 g, 0.201 mmol) was dissolved in CH_2Cl_2 (5 mL). A CH_2Cl_2 solution (5 mL) of [PtClPh(cod)] (0.0831 g, 0.200 mmol) was added dropwise, and the solution was stirred for 1 h and then cooled to 0 °C. Sodium borohydride (0.0152 g, 0.400 mmol) was added, and methanol (2 mL) was introduced very slowly. The solution turned brown. After 1 h, NH_4PF_6 (0.0652 g, 0.400 mmol) was added, and the mixture was stirred for 15 min. The product was isolated as described for the symmetrical complexes and obtained as a yellow powder (0.173 g, 57%). Anal. Found: C, 49.19; H, 3.97. Calcd for $C_{58}H_{55}F_6P_5Pt_2$: C, 49.37; H, 3.93.

[PhPt(μ-H)(μ-dppm)$_2$PtMe]PF_6 was prepared analogously from [PtMe(dppm-*P,P*)(dppm-*P*)]PF_6, [PtClPh(cod)], $NaBH_4$, and NH_4PF_6 and obtained as an off-white solid in 64% yield. Anal. Found: C, 48.66; H, 4.02. Calcd for $C_{57}H_{53}F_6P_5Pt_2$: C, 49.01; H, 3.82.

[EtPt(μ-H)(μ-dppm)$_2$PtMe]PF_6 was prepared analogously from [PtEt(dppm-*P,P*)(dppm-*P*)]PF_6, [PtClMe(cod)], $NaBH_4$, and NH_4PF_6, and obtained as an off-white solid in 59% yield. Anal. Found: C, 46.84; H, 3.88. Calcd for $C_{53}H_{53}F_6P_5Pt_2$: C, 47.19; H, 3.96.

Preparation of [MePt(μ-H)(μ-dppm)$_2$PdMe]PF$_6$. [$Pd_2(\mu$-$Cl)_2Me_2(AsPh_3)_2$] (0.0926 g, 0.100 mmol) was suspended in CH_2Cl_2 (5 mL). A CH_2Cl_2 solution (5 mL) of [PtMe(dppm-*P,P*)(dppm-*P*)]PF_6 (0.225 g, 0.200 mmol) was added dropwise. The palladium complex dissolved, and the solution was stirred for 1 h and then cooled to 0 °C. $NaBH_4$ (0.0152 g, 0.400 mmol) was added, methanol (2 mL) was introduced slowly, and the mixture was stirred for 1 h. NH_4PF_6 (0.0978 g, 0.600 mmol) was added, and the mixture was stirred for a further 15 min. The product was isolated as described above and was obtained as a yellow powder (0.240 g, 96%). Anal. Found: C, 49.63; H, 4.07. Calcd for $C_{52}H_{51}F_6P_5PdPt$: C, 50.12; H, 4.13.

[EtPt(μ-H)(μ-dppm)$_2$PdMe]PF_6 was prepared similarly and obtained as an off-white powder in 45% yield. Anal. Found: C, 50.27; H, 4.15. Calcd for $C_{53}H_{53}F_6P_5PdPt$: C, 50.51; H, 4.24.

[PhPt(μ-H)(μ-dppm)$_2$PdMe]PF_6 was prepared similarly and obtained as an off-white powder in 69% yield. Anal. Found: C, 52.28; H, 4.16. Calcd for $C_{57}H_{53}F_6P_5PdPt$: C, 52.33; H, 4.08.

Preparation of [MePt(μ-H)(μ-dppm)$_2$PdPh]PF$_6$. To a suspension of [$Pd_2(\mu$-$Cl)_2Ph_2(AsPh_3)_2$] (0.105 g, 0.100 mmol) in CH_2Cl_2 (5 mL) was added dropwise [PtMe(dppm-*P,P*)(dppm-*P*)]PF_6 (0.225 g, 0.200 mmol) in CH_2Cl_2 (5 mL). After 1 h, the reaction mixture was cooled to 0 °C and $NaBH_4$ (0.015 g, 0.400 mmol) was added, methanol (2 mL) was introduced slowly, and the mixture was stirred for 1 h. NH_4PF_6 (0.065 g, 0.400 mmol) was introduced, and the mixture was stirred for a further 15 min. The product was isolated as described above and was obtained as a white powder (0.201 g, 76%). Anal. Found: C, 52.48; H, 4.13. Calcd for $C_{57}H_{53}F_6P_5PdPt$: C, 52.32; H, 4.08.

[EtPt(μ-H)(μ-dppm)$_2$PdPh]PF_6 was prepared similarly and obtained as a yellow powder in 75% yield. Anal. Found: C, 52.45; H, 4.18. Calcd for $C_{58}H_{55}F_6P_5PdPt$: C, 52.68; H, 4.23.

[PhPt(μ-H)(μ-dppm)$_2$PdPh]PF_6 was prepared similarly and obtained as a yellow powder in 92% yield. Anal. Found: C, 54.45; H, 4.20. Calcd for $C_{62}H_{55}F_6P_5PdPt$: C, 54.34; H, 4.05.

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