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Synthesis and Ligand Substitution Reactions of a Mesitylphosphido-Bridged Platinum(II) Dimer

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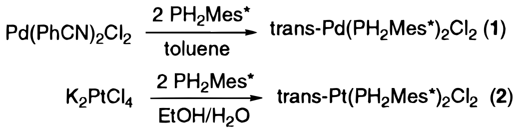
The stable primary phosphine complexes *trans*-M(PH_2Mes^*)$_2$$Cl_2$ (**1**, M = Pd; **2**, M = Pt; Mes* = 2,4,6-(*t*-Bu)$_3$$C_6H_2$) were prepared from Pd(PhCN)$_2$$Cl_2$ and K_2PtCl_4, respectively. Reaction of Pt(COD)Cl_2 (COD = 1,5-cyclooctadiene) with less bulky arylphosphines gives the unstable *cis*-Pt(PH_2Ar)$_2$$Cl_2$ (**3**, Ar = Is = 2,4,6-(*i*-Pr)$_3$$C_6H_2$; **4**, Ar = Mes = 2,4,6-$Me_3C_6H_2$). Spontaneous dehydrochlorination of **4** or direct reaction of K_2PtCl_4 with 2 equiv of PH_2Mes gives the insoluble primary phosphido-bridged dimer [Pt(PH_2Mes)(μ-PHMes)Cl]$_2$ (**5**), which was characterized spectroscopically, including solid-state ^{31}P NMR studies. The reversible reaction of **5** with PH_2Mes gives [Pt(PH_2Mes)$_2$(μ-PHMes)]$_2$[Cl]$_2$ (**6**), while PEt_3 yields [Pt(PEt_3)$_2$(μ-PHMes)]$_2$[Cl]$_2$ (**7**), which on recrystallization forms [Pt(PEt_3)(μ-PHMes)Cl]$_2$ (**8**). Complex **5** and PPh_3 afford [Pt(PPh_3)(μ-PHMes)Cl]$_2$ (**9**). Addition of 1,2-bis(diphenylphosphino)ethane (dppe) to **5** gives the dicationic [Pt(dppe)(μ-PHMes)]$_2$[Cl]$_2$ (**10-Cl**), which was also obtained as the tetrafluoroborate salt **10-BF$_4$** by deprotonation of [Pt(dppe)(PH_2Mes)Cl][BF_4] (**11**) with Et_3N or by reaction of [Pt(dppe)(μ-OH)]$_2$[BF_4]$_2$ with 2 equiv of PH_2Mes. Complexes **8**, **9**, and **10-Cl**·2CH_2Cl_2·2H_2O were characterized crystallographically.

Introduction

Many dinuclear metal complexes with bridging secondary phosphido (μ-PR_2) ligands are known,[1] but the corresponding μ-PHR primary derivatives are less common.[2] Such complexes are of interest, since the P−H bond is reactive. For example, M−PHR groups are precursors to phosphinidene (PR) ligands, formed by further proton transfer from phosphorus,[3] and are proposed intermediates in metal-catalyzed olefin hydrophosphination, in which alkenes undergo formal insertion into the P−H bond.[4]

Primary phosphido complexes have been prepared by dehydrohalogenation of primary phosphine halide complexes.[5] For example, *cis*-Pd(PH_2Cy)$_2$$Cl_2$ (Cy = cyclo-C_6H_{11}) loses HCl to form [Pd(PH_2Cy)(μ-PHCy)Cl]$_2$,[6] while related chemistry with PH_2Ph was claimed to result in [Pd(PH_2Ph)$_2$Cl]$_2$(μ-PPh) as a result of further loss of HCl.[7] We report here the synthesis of related Pd(II) and Pt(II) chloride complexes of sterically demanding primary arylphosphines. The dehydrochlorination of one such compound leads to formation of the primary phosphido-bridged Pt(II) dimer [Pt(PH_2Mes)(μ-PHMes)Cl]$_2$ (**5**; Mes = 2,4,6-$Me_3C_6H_2$). Ligand substitution reactions of **5** give a series of other phosphido-bridged dimers.

Scheme 1



$$Pd(PhCN)_2Cl_2 \xrightarrow[\text{toluene}]{2\ PH_2Mes^*} trans\text{-}Pd(PH_2Mes^*)_2Cl_2\ (\mathbf{1})$$

$$K_2PtCl_4 \xrightarrow[\text{EtOH/H}_2\text{O}]{2\ PH_2Mes^*} trans\text{-}Pt(PH_2Mes^*)_2Cl_2\ (\mathbf{2})$$

Results and Discussion

The complexes *trans*-M(PH_2Mes^*)$_2$$Cl_2$ (Mes* = 2,4,6-(*t*-Bu)$_3$$C_6H_2$; M = Pd (**1**), Pt (**2**)) were prepared by addition of 2 equiv of the phosphine to Pd(PhCN)$_2$$Cl_2$ or to K_2PtCl_4 (Scheme 1). The palladium complex could also be made directly from $PdCl_2$ in hot toluene, or from $PdCl_2$ in acidic ethanol. These air- and water-stable yellow solids are characterized by their distinctive ^{31}P and ^1H NMR spectra (AA′X_2X′$_2$ spin systems). The P−P coupling constants (for **1**, $^2J_{PP}$ = 668 Hz; for **2**, $^2J_{PP}$ = 596 Hz) and the Pt−P coupling constant of 2707 Hz for **2** indicate that **1** and **2** are the trans isomers, as expected for the

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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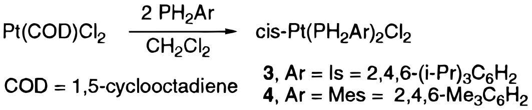
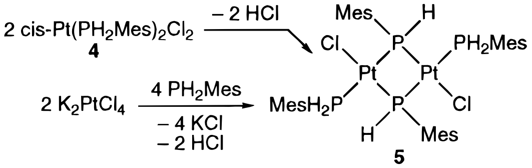
Scheme 2



Scheme 3



bulky PH_2Mes^* ligand.[8] One large and one small P−H coupling are also observed (for **1**, $^1J_{PH} = 374$, $^3J_{PH} = 4$ Hz; for **2**, $^1J_{PH} = 389$, $^3J_{PH} = 1$ Hz). IR spectroscopy confirms the presence of P−H bonds (for **1**, ν_{PH} 2410 cm^{-1}; for **2**, ν_{PH} 2409 cm^{-1}). These complexes are stable with respect to dehydrochlorination and remain unchanged in solution for weeks.

Reactions of $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene) with the less sterically demanding phosphines (L) PH_2Is (Is = 2,4,6-(i-Pr)$_3C_6H_2$) and PH_2Mes gave the complexes *cis*-PtL_2Cl_2 (**3** and **4**; Scheme 2), as determined from ^{31}P NMR spectroscopy. In these cases, spectral simulation affords characteristically smaller cis $^2J_{PP}$ values of 15 Hz in each case, while the $^1J_{PtP}$ couplings of 3317 and 3340 Hz are also consistent with the cis geometry. The P−H coupling constants (for **3**, $^1J_{PH} = 420$, $^3J_{PH} = 5$ Hz; for **4**, $^1J_{PH} = 423$, $^3J_{PH} = 5$ Hz) and IR spectra (for **3**, ν_{PH} 2399, 2367 cm^{-1}) are similar to those observed for **1** and **2**.[9]

Complexes **3** and **4** could not be isolated in analytically pure form because they decompose in solution, producing white solids that are insoluble in common solvents.[10] For example, complex **4** in CH_2Cl_2 deposited a precipitate, identified as the phosphido-bridged Pt(II) complex $[Pt(PH_2Mes)(\mu\text{-}PHMes)Cl]_2$ (**5**; Scheme 3). Moreover, the reaction of K_2PtCl_4 in water with 2 equiv of PH_2Mes led directly to solid **5**. This material is thermally stable and does not melt up to 250 °C. Powder X-ray diffraction studies show that when it is formed rapidly, as in the decomposition of **4** in CH_3NO_2 or from K_2PtCl_4 in water, it is amorphous. Slower precipitation from CH_2Cl_2 solutions of **4**, however, gives crystalline material. In some cases, we observed by elemental analysis and/or CP/MAS ^{31}P NMR (see below) that isolated **5** was contaminated by complex **4**, which could be removed by extraction with CH_2Cl_2.

Elemental analysis and the FAB mass spectrum of complex **5**, which shows a peak at m/z 1052.0 ($(M - Me)^+$) and several fragments corresponding to loss of Me, Mes, or PH_2Mes groups, are consistent with the formulation of **5**. The IR (KBr) spectrum of **5** shows a P−H stretch at 2366 cm^{-1}; when deuterium-labeled **5** was prepared from PD_2Mes, this band was significantly reduced in intensity, but no ν_{PD} band could be confidently assigned.

Titration of the CH_2Cl_2 solution remaining after **5** precipitates showed that approximately 2 equiv of acid (presumably HCl) was formed; this was also observed for the aqueous filtrate in the alternative synthesis from K_2PtCl_4. Loss of HCl was greatly accelerated by addition of Et_3N to a CH_2Cl_2 solution of **4**, which resulted in the immediate precipitation of **5**. GC−MS analysis of the volatile materials formed in the reaction of $Pt(COD)Cl_2$ with PH_2Mes in CH_2Cl_2 indicated that COD was released.

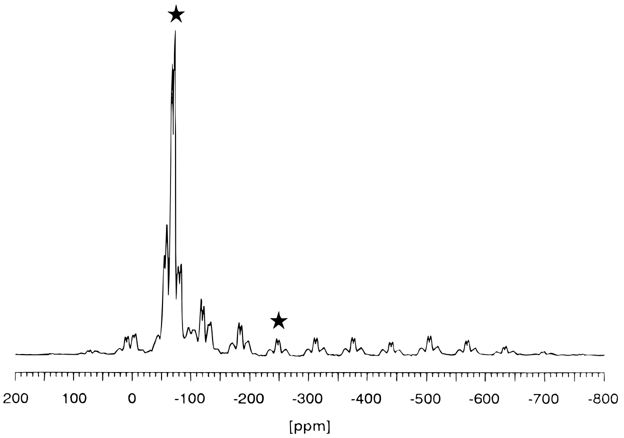


Figure 1. ^{31}P CP/MAS NMR spectrum of a powder sample of **5** obtained at 81.0 MHz. The isotropic regions are indicated by asterisks. Conditions: spinning rate, 5.2 kHz; ^1H $\pi/2$ pulse width, 3.4 μs; contact time, 5 ms; recycle delay, 8 s; 422 scans.

The structure proposed for **5** is consistent with these data and with literature reports of the formation of closely related μ-phosphido dimers from primary and secondary phosphines. In particular, similar Pt(II) chemistry with diphenylphosphine gives $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl)]_2$,[11] and the synthesis[6] of $[Pd(PH_2Cy)(\mu\text{-}PHCy)Cl]_2$, mentioned above, is directly related. However, the insolubility of **5** (in contrast, the above dimers are soluble in organic solvents) was puzzling and prevented further characterization by solution NMR. A solid-state ^{31}P NMR study provided more evidence for the proposed structure.

The ^{31}P CP/MAS NMR spectrum of **5** (Figure 1) shows two apparent doublet signals, each flanked by Pt satellites, in an approximately 1:1 ratio. The isotropic chemical shifts of these peaks are −67 and −247 ppm. The solution ^{31}P NMR spectra of related complexes, *e.g.* $[Pt(PEt_3)(\mu\text{-}PPh_2)Cl]_2$, have been analyzed in detail by Brandon and Dixon[12] and are analogous to the one observed here, except for the much greater natural line width of the solid-state ^{31}P NMR spectrum. The peak at −67 ppm can be assigned to the terminal PH_2Mes group of **5**, while the chemical shift of the peak at much lower frequencies, −247 ppm, is consistent with the literature on phosphido-bridged dimers without metal−metal interactions.[1] Each phosphorus site of **5** consists of two chemically equivalent but magnetically nonequivalent ^{31}P nuclei, giving rise to an AA′XX′ spin system. For such spin systems, the apparent doublet splitting in the AA′ and XX′ regions of the spectrum (here 360 Hz) is known to correspond approximately to the sum of J_{AX} and $J_{AX'}$. This observation is similar to the results for $[Pt(PEt_3)(\mu\text{-}PPh_2)Cl]_2$ ($J_{AX} + J_{AX'} = 378.8$ Hz) and $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl]_2$ ($J_{AX} + J_{AX'} = 394.4$ Hz).[12]

For the terminal phosphine, $^1J_{PtP}$ is 1960 ± 20 Hz, consistent with the results for $[Pt(PEt_3)(\mu\text{-}PPh_2)Cl]_2$ ($^1J_{PtP} = 2171.8$ Hz) and $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl]_2$ ($^1J_{PtP} = 2184.0$ Hz). For the bridging phosphido ligand, the $^1J_{PtP}$ couplings (1954 ± 50 (trans to PH_2Mes) and 2503±50 Hz (trans to Cl)) reflect the trans influence. These results are also similar to those observed for $[Pt(PEt_3)(\mu\text{-}PPh_2)Cl]_2$ (1690.5 and 2634.7 Hz) and $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl]_2$ (1991.1 and 2364.2 Hz).[12]

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[9] Related cis complexes of 1-adamantylphosphine have been reported recently: Goerlich, J. R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 898−907.

[10] Complex **5** does not dissolve in petroleum ether, diethyl ether, benzene, toluene, THF, CH_2Cl_2, $CHCl_3$, CH_3NO_2, dioxane, CS_2, DMSO, DMF, or chlorobenzene.

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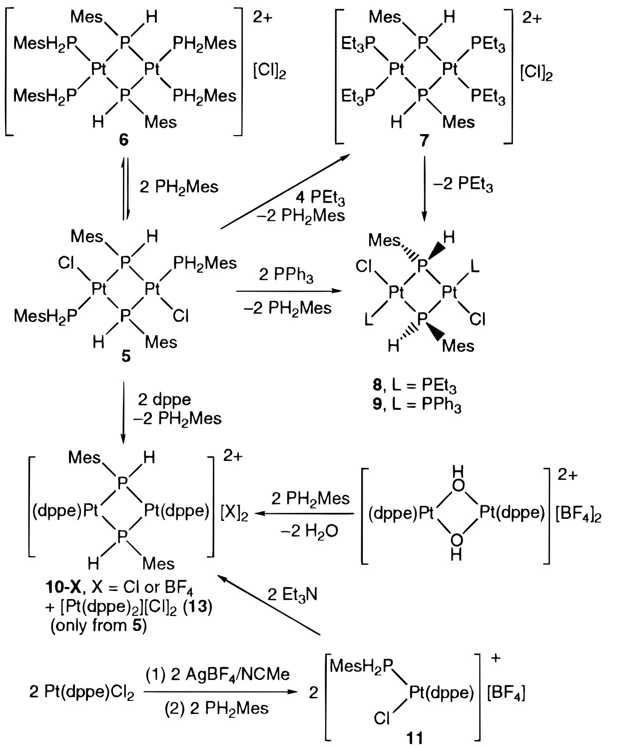
[12] Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188−1200.

Figure 1 demonstrates that the peak due to the phosphido group exhibits many spinning sidebands at multiples of the spinning frequency, in contrast to the peak due to the terminal PH_2Mes ligand, which has only first-order spinning sidebands. This indicates drastic differences in the chemical shift anisotropies (CSA) of these two species.[13] Analysis of the ^{31}P CP NMR spectrum of a static powder sample of **5** yields the principal components of the chemical shift tensors: for the PH_2Mes ligand, δ_{11} −27, δ_{22} −62, δ_{33} −112 ppm; for the μ-PHMes ligand, δ_{11} 28, δ_{22} −85, δ_{33} −684 ppm. The CSA of the terminal ligand is typical of phosphines coordinated to platinum.[14] Obviously, the high shielding observed for the ^{31}P of the phosphido group as compared to the terminal ligand arises mainly from the direction corresponding to δ_{33}. So far, there are only very few phosphorus compounds known with such high shielding of the phosphorus nucleus along a particular direction (note that the chemical shift of the free ^{31}P atom[15] is −632 ppm). Such molecules are linear, where for reasons of symmetry[16] there is no paramagnetic contribution to the direction along the molecular axis (*e.g.* PN,[17] HCP[18]), or are highly strained cyclic molecules such as 1,2,3-triphenylphosphirene[19] and P_4.[20] Unfortunately, there are no reasonable interpretations of these effects available at this time. Note, however, that the phosphorus nuclei of phosphido groups bridging formal metal−metal bonds are usually much less shielded than in corresponding terminal phosphines.[21]

Although **5** is insoluble, it reacts with donor ligands (Scheme 4). A slurry of **5** in a polar solvent (CH_3NO_2 or CH_2Cl_2) rapidly reacted with an excess of PH_2Mes or PEt_3 at room temperature to give a homogeneous yellow solution; $^{31}P\{^1H\}$ NMR monitoring suggested that the ionic compounds $[PtL_2(\mu\text{-PHMes})]_2[Cl]_2$ (**6**, L = PH_2Mes; **7**, L = PEt_3) were formed. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of PH_2Mes and **6** in CD_2Cl_2 at room temperature shows broad peaks at δ −76 (coordinated PH_2-Mes), −147 (free PH_2Mes), and −215 ppm (μ-PHMes), consistent with rapid exchange of the terminal PH_2Mes groups.[22] However, at −60 °C this exchange is slowed and the peak assigned to free PH_2Mes is sharp, while that at δ −76 is resolved as a complex multiplet. The peak assigned to coordinated PHMes, however, remains broad. From these observations, we cannot determine if the compound exists as a mixture of syn and anti isomers differing in the relative stereochemistry of the phosphido ligands. Similarly, the $^{31}P\{^1H\}$ NMR spectrum of a mixture of PEt_3 and **7** in CH_3NO_2 shows a multiplet at δ 17.6 (coordinated PEt_3), resonances at δ −12.4 (free PEt_3) and −152.0 (free PH_2Mes), and a broad signal at δ −252.2 (μ-PHMes). The ionic formulation of complexes **6** and **7** is consistent with solution conductivity measurements in CH_3NO_2, which show that these compounds are 2:1 electrolytes.[23]

Scheme 4



The reaction of **5** with PH_2Mes is reversible; attempted recrystallization of **6** gave the insoluble starting material **5**. Similarly, attempts to recrystallize the PEt_3 complex **7** produced another insoluble compound, which was identified as $[Pt(PEt_3)(\mu\text{-PHMes})Cl]_2$ (**8**) by elemental analysis, IR spectroscopy, FAB mass spectroscopy, and X-ray crystallography (see below). The IR spectrum of **8** shows ν_{PH} at 2374 cm^{-1}; the FAB mass spectrum shows a peak at *m/z* 927.2 ($(M - 2Cl - H)^+$) and several fragments corresponding to loss of PEt_3, Cl, and Me groups.

The related reaction of **5** with the larger and less nucleophilic PPh_3 required elevated temperature and led to the formation of the insoluble yellow $[Pt(PPh_3)(\mu\text{-PHMes})Cl]_2$ (**9**) (Scheme 4). In this case, no soluble intermediate was observed. Heating of the reaction mixture (THF, 55 °C, 8 days) gave X-ray-quality crystals. Complex **9** was characterized by elemental analysis, IR spectroscopy, FAB mass spectroscopy, and X-ray crystallography (see below). In the IR (KBr) spectrum of **9** ν_{PH} 2380 cm^{-1} is observed; the FAB mass spectrum of **9** shows peaks at *m/z* 1252.1 ($(M - Cl)^+$) and 1216.2 ($(M - 2Cl)^+$).

Addition of 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) to a CH_2Cl_2 slurry of **5** rapidly gave a solution containing a mixture of $[Pt(dppe)(\mu\text{-PHMes})]_2[Cl]_2$ (**10-Cl**) and $[Pt(dppe)_2][Cl]_2$ (**13**) (Scheme 4), as shown by ^{31}P NMR. The $^{31}P\{^1H\}$ NMR spectrum of **13** has been reported elsewhere[24] and shows a peak at δ 47.2 ($^1J_{PtP}$ = 2374 Hz). Separation of **10-Cl** from **13** by recrystallization or by chromatography was difficult; therefore, **10** was prepared independently as the BF_4 salt **10-BF$_4$** (Scheme 4).

Addition of $AgBF_4$ to $Pt(dppe)Cl_2$ followed by treatment with PH_2Mes gave the intermediate complex $[Pt(dppe)(PH_2Mes)Cl][BF_4]$ (**11**), which was characterized spectroscopically. The ^{31}P-

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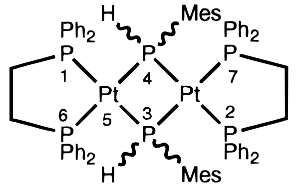

Figure 2. Atom labeling for complex **10**.

{^{1}H} NMR spectrum of **11** shows three signals due to the inequivalent phosphorus nuclei; the coordinated primary phosphine resonates at δ −70.5 (dd, $^2J_{PP} = 398$ Hz, $^2J_{PP} = 18$ Hz, $^1J_{PtP} = 2180$ Hz). Treatment of **11** with Et_3N gave pure **10-BF$_4$**. We assume that this reaction proceeds by initial deprotonation of the complexed primary phosphine, followed by formation of the phosphido bridges with displacement of chloride as an anion. Alternatively, **10-BF$_4$** can be prepared from the known[25] hydroxo complex $[Pt(dppe)(\mu\text{-}OH)]_2[BF_4]_2$ by addition of PH_2Mes (Scheme 4), as evident from $^{31}P\{^1H\}$ NMR spectroscopy.

$^{31}P\{^1H\}$ NMR spectroscopy shows that dication **10** exists in solution as two isomers **10a** (complex multiplets at δ 55.2 (dppe) and −273.9 (μ-PHMes)) and **10b** (complex multiplets at δ 51.6 (dppe) and −243.3 (μ-PHMes)). From the available data, we cannot tell which of these is the syn and which is the anti isomer. When **10-Cl** is prepared from **5**, the initial ratio of isomers **10a**:**10b** is approximately 2:1; after several days in CH_2Cl_2 the ratio changes to about 1:1. However, when **10-BF$_4$** is prepared by either of the two methods described above, the initial ratio of the isomers **10a**:**10b** is 1:2 and further changes in the ratio were not observed. Note that the ^{31}P chemical shifts for the phosphido ligands differ for **10-Cl** and **10-BF$_4$**; we have not investigated the reasons for this observation.

The $^{31}P\{^1H\}$ NMR spectra of cations **10a**,**b** are similar to those of the closely related[12] secondary phosphido complex $[Pt(dppe)(\mu\text{-}PPh_2)]_2[Cl]_2$, whose ^{31}P NMR spectrum has been analyzed in detail by Brandon and Dixon and which displays similar coupling constants. For **10a-Cl**, ^{31}P NMR spectral simulation gives the following coupling constants (the labeling in Figure 2 and the sign convention follow Brandon and Dixon): $^4J_{1,2} = 7.0$, $^2J_{1,3} = 292.5$, $^2J_{1,4} = 0$, $^1J_{1,5} = 2180$, $^2J_{1,6} = 0$, $^4J_{1,7} = 0$, $^3J_{2,5} = 58$, $^2J_{3,4} = -182$, and $^1J_{3,5} = 1636$ Hz. For **10b-Cl**, $^4J_{1,2} = 5.0$, $^2J_{1,3} = 286.5$, $^2J_{1,4} = 0$, $^1J_{1,5} = 2236$, $^2J_{1,6} = 0$, $^4J_{1,7} = 0$, $^3J_{2,5} = 50$, $^2J_{3,4} = -165$, and $^1J_{3,5} = 1632$ Hz. The $^1J_{PtP}$ ($J_{1,5}$) value for the dppe ^{31}P nuclei (2180 and 2236 Hz) is larger for **10a**,**b** than for $[Pt(dppe)(\mu\text{-}PPh_2)]_2[Cl]_2$ (2112.6 Hz), indicating that the μ-PPh_2 ligand has a larger trans influence than the μ-PHMes ligand.

The mixture of isomers **10a**,**b** was also characterized by ^{1}H NMR spectroscopy. The Ar and Me groups of the two isomers give rise to well-resolved signals, although peaks due to the P−H protons could not be observed. The ^{1}H NMR spectrum of **10-BF$_4$** shows peaks due to three inequivalent Me groups and two inequivalent Mes ring protons for each of the isomers **10a** and **10b**. Similarly, the ^{13}C NMR spectrum exhibits two sets of three signals assigned to the mesityl methyl carbons of **10a**,**b**. These results are consistent with restricted rotation around the P−Mes bonds, which probably arises as a result of interaction between the Mes and the dppe Ph groups. The ^{1}H NMR spectrum also shows signals due to six different types of dppe aryl protons per isomer. This confirms that the two phenyl groups bound to a dppe phosphorus are inequivalent, as required by symmetry.

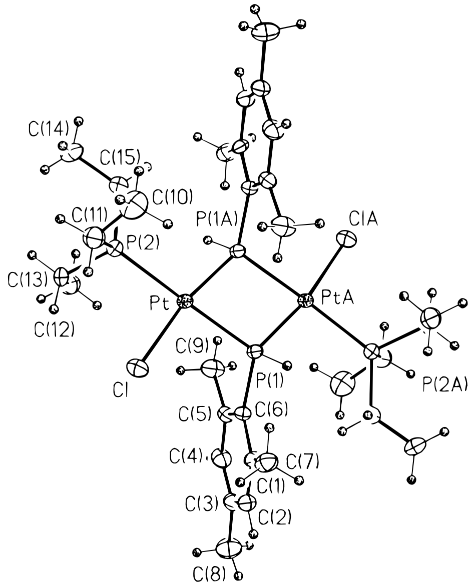

Figure 3. ORTEP diagram for $[Pt(PEt_3)(\mu\text{-}PHMes)Cl]_2$ (**8**). Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity, except for the P−H atoms, which were treated as idealized contributions.

Although complex **8** is insoluble in organic solvents, crystals of it were obtained on attempted recrystallization of dication **7** from CH_2Cl_2/Et_2O. Similarly, the heterogeneous reaction of insoluble **5** with PPh_3 in hot THF gave crystals of insoluble **9** directly from the reaction mixture. Suitable crystals of **10-Cl** as a methylene chloride/water solvate were grown by diffusion of Et_2O into a CH_2Cl_2 solution.

Crystal, data collection, and refinement parameters for complexes **8**, **9**, and **10-Cl**·$2CH_2Cl_2$·$2H_2O$ are given in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are included as Supporting Information. ORTEP diagrams are shown in Figures 3−5. Selected bond lengths and angles appear in Tables 2 and 3, with data for analogous platinum μ-phosphido dimers for comparison. Further details of the structure determinations are given in the Experimental Section and the Supporting Information.

All three complexes crystallize as the more symmetrical anti isomer, as observed previously for other μ-phosphido dimers.[26] The central Pt_2P_2 rings are planar, and the ideal square-planar geometry at Pt(II) is distorted since the core P−Pt−P angle is 76−77°, as previously described by Carty[11] for $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl]_2$ and $[Pt(dppe)(\mu\text{-}PPh_2)]_2[Cl]_2$. The data in Tables 2 and 3 show that bond lengths and angles in these rings are relatively insensitive to substitution. For both **8** and **9**, the difference between the Pt−PHMes (trans to PR_3, R = Et or Ph) bond length (2.323(2) and 2.318(2) Å, respectively) and the Pt−PHMes (trans to Cl) bond length (2.265(2) and 2.268(2) Å) may be rationalized by the greater trans influence of a tertiary phosphine in comparison to chloride.[27]

The Pt−Cl bond length in **8** (2.376(2) Å) is significantly longer than that in **9** (2.355(2) Å), perhaps because of the relative cis influences of PEt_3 and PPh_3.[28] However, these bond lengths may also be affected by the different PR_3−Pt−Cl (δ) and PR_3−Pt−PHMes (γ) angles observed in these compounds.

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(25) Scarcia, V.; Furlani, A.; Longato, B.; Corain, B.; Pilloni, G. *Inorg. Chim. Acta* **1988**, *153*, 67−70.

(26) For examples, see: (a) Reference 2 a. (b) Brown, M. P.; Buckett, J.; Harding, M. M.; Lynden-Bell, R. M.; Mays, M. J.; Woulfe, K. W. *J. Chem. Soc., Dalton Trans.* **1991**, 3097−3102. (c) Clegg, W.; Morton, S. *Inorg. Chem.* **1979**, *18*, 1189−1192.

(27) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335−422.

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Table 1. Crystallographic Data for **8**, **9**, and **10-Cl**$\cdot 2CH_2Cl_2 \cdot 2H_2O$

	8	**9**	**10-Cl**$\cdot 2CH_2Cl_2 \cdot 2H_2O$
formula	$C_{30}H_{54}Cl_2P_4Pt_2$	$C_{54}H_{52}Cl_2P_4Pt_2$	$C_{72}H_{78}Cl_4O_2P_6Pt_2$
fw	999.69	1285.92	1693.14
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	7.804(4)	10.210(3)	12.449(7)
b, Å	12.724(6)	16.226(8)	12.510(7)
c, Å	18.618(15)	15.066(5)	12.926(7)
α, deg			77.52(4)
β, deg	92.53(5)	90.21(4)	65.80(4)
γ, deg			81.87(5)
V, Å^3	1847(2)	2496(2)	1790(2)
Z	2	2	1
D(calc), g cm^{-3}	1.798	1.711	1.571
μ(Mo Kα), cm^{-1}	79.02	58.69	42.30
temp, K	296	296	296
radiation		Mo Kα (λ = 0.710 73 Å)	
$R(F)$, %^{a}	3.02 (4.24)^b	3.54 (6.25)^b	2.84 (3.73)^b
$R(\mathrm{w}F^2)$, %	6.89 (7.42)^b	6.95 (7.47)^b	6.16 (6.31)^b

^{a} Quantity minimized $\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[(wF_o{}^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$; $R(\mathrm{w}) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. ^{b} Residual based on all data.

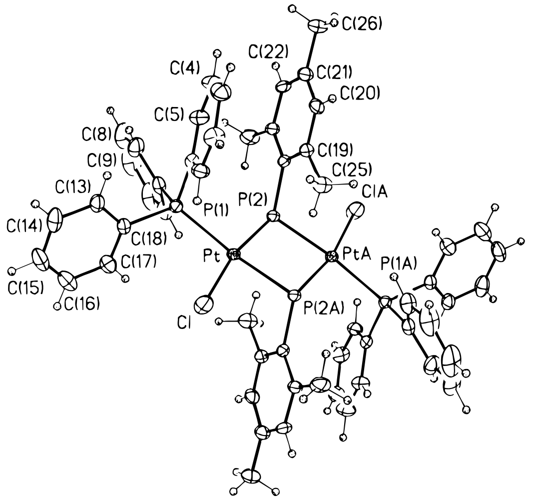

Figure 4. ORTEP diagram for $[Pt(PPh_3)(\mu\text{-}PHMes)Cl]_2$ (**9**). Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

Comparison of the Pt−P(dppe) bond lengths in **10** (average 2.310(2) Å) and $[Pt(dppe)(\mu\text{-}PPh_2)]_2[Cl]_2$ (2.331(3) Å)[11] indicates that the μ-PPh_2 ligand has a greater trans influence than μ-PHMes, consistent with the results from the ^{31}P NMR analysis above.

No close intermolecular contacts or unusual packing was observed in the structures of **8** or **9**, so their lack of solubility, and that of **5**, remains mysterious. The μ-PHR group is present in these compounds and in Woollins' insoluble[29] $[Pt(PPh_2Me)_2(\mu\text{-}PHPh)]_2{}^{4+}$, but $[Pt(PHPh_2)(\mu\text{-}PPh_2)Cl)]_2$ and $[Pd(PH_2Cy)(\mu\text{-}PHCy)Cl]_2$, mentioned above,[6,11] as well as **10**, are soluble in common solvents. However, Leoni et al. recently reported that $\{Pt[PH(t\text{-}Bu)_2][\mu\text{-}P(t\text{-}Bu)_2]H\}_2$ is only sparingly soluble,[30] and an understanding of the effect of ligand substituents on the solubility of such dimers is evidently not yet available.

In conclusion, the primary phosphine complex *cis*-$Pt(PH_2Mes)_2Cl_2$ (**4**) decomposes under mild conditions to form the phosphido-bridged Pt(II) dimer $[Pt(PH_2Mes)(\mu\text{-}PHMes)Cl]_2$ (**5**), which, although insoluble, reacts with other phosphine ligands to give complexes **6**−**10**. NMR and X-ray structural data have been used to characterize the properties of the μ-phosphido ligand in this series of compounds. Comparison of precursors **3** and **4** with the stable PH_2Mes^* complexes **1** and **2** suggests that a cis geometry (probably related to the steric bulk of the phosphine ligands) is required for dehydrochlorination and the formation of bridging phosphido complexes. We are continuing to explore the reactivity of **5** and the related phosphido complexes **6**−**10**, both as precursors to phosphinidene ligands by further proton transfer from phosphorus and as model intermediates for olefin hydrophosphination.

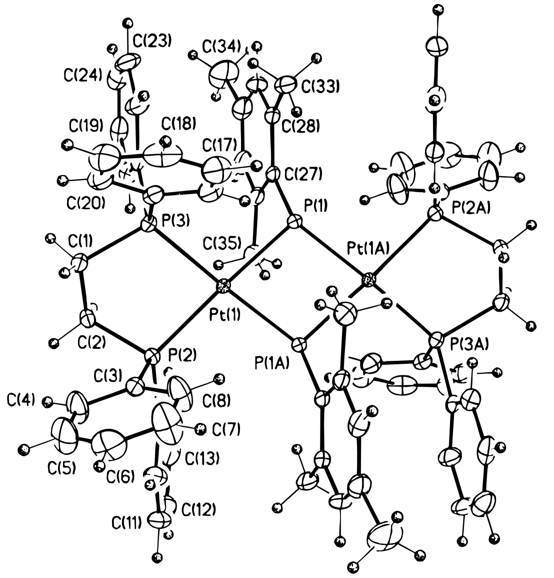

Figure 5. ORTEP diagram for $[Pt(dppe)(\mu\text{-}PHMes)]_2[Cl]_2 \cdot 2CH_2Cl_2 \cdot 2H_2O$ (**10-Cl**$\cdot 2CH_2Cl_2 \cdot 2H_2O$). Only the cation is shown. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

Experimental Section

General Considerations. Unless noted otherwise, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. All solvents were dried and distilled prior to use from Na/benzophenone (petroleum ether (bp 38−53 °C), ether, THF, toluene) or CaH_2 (CH_2Cl_2).

NMR spectra of all solutions examined in this study were recorded by using a Varian Unity Plus 300 spectrometer. ^1H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz. Unless noted otherwise, peaks in NMR spectra are singlets.

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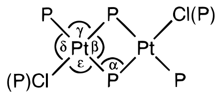
(30) Leoni, P.; Manetti, S.; Pasquali, M. *Inorg. Chem.* **1995**, *34*, 749−752.

Table 2. Selected Bond Lengths (Å) for Phosphido-Bridged Platinum Dimers

complex	Pt---Pt	Pt−PR$_3$	Pt−PR$_2$[a]	Pt−PR$_2$[b]	Pt−Cl
[Pt(PEt$_3$)(μ-PHMes)Cl]$_2$ (**8**)	3.60	2.311(2)	2.323(2)	2.265(2)	2.376(2)
[Pt(PPh$_3$)(μ-PHMes)Cl]$_2$ (**9**)	3.60	2.311(2)	2.318(2)	2.268(2)	2.355(2)
[Pt(PHPh$_2$)(μ-PPh$_2$)Cl]$_2$·C$_3$H$_6$O[c]	3.585(1)	2.313(3)	2.329(3)	2.260(3)	2.379(4)
[Pt(dppe)(μ-PPh$_2$)]$_2$[Cl]$_2$·2.5C$_2$H$_4$Cl$_2$[c]	3.699(1)	2.331(3)	2.362(3)		
		2.331(3)	2.335(3)		
[Pt(dppe)(μ-PHMes)]$_2$[Cl]$_2$·2CH$_2$Cl$_2$·2H$_2$O (**10-Cl**·2CH$_2$Cl$_2$·2H$_2$O)	3.70	2.302(2)	2.356(2)		
		2.318(2)	2.348(2)		
[Pt(PPh$_2$Me)$_2$(μ-PHPh)]$_2$[Cl]$_4$·1.5CH$_2$Cl$_2$[d]	3.7	2.341(3)	2.319(3)		
		2.338(3)	2.330(3)		
[Pt(PPh$_2$Me)$_2$(μ-PHPh)]$_2$[Cl]$_2$·[PhPO$_2$OH]$_2$·[PhPO(OH)$_2$][d]	3.7	2.336(1)	2.334(1)		
		2.339(2)	2.326(2)		

[a] Trans to PR$_3$. [b] Trans to Cl. [c] Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349−1354. [d] Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chim. Acta* **1990**, *172*, 159−163.

Table 3. Selected Bond Angles (deg) for Phosphido-Bridged Platinum Dimers



complex	α	β	γ	δ	ϵ
[Pt(PEt$_3$)(μ-PHMes)Cl]$_2$ (**8**)	103.58(9)	76.42(9)	101.38(9)	88.73(9)	93.47(9)
[Pt(PPh$_3$)(μ-PHMes)Cl]$_2$ (**9**)	103.32(6)	76.68(6)	97.28(5)	94.33(6)	91.57(6)
[Pt(PHPh$_2$)(μ-PPh$_2$)Cl]$_2$·C$_3$H$_6$O[a]	102.8(0)	77.2(0)	94.8(1)	93.2(1)	94.8(1)
[Pt(dppe)(μ-PPh$_2$)]$_2$[Cl]$_2$·2.5C$_2$H$_4$Cl$_2$[a]	103.9(0)	76.1(0)	99.6(1)		
			101.9(1)		
[Pt(dppe)(μ-PHMes)]$_2$[Cl]$_2$·2CH$_2$Cl$_2$·2H$_2$O (**10-Cl**·2CH$_2$Cl$_2$·2H$_2$O)	103.81(6)	76.19(6)	99.34(6)		
			101.24(6)		
[Pt(PPh$_2$Me)$_2$(μ-PHPh)]$_2$[Cl]$_4$·1.5CH$_2$Cl$_2$[b]	104.9(1)	75.1(1)	95.5(1)		
			93.5(1)		
[Pt(PPh$_2$Me)$_2$(μ-PHPh)]$_2$[Cl]$_2$·[PhPO$_2$OH]$_2$·[PhPO(OH)$_2$][b]	105.4(1)	74.6(1)	95.9(1)		
			93.3(1)		

[a] Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349−1354. [b] Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chim. Acta* **1990**, *172*, 159−163.

Solid-state ^{31}P CP/MAS spectra were obtained using Bruker MSL-200 (B_0 = 4.7 T) and AMX-400 (B_0 = 9.4 T) spectrometers. Powdered samples were packed into 7 mm o.d. (4.7 T) or 4 mm o.d. (9.4 T) zirconia rotors. Spectra were acquired after cross-polarization and under high-power proton decoupling and are referenced with respect to external H$_3$PO$_4$ (85%) via external NH$_4$H$_2$PO$_4$ at 0.8 ppm. The isotropic positions were determined as the peaks invariant to changes in MAS rates or the strength of the applied magnetic field.

IR spectra were recorded on a Perkin-Elmer 1600 series FTIR machine. Only the ν_{PH} values (when observed) are reported; full IR spectra are given in the Supporting Information. GC−MS spectra were obtained on a Hewlett-Packard 5890 Series II instrument. Conductivity measurements were done by using a Fisher Digital Conductivity Meter. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory, Oneida Research Services, Inc. (complex **5**), or Quantitative Technologies, Inc. (complex **10**). Low-resolution FAB mass spectroscopy was performed by S. L. Mullen on a VG ZAB-SE instrument at the University of Illinois. MS results are reported in *m*/*z* units and percent intensity, and assignments are made using the most intense peak in an envelope, calculated[31] for the isotopomer containing the most abundant isotopes ^{194}Pt and ^{35}Cl.

Unless noted otherwise, reagents were from commercial suppliers. The following compounds were made by the literature procedures: PH$_2$Mes*,[32] PH$_2$Mes,[33] PH$_2$Is,[34] Pt(COD)Cl$_2$,[35] Pt(dppe)Cl$_2$,[24] [Pt(dppe)(μ-OH)]$_2$[BF$_4$]$_2$.[25]

[*trans*-Pd(PH$_2$Mes*)$_2$Cl$_2$] (1). In the air, a solution of PH$_2$Mes* (152 mg, 0.55 mmol) in 5 mL of toluene was added, with stirring, to a suspension of Pd(PhCN)$_2$Cl$_2$ (100 mg, 0.26 mmol) in 15 mL of toluene. The orange solution instantly lightened, and on complete addition it was lemon yellow with some orange solid remaining. After 3.5 h the reaction mixture was filtered through Celite, which was washed with 2 × 5 mL of toluene. The solvent was removed from the orange filtrate with a rotary evaporator. Crystallization of the light orange residue from hot toluene/petroleum ether at −80 °C gave 114 mg (60% yield) of yellow solid in three crops. The compound may also be recrystallized from chloroform/petroleum ether or dichloromethane/petroleum ether. It may also be prepared directly from PdCl$_2$ and PH$_2$Mes* in hot toluene or in acidic aqueous ethanol. ^{1}H NMR (C$_6$D$_6$): δ 7.51 (4H, Ar), 6.4−5.1 (m, 4H, PH$_2$), 1.66 (36H, *o*-*t*-Bu), 1.19 (18H, *p*-*t*-Bu). In the ^{13}C{^{1}H} NMR spectra of both **1** and **2** (see below), the multiplicities reported for the Mes* aryl resonances refer to apparent splitting patterns. Accordingly, the values reported for *J* do not reflect true coupling constants. For a more detailed discussion of these AXX′ spin systems, see ref 8. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 156.7 (t, J = 3.6, *o* Ar), 152.8 (*p* Ar), 123.8 (t, J = 4.4, Ar), 114.3 (broad, Ar), 38.7 (*C*Me$_3$), 35.4 (*C*Me$_3$), 33.9 (C*Me*$_3$), 31.3 (C*Me*$_3$). ^{31}P NMR (CDCl$_3$): δ −66.2 (m). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −66.2. IR (KBr): 2410 cm^{-1}. Anal. Calcd for C$_{36}$H$_{62}$Cl$_2$P$_2$Pd: C, 58.89; H, 8.53. Found: C, 58.94; H, 8.59.

[*trans*-Pt(PH$_2$Mes*)$_2$Cl$_2$] (2). A slurry of PH$_2$Mes* (1000 mg, 3.59 mmol) in 40 mL of EtOH was added to a red solution of K$_2$PtCl$_4$ (745 mg, 1.79 mmol) in 15 mL of degassed water. The resulting pink slurry was stirred for 4 days, after which most of the red color had disappeared. In the air, the mixture was filtered on a fine frit and washed with water. The solid was dissolved in CH$_2$Cl$_2$, and the resulting solution was dried over MgSO$_4$. The solvent was removed in vacuo to give 1138 mg of pale yellow powder (77%). An analytical sample was recrystallized from CH$_2$Cl$_2$/petroleum ether to give light yellow feathery crystals. ^{1}H NMR (CDCl$_3$): δ 7.52 (4H, Ar), 6.34−5.05 (m, 4H, PH$_2$), 1.69 (36H,

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(31) Isotope Version 1.6, by Les Arnold, University of Waikato, New Zealand, 1991.
(32) Cowley, A. H.; Norman, N. C.; Pakulski, M. *Inorg. Synth.* **1990**, *27*, 235−240.
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(34) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156−1163.
(35) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521−6528.

o t-Bu), 1.31 (18H, *p t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.9 (t, J = 3.3, *o* Ar), 152.8 (*p* Ar), 123.7 (t, J = 4.7, Ar), 113.1 (t, J = 23.1, Ar), 38.8 ($\mathit{C}Me_3$), 35.3 ($\mathit{C}Me_3$), 33.8 ($C\mathit{Me}_3$), 31.3 ($C\mathit{Me}_3$). ^{31}P NMR ($CDCl_3$): δ −64.8 (m, $^1J_{PtP}$ = 2707). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −64.8 ($^1J_{PtP}$ = 2707). IR (KBr): 2409 cm^{-1}. Anal. Calcd for $C_{36}H_{62}Cl_2P_2Pt$: C, 52.54; H, 7.61. Found: C, 52.23; H, 7.72.

***cis*-Pt(PH_2Is)$_2$$Cl_2$ (3).** A solution of PH_2Is (316 mg, 1.34 mmol) in CH_2Cl_2 (1 mL) was added to a slurry of Pt(COD)Cl_2 (200 mg, 0.53 mmol) in CH_2Cl_2 (5 mL) to give a white suspension. The reaction mixture was stirred for 2 h. The solvent was removed in vacuo, and the residue was washed with petroleum ether to give 230 mg (60% yield) of a white solid. Complex **3** was not obtained in analytically pure form; attempted recrystallization or chromatography on silica was unsuccessful. ^1H NMR (CD_2Cl_2): δ 7.20 (d, J = 4, 4H, Ar), 4.95 (m, 4H, PH_2), 3.14 (septet, J = 6.5, 4H, *o*-C*H*(CH_3)$_2$), 2.90 (septet, J = 7, 2H, *p*-C*H*(CH_3)$_2$), 1.30 (d, J = 6.5, 24H, *o*-CH(C*H*$_3$)$_2$), 1.22 (d, J = 6.9, 12H, *p*-CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 154.6 (Ar), 153.0 (Ar), 122.7 (Ar), 35.0 (*C*HMe$_2$), 33.4 (*C*HMe$_2$), 24.4 (Me), 24.0 (Me). The ipso Ar C peak was not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −80.6 ($^1J_{PtP}$ = 3317). ^{31}P NMR (CD_2Cl_2): δ −80.6 (m, $^1J_{PtP}$ = 3317). IR (KBr): 2399, 2367 cm^{-1}.

***cis*-Pt(PH_2Mes)$_2$$Cl_2$ (4).** A solution of PH_2Mes (24 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) was added to Pt(COD)Cl_2 (30 mg, 0.08 mmol) slurried in CH_2Cl_2 (1 mL), and the resulting mixture was stirred for 2 min to give a yellow solution. The solvent was removed to afford 38 mg of an off-white residue, which was washed with diethyl ether (15 mL). ^1H NMR (CD_2Cl_2): δ 6.89 (m, 4H, Ar), 5.04 (m, 4H, PH_2), 2.36 (m, 12H, *o*-CH_3), 2.23 (6H, *p*-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −82.7 ($^1J_{PtP}$ = 3340). ^{31}P NMR (CD_2Cl_2): δ −82.7 (m, $^1J_{PtP}$ = 3340). Attempted recrystallization of the complex from a CH_2Cl_2/Et_2O mixture gave insoluble **5**. Attempts at purifying complex **4** by chromatography on silica were unsuccessful.

[Pt(PH_2Mes)(μ-PHMes)Cl]$_2$ (5). A slurry of Pt(COD)Cl_2 (50 mg, 0.13 mmol) in CH_2Cl_2 (4 mL) was mixed with PH_2Mes (56 mg, 0.37 mmol) and stirred for 3 h, during which time an insoluble solid precipitated. The solid was collected, washed with diethyl ether (2 × 10 mL), and dried in vacuo to afford 98 mg (80% yield) of the off-white product. Anal. Calcd for $C_{36}H_{50}Cl_2P_4Pt_2$: C, 40.49; H, 4.73; Cl, 6.64. Found: C, 39.78; H, 4.64; Cl, 6.78. IR (KBr): 2366 cm^{-1}. ^{31}P CP/MAS NMR: δ −67 (m, $^1J_{PtP}$ = 1960), −247 (m, $^1J_{PtP}$ = 1954, 2503). Low-resolution FAB MS (3-NBA): 1052.0 [20, (M − Me)$^+$], 991.0 [18, (M − 5Me −H)$^+$], 961.0 [15, (M − 7Me)$^+$], 903.9 [28, (M − Mes − 3Me)$^+$], 856.9 [18, (M − Mes − 6Me)$^+$], 841.9 [20, (M − Mes − 7Me)$^+$], 763.0 [20, (M − 2PH_2Mes − H)$^+$]. Melting point: >250 °C.

The GC−MS spectrum of the mother liquor, separated from **5** by distillation at room temperature, showed one peak with *m*/*z* 108, 93, 80, 67, 54, 39, 32 (COD). The mother liquor was titrated with a 0.0999 M methanol solution of KOH with thymol blue used as an indicator.[36] In two separate experiments, 1.9 and 1.6 equiv of an acid were formed per equivalent of complex **5**.

Synthesis of 5 from K_2PtCl_4. A solution of K_2PtCl_4 (500 mg, 1.2 mmol) in H_2O (30 mL) was treated with PH_2Mes (385 mg, 2.5 mmol) to give a yellow solid, which was collected and washed with water (40 mL) and petroleum ether (20 mL) to give 500 mg (47% yield) of complex **5**. The $^{31}P\{^1H\}$ CP/MAS NMR spectrum showed that **5** was contaminated by complex **4**: δ −67 (m), −85 (complex **4**), −247 (m). Elemental analysis also showed that this sample was impure: Anal. Calcd for $C_{36}H_{50}Cl_2P_4Pt_2$: C, 40.49; H, 4.73. Found: C, 45.83; H, 5.67. IR (KBr): 2367 cm^{-1}. X-ray powder diffraction showed that the complex was amorphous. Titration of the mother liquor in two separate experiments showed that 1.7 and 1.9 equiv of an acid were formed per equivalent of dimer **5**.

Synthesis of 5 in the Presence of Et_3N. A solution of Et_3N (27 mg, 0.27 mmol) in THF (2 mL) was added to the solution obtained by mixing a slurry of Pt(COD)Cl_2 (50 mg, 0.13 mmol) and PH_2Mes (40 mg, 0.27 mmol). A yellow solid precipitated immediately. It was collected and dried in vacuo. IR (KBr): 2348 cm^{-1}. We do not understand the origin of the small differences in the P−H stretching frequency observed between this and other samples of **5** prepared in different ways.

PD_2Mes. MesBr (10 g, 50.2 mmol) was dissolved in THF (150 mL) and cooled to −78 °C. Cold (−78 °C) *n*-BuLi (34.0 mL of 1.6 M hexane solution, 54 mmol) was added, and the resulting mixture was stirred for 2 h at −78 °C. This cold mixture was added slowly to a solution of PCl_3 (7.55 g, 55.0 mmol) in THF (15 mL) at −78 °C. The mixture was warmed to room temperature; the volatile materials were pumped off, and the residue was extracted with diethyl ether (2 × 50 mL). The diethyl ether solution was added to a slurry of $LiAlD_4$ (4.2 g, 10.0 mmol) in diethyl ether (100 mL) at −78 °C and stirred for 30 min. During this time it was warmed to room temperature and then quenched with a saturated aqueous solution of NH_4Cl (40 mL). The organic phase was separated and dried over $MgSO_4$. The solvent was removed, and the yellow viscous residue was distilled under vacuum to give 3.4 g (43% yield) of PD_2Mes. Analysis of the $^{31}P\{^1H\}$ NMR spectrum suggested that the product was a mixture of PD_2Mes (δ −157.8 (five-line multiplet, $^1J_{PD}$ = 32), 80%), PHDMes (−156.7 (three-line multiplet, $^1J_{PD}$ = 32), 15%), and PH_2Mes (−155.7, 5%).

[Pt(PD_2Mes)(μ-PDMes)Cl]$_2$ (5-D). A slurry of Pt(COD)Cl_2 (370 mg, 0.99 mmol) in CH_2Cl_2 (3 mL) and PD_2Mes (318 mg, 2.1 mmol) were mixed together and stirred for 10 min, during which time a white solid precipitated. The solvent was decanted, and the solid was washed with CH_2Cl_2 (10 mL) and petroleum ether (5 mL) to give 340 mg (69% yield) of the title complex. Anal. Calcd for $C_{36}H_{44}D_6Cl_2P_4Pt_2$: C, 40.26; H, 5.26; Cl, 6.6. Found: C, 39.30; H, 4.77; Cl, 9.19. IR (KBr): 2384 cm^{-1} (weak). $^{31}P\{^1H\}$ CP/MAS NMR: δ −67 (m), −85 (complex **4-D** present as an impurity), −247 (m).

[Pt(PH_2Mes)$_2$(μ-PHMes)]$_2$[Cl]$_2$ (6). Complex **5** (80 mg, 0.08 mmol) was slurried in CH_2Cl_2 (1.5 mL). Addition of PH_2Mes (68 mg, 0.45 mmol) resulted in a yellow solution. $^{31}P\{^1H\}$ NMR (CH_2Cl_2) (20 °C): δ −76.0 (br), −147.0 (br), −215.0 (br). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) (−60 °C): δ −76.0 (m), −147.0, −215.0 (br).

[Pt(PEt_3)$_2$(μ-PHMes)]$_2$[Cl]$_2$ (7). Complex **5** (40 mg, 0.04 mmol) was slurried in CH_2Cl_2 (1.5 mL). Addition of PEt_3 (30 mg, 0.25 mmol) resulted in a yellow solution. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 14.6 (m), −12.4, −152.0, −252.2 (m).

Solution Conductivity Measurements on 6 and 7. Complex **5** (32 mg, 0.03 mmol) was slurried in CH_3NO_2 (30 mL). Addition of PH_2Mes (15 mg, 0.1 mmol) led to a yellow solution, whose specific conductivity was 0.146 Ω^{-1}. In a similar experiment PEt_3 (10 mg, 0.13 mmol) was added to a slurry of **5** (32 mg, 0.03 mmol) in CH_3NO_2 (30 mL) to give a yellow solution, whose specific conductivity was 0.156 Ω^{-1}. With the concentrations and apparatus used, these values correspond to molar conductivities of 146 and 156 Ω^{-1} cm^2 mol^{-1}, respectively.

[Pt(PEt_3)(μ-PHMes)Cl]$_2$ (8). Addition of PEt_3 (40 mg, 0.34 mmol) to a slurry of **5** (100 mg, 0.094 mmol) in CH_2Cl_2 (10 mL) resulted in a yellow solution, from which 50 mg (54% yield) of X-ray-quality crystals were obtained by addition of diethyl ether (5 mL) at room temperature over a period of a few days. Anal. Calcd for $C_{30}H_{54}Cl_2P_4Pt_2$: C, 36.03; H, 5.46. Found: C, 35.93; H, 5.13. IR (KBr): 2374 cm^{-1}. Low-resolution FAB MS (3-NBA): 1081.3 [30, (M − 2Cl + PH_2Mes + H)$^+$], 927.2 [49, (M − 2Cl − H)$^+$], 720.0 [15, (M − 2Cl − PEt_3 − 6Me)$^+$], 632.0 [15, (M − 2Cl −2PEt_3 − 4Me)$^+$], 603.0 [26, (M − 2Cl − 2PEt_3 − 6Me + H)$^+$].

[Pt(PPh_3)(μ-PHMes)Cl]$_2$ (9). PPh_3 (210 mg, 0.8 mmol) was added to a slurry of **5** (200 mg, 0.19 mmol) in THF (10 mL), and the resulting mixture was heated at 55 °C for 8 days. During this time an insoluble yellow solid, some of which was X-ray-quality crystals, formed. It was collected, washed with THF (2 × 10 mL), and dried under vacuum to give 120 mg (53% yield) of complex **9**. Anal. Calcd for $C_{54}H_{54}Cl_2P_4Pt_2$: C, 50.35; H, 4.23. Found: C, 50.42; H, 4.25. IR (KBr): 2380 cm^{-1}. Low-resolution FAB MS (3-NBA): *m*/*z* 1369.0 [10, (M − 2Cl + PH_2Mes + H)$^+$], 1252.1 [61, (M − Cl)$^+$], 1216.2 [44, (M − 2Cl)$^+$].

[Pt(dppe)(μ-PHMes)]$_2$[Cl]$_2$ (10-Cl). A solution of dppe (62 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was added to complex **5** (70 mg, 0.07 mmol) to afford a yellow solution. Addition of diethyl ether (1 mL) precipitated a white solid, which was collected and dried to give 105 mg (76% yield) of **10-Cl**. The $^{31}P\{^1H\}$ NMR spectrum showed that a mixture of isomers **10a**,**b** and [Pt(dppe)$_2$]Cl_2 (**13**) was formed. Attempts

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[36] Kucharsky, J.; Safarik, L. *Titrations in Non-Aqueous Solutions*; Elsevier: New York, 1965; pp 97−98.

at separating **10-Cl** from **13** by recrystallization or by chromatography were unsuccessful, but on one occasion X-ray-quality crystals of **10-Cl** were grown by diffusion of diethyl ether into a CH_2Cl_2 solution at room temperature. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) for the mixture of **10-Cl** and **13**: δ 55.2 (m), 51.6 (m), 47.2 ($^1J_{PtP}$ = 2374, **13**), −243.3 (m), −273.9 (m).

X-ray Crystallographic Studies on Complexes 8, 9, and 10-Cl·2CH$_2$Cl$_2$·2H$_2$O. Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences were uniquely consistent with the reported space groups for **8** and **9**. No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **10**. The structure was solved and refined in the centrosymmetric space group, which yielded chemically reasonable and computationally stable results. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were applied to the data sets. In each case, the compound molecule was centered on an inversion point. A methylene chloride solvent molecule and an adventitious water molecule were located in the asymmetric unit of **10**. The remaining peaks in the difference map of **9** (maximum 1.72 e Å^{-3}) occur at positions <1 Å from the platinum atom and were considered as noise. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions except on the solvent molecules of **10**, which were ignored. All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

[Pt(dppe)(PH$_2$Mes)Cl][BF$_4$] (11). To a slurry of Pt(dppe)Cl_2 (480 mg, 0.72 mmol) in CH_2Cl_2 (15 mL) was added a solution of $AgBF_4$ (140 mg, 0.72 mmol) in CH_3CN (4 mL). AgCl precipitated immediately and was filtered off. Then, PH_2Mes (25 mg, 0.16 mmol) was added to the filtrate to give a pale yellow solution. The solution was concentrated to ca. 5 mL, and diethyl ether (3 mL) was added. A white solid precipitated over a period of a few hours and was filtered and dried under vacuum to give 450 mg of complex **11** (72% yield). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CH_3CN): δ 51.3 (d, $^2J_{PP}$ = 398, $^1J_{PtP}$ = 2612), 41.5 (d, $^2J_{PP}$ = 18, $^1J_{PtP}$ = 3288), −70.5 (dd, $^2J_{PP}$ = 398, $^2J_{PP}$ = 18, $^1J_{PtP}$ = 2180).

[Pt(dppe)(μ-PHMes)]$_2$[BF$_4$]$_2$ (10-BF$_4$). Complex **11** (40 mg, 0.04 mmol) was slurried in THF (2 mL), and Et_3N (0.006 mL, 0.04 mmol) was added to give a yellow solution. Addition of petroleum ether precipitated a white solid. The solution was decanted, and the solid was washed with H_2O (10 mL), washed with ether (50 mL), and dried under vacuum to give 65 mg (68% yield) of **10-BF$_4$** as a mixture of isomers. Anal. Calcd for $C_{70}H_{72}B_2F_8P_6Pt_2$: C, 50.55; H, 4.37. Found: C, 50.20; H, 4.53.

Because of the large $^{31}P-^{31}P$ coupling, the resonances in the ^1H and ^{13}C NMR spectra are not first-order multiplets. Therefore, the multiplicities reported refer to apparent splitting patterns, and the values reported for J do not reflect true coupling constants. Data from the $^1H\{^{31}P\}$ NMR spectrum were used to assign the J_{PH} couplings reported. ^1H NMR (CD_2Cl_2): δ 8.02 (dm, J = 2.3, J_{PH} = 10.0, 8H, *m* or *o* Ar, isomer **a**), 7.91 (dd, J = 8.1, J_{PH} = 12.3, 8H, *m* or *o* Ar, isomer **b**), 7.83 (m, 12H, *m* or *o* Ar + *p* Ar, **a**), 7.64 (m, 12H, *m* or *o* Ar + *p* Ar, **b**), 7.36 (t, J = 8, 4H, *p* Ar, **b**), 7.19 (t, J = 7.2, 4H, *p* Ar, **a**), 7.11 (dt, J = 7.5, J_{PH} = 2.7, 8H, *m* or *o* Ar, **b**), 6.93 (dt, J = 7.8, J_{PH} = 2.7, 8H, *m* or *o* Ar, **a**), 6.83 (dd, J = 7.8, J_{PH} = 12.3, 8H, *m* or *o* Ar, **b**), 6.63 (dd, J = 7.8, J_{PH} = 12.3, 8H, *m* or *o* Ar, **a**), 6.21 (2H, Mes, **b**), 5.91 [4H, Mes, **a**; in $CDCl_3$ this signal is resolved as two peaks, δ 6.03 (2H) and 5.79 (2H)], 5.66 (2H, Mes, **b**), 2.95 (6H, Me, **a**), 2.50 (br m, 4H, CH_2, **a**), 2.36 (6H, Me, **b**), 2.25 (br m, 4H, CH_2, **b**), 2.12 (6H, Me, **b**), 2.08 (6H, Me, **a**), 1.9 (br m, 4H, CH_2, **b**), 1.7 (br, 4H, CH_2, **a**), 1.40 (6H, Me, **b**), 1.28 (6H, Me, **a**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 141.0 (Ar), 140.2 (Ar), 140.0 (Ar), 139.5 (Ar), 134.9 (d, J = 11.6, Ar), 134.2 (Ar), 133.2 (Ar), 132.6 (Ar), 132.1 (Ar), 131.6 (d, J = 11, Ar), 131.2 (Ar), 131.0 (Ar), 130.4 (d, J = 25.0), 129.3 (m, Ar), 128.6 (Ar), 127.1 (Ar), 126.9 (Ar), 126.2 (m, Ar), 125.5 (d, J = 11, Ar), 124.7 (Ar), 32.5 (m, CH_2), 32.0 (m, CH_2), 30.5 (m, CH_2), 30.0 (m, CH_2), 26.4 (m, Me), 25.8 (m, Me), 23.7 (Me), 22.8 (Me), 21.8 (Me), 20.8 (d, J = 4, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.3 (m), 51.6 (m), −251.1 (m), −275.1 (m).

Synthesis of 10-BF$_4$ from [Pt(dppe)(μ-OH)]$_2$[BF$_4$]$_2$. To a solution of [Pt(dppe)(μ-OH)]$_2$[BF$_4$]$_2$ (30 mg, 0.022 mmol) in CH_2Cl_2 (1.5 mL) was added PH_2Mes (7 mg, 0.046 mmol) to afford a pale yellow solution. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 55.3 (m), 51.6 (m), −251.1 (m), −275.1 (m).

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, H-atom coordinates, and all bond distances and angles for **8**, **9**, and **10-Cl**·2CH$_2$Cl$_2$·2H$_2$O and text giving additional IR, mass spectral, and X-ray powder diffraction data (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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