Cyclometalation of Dimesitylphosphine in Cationic Palladium(II) and Platinum(II) Complexes: P−H vs C−H Activation

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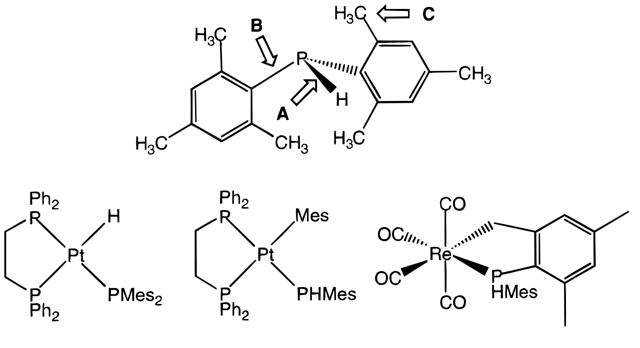
The cationic complexes [M(dppe)(R)($PHMes_2$)][OTf] (M = Pd, R = Me (**1**), Ph (**2**); M = Pt, R = Me (**3**), Et (**4**); dppe = $Ph_2PCH_2CH_2PPh_2$, Mes = 2,4,6-$Me_3C_6H_2$, OTf = OSO_2CF_3) were prepared by the reaction of the corresponding M(dppe)(R)(X) (X = Cl, I) with AgOTf and $PHMes_2$. When they were allowed to stand in THF or CH_2Cl_2 solution, the Pd complexes underwent cyclometalation, forming [Pd(dppe)($CH_2C_6H_2(Me)_2PHMes$)][OTf] (**5**). Thermolysis of Pt complexes **3** and **4** gave [Pt(dppe)($CH_2C_6H_2(Me)_2PHMes$)][OTf] (**6**), along with ethylene in the latter case. Reaction of Pt(dppe)(Et)(Cl) with AgOTf generated $[Pt(dppe)(H)]_2^{2+}$, which on treatment with $PHMes_2$ also yielded **6**. Treatment of **1**, **2** and **3**, **4** with triflic acid gave **5** and **6**, respectively. The cyclometalation of **1** is acid-catalyzed; the intermediacy of $[Pd(dppe)(PHMes_2)]^{2+}$ in these reactions was supported by formation of **5** from sources of the $[Pd(dppe)]^{2+}$ fragment and dimesitylphosphine.

Introduction

The chemistry of secondary phosphines (PHR_2) is usually dominated by the reactive P−H bond. Oxidative addition of this bond or deprotonation of coordinated secondary phosphines often leads to phosphido complexes.[1] Recently, for example, we showed that treatment of Pt(dppe)(*trans*-stilbene) with dimesitylphosphine ($PHMes_2$; Mes = 2,4,6-$Me_3C_6H_2$) led to initial formation of Pt(dppe)($PMes_2$)(H) (dppe = $Ph_2PCH_2CH_2PPh_2$; reaction at site A in Chart 1). However, this was followed by an unusual P−C oxidative addition (site B) to give the thermodynamic product Pt(dppe)(Mes)(PHMes).[2] Another potentially reactive site (C) in dimesitylphosphine is the ortho-substituted methyl group, as observed recently in rhenium carbonyl chemistry.[3] Trimesitylphosphine ($PMes_3$) readily undergoes analogous cyclometalation reactions[4] at Pd(II) and Pt(II),[5] and the Pd complex $[Pd(CH_2C_6H_2(Me)_2PMes_2)(\mu\text{-}OAc)]_2$ and related compounds are excellent catalyst precursors for the Heck reaction.[6] Here we report cyclometalation of dimesitylphosphine at Pd(II) and Pt(II) centers, in which the methyl C−H bond is activated selectively in the presence of the P−H bond. Evidence for an acid-catalyzed cyclometalation pathway involving cationic, coordinatively unsaturated intermediates is also presented.

Chart 1. Three Potentially Reactive Sites in Dimesitylphosphine and Metal Complexes Formed from It by Activation of P−H, P−C, and C−H Bonds, Respectively



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[1] For examples, see: (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1964**, 2433−2445. (b) Hayter, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 3046−3053. (c) Bader, A.; Nullmeyers, T.; Pabel, M.; Salem, G.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1995**, *34*, 384−389. (d) Leoni, P. *Organometallics* **1993**, *12*, 2432−2434. (e) Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, England, 1990; Vol. 1; pp 567−641.

[2] Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125−127.

[3] Florke, U.; Haupt, H.-J. *Z. Kristallogr. New Cryst. Struct.* **1998**, *213*, 269−270.

[4] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 297−300. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424.

[5] (a) Dias, S. A.; Alyea, E. C. *Transition Met. Chem.* **1979**, *4*, 205−206. (b) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Organometallics* **1989**, *8*, 1188−1191. (c) Alyea, E. C.; Malito, J. *J. Organomet. Chem.* **1988**, *340*, 119−126. (d) We found (see the Supporting Information) that reaction of $PHMes_2$ with $Pd(OAc)_2$ did not give analogous cyclometalated complexes.

[6] (a) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Ofele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357−1364. (b) Herrmann, W. A.; Bohm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23−41.

10.1021/om000164o CCC: $19.00
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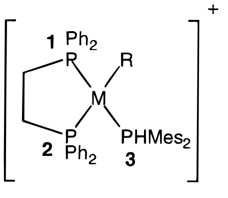
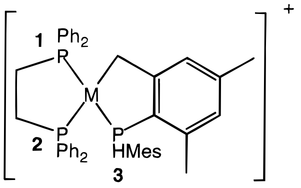
Table 1. Selected NMR and IR Data for Complexes 1−6 and 9−10[a,b]



1-4, **9-10**

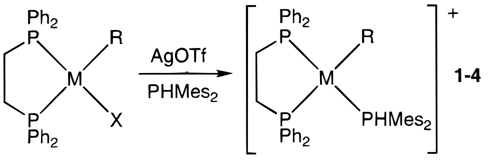


5-6

compd (M, R)	$\delta(P_1)$ (J_{Pt-P})	$\delta(P_2)$ (J_{Pt-P})	$\delta(P_3)$ (J_{Pt-P})	J_{12}	J_{13}	J_{23}	δ(PH)	J_{PH}	ν(PH)
1 (Pd, Me)[c]	59.5	42.7	−47.2	33	367	26	6.52	357, 12	2318
2 (Pd, Ph)	50.6	44.6	−49.9	24	361	*b*	6.38	358, 19	2329
3 (Pt, Me)	54.9 (2846)	49.6 (1692)	−42.8 (2553)	4	379	17	7.01	378	*b*
4 (Pt, Et)	53.6 (3011)	47.4 (1506)	−43.6 (2713)	4	375	17	7.09	382	*b*
9 (Pd, Cl)	62.8	65.5	−43.3	4	418	23	6.14	369, 13	2402
10 (Pd, NCMe)[d]	67.3	67.0	−43.9	*b*	337	20	5.92	386, 10	2397
5 (Pd)	54.7	43.8	−14.8	29	339	30	6.53	364, 12	2381
6 (Pt)	50.1 (2767)	44.2 (1788)	−17.7 (2632)	7	352	15	*b*	362[e]	2390

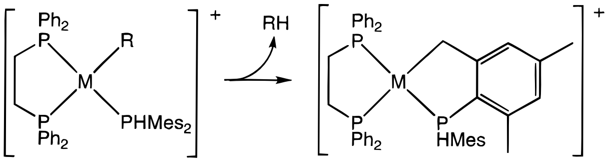
[a] Solvents: CD_2Cl_2 for **1**, **2**, **5**, **6**, and **10**; acetone-d_6 for **3**, **4**, and **9**. ^{31}P NMR chemical shift reference: external 85% H_3PO_4. Coupling constants are in Hz. IR data are in cm^{-1} for KBr pellets. [b] Not observed. [c] For the $^{13}CH_3$-labeled **1a**, $J_{P_2-C} = 80$ Hz. [d] Dication. [e] From the ^{31}P NMR spectrum.

Scheme 1



M = Pd, X = Cl, R = Me (**1**); X = I, R = $^{13}CH_3$ (**1a**), Ph (**2**)
M = Pt, X = Cl, R = Me (**3**), Et (**4**)

Scheme 2



M = Pd, R = Me (**1**), $^{13}CH_3$ (**1a**), Ph (**2**)
M = Pt, R = Me (**3**)

M = Pd (**5**)
M = Pt (**6**)

Results and Discussion

The complexes [Pd(dppe)(Me)(PHMes$_2$)][OTf] (**1**; OTf = OSO_2CF_3), [Pd(dppe)(Ph)(PHMes$_2$)][X] (**2**), and [Pt(dppe)(Me)(PHMes$_2$)][OTf] (**3**) were prepared by the reaction of Pd(dppe)(R)(X′) (R = Ph, X′ = I; R = Me, X′ = Cl, I; X = BF_4, OTf) and Pt(dppe)(Me)(Cl) with AgOTf or $AgBF_4$ and subsequent addition of PHMes$_2$ (Scheme 1). The synthesis of [Pt(dppe)(Et)(PHMes$_2$)][OTf] (**4**) requires that PHMes$_2$ be added *before* AgOTf (see below). The complexes were isolated in good yields as yellow crystalline solids and characterized by spectroscopy and by elemental analysis. The ^{31}P NMR data for **1**−**4** as well as selected ^{1}H NMR and IR data characterizing the PH groups are summarized in Table 1.

On standing in THF or CH_2Cl_2 solution over a period of 2−5 days, complexes **1** and **2** started to decompose; heating or prolonged standing at room temperature led to complete reaction. The decomposition rates varied widely, depending on the sample (see below), and depended on the solvent; qualitatively, reaction occurred faster in THF or CH_2Cl_2 than in acetone and did not occur at all in acetonitrile.[7] Spiking confirmed that the same Pd-containing product formed from **1** and **2**, suggesting the loss of the phenyl and methyl ligands and formation of the cyclometalated complex [Pd(dppe)-($CH_2C_6H_2(Me)_2$PHMes)][OTf] (**5**) (Scheme 2).

The loss of methane and benzene from **1** and **2** was observed directly. The reaction of Pd(dba)(dppe)[8] (formed in situ by the addition of 1 equiv of dppe to Pd(dba)$_2$) with $^{13}CH_3I$ gave Pd(dppe)($^{13}CH_3$)(I) in good yield.[9] This labeled precursor was converted to [Pd(dppe)($^{13}CH_3$)(PHMes$_2$)][OTf] (**1a**), which decomposed in CD_2Cl_2 in a sealed NMR tube after 2 days to give $^{13}CH_4$, observed as a doublet at δ 0.26 ($^1J_{CH} = 126$) in the ^{1}H NMR spectrum and a quintet at δ −4.39 ($^1J_{CH} = 126$) in the ^{13}C NMR spectrum.[10] No ^{13}C incorporation in the decomposition product was observed. Phenyl complex **2** decomposed in CD_2Cl_2 to give benzene (δ 7.35), confirmed by adding a small amount of benzene to the solution.

Cationic complex **5** was obtained as a yellow solid by recrystallization from THF/petroleum ether and characterized by NMR and IR spectroscopy and FAB mass spectroscopy as well as by X-ray crystallography. The dppe $^{31}P\{^1H\}$ NMR signals (Table 1, CD_2Cl_2) of **5** do not change much as compared to **1** and **2**; the phosphine peak, however, shifts downfield to δ −14.8 ($^2J_{PP} = 339$, 30 Hz), which is consistent with the formation of a chelating ligand.[11] The P−H coupling constant ($^1J_{PH} = 371$ Hz) indicates that the proton is not removed from the phosphorus. The FAB mass spectrum shows the parent ion peak at *m*/*z* 773.1. The diastereotopic Pd−CH_2 protons give rise to an AB quartet at δ 3.51−3.43 ($^2J_{HH} = 15$ Hz) in the $^1H\{^{31}P\}$ NMR spectrum (CD_2Cl_2), consistent with data for other cyclometalated com-

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(7) See the Supporting Information for details. See also ref 18.

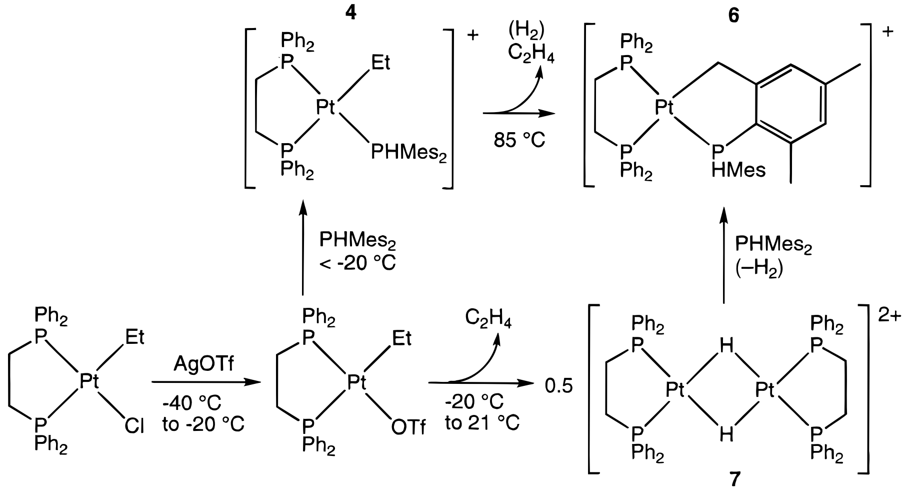
(8) Herrmann, W. A.; Thiel, W. R.; Brossner, C.; Ofele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51−60.

(9) See the Supporting Information for synthetic details. For a similar preparation of Pd(bipy)(Me)(I), see: Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210−220.

(10) (a) Alei, M. J.; Wageman, W. E. *J. Chem. Phys.* **1978**, *68*, 783−784. (b) Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8−10.

(11) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435−1439.

Scheme 3



pounds.[12] In the $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) the cyclometalated CH_2 group gives rise to a doublet at δ 40.6 ($^2J_{PC}$ = 82 Hz).

Thermolysis of the Pt cations **3** and **4** led to the formation of the analogous cyclometalated Pt complex $[Pt(dppe)(CH_2C_6H_2(Me)_2PHMes)][OTf]$ (**6**) (Schemes 2 and 3). Ethylene was also observed by ^1H NMR in a sealed NMR tube experiment with **4**, which suggests that heating of **4** leads to β-elimination and formation of $[Pt(dppe)(H)(PHMes_2)]^+$, which decomposes with the loss of H_2 (see below). Spectral data for **6** (Table 1) are similar to those for the Pd analogue **5**, including an AB pattern of $^1H\{^{31}P\}$ NMR signals for the Pt–CH_2 protons at δ 3.56 ($^2J_{HH}$ = 17, $^2J_{Pt-H}$ = 67 Hz, $CDCl_3$) and 3.42 ($^2J_{Pt-H}$ = 54 Hz).

Cyclometalated complex **6** could also be prepared at room temperature by adding AgOTf to Pt(dppe)(Et)(Cl) *before* addition of $PHMes_2$. However, when the reaction was conducted at −78 or −40 °C ethyl phosphine complex **4** was formed (Scheme 3). To better understand this behavior, we added AgOTf to a solution of Pt(dppe)(Et)(Cl) in CH_2Cl_2; this gave the dinuclear dication $[Pt(dppe)(H)]_2^{2+}$ (**7**; Scheme 3) as the major product. The $^{31}P\{^1H\}$ NMR (CH_2Cl_2) spectrum of this reaction mixture showed a major signal at δ 38.9 (J_{Pt-P} = 4167 Hz), and the ^1H NMR (CD_2Cl_2) spectrum included a hydride resonance at δ −4.39 ($^2J_{PH}$ = 10, 64, $^1J_{Pt-H}$ = 592 Hz). Several related dications have been prepared with bulkier, more electron-rich diphosphines.[13] This reaction was not clean (for example, another hydride signal was observed at δ −4.11), and complex **7** decomposed in solution. Treatment of the reaction mixture with $PHMes_2$ gave **6** as the major product (Scheme 3).

Treatment of Pt(dppe)(Et)(Cl) with AgOTf at −78 °C in CD_2Cl_2, followed by warming of the solution, was monitored by NMR (Scheme 3). From −40 to −30 °C, most of the Pt(dppe)(Et)(Cl) was converted to what is presumably Pt(dppe)(Et)(OTf) ($^{31}P\{^1H\}$ NMR δ 52.7 (J_{Pt-P} = 1644 Hz), 46.7 (J_{Pt-P} = 4886 Hz); compare Pt(dppe)(Me)(OTf), $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 56.0 (J_{Pt-P} = 1853 Hz), 36.0 (J_{Pt-P} = 4646 Hz)).[14] At −20 °C, the chloro complex had all reacted and signals were observed due to $[Pt(dppe)(H)]_2^{2+}$ (**7**) and to ethylene (δ 5.39). From −20 to 21 °C, signals due to **7** and ethylene increased in intensity, although Pt(dppe)(Et)(OTf) remained the major constituent of the reaction mixture. These observations are consistent with the synthetic results; ethyl complex **4** is presumably formed from Pt(dppe)(Et)(OTf) at low temperature before it decomposes by β-elimination.

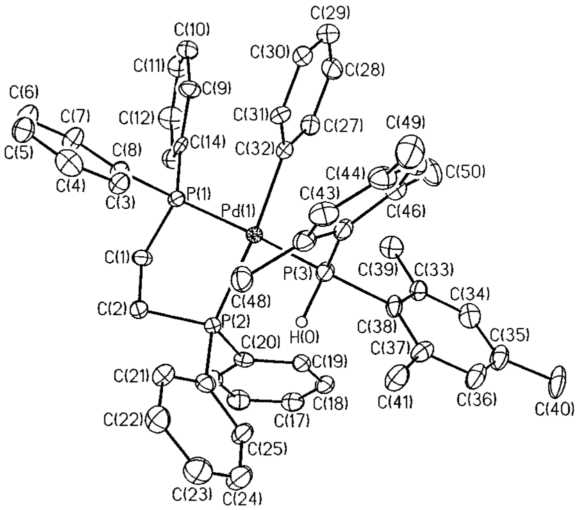


Figure 1. ORTEP diagram of **2** with thermal ellipsoids at 30% probability. Tetrafluoroborate anion and hydrogen atoms, except the hydrogen atom of the phosphine, are omitted for clarity.

The cyclometalated complex **5** and precursors **2** and **4** were also characterized by X-ray crystallography. The structure of **4** was suitable only for establishing the atom connectivity and is reported in the Supporting Information. The crystal structures of **2** as the tetrafluoroborate salt and **5** as the triflate salt with cocrystallized toluene are shown in Figures 1 and 2. Data collection and structure refinement are summarized in Table 2, selected bond lengths and angles appear in Table 3, and additional details are given in the Experimental Section and the Supporting Information.

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[12] (a) Fornies, J.; Martin, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Organometallics* **1996**, *15*, 1826−1833. (b) Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359−2361.

[13] Mole, L.; Spencer, J. L.; Litster, S. A.; Redhouse, A. D.; Carr, N.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 2315−2321.

[14] Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408−1418.

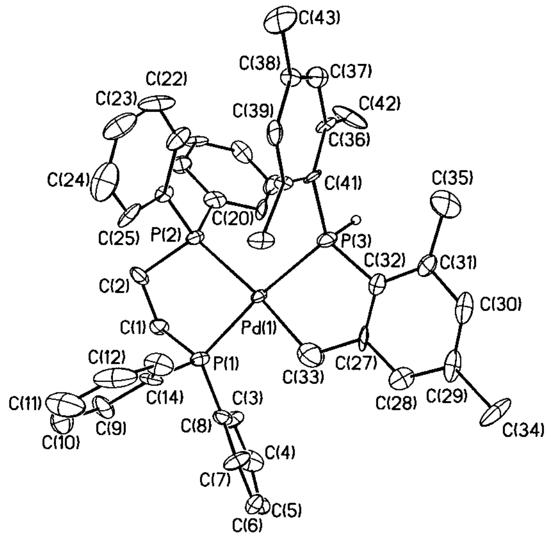


Figure 2. ORTEP diagram of **5**·$0.5C_7H_8$ with thermal ellipsoids at 50% probability. Triflate anion, solvent molecule, and hydrogen atoms, except the hydrogen atom of the phosphine, are omitted for clarity.

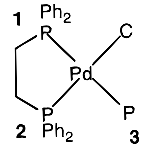
Table 2. Crystallographic Data for $[(Pd(dppe)(Ph)(PHMes_2)][BF_4]$ (2) and $[Pd(dppe)(CH_2C_6H_2(Me)_2PHMes)][CF_3SO_3]$ (5)·0.5 Toluene.

	2	5·0.5(toluene)
formula	$C_{50}H_{52}F_4P_3BPd$	$C_{48.5}H_{50}F_3O_3P_3PdS$
fw	939.04	969.26
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.1139(2)	11.4171(2)
b, Å	13.0924(2)	14.0653(2)
c, Å	13.9935(2)	16.5162(2)
α, deg	88.5821(4)	86.0325(8)
β, deg	82.5610(3)	82.0153(3)
γ, deg	83.9039(6)	72.8459(8)
V, Å^3	2188.09(5)	2508.58(5)
Z	2	2
cryst color, habit	yellow plate	colorless plate
D(calcd), g cm^{-3}	1.425	1.283
μ(Mo Kα), cm^{-1}	5.86	5.55
temp, K	203(3)	173(2)
diffractometer	Siemens P4/CCD	
radiation	Mo Kα (λ = 0.710 73 Å)	
R(*F*), %^{a}	5.67	7.56
R(*wF*^{2}), %^{a}	16.54	25.85

^{a} Quantity minimized: $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

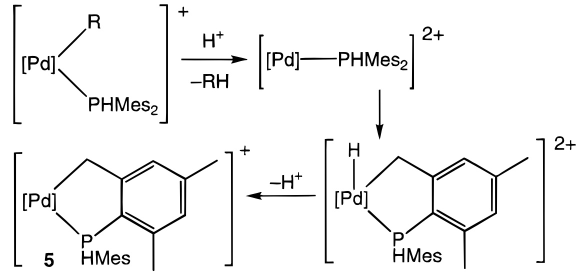
Bulky ligands and the associated steric interactions are known to promote cyclometalation.[4] The shortest calculated Pd−C and Pd−H distances for dimesitylphosphine in **2**, 3.447(7) and 2.845(7) Å, respectively, do not suggest any unusual interaction between the mesityl Me groups and the metal center. However, it was noted previously that due to the repulsive nature of axial CH−Pd interactions such positions are normally avoided; therefore, the presence of hydrogen in an axial position (Mes Me group above the square plane) may serve as an indication of steric strain.[15]

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Pd(dppe)(Ph)(PHMes_2)][BF_4]$ (2) and $[Pd(dppe)(CH_2C_6H_2(Me)_2PHMes)][OTf]$ (5)



	2	5
Pd−P(1)	2.3013(15)	2.381(3)
Pd−P(2)	2.3559(15)	2.415(3)
Pd−P(3)	2.3446(16)	2.380(3)
Pd−C	2.055(6)	2.137(13)
P(1)−Pd−P(2)	85.12(5)	84.54(9)
P(3)−Pd−C	91.97(17)	82.7(3)
P(3)−Pd−P(2)	94.82(6)	102.74(10)
C−Pd−P(1)	88.21(17)	90.0(3)

Scheme 4^a



^{a} [Pd] = Pd(dppe).

Several significant structural changes occur on conversion of **2** to cyclometalated **5** (Table 3). As expected, the C−Pd−PHMes$_2$ angle decreases from 91.97(17)° in **2** to 82.7(3)° in the five-membered ring of **5**. Perhaps to relieve strain in this ring, the Pd−P and Pd−C bond lengths in it are slightly longer than in precursor **2**. The Pd−P(dppe) bond lengths in **5** are also somewhat longer than in **2**; perhaps this occurs to minimize steric interactions with the relatively inflexible cyclometalated ring and its substituents. Other structural features, like the square-planar geometry and dppe bite angle, remain essentially unchanged.[16]

Mechanism of Cyclometalation. The erratic rates observed for cyclometalation suggested an acid-catalyzed mechanism (Scheme 4), analogous to a similar pathway proposed by Thorn in a related Pt(II) system.[17] Protonation of **1** or **2** by adventitious acid, followed by reductive elimination of CH_4 or C_6H_6, could give $[Pd(dppe)(PHMes_2)]^{2+}$ (**8**). Benzylic C−H activation followed by loss of a proton would then give **5**. According to this mechanism, added acid should speed up cyclometalation, added acid scavenger should slow it down, and the proposed intermediate, $[Pd(dppe)(PHMes_2)]^{2+}$, if prepared independently, should form cyclometalated **5**. These predictions were tested, as described below, and the results are consistent with the proposed mechanism.[18]

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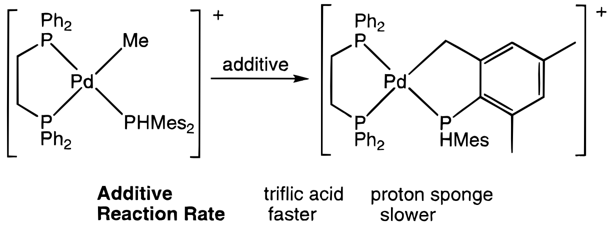
[15] (a) Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1414−1417. (b) As noted by a reviewer, more recent work has suggested that such M−H−C interactions have an attractive component. For a recent discussion, see: Hambley, T. W. *Inorg. Chem.* **1998**, *37*, 3767−3774.

[16] The average dppe−Pd bite angle is 85.03°; see: Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1529.

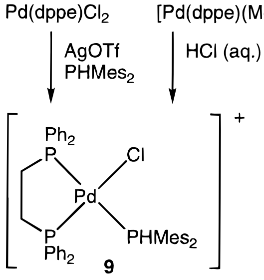
[17] Thorn, D. L. *Organometallics* **1998**, *17*, 348−352.

[18] The variation of cyclometalation rate with sample made it difficult to reliably establish the effect of added reagents, solvent, or conditions on the rate. To minimize these difficulties, when investigating one such variable, we used samples of **1** from the same synthetic batch, solvents from the same storage container, and groups of NMR tubes that had been cleaned and dried side by side.

Scheme 5



Scheme 6



1. Added Acid. In NMR tubes, three separate acetone solutions of **1** were treated with 1 equiv (1), 0.5 equiv (2), and 0.05 equiv (3) of triflic acid and then heated to 50 °C (Scheme 5). The reaction of the Pd−C bond with the strong acid is slow, according to ^{31}P NMR monitoring. After 5 h, no reaction was seen in sample 3 and in a control sample (4) containing no HOTf, while samples 1 and 2 showed 10% and 8% conversion to **5**, respectively. After 23 h of heating 70% conversion was observed for sample 1, 50% for sample 2, 13% for sample 3, and only a trace of **5** was seen for sample 4. After 72 h of heating samples 1 and 2 had reacted completely, a trace of **1** remained in sample 3, and 44% conversion was observed for sample 4.

2. Added Base. Proton Sponge (1,8-bis(dimethylamino)naphthalene) was chosen as a base, since it reacts very slowly with the coordinated dimesitylphosphine in **1**. Two samples of **1** in THF were prepared, 0.2 equiv of Proton Sponge was added to one of them, and the samples were heated to 50 °C (Scheme 5). After 2 days of heating, considerable cyclometalation (ca. 50%) occurred in the control sample, while no **5** formed in the sample containing Proton Sponge; instead, minor decomposition occurred. After 4 days of heating the base-free sample showed complete conversion to **5** and only a trace (less than 5%) of **5** was observed in the sample containing Proton Sponge.

3. The Proposed Intermediate [Pd(dppe)(PHMes$_2$)]$^{2+}$ (8). To generate **8**, we planned to abstract chloride from [Pd(dppe)(PHMes$_2$)(Cl)][OTf] (**9**), with Ag$^+$. Complex **9** was prepared either by treatment of **1** with aqueous HCl or by reaction of Pd(dppe)Cl$_2$ with AgOTf and PHMes$_2$ in THF (Scheme 6; see Table 1 for selected NMR and IR data). As desired, silver(I) salts removed chloride from **9**; the results depended on counterion and solvent (Scheme 7). Treatment of **9** with AgOTf in acetonitrile gave mostly [Pd(dppe)(PHMes$_2$)(NCMe)][OTf] (**10**), which was also the major product formed on reaction of 1 equiv of HOTf with **1** in acetonitrile or from Pd(dppe)Cl$_2$, AgOTf, and PHMes$_2$ in acetonitrile. Although this acetonitrile complex (Table 1) could not be obtained pure, it did not undergo cyclometalation to give **5**.

Reaction of **9** with AgOTf in THF gave PHMes$_2$ and the known Pd(dppe)(OTf)$_2$ (**11**).[19] A similar reaction in acetone gave **11**, PHMes$_2$, and a small amount of **5**; on standing, triflate complex **11** was slowly converted to **5**. Treatment of independently prepared **11** with PHMes$_2$ in THF or acetone gave **5** on heating or standing at room temperature. In acetone, [Pd(dppe)(PHMes$_2$)(OTf)][OTf] (**12**) was cleanly formed initially; the same complex is also apparently formed in THF, although the ^{31}P NMR spectra are not as well resolved as in acetone.[20] Reaction of **11** with PHMes$_2$ in acetonitrile, however, gives **10**. These results are consistent with the intermediacy of the fragments [Pd(dppe)(PHMes$_2$)(L)]$^{2+}$ and [Pd(dppe)(PHMes$_2$)(X)]$^+$ in cyclometalation and the requirement for a vacant coordination site in [Pd(dppe)(PHMes$_2$)]$^{2+}$ via dissociation of L (solvent) or X (counterion).

Reactions with more weakly coordinating anions are consistent with this idea (Scheme 7). Treatment of Pd(dppe)Cl$_2$ with 1.2 equiv of AgBF$_4$ and 1 equiv of PHMes$_2$ in THF gave a 1:4 ratio of cyclometalated **5** and chloro complex **9** after 2 days. Addition of another 0.8 equiv of AgBF$_4$ gave complete conversion to **5**. Similar reactions involving Pd(dppe)Cl$_2$, 2 equiv of AgBF$_4$, and 1 equiv of PHMes$_2$ in THF or acetone also afforded **5**, but the formation of 1 equiv of acid complicated isolation of the product. Attempts to run the reaction in the presence of base (for example, K$_2$CO$_3$), were not successful.

These experiments are consistent with the proposed acid-catalyzed mechanism, but do not rule out other possible pathways. For example, direct benzylic oxidative addition, followed by loss of RH, would give **5** (path A, Scheme 8).[21] Alternatively (path B), P−H oxidative addition and reductive elimination could form [Pd(dppe)(PMes$_2$)]$^+$. Benzylic oxidative addition and P−H reductive elimination would then yield **5**.

We attempted to test the latter mechanism by monitoring decomposition of [Pd(dppe)(^{13}CH$_3$)(PDMes$_2$)][OTf] (**1b**) by NMR. Assuming no complications from isotope effects, cyclometalation of **1b** via P−H activation (path B) should give ^{13}CH$_3$D, whereas C−H activation (path A) or an acid-catalyzed pathway (Scheme 4) should give ^{13}CH$_4$. Complex **1b** was prepared by H−D exchange between **1a** and D$_2$O. Unfortunately, when **1b** was heated, H−D scrambling was faster than cyclometalation and caused partial conversion to **1a** before cyclometalation occurred. NMR monitoring showed that the methane formed was mostly ^{13}CH$_4$ with ca. 5% CH$_3$D. In contrast, decomposition of **1b** formed by addition of DOTf to **1a** gave mostly ^{13}CH$_3$D with a small amount of ^{13}CH$_4$. Details of these experiments can be found in the Supporting Information, but the lability of the P−H(D) bond and its likely exchange with adventitious or deliberately added proton sources made them inconclusive; we cannot tell if the P−H(D) proton in **1** is incorporated in the methane formed.

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[20] Complex **12** is described as a triflate complex for convenience, although it is possible that solvent and/or water displaces triflate from Pd in **12**, as in acetonitrile complex **10**.

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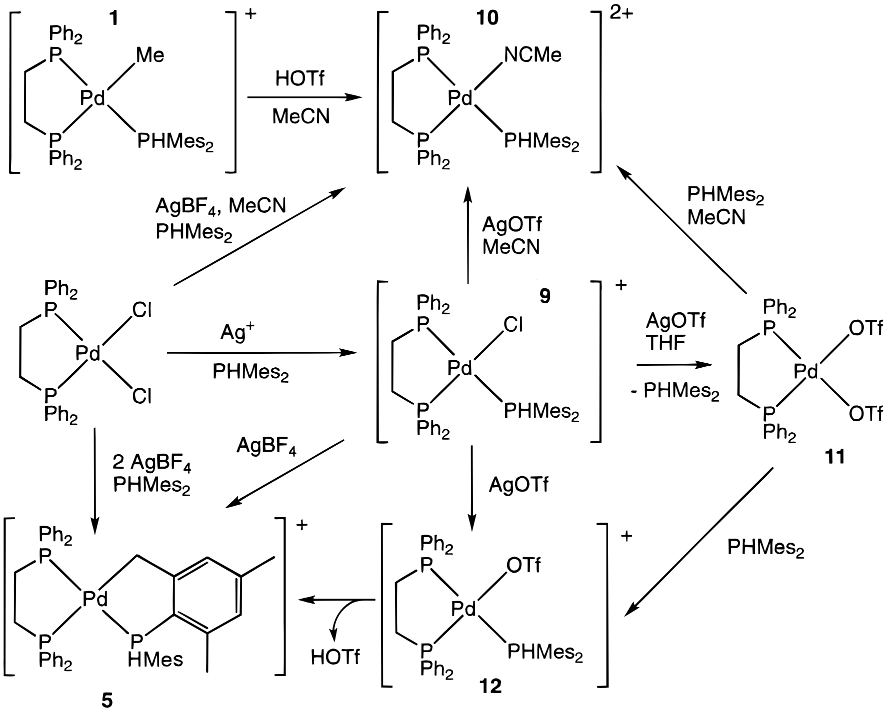
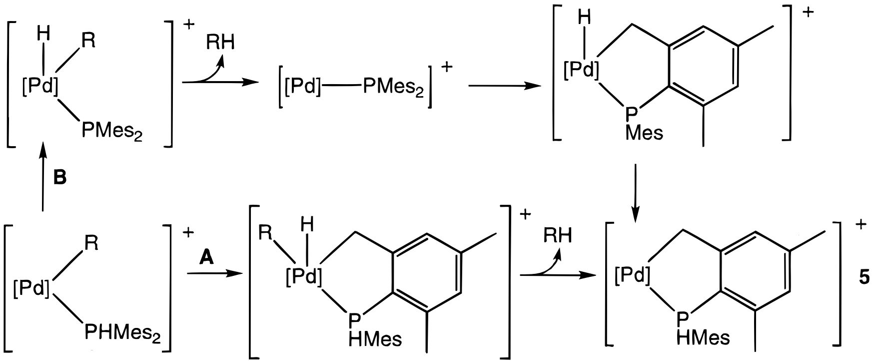
Scheme 7



Scheme 8



Conclusions

The cationic Pd(II) and Pt(II) complexes [M(dppe)(R)-(PHMes$_2$)]$^+$ (**1**−**4**) decompose by cyclometalation of a mesityl methyl group, while the usually reactive PH group remains intact in the final product. Mechanistic studies of cyclometalation of the Pd(II) complexes are consistent with an acid-catalyzed pathway via the coordinatively unsaturated fragment [Pd(dppe)(PHMes$_2$)]$^{2+}$. However, we have not been able to rule out other possible mechanisms or to establish the source or nature of the proposed acid catalyst.[22]

Experimental Section

General Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and toluene were dried and distilled before use by employing Na/benzophenone. CH$_2$Cl$_2$ was distilled from CaH$_2$. Acetone and acetonitrile were degassed by purging with N$_2$ and stored over molecular sieves.

Unless otherwise noted, all NMR spectra were recorded by using a Varian 300 MHz spectrometer. ^{1}H or ^{13}C NMR chemical shifts are reported vs Me$_4$Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H$_3$PO$_4$ (85%) used as an external reference. Coupling constants are reported in Hz. Unless otherwise noted, absolute values are reported for all experimental coupling constants. Unless otherwise noted, peaks in NMR spectra are singlets. Infrared spectra were recorded on KBr pellets using a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Low-resolution FAB mass spectroscopy was performed by S. L. Mullen on a VG ZAB-SE instrument at the University of Illinois.

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[22] A reviewer suggested that adventitious water might be the impurity responsible for catalyzing cyclometalation. There is precedent for this idea (see: Cave, G. W. V.; Fanizzi, F. P.; Deeth, R. J.; Errington, W.; Rourke, J. P. *Organometallics* **2000**, *19*, 1355−1364), and we cannot rule it out.

Unless otherwise noted, reagents were obtained from commercial suppliers. The following compounds were made by the literature procedures: Pd(dppe)(Ph)I,[23] Pd(dba)$_2$,[24] Pd(dppe)(Me)(Cl),[25] PHMes$_2$,[26] Pt(dppe)(Et)(Cl),[27] Pt(dppe)(Me)(Cl),[28] Pd(dppe)Cl$_2$,[29] and Pd(dppe)(OTf)$_2$.[19]

[Pd(dppe)(Me)(PHMes$_2$)][OTf] (1). Pd(dppe)(Me)(Cl) (118 mg, 0.21 mmol) was suspended in a mixture of 2 mL of THF and 0.5 mL of MeCN. AgOTf (55 mg, 0.21 mmol) and PHMes$_2$ (57 mg, 0.21 mmol) were introduced simultaneously with constant stirring to produce a dark gray precipitate. The reaction was protected from light. After 60 min of stirring the solution was filtered and its volume was reduced to 2 mL. Petroleum ether was added, and the solution was cooled to −25 °C. The product was obtained as 160 mg (80% yield) of yellow solid, which decomposed partially on attempted recrystallization. Anal. Calcd for $C_{46}H_{50}SO_3F_3P_3Pd$: C, 58.82; H, 5.37. Found: C, 57.26; H, 5.36. We were unable to obtain satisfactory analyses despite numerous attempts, presumably because of this decomposition.

^{1}H NMR (CD$_2$Cl$_2$): δ 7.66−7.28 (m, 20H, Ar), 6.77 (d, $^4J_{PH}$ = 3, 4H, Ar), 6.52 (dd, $^1J_{PH}$ = 357, $^3J_{PH}$ = 12, 1H, PH), 2.60−2.44 (m, 4H, dppe CH$_2$), 2.23 (6H, Mes), 2.17 (12H, Mes), 0.35 (ddd, $^3J_{PH}$ = 5, 6, 8, 3H, Me). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 142.4 (d, J_{PC} = 7), 142.0 (d, J_{PC} = 8), 141.5 (d, J_{PC} = 2), 133.7−133.4 (m), 133.3 (d, J_{PC} = 12), 133.1 (d, J_{PC} = 11), 132.6 (d, J_{PC} = 12), 132.1 (dd, J_{PC} = 45, 3), 130.8−130.6 (m), 130.6 (d, J_{PC} = 8), 129.9, 129.8 (d, J_{PC} = 11), 129.6, 129.4 (d, J_{PC} = 10), 128.2 (d, J_{PC} = 47), 28.3−27.1 (m, dppe CH$_2$), 23.3 (d, $^2J_{PC}$ = 9, Mes), 21.0 (Mes), 5.3 (d, $^2J_{PC}$ = 77, Me). IR: 3054, 2966, 2919, 2318 (PH), 1604, 1437, 1264, 1157, 1104, 1031, 853, 749.

[Pd(dppe)(^{13}CH$_3$)(PHMes$_2$)][OTf] (1a) was prepared similarly from Pd(dppe)(^{13}CH$_3$)(I). Selected spectral data: ^{1}H NMR (CD$_2$Cl$_2$) δ 0.35 (m, Me, $^1J_{CH}$ = 134); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 5.3 (dm, $^2J_{PC}$ = 80, Me).

[Pd(dppe)(Ph)(PHMes$_2$)][BF$_4$] (2). Pd(dppe)(Ph)(I) (46 mg, 0.07 mmol) was dissolved in THF. AgBF$_4$ (13 mg, 0.07 mmol) was added as a MeCN solution to produce a gray precipitate. The reaction mixture was protected from light and stirred for 15 min. It was then filtered, and PHMes$_2$ (18 mg, 0.07 mmol) was added with stirring to the pale yellow solution. After 60 min of stirring the solution was filtered and the volume of the solution was reduced to 3 mL. Petroleum ether was added, and cooling to −25 °C gave the product as 29 mg (52% yield) of yellow crystals. Additional recrystallization gave yellowish crystals of X-ray quality. Anal. Calcd for $C_{50}H_{52}BF_4P_3Pd$: C, 63.95; H, 5.58. Found: C, 63.83; H, 5.78.

^{1}H NMR (CD$_2$Cl$_2$): δ 7.58−7.34 (m, 16H, Ar), 7.31−7.21 (m, 4H, Ar), 6.66 (d, 4H, $^4J_{PH}$ = 3), 6.62−6.42 (m, 5H, Ar), 6.38 (dd, 1H, $^1J_{PH}$ = 358, $^3J_{PH}$ = 14), 2.52 (m, 4H, dppe CH$_2$), 2.17 (6H, Mes), 2.05 (br, 12H, Mes). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 154.0 (m, J_{PC} = 100, quat), 142.2 (d, J_{PC} = 8), 141.5 (quat), 136.7 (m), 133.7 (d, J_{PC} = 11), 132.8 (d, J_{PC} = 12), 132.2 (m), 130.3 (d, J_{PC} = 8), 129.7 (d, J_{PC} = 10), 129.5 (d, J_{PC} = 10), 129.2, 128.8 (d, J_{PC} = 12), 127.9, 127.8 (d, J_{PC} = 7), 123.6, 121.1 (m, J_{PC} = 45, quat), 27.7 (dd, J_{PC} = 26, 18, dppe CH$_2$), 26.6 (dd, J_{PC} = 26, 18, dppe CH$_2$), 23.2 (m, Mes), 21.0 (Mes). IR: 3052, 2966, 2918, 2329 (PH), 1602, 1563, 1469, 1435, 1103, 1053 (BF$_4$), 729, 693.

[Pt(dppe)(Me)(PHMes$_2$)][OTf] (3). To a slurry of Pt(dppe)(Me)(Cl) (201 mg, 0.312 mmol) in THF (10 mL) prepared in the air were added CH$_3$CN (0.5 mL), a solution of AgOTf (80 mg, 0.312 mmol) in THF (1 mL), and a solution of PHMes$_2$ in THF (2 mL), and the resulting purple mixture was stirred for 12 h. The reaction mixture was filtered through Celite to give a clear solution, and solvent was removed under vacuum. The solid residue was dissolved in toluene, and addition of diethyl ether and cooling to −25 °C gave the final product in three crops as 246 mg (77% yield) of white solid. Anal. Calcd for $C_{46}H_{50}F_3O_3P_3PtS$: C, 53.75; H, 4.90. Found: C, 53.52; H, 5.09.

^{1}H NMR (acetone-d_6): δ 7.88−7.78 (m, 4H, Ar), 7.74−7.58 (m, 10H, Ar), 7.54−7.38 (m, 6H, Ar), 7.01 (dm, $^1J_{PH}$ = 378, 1H, PH), 6.90 (4H, Ar), 3.04−2.60 (m, 4H, CH$_2$), 2.31 (12H, *o*-Me), 2.28 (6H, *p*-Me), 0.52−0.43 (m, $^2J_{Pt-H}$ = 60, 3H, Me). ^{13}C{^{1}H} NMR (acetone-d_6): δ 143.3−142.8 (m, quat Ar), 142.2 (d, J_{PC} = 2, quat Ar), 134.4−133.8 (m, Ar), 133.8−133.3 (m, Ar), 133.0 (d, J_{PC} = 3, Ar), 132.5 (d, J_{PC} = 2, Ar), 131.2 (d, J_{PC} = 8, Ar), 130.3 (d, J_{PC} = 11, Ar), 129.8 (d, J_{PC} = 10, Ar), 129.1 (quat Ar), 128.4 (quat Ar), 29.1−28.1 (m, dppe CH$_2$), 23.5 (d, J_{PC} = 9, *o*-Me), 21.0 (*p*-Me), −1.4 (dm, J_{PC} = 73, Me, Pt satellites were not resolved). IR: 3056, 2933, 1600, 1433, 1267, 1222, 1150, 1104, 1030, 877, 853, 821, 751, 695, 636, 532, 487, 433.

[Pt(dppe)(Et)(PHMes$_2$)][OTf] (4). To a slurry of Pt(dppe)(Et)(Cl) (196 mg, 0.30 mmol) in THF (2 mL) was added a solution of PHMes$_2$ (85 mg, 0.31 mmol) in THF (1 mL) followed by a solution of AgOTf (81 mg, 0.31 mmol) in 1 mL of THF. The resulting purple slurry was stirred for 2 h and then filtered through Celite to give a yellow solution. The solvent was removed under vacuum, the tan solid residue was dissolved in THF, and addition of diethyl ether and cooling to −30 °C gave the product in three crops as 210 mg of white, air-stable solid (68% yield). Anal. Calcd for $C_{47}H_{52}F_3O_3P_3PtS$: C, 54.18; H, 5.03. Found: C, 53.88; H, 5.03.

^{1}H NMR (acetone-d_6): δ 7.84−7.34 (m, 20H, Ar), 7.09 (dm, $^1J_{PH}$ = 382, 1H, PH), 6.85 (4H, Ar), 2.86−2.60 (m, 4H, dppe CH$_2$), 2.30 (br, 12H, *o*-Me), 2.23 (6H, *p*-Me), 1.52−1.18 (m, 2H, ethyl CH$_2$), 0.37−0.11 (m, 3H, ethyl CH$_3$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 143.3−143.0 (m, quat Ar), 142.3 (d, J_{PC} = 2, quat Ar), 134.7−134.1 (m, Ar), 134.1−133.4 (m, Ar), 133.1 (d, J_{PC} = 2, Ar), 132.7−132.4 (m, Ar), 131.3 (d, J_{PC} = 8, Ar), 130.6 (quat Ar), 130.3 (d, J_{PC} = 11, Ar), 129.9 (d, J_{PC} = 10, Ar), 128.7 (quat Ar), 127.9 (quat Ar), 29.1−28.0 (m, dppe CH$_2$),

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23.8−23.4 (m, *o*-Me), 21.0 (*p*-Me), 15.1 (d, $J_{PC} = 3$, ethyl CH_3), ethyl CH_2 was not resolved. IR: 3054, 2915, 1603, 1437, 1271, 1222, 1191, 1148, 1103, 1030, 877, 853, 821, 750, 695, 636, 531, 486, 432.

[Pd(dppe)(PH(Mes)(CH$_2$C$_6$H$_2$Me$_2$))][OTf] (5). [Pd(dppe)(Me)(PHMes$_2$)][OTf] (42 mg, 0.04 mmol) was dissolved in 1 mL of acetone, HOTf (395 μL, 1 vol % solution in acetone, 0.04 mmol) was added via microliter syringe, and the solution was heated for 3 days at 60 °C. The solution was filtered, diethyl ether was added, and cooling to −25 °C gave the product as 35 mg (85% yield) of orange solid. Slow evaporation of THF from a solution in toluene/THF (5:1) gave crystals of X-ray quality. Anal. Calcd for $C_{45}H_{46}SO_3F_3P_3Pd$: C, 58.54; H, 5.02. Found: C, 57.60; H, 5.25.

^{1}H NMR (CD_2Cl_2): δ 7.70−7.32 (m, 17H, Ar), 7.36−7.29 (m, 2H, Ar), 7.13−6.62 (m, 5H), 6.53 (dd, $^1J_{PH} = 364$, $^3J_{PH} = 12$, 1H, P−H), 3.54 (m, $^2J_{HH} = 15$, 1H, CH_2), 3.49 (m, $^2J_{HH} = 15$, 1H, CH_2), 2.64−2.30 (m, 4H, dppe CH_2), 2.27 (3H, Me), 2.25 (3H, Me), 1.94 (broad, 6H, Me), 1.92 (3H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.3 (m, $J_{PC} = 41$, Ar), 143.7, 142.7, 142.1, 141.7, 133.9−133.3 (m, Ar), 132.8−132.5 (m, Ar), 131.8 (d, $J_{PC} = 13$, Ar), 131.2 (m, Ar), 130.8−129.3 (m, Ar), 128.9−127.6 (m, Ar), 122.6, 122.0−121.6 (m), 120.0, 40.6 (d, $^2J_{PC} = 83$), 28.9−28.5 (m, dppe CH_2), 23.7−23.3 (m, Me), 22.8−22.4 (m, Me), 21.2−21.0 (m, Me), 21.1−20.0 (m, Me). IR: 3054, 3023, 2963, 2916, 2865, 2381 (PH), 1603, 1563, 1436, 1266 (OTf), 1223, 1151, 1104, 852, 809, 749, 694, 637. FAB-MS (3-NBA): 773.1 (M^+), 695.1, 587.1, 545.1, 476.0, 427.0.

[Pt(dppe)(PH(Mes)(CH$_2$C$_6$H$_2$Me$_2$))][OTf] (6). In the air, a 25 mL ampule was charged with a solution of [Pt(dppe)(Me)(PHMes$_2$)][OTf] (410 mg, 0.40 mmol) in $Cl_2HCCHCl_2$ (6 mL). The ampule was evacuated, and the solution was heated at 95−100 °C for 4 days. Solvent was then removed under reduced pressure to give the crude product as a white solid, which was redissolved in THF/toluene (1:1) and crystallized by the addition of diethyl ether and petroleum ether and cooling to −25 °C to give the product as 212 mg (53% yield) of white solid. Anal. Calcd for $C_{45}H_{46}SO_3F_3P_3Pt$: C, 53.41; H, 4.58. Found: C, 52.89; H, 4.93.

^{1}H NMR (CD_2Cl_2): δ 8.2−6.5 (m, 25H, Ar and PH), 3.8−3.2 (m, 2H, Pt−CH_2), 2.8−2.2 (m, 4H, dppe CH_2), 2.27 (3H, Me), 2.25 (3H, Me), 1.98 (br, 3H, Me), 1.91 (3H, Me), 1.89 (br, 3H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.9−157.6 (m), 144.1, 142.9−142.0 (m), 139.9, 134.2−134.0 (m), 133.8−133.3 (m), 133.0−132.6 (m), 131.9−131.7 (m), 131.2 (m), 130.9−130.4 (m), 130.1−129.1 (m), 128.1−127.1 (m), 126.0−125.2 (m), 122.6, 121.4, 120.9, 120.1, 35.5 (d, $^2J_{PC} = 76$, $^1J_{Pt-C} = 507$), 30.5 (dd, $J_{PC} = 16, 34$), 29.5 (dd, $J_{PC} = 15, 38$), 22.7 (broad), 22.0 (broad), 21.1 (m), 20.2 (m). IR: 3054, 3023, 2964, 2917, 2859, 2390, 1600, 1564, 1436, 1263, 1150, 1104, 1030, 852, 820, 751, 695.

[Pd(dppe)(Cl)(PHMes$_2$)][OTf] (9). To a slurry of Pd(dppe)Cl_2 (89 mg, 0.16 mmol) in 2 mL of THF/MeCN (10:1) was added AgOTf (40 mg, 0.16 mmol) and PHMes$_2$ (42 mg, 0.16 mmol), and the reaction mixture was stirred for 5 min. The solution was filtered, petroleum ether was added, and cooling to −30 °C gave the product as 136 mg (92% yield) of orange solid. Anal. Calcd for $C_{45}H_{47}P_3O_3F_3SClPd$: C, 56.36; H, 4.94. Found: C, 56.22; H, 5.30.

^{1}H NMR (CD_2Cl_2): δ 8.04−7.76 (m, 8H, Ph), 7.70−7.42 (m, 12H, Ph), 6.83 (d, 4H, $^4J_{PH} = 4$, Mes), 6.14 (dd, $^3J_{PH} = 13$, $^1J_{PH} = 369$, 1H, PH), 3.48−3.26 (m, 2H, CH_2), 2.85−2.62 (m, 2H, CH_2), 2.26 (broad, 12H, Me), 2.23 (broad, 6H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.5 (d, $J_{PC} = 8$), 142.2 (d, $J_{PC} = 3$), 133.8 (d, $J_{PC} = 3$), 133.5 (dd, $J_{PC} = 2, 11$), 133.2 (broad d, $J_{PC} = 11$), 132.9 (d, $J_{PC} = 3$), 130.8 (d, $J_{PC} = 8$), 129.9 (d, $J_{PC} = 12$), 129.8 (d, $J_{PC} = 12$), 127.6 (dm, $J_{PC} = 50$), 125.3 (dm, $J_{PC} = 56$), 24.3−23.9 (m), 23.7 (d, $J_{PC} = 88$), 21.1. IR: 3055, 3023, 2960, 2918, 2402 (P−H), 2294, 1603, 1558, 1437, 1259 (OTf), 1223, 1152, 1103, 1030, 853, 750.

[Pd(dppe)(PHMes$_2$)(NCMe)][X] (X = OTf, BF$_4$) (10). Method 1. To a solution of **9** (46 mg, 0.05 mmol) in 1 mL of MeCN was added AgOTf (12 mg, 0.05 mmol), and the resulting slurry was filtered to give an orange solution.

Method 2. To a slurry of Pd(dppe)Cl_2 (41 mg, 0.07 mmol) in 2 mL of MeCN was added AgOTf (37 mg, 0.14 mmol) and PHMes$_2$ (19 mg, 0.07 mmol), and the resulting slurry was stirred for 5 min. The reaction mixture was filtered to give an orange solution.

Method 3. To a slurry of Pd(dppe)Cl_2 (68 mg, 0.12 mmol) in 3 mL of THF was added AgBF$_4$ (23 mg, 0.12 mmol) in acetonitrile (1 mL) and PHMes$_2$ (32 mg, 0.12 mmol). No visible reaction occurred. The ^{31}P NMR spectrum of the reaction mixture showed PHMes$_2$ and a small amount of the product **10**. An additional 1.2 equiv of AgBF$_4$ was added to the reaction mixture, the solid dissolved, and the solution turned orange. The mixture was filtered, diethyl ether was added, and cooling to −25 °C gave a pale yellow solid which was washed with diethyl ether and dried under vacuum. The ^{31}P NMR spectrum of the solid showed the product as well as a small amount of "Pd(dppe)(BF$_4$)$_2$" ($^{31}P\{^1H\}$ NMR δ 77) and an unidentified impurity.

^{1}H NMR (CD_2Cl_2): δ 7.84−7.62 (m, 15H), 7.58−7.40 (m, 5H), 6.84 (d, 4H, $^4J_{PH} = 4$), 5.92 (dd, 1H, $^1J_{PH} = 386$, $^3J_{PH} = 10$), 3.38−3.16 (m, 2H, CH_2), 2.75−2.50 (m, 2H, CH_2), 2.24 (6H, Me), 2.17 (12H, Me), 1.83 (broad, 3H, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.3 (d, $J_{PC} = 3$), 142.2 (dd, $J_{PC} = 2, 9$), 134.6 (m), 134.0 (d, $J_{PC} = 3$), 133.6−132.9 (m), 131.4 (d, $J_{PC} = 9$), 131.9−130.6 (m), 130.3 (d, $J_{PC} = 12$), 128.6, 125.7 (dm, $J_{PC} = 50$), 124.6, 123.9−123.1 (m), 117.6 (dm, $J_{PC} = 51$, CN), 32.4 (dd, $J_{PC} = 13, 37$, CH_2), 23.3 (d, $^3J_{PC} = 9$, Me), 22.7 (dd, $J_{PC} = 8, 34$, CH_2), 21.1 (Me), 2.6 (m, Me). IR: 3058, 2965, 2923, 2319, 2291, 1603, 1558, 1438, 1410, 1380, 1269, 1158, 1104, 1030, 998, 931, 853, 817, 752, 723.

Crystallographic Structural Determination. Crystal data and data collection and refinement parameters are given in Table 2. No evidence of symmetry higher than triclinic was observed in the diffraction data of **2** and **5**. The centrosymmetric space group option $P\bar{1}$ was chosen for both structures, which yielded chemically reasonable and computationally stable results of refinement. The palladium atom in structure **2** was located by Patterson synthesis, and the structure of **5** was solved by direct methods. Both structures were completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Empirical SADABS absorption correction was applied to the data set of **5**. The asymmetric unit of **2** contains one palladium cation and a tetrafluoroborate anion, and the asymmetric unit of **5** contains one palladium cation, a triflate anion, and half of a molecule of toluene which is disordered over an inversion center. All non-hydrogen atoms, except C(50) of the disordered toluene molecule in **5**, were refined with anisotropic displacement parameters. The hydrogen atom on phosphorus in both structures was located from a difference map, and the thermal parameters were refined. The hydrogen atoms of the toluene molecule in **5** were ignored, and the remaining hydrogen atoms were treated as idealized contributions. The relatively high *R* factor of the structure of **5** may be attributed to the high thermal activity associated with the triflate counterion and the disordered toluene molecule. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.[30]

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Supporting Information Available: Details of the crystal structure determinations and additional experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] Sheldrick, G. Siemens XRD, Madison, WI.