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Synthesis and Structures of Palladium and Platinum A-Frame Complexes Bridged by a Novel Binucleating Ligand, *N*,*N*′-Bis[(2-diphenylphosphino)phenyl]formamidine

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A novel binucleating ligand, *N*,*N*′-bis[(2-diphenylphosphino)phenyl]formamidine (Hdpfam), has been prepared and utilized for the synthesis of homo- and heterobimetallic palladium/platinum complexes $M_2R_2(\mu\text{-}X)(\mu\text{-dpfam})$ (M = Pd, Pt; R = Me, *p*-Tol, Cl; X = Cl, Br, I; dpfam = *N*,*N*′-bis[(2-diphenylphosphino)phenyl]formamidinate). Treatment of Hdpfam with 2 equiv of MRX(tmeda) or MRX(cod) in the presence of tmeda produced the homobimetallic complexes. The heterobimetallic complex $PdPtMe_2(\mu\text{-}Cl)(\mu\text{-dpfam})$ was obtained by the reaction of PdMeCl(cod) with PtMe(dpfam), which was produced from $PtMe_2$(cod) and Hdpfam. The crystal structures of $Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-dpfam})$ and $Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dpfam})$ have been determined by X-ray analysis. The results indicate that both complexes have P−M−Cl−M−P A-frame structures, in which each metal center has a slightly distorted square-planar geometry and the nonbridging σ-donor ligands (Cl or Me) and μ-Cl are in a cis orientation. Treatment of $Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dpfam})$ with $NaBH_4$ gave the hydride-bridged complex $Pt_2Me_2(\mu\text{-}H)(\mu\text{-dpfam})$.

Introduction

Recently, catalysis using bimetallic complexes has attracted considerable interest.[1] Two metal centers in close proximity have the potential to have a cooperative effect, both improving the efficiency and selectivity of catalyzation and promoting reactions that are not possible using a single metal center. The chemistry of bimetallic metal complexes containing bridging ligands, such as bis(diphenylphosphino)methane (dppm) and (diphenylphosphino)pyridine, has developed remarkably over the last 30 years.[2] In particular, dipalladium and diplatinum complexes have received considerable attention.[3−5] However, the application of such complexes as catalysts is extremely rare.[6] We think the geometry of the bimetallic complexes may be responsible for this lack of catalytic activity. In several important reactions on a metal center, the existence of two ligands or vacant sites in a cis orientation is essential. Although dipalladium and diplatinum complexes are known to adopt several geometries,[2] other ligand molecules (Y) attach to metal centers in a trans orientation in all geometries, as illustrated in Chart 1. In contrast, binucleating tetradentate ligands have a natural preference for the cis arrangement of Y (Chart 1). Although there are only a few reports regarding the synthesis of this type of bimetallic complex,[7] such complexes have proven high

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(5) Recent examples for palladium and platinum heterobimetallic complexes: (a) Xu, C.; Anderson, G. K. *Organometallics* **1996**, *15*, 1760. (b) Xu, C.; Anderson, G. K. *Organometallics* **1994**, *13*, 3981. (c) Fallis, K. A.; Xu, C.; Anderson, G. K. *Organometallics* **1993**, *12*, 2243. For trimetallic complexes: (d) Tanase, T.; Begam, R. A. *Organometallics* **2001**, *20*, 106. (e) Tanase, T.; Takahata, H.; Ukaji, H.; Hasegawa, M.; Yamamoto, Y. *J. Organomet. Chem.* **1997**, *538*, 247. (f) Tanase, T.; Takahata, H.; Hasegawa, M.; Yamamoto, Y. *J. Organomet. Chem.* **1997**, *545−546*, 531.

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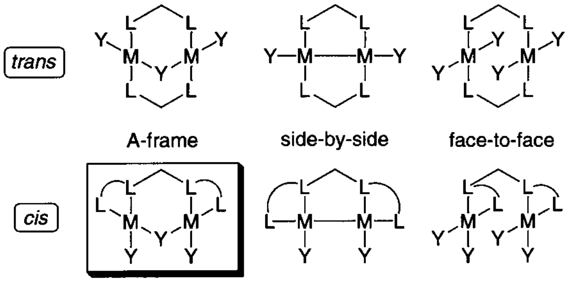
Chart 1

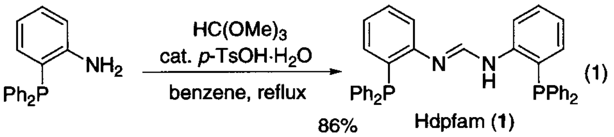


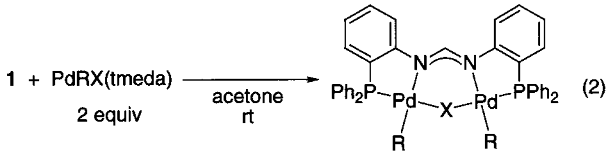
(M = metal, L = P or N, Y = other ligands)

efficiency in catalysis. Stanley reported a dirhodium complex bridged by a tetraphosphine ligand that exhibited higher regioselectivity and reactivity for the hydroformylation of α-olefins than the related monometallic complexes.[8] Here, we report on the preparation of a novel binucleating ligand for cis bimetallic complexes and the synthesis of several palladium and platinum A-frame complexes.

Results and Discussion

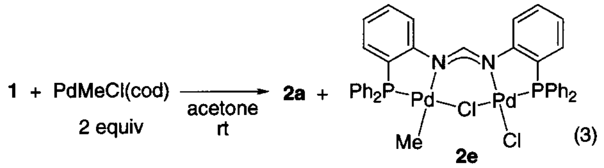
Synthesis of Homobimetallic Palladium and Platinum Complexes. *N*,*N*′-Bis[(2-diphenylphosphino)phenyl]formamidine (**1**, Hdpfam) was prepared by heating a mixture of 2-(diphenylphosphino)aniline and 0.5 equiv of trimethyl orthoformate in the presence of catalytic amounts of TsOH•H$_2$O (eq 1). Reactions with trialkyl orthoacetates or orthobenzoates did not give the corresponding amidines. Treatment of **1** with 2 equiv of PdRX(tmeda) (R = Me, *p*-Tol; X = Cl, Br, I; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in acetone at room temperature resulted in the formation of the dipalladium complex Pd$_2$R$_2$(μ-X)(μ-dpfam) (**2a**−**d**) (eq 2).



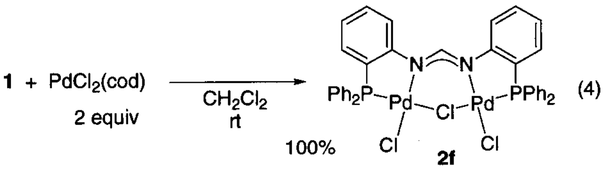


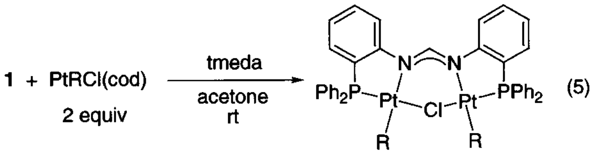
2a; R = Me, X = Cl (86%)
2b; R = *p*-Tol, X = Cl (86%)
2c; R = *p*-Tol, X = Br (71%)
2d; R = *p*-Tol, X = I (92%)

However, the reaction of **1** with the corresponding cycooctadiene complex PdMeCl(cod) gave the monomethyldipalladium complex **2e** as a major product (**2e**:**2a** = 80:20) (eq 3). The complex **2e** may be formed by cleavage of the palladium−carbon bond of **2a** with HCl. Since HCl was generated in equimolar amounts with **2a** as a byproduct, the monomethyldipalladium species **2e** was selectively obtained without the formation of the trichlorodipalladium complex **2f**. Actually, treatment of **2a** with a stoichiometric amount of HCl (formed from acetyl chloride and methanol) in benzene afforded the complex **2e**. Furthermore, the addition of excess amounts of bases, such as tmeda and diisopropylethylamine, suppressed the formation of **2e** in the reaction of **1** and PdMeCl(cod) to afford **2a** selectively (eq 3). The trichlorodipalladium compound **2f** was prepared by the reaction of **1** with 2 equiv of PdCl$_2$(cod) in CH$_2$Cl$_2$ (eq 4). In a similar manner, the dimethyl- and di-*p*-tolyldiplatinum complexes **3a** and **3b** were also obtained by the reaction of **1** with PtMeCl(cod) or Pt(*p*-Tol)Cl(cod) in the presence of tmeda in acetone (eq 5).



in the absence of amines; **2a**:**2e** = 20/80 (91%)
in the presence of tmeda; **2a**:**2e** = 100/0 (90%)
in the presence of *i*Pr$_2$NEt; **2a**:**2e** = 100/0 (78%)





3a; R = Me (88%)
3b; R = *p*-Tol (89%)

Characterizations of A-Frame Complexes. Crystallization of **2f** by vapor diffusion of diethyl ether into a solution of CH$_2$Cl$_2$ afforded a red crystal suitable for X-ray analysis. The lattice contains two molecules of CH$_2$Cl$_2$ per **2f**. There are no significant interactions between **2f** and the solvent molecules. The molecular structure of **2f** is shown in Figure 1, and selected bond distances and angles are presented in Table 1. The complex **2f** adopts a symmetrical A-frame structure with chlorine at the apex of "A" and two phosphines at the bottom. The μ-Cl ligand is positioned symmetrically relative to the metal centers with Pd(1)−Cl(1) = 2.405(4) Å and Pd(2)−Cl(1) = 2.398 Å, which is longer than the other Pd−Cl bond (Pd(1)−Cl(2) = 2.285(5) Å, Pd(2)−Cl(3) = 2.276(5) Å). Each palladium center has a square-planar geometry with two chloro ligands in a cis orientation. The N−Pd−P angles (84.0(4), 84.2(4)°) are

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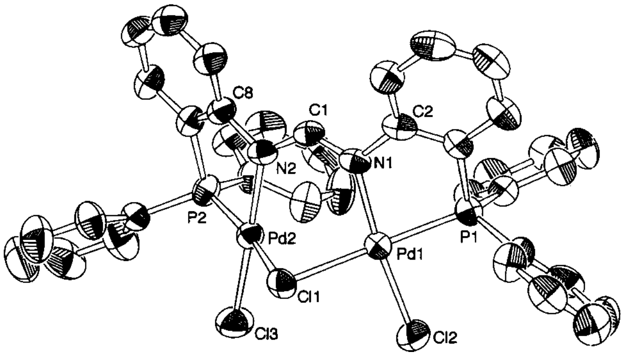

Figure 1. Molecular structure of $Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**2f**), showing 50% thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 2f

Pd(1)−C1(1)	2.405(4)	Pd(1)−C1(2)	2.285(5)
Pd(1)-P(1)	2.200(4)	Pd(1)−N(1)	2.04(1)
Pd(2)−Cl(1)	2.398(4)	Pd(2)−Cl(3)	2.276(5)
Pd(2)−P(2)	2.189(4)	Pd(2)−N(2)	2.05(1)
N(1)−C(1)	1.32(2)	N(2)−C(1)	1.31(2)
Cl(1)−Pd(1)-Cl(2)	93.4(2)	Cl(2)−Pd(1)−P(1)	90.1(2)
P(1)−Pd(1)−N(1)	84.0(4)	Cl(1)−Pd(1)−N(1)	93.3(4)
Cl(1)−Pd(1)−P(1)	166.0(2)	Cl(2)−Pd(1)−N(1)	172.7(4)
Pd(1)−N(1)−C(1)	126.0(10)	Pd(1)−N(1)−C(2)	116(1)
C(1)−N(1)−C(2)	115(1)		
Cl(1)−Pd(2)−Cl(3)	93.1(2)	Cl(3)−Pd(2)−P(2)	88.4(2)
P(2)−Pd(2)−N(2)	84.2(4)	Cl(1)−Pd(2)−N(2)	94.6(4)
Cl(1)−Pd(2)−P(2)	169.9(2)	Cl(3)−Pd(2)−N(2)	172.2(4)
Pd(2)−N(2)−C(1)	127(1)	Pd(2)−N(2)−C(8)	115.2(10)
C(1)−N(2)−C(8)	116(1)		
Pd(1)−Cl(1)−Pd(2)	84.8(1)	N(1)−C(1)−N(2)	130(1)

slightly acute due to the bidentate PC_6H_4N units,[9] and both the μ-Cl−Pd−P angles (166.0(2), 169.9(2)°) and the Cl−Pd−N angles (172.7(4), 172.2(4)°) are distorted. The geometries of both nitrogens are almost planar, $\sum\phi(N1) = 357.0°$ and $\sum\phi(N2) = 358.2°$, and C(1) is positioned symmetrically relative to the nitrogen atoms (C(1)−N(1) = 1.32(2) Å, C(1)−N(2) = 1.31(2) Å), indicating that the double bond of the amidinate is delocalized. The Pd−Pd distance is 3.24 Å, indicating that there is no significant metal−metal interaction.[3c,e−h,j−l,10]

The structure of the diplatinum complex **3a** was also determined by X-ray analysis. The lattice contains one molecule of CH_2Cl_2 per **3a**. There are no significant interactions between **3a** and the solvent molecule. The molecular structure is shown in Figure 2, and selected bond and angles are presented in Table 2. The complex **3a** adopts an A-frame structure similar to **2f**. The μ-Cl ligand is positioned symmetrically relative to the metal centers with Pt(1)−Cl(1) = 2.462(8) Å and Pt(2)−Cl(1) = 2.444(5) Å. Each platinum center has a slightly distorted square-planar geometry (P−Pt−N = 82.9(3) and 81.8(3)°).[11] The Pt−P bond lengths are short due to the low trans influence of μ-Cl (Pt(1)−P(1) = 2.176(6)°, Pt(2)−P(2) = 2.179(5)°). Similar to **2f**, the geometries of both nitrogens are almost planar and the distances between the amidine carbon and the nitrogens are equal ($\sum\phi(N1) = \sum\phi(N2) = 359°$; C(1)−N(1) = C(1)−N(2) = 1.33 Å). The Pt−Pt separation of 3.16 Å falls well outside the range considered typical of Pt−Pt single bonds.[4a−e,g−k,12]

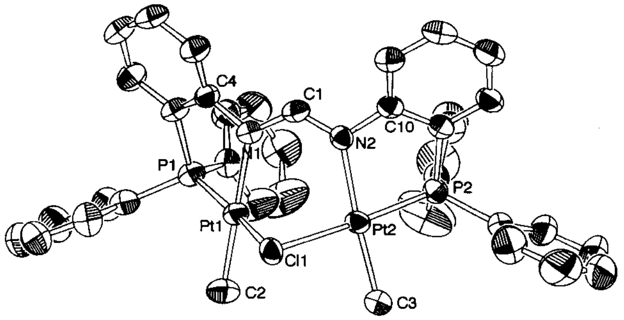

Figure 2. Molecular structure of $Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**3a**), showing 50% thermal ellipsoids.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a

Pt(1)−C1(1)	2.462(8)	Pt(1)−C(2)	2.069(10)
Pt(1)−P(1)	2.176(6)	Pt(1)−N(1)	2.132(8)
Pt(2)−Cl(1)	2.444(5)	Pt(2)−C(3)	2.07(1)
Pt(2)−P(2)	2.179(5)	Pt(2)−N(2)	2.144(8)
N(1)−C(1)	1.33(1)	N(2)−C(1)	1.33(1)
Cl(1)−Pt(1)−C(2)	90.2(4)	P(1)−Pt(1)−C(2)	94.4(4)
P(1)−Pt(1)−N(1)	82.9(3)	Cl(1)−Pt(1)−N(1)	92.7(3)
Cl(1)−Pt(1)−P(1)	168.60(9)	N(1)−Pt(1)−C(2)	176.7(3)
Pt(1)−N(1)−C(1)	127.8(6)	Pt(1)−N(1)−C(4)	114.0(6)
C(1)−N(1)−C(4)	116.8(7)		
Cl(1)−Pt(2)−C(3)	89.2(4)	P(2)−Pt(2)−C(3)	94.7(4)
P(2)−Pt(2)−N(2)	81.8(3)	Cl(1)−Pt(2)−N(2)	94.1(3)
Cl(1)−Pt(2)−P(2)	174.31(9)	N(2)−Pt(2)−C(3)	176.5(4)
Pt(2)−N(2)−C(1)	127.6(6)	Pt(2)−N(2)−C(10)	113.7(5)
C(1)−N(2)−C(10)	117.3(7)		
Pt(1)−Cl(1)−Pt(2)	80.3(2)	N(1)−C(1)−N(2)	125.7(8)

The $^{31}P\{^1H\}$ NMR spectra of the symmetrical dipalladium complexes **2a**−**d**,**f** exhibit a single resonance between 32.00 and 46.38 ppm, that of the methyl complex **2a** appearing at a higher frequency than those of the aryl complexes **2b**−**d** (Table 3). The P atoms attached to platinum in **3a**,**b** give rise to single reso-

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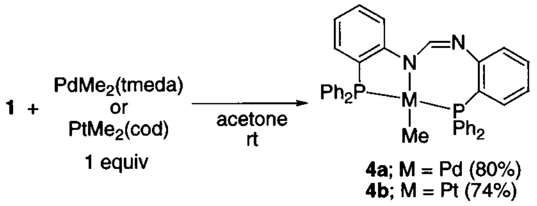
Table 3. ^1H and $^{31}P\{^1H\}$ NMR Data for Complexes 2−6 in $CDCl_3$ Solution

complex	δ(P), ppm	$^1J_{PtP}$ (Hz)	δ(H) (amidine), ppm	δ(H) (methyl), ppm	J_{PH} (Hz)	$^2J_{PtH}$ (Hz)
$Pd_2Me_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**2a**)	40.67		8.25	0.64	2.0	
$Pd_2Tol_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**2b**)	34.45		8.11			
$Pd_2Tol_2(\mu\text{-}Br)(\mu\text{-}dpfam)$ (**2c**)	33.75		8.06			
$Pd_2Tol_2(\mu\text{-}I)(\mu\text{-}dpfam)$ (**2d**)	32.00		8.00			
$Pd_2MeCl(\mu\text{-}Cl)(\mu\text{-}dpfam)$ **2e**[a]	40.14, 46.33		8.13	0.69	1.9	
$Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**2f**)[a]	46.38		8.02			
$Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**3a**)	18.53	5154	8.79[b]	0.71	2.3	66
$Pt_2Tol_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**3b**)	16.65	4966	8.37[b]			
PdMe(dpfam) (**4a**)	19.01,[c] 35.46[c]			7.72	0.24	6.0
PtMe(dpfam) (**4b**)	20.54[d]	2368	7.81[b]	0.37	6.1, 6.8	73
	35.70[d]	3002				
$PdPtMe_2(\mu\text{-}Cl)(\mu\text{-}dpfam)$ (**5**)	39.00		8.55[b]	0.66	1.7	
	20.22	5079		0.70	2.4	*e*
$Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dpfam)$ (**6**)	31.10	*f*	10.13	0.93	*e*	*e*

[a] In CD_2Cl_2. [b] $^3J_{PtH}$ values were unresolved. [c] $^2J_{PP}$ = 402 Hz. [d] $^2J_{PP}$ = 424 Hz. [e] Unresolved. [f] $^1J_{PtP}$ = 3863 Hz, $^2J_{PtP}$ = 391 Hz, $^3J_{PP}$ = 68 Hz.

nances at 18.53 and 16.65 ppm, respectively, with ^{195}Pt satellites. The $^1J_{PtP}$ values, 5154 Hz for **3a** and 4966 Hz for **3b**, are larger than those for the corresponding mononuclear complex PtMeCl[2-aminophenyl(diphenylphosphine)] (4617 Hz),[13] indicating the lower trans influence of μ-Cl compared to nonbridging Cl, consistent with the short Pt−P bond lengths.[14]

Synthesis of Monometallic and Heterobimetallic Palladium and Platinum Complexes. Treatment of **1** and 1 equiv of $PdMe_2$(tmeda) or $PtMe_2$(cod) in acetone at room temperature caused the evolution of methane and produced the monometallic complexes PdMe(dpfam) (**4a**) and PtMe(dpfam) (**4b**) (eq 6). The reaction of **1** with 1 equiv of PtMeCl(cod) in the presence of excess tmeda also afforded **4b**, although treatment of **1** with 1 equiv of PdMeCl(tmeda) resulted in the formation of small amounts of the bimetallic complex **2a**. These monometallic complexes **4a**,**b** were characterized by $^{31}P\{^1H\}$ and ^1H NMR analysis. The $^{31}P\{^1H\}$ NMR spectra of **4a** exhibit two sets of doublets at 19.01 and 35.46 ppm ($^2J_{PP}$ = 402 Hz). Similarly, those of **4b** exhibit two sets of doublets with ^{195}Pt satellites at 20.54 ($^1J_{PtP}$ = 2368 Hz) and 35.70 ($^1J_{PtP}$ = 3002 Hz) ppm, with a $^2J_{PP}$ value of 424 Hz. In the ^1H NMR spectra, the methyl group of **4a** produces a triplet at 0.24 ppm ($^3J_{PH}$ = 6.0 Hz), and a double doublet is observed with ^{195}Pt satellites at 0.37 ppm ($^3J_{PH}$ = 6.1 and 6.8 Hz, $^1J_{PtH}$ = 73 Hz) in the case of **4b**. These results indicate that the two phosphine atoms coordinate to the metal centers.



4a; M = Pd (80%)
4b; M = Pt (74%)

(6)

The structure of **4b** was determined by X-ray analysis. The molecular structure is shown in Figure 3, and selected bond distances and angles are presented in Table 4. The molecule exhibits a slightly distorted square planar geometry about the platinum with a N(1)−Pt(1)−C(1) angle of 171.0(2)°, a P(1)−Pt(1)−P(2) angle of 170.51(5)°, and a P(1)−Pt(1)−N(1) angle of 82.8(1)°. There is no significant difference between the bond lengths Pt(1)−P(1) and Pt(1)−P(2). While the nitrogen atom N(1) of the amidinate exists in the ideal position around the square-planar platinum center, the Pt(1)−N(2) distance is too long to consider the coordination of the nitrogen atom N(2) to the platinum center. The bond lengths N(1)−C(2) of 1.374(6) Å and N(2)−C(2) of 1.277(7) Å coincide with typical lengths of sp^2 C−N single bonds and C=N double bonds, respectively, indicating that the double bond of the amidinate is almost localized, although the torsion angle N(1)−C(2)−N(2)−C(26) of −10.3(10)° is not consistent with the ideal double bond.

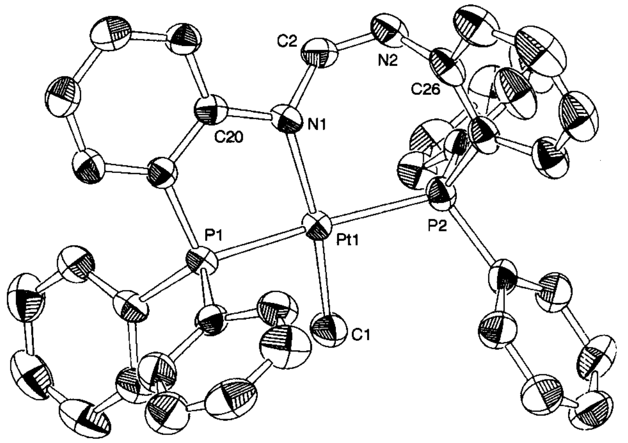


Figure 3. Molecular structure of PdMe(dpfam) (**4b**), showing 50% thermal ellipsoids.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 4b

Pt(1)−C(1)	2.067(6)	Pt(1)−N(1)	2.126(4)
Pt(1)−P(1)	2.257(1)	Pt(1)−P(2)	2.287(1)
N(1)−C(2)	1.374(6)	N(2)−C(2)	1.277(7)
P(1)−Pt(1)−C(1)	90.6(2)	P(1)−Pt(1)−N(1)	82.8(1)
P(2)−Pt(1)−N(1)	96.4(1)	P(2)−Pt(1)−C(1)	91.1(2)
N(1)−Pt(1)−C(1)	171.0(2)	P(1)−Pt(1)−P(2)	170.51(5)
Pt(1)−N(1)−C(2)	119.6(3)	Pt(1)−N(1)−C(20)	117.9(3)
C(2)−N(1)−C(20)	114.4(4)	N(1)−C(2)−N(2)	130.4(5)
C(2)−N(2)−C(26)	123.9(5)		

The isolated **4b** reacts with 1 equiv of PtMeCl(cod) in benzene to give the bimetallic platinum complex **3a** (Scheme 1). Similarly, the dipalladium complex **2a** is formed quantitatively by treatment of **4a** with 1 equiv

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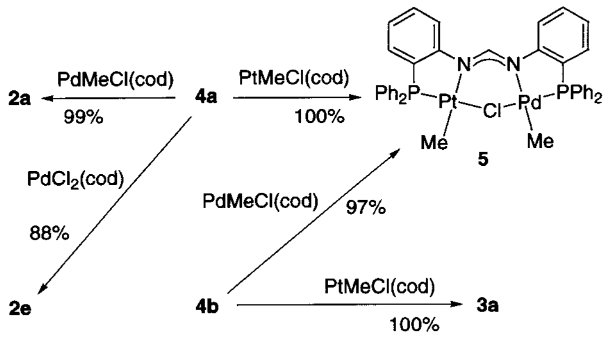
(13) Pfeiffer, J.; Kickelbick, G.; Schubert, U. *Organometallics* **2000**, *19*, 62.

(14) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.

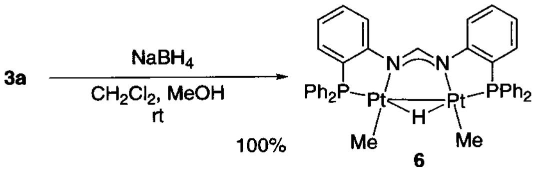
Scheme 1



of PdMeCl(cod). The reaction of **4a** with $PdCl_2$(cod) affords the complex **2e** in pure form.

The synthesis of the palladium and platinum heterobimetallic complex **5** was then investigated. Both the reaction of **4a** with PtMeCl(cod) and the reaction of **4b** with PdMeCl(cod) afford the complex **5** selectively, without the formation of the homobimetallic complexes **2a** and **3a**. The $^{31}P\{^1H\}$ NMR spectra for **5** exhibit two single resonances at 20.22 ppm ($^1J_{PtP} = 5079$ Hz) and 39.00 ppm, which are close to those of the corresponding homobimetallic complexes **3a** and **2a** (Table 3), respectively. In the ^1H NMR spectra, the methyl groups on the palladium and the platinum also exhibit chemical shifts and *J* values similar to those of **3a** and **2a**. The chemical shift of the amidine proton of **5** (8.55 ppm) is between those of **3a** and **2a** (8.79 and 8.25 ppm).

Synthesis and Structure of a Hydride-Bridged Platinum A-Frame Complex. The diplatinum complex **3a** was converted to the corresponding hydride-bridged derivative **6** by treatment of $NaBH_4$ in CH_2Cl_2 and MeOH (eq 7).[12e,15] The structure of **6** was determined by X-ray analysis. The molecular structure is shown in Figure 4, and selected bond distances and angles are presented in Table 5. The Pt–Pt length in **6** (2.8000(6) Å) is slightly longer than the Pt–Pt distances (2.620(1)–2.769(1) Å) in the "side-by-side" binuclear platinum complexes, in which all structural features are compatible with the presence of covalent Pt–Pt bonding.[12g,16] It is, however, shorter than the Pt–Pt separation (2.867(2)–2.932(1) Å) in the dppm- and hydride-bridged platinum A-frame complexes, in which a weak metal–metal bonding interaction is suggested,[5d,12e] indicating the presence of a stronger interaction between the platinum centers in **6**. The shorter distance can be accounted for by the weaker trans influence of Ph_2P in **6** compared with the alkyl groups in the dppm- and hydride-bridged complexes[12e] or the shorter distance between two nitrogen atoms in the amidinate compared with two phosphine atoms in dppm. The interaction between two platinums was also confirmed by $^{31}P\{^1H\}$ analysis. The spectrum of **6** exhibits a typical AA′XX′ spin system together with ^{195}Pt atoms ($^1J_{PtP} = 3863$ Hz, $^2J_{PtP} = 391$ Hz, $^3J_{PP} = 68$ Hz), which is very similar to that previously reported for a linear P–Pt–Pt–P system.[17]



6 (7)

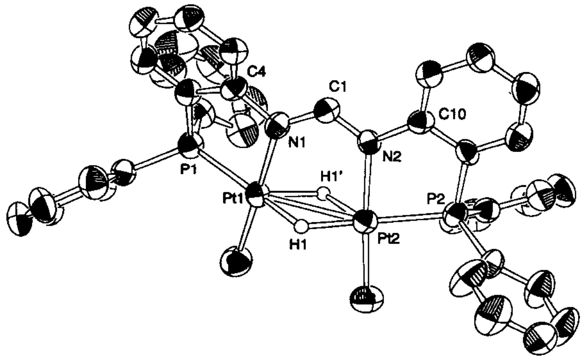


Figure 4. Molecular structure of $Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dpfam)$ (**6**), showing 50% thermal ellipsoids.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Pt(1)–Pt(2)	2.8000(6)		
Pt(1)–C(2)	2.060(10)	Pt(1)–P(1)	2.217(2)
Pt(1)–N(1)	2.116(6)	Pt(2)–C(3)	2.056(10)
Pt(2)–P(2)	2.210(2)	Pt(2)–N(2)	2.138(6)
N(1)–C(1)	1.32(1)	N(2)–C(1)	1.32(1)
Pt(2)–Pt(1)–C(2)	99.2(3)	P(1)–Pt(1)–C(2)	94.9(3)
P(1)–Pt(1)–N(1)	83.2(2)	Pt(2)–Pt(1)–N(1)	82.7(2)
Pt(2)–Pt(1)–P(1)	156.34(6)	N(1)–Pt(1)–C(2)	178.1(4)
Pt(1)–N(1)–C(1)	125.7(5)	Pt(1)–N(1)–C(4)	115.7(5)
C(1)–N(1)–C(4)	118.1(7)		
Pt(1)–Pt(2)–C(3)	100.3(3)	P(2)–Pt(2)–C(3)	92.9(3)
P(2)–Pt(2)–N(2)	83.4(2)	Pt(1)–Pt(2)–N(2)	83.6(2)
Pt(1)–Pt(2)–P(2)	156.87(5)	N(2)–Pt(2)–C(3)	176.2(4)
Pt(2)–N(2)–C(1)	124.0(5)	Pt(2)–N(2)–C(10)	118.3(5)
C(1)–N(2)–C(10)	117.7(6)		
N(1)–C(1)–N(2)	122.5(7)		

In the X-ray analysis, the hydrogen atom H(1) was found by difference Fourier synthesis to be disordered between the Pt(1) and Pt(2) atoms. The two hydrogen atoms H(1) and H(1′), where the occupancies of 0.6 and 0.4 are assigned, are positioned symmetrically relative to the metal centers (Pt(1)–H(1) = 1.66(7) Å, Pt(2)–H(1) = 1.63(8) Å; Pt(1)–H(1′) = 1.70(8) Å, Pt(2)–H(1′) = 1.69(8) Å). These Pt–H lengths are shorter than the distances previously reported for a hydride-bridged platinum A-frame complex, as is the case for the Pt–Pt distances as well.[5d] Although the hydride H(1) is arranged in a trans position to the phosphines, the P–Pt–H angles are not linear (P(1)–Pt(1)–H(1) = 164(2)° and P(2)–Pt(2)–H(1) = 168(2)°). Considering that the Pt–Pt–P angles are also bent (Pt(2)–Pt(1)–P(1) = 156.33(6)° and Pt(1)–Pt(2)–P(2) = 156.85(5)°), these nonlinearities may be related to a three-center–two-electron bond in the bridging $Pt_2(\mu\text{-}H)$ unit.[12e,15,18] The presence of a symmetrical bridging hydride in **6** is also

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[16] (a) Brown, M. P.; Cooper, S. J.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 1117. (b) Brown, M. P.; Fisher, J. R.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 931. (c) Few, A. A.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1980**, 624. (d) Manojlović-Muir, L.; Muir, K. W.; Solomum, T. *J. Organomet. Chem.* **1979**, *179*, 479. (e) Manojlović-Muir, L.; Muir, K. W.; Solomum, T. *Acta Crystallogr., Sect. B* **1979**, *35*, 1237.

[17] Kühn, A.; Werner, H. *J. Organomet. Chem.* **1979**, *179*, 421.

[18] See also refs 3a,b,d.

revealed in the ^{1}H NMR spectrum. A resonance at −4.06 ppm, with the appearance of a 1:8:18:8:1 quintet due to coupling with ^{195}Pt and with each peak further split into a 1:2:1 triplet due to coupling with ^{31}P, was observed ($^1J_{PtH} = 780$ Hz, $^2J_{PH} = 93$ Hz). The two hydrogen atoms H(1) and H(1′) are equivalent in solution because of a fast flipping of the P−Pt−Pt−P system.

Summary

In this study, a series of dpfam- and halide-bridged palladium and platinum A-frame complexes were synthesized. A palladium and platinum heterobimetallic complex was also prepared via the monometallic complexes. Treatment of the chloride-bridged platinum A-frame complex with $NaBH_4$ afforded the hydride-bridged complex. The tetradentate ligand dpfam permits flexible metal−metal distances. The Pd−Pd distance in the chloride-bridged complex **2f** is longer than that in the related dppm- and chloride-bridged palladium complexes (3.24 vs 3.03 Å).[10c] In contrast, the hydride-bridged complex **6** exhibits shorter Pt−Pt distances than dppm- and hydride-bridged complexes (2.8006(9) Å vs 2.867(2)−2.932(1) Å).[5d,12e] In all of the complexes, the metal centers have a distorted-square-planar geometry with two ligands other than dpfam in a cis orientation, which is expected to exhibit different reactivities than the well-known dppm-bridged A-frame complexes. Reductive elimination, insertion, and oxidative addition on the dpfam-bridged A-frame complexes and application in catalysis are currently under investigation.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. The compounds 2-(diphenylphosphino)aniline,[19] PdMeCl(tmeda),[20] $PdMe_2$(tmeda),[20] PdMeCl(cod),[21] Pd(*p*-Tol)Cl(tmeda),[22] Pd(*p*-Tol)Br(tmeda),[22] Pd(*p*-Tol)I(tmeda),[22] PtMeCl(cod),[23] $PtMe_2$(cod),[23] and Pt(*p*-Tol)Cl(cod)[23] were prepared by literature methods.

NMR spectra were recorded by using a Bruker DPX-400 or Bruker DRX-500 spectrometer. ^{1}H NMR chemical shifts were measured relative to tetramethylsilane in $CDCl_3$ or relative to the residual solvent peak in CD_2Cl_2. Phosphorus chemical shifts were determined relative to 85% H_3PO_4 as an external standard.

Preparation of Hdpfam (1). A solution of 2-(diphenylphosphino)aniline (5.6 g, 20 mmol), trimethyl orthoformate (1.1 mL, 10 mmol), and a catalytic amount of *p*-TsOH·H_2O in benzene (10 mL) was gently refluxed for 12 h, while distilling off the methanol generated. After cooling and addition of saturated $NaHCO_3$ (10 mL), the reaction mixture was extracted with benzene (2 × 30 mL). The combined extracts were dried over anhydrous Na_2SO_4 and evaporated to give a yellow oil. Diisopropyl ether (20 mL) was added to the oil, and the mixture was refluxed for 1 h. After the mixture was cooled to room temperature, white precipitates were collected by filtration, washed with cold diisopropyl ether, and dried to yield 4.8 g (86%) of the analytically pure product as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (m, 2H), 6.95 (m, 2H), 7.22 (m, 2H), 7.24−7.36 (m, 22H), 7.57 (s, 1H, NC*H*N), 7.65 (br s, 1H, N*H*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −19.25, −15.02. Anal. Calcd for $C_{37}H_{30}N_2P_2$: C, 78.71; H, 5.36; N, 4.96. Found: C, 78.41; H, 5.46; N, 5.07. Mp: 164−165 °C.

Pd_2Me_2(μ-Cl)(μ-dpfam) (2a). To a solution of **1** (0.28 g, 0.50 mmol) in acetone (20 mL) was added PdMeCl(tmeda) (0.27 g, 1.0 mmol). The mixture was stirred at room temperature overnight to give a pale yellow precipitate, which was collected by filtration after the addition of H_2O (20 mL) to the suspension, washed with H_2O, MeOH, and ether and dried. Yield: 0.36 g, 86%. This complex slowly reacted with halogenated solvents, such as $CHCl_3$ and CH_2Cl_2, to give **2e**,**f** by cleavage of the methylpalladium group. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.64 (d, ^3J(P,H) = 2.0 Hz, 6H, Pd*Me*), 6.90 (m, 2H), 7.03 (m, 2H), 7.10 (m, 2H), 7.26−7.36 (m, 12H), 7.44 (m, 4H), 7.59 (m, 8H), 8.25 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 40.67. Anal. Calcd for $C_{39}H_{35}ClN_2P_2Pd_2$: C, 55.63; H, 4.19; N, 3.33; Cl, 4.21. Found: C, 55.69; H, 4.51; N, 3.18; Cl, 4.31. Mp: >260 °C.

Pd_2(*p*-Tol)$_2$(μ-Cl)(μ-dpfam) (2b). This complex was prepared in a manner similar to that above from **1** (56 mg, 0.10 mmol) and Pd(*p*-Tol)Cl(tmeda) (70 mg, 0.20 mmol) and isolated as a beige powder (86 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 6H, C_6H_4*Me*), 6.47 (d, *J* = 8.0 Hz, 4H, C_6*H_4*Me-3,5), 6.85 (m, 4H, C_6*H_4*Me-2,6), 6.95−7.02 (m, 4H), 7.20−7.35 (m, 14H), 7.41 (m, 4H), 7.48 (m, 8H), 8.11 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 34.45. Anal. Calcd for $C_{51}H_{43}ClN_2P_2Pd_2$: C, 61.62; H, 4.36; N, 2.82; Cl, 3.57. Found: C, 61.68; H, 4.56; N, 2.82; Cl, 3.33. Mp: >260 °C.

Pd_2(*p*-Tol)$_2$(μ-Br)(μ-dpfam) (2c). This complex was prepared in a manner similar to that for **2a** from **1** (56 mg, 0.10 mmol) and Pd(*p*-Tol)Br(tmeda) (79 mg, 0.20 mmol) and isolated as a pale yellow powder (74 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 6H, C_6H_4*Me*), 6.48 (d, *J* = 7.6 Hz, 4H, C_6*H_4*-Me-3,5), 6.87 (m, 4H, C_6*H_4*Me-2,6), 6.93−7.01 (m, 4H), 7.20−7.35 (m, 14H), 7.41 (m, 4H), 7.48 (m, 8H), 8.06 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 33.75. Anal. Calcd for $C_{51}H_{043}BrN_2P_2Pd_2$: C, 58.98; H, 4.17; N, 2.70; Br, 7.69. Found: C, 59.19; H, 4.35; N, 2.79; Br, 7.63. Mp: >260 °C.

Pd_2(*p*-Tol)$_2$(μ-I)(μ-dpfam) (2d). This complex was prepared in manner similar to that for **2a** from **1** (0.28 g, 0.50 mmol) and Pd(*p*-Tol)I(tmeda) (0.44 g, 1.0 mmol) and isolated as a pale yellow powder (0.50 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (s, 6H, C_6H_4*Me*), 6.46 (d, *J* = 7.9 Hz, 4H, C_6*H_4*-Me-3,5), 6.88 (m, 4H, C_6*H_4*Me-2,6), 6.93 (m, 2H), 6.97 (m, 2H), 7.23−7.33 (m, 14H), 7.40 (m, 4H), 7.47 (m, 8H), 8.00 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 32.00 Anal. Calcd for $C_{51}H_{43}IN_2P_2Pd_2$: C, 56.43; H, 3.99; N, 2.58; I, 11.69. Found: C, 56.14; H, 4.12; N, 2.91; I, 11.70. Mp: >260 °C.

Reaction of 1 with PdMeCl(cod). To a solution of **1** (56 mg, 0.10 mmol) in acetone (4 mL) was added PdMeCl(cod) (53 mg, 0.20 mmol). The mixture was stirred at room temperature overnight to give an orange precipitate, which was collected by filtration after the addition of H_2O (4 mL) to the suspension, washed with H_2O, MeOH, and ether, and dried. The mixture of **2a** and **2e** (20:80, determined by ^{1}H NMR) was obtained in 91% yield (78 mg).

Reaction of 1 with PdMeCl(cod) in the Presence of Amines. To a solution of **1** (56 mg, 0.10 mmol) and tmeda (30 μL, 0.20 mmol) in acetone (4 mL) was added PdMeCl(cod) (53 mg, 0.20 mmol). The mixture was stirred at room temperature overnight to give a pale yellow precipitate, which was collected by filtration after H_2O (20 mL) was added to the suspension, washed with H_2O, MeOH, and ether, and dried. The complex **2a** was obtained as the sole product in 90% yield (76 mg). Using *i*-Pr_2NEt (70 μL, 0.4 mmol) instead of tmeda, **2a** was obtained in 78% yield (66 mg).

Reaction of 2a with HCl. To a solution of **2a** (0.17 g, 0.2 mmol) in benzene (20 mL) and methanol (1 mL) was added a solution of acetyl chloride (14 μL, 0.2 mmol) in benzene (1 mL).

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The mixture was stirred at room temperature overnight to give an orange precipitate. After the mixture was evaporated to ca. 5 mL, the precipitate was collected by filtration, washed with ether, and dried. The mixture of **2a**, **2e**, and **2f** (4:90:6, determined by ^{1}H NMR) was obtained in 95% yield (0.16 g).

$Pd_2Cl_2(\mu$-Cl)(μ-dpfam) (2f). To a solution of **1** (0.28 g, 0.50 mmol) in CH_2Cl_2 (20 mL) was added $PdCl_2$(cod) (0.29 g, 1.0 mmol). The mixture was stirred at room temperature overnight. Addition of ether to the reaction mixture led to the precipitation of a orange powder, which was collected by filtration, washed with ether, and dried. Yield: 0.44 g, 100%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.10 (m, 2H), 7.16 (m, 2H), 7.24 (m, 2H), 7.39−7.47 (m, 12 H), 7.57 (m, 4H), 7.75 (m, 8H), 8.02 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 46.38. Anal. Calcd for $C_{37}H_{29}Cl_3N_2P_2Pd_2$: C, 50.34; H, 3.31; N, 3.17; Cl, 12.05. Found: C, 50.01; H, 3.68; N, 3.21; Cl, 12.49. Mp: >260 °C.

$Pt_2Me_2(\mu$-Cl)(μ-dpfam) (3a). To a solution of **1** (56 mg, 0.10 mmol) and tmeda (30 μL, 0.20 mmol) in acetone (4 mL) was added PtMeCl(cod) (71 mg, 0.20 mmol). The mixture was stirred at room temperature overnight to give a white precipitate, which was collected by filtration after H_2O (20 mL) was added to the suspension, washed with H_2O, MeOH, and ether, and dried. Yield: 90 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71 (d, ^3J(P,H) = 2.3 Hz, ^2J(Pt,H) = 66 Hz, 6H, Pt*Me*), 6.92 (m, 2H), 7.17 (m, 4H), 7.31 (m, 10H), 7.43 (m, 4H), 7.63 (m, 8H), 8.79 (s, ^3J(Pt,H) = 30 Hz, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 18.53, ^1J(Pt,P) = 5154 Hz. Anal. Calcd for $C_{39}H_{35}ClN_2P_2Pt_2$: C, 45.96; H, 3.46; N, 2.75; Cl, 3.48. Found: C, 46.25; H, 3.58; N, 2.85; Cl, 3.38. Mp: >260 °C.

Pt_2(*p*-Tol)$_2$(μ-Cl)(μ-dpfam) (3b). This complex was prepared in a manner similar to that for **3a** from **1** (56 mg, 0.10 mmol), tmeda (30 μL, 0.20 mmol), and Pt(*p*-Tol)Cl(tmeda) (86 mg, 0.20 mmol) and isolated as a white powder (0.10 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 6H, C_6H_4*Me*), 6.41 (m, 4H, C_6H_4Me-3,5), 6.87 (d+br satellites, ^3J(H,H) = 7.9 Hz, 4H, C_6H_4Me-2,6), 7.03 (m, 2H), 7.10 (m, 2H), 7.25−7.37 (m, 12H), 7.41 (m, 4H), 7.56 (m, 8H), 8.37 (s+br satellites, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 16.65 (^1J(Pt,P) = 4966 Hz). Anal. Calcd for $C_{51}H_{43}ClN_2P_2Pt_2$: C, 52.29; H, 3.70. Found: C, 51.91; H, 3.65. Mp: >260 °C.

PdMe(dpfam) (4a). To a solution of **1** (56 mg, 0.10 mmol) in acetone (4 mL) was added $PdMe_2$(tmeda) (25 mg, 0.10 mmol). The mixture was stirred at room temperature overnight to give a yellow precipitate, which was collected by filtration, washed with a small amount of acetone, and dried. Yield: 55 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (t, ^3J(P,H) = 6.0 Hz, 3H, PdMe), 6.6−6.9 (br, 5H), 7.1−7.7 (br, 23H), 7.72 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 19.01 (d, ^2J(P,P) = 402 Hz), 35.46 (d, ^2J(P,P) = 402 Hz). Anal. Calcd for $C_{38}H_{32}N_2P_2Pd$: C, 66.62; H, 4.71; N, 4.09. Found: C, 66.64; H, 4.83; N, 4.12. Mp: 231−233 °C dec.

PtMe(dpfam) (4b). This complex was prepared in a manner similar to that above from **1** (56 mg, 0.10 mmol) and $PtMe_2$(cod) (33 mg, 0.10 mmol) and isolated as a yellow powder (57 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.37 (dd, ^3J(P,H) = 6.1, 6.8 Hz, ^2J(Pt,H) = 73 Hz, 3H, PtMe), 6.68−6.77 (m, 2H), 6.80−6.87 (m, 2H), 6.92 (dd, J = 4.7, 7.8 Hz, 1H), 7.24−7.32 (m, 2H), 7.38−7.56 (m, 13H), 7.61 (m, 4H), 7.69 (m, 4H), 7.81 (s+br satellites, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 20.54 (d, ^2J(P,P) = 424 Hz, ^1J(Pt,P) = 2368 Hz), 35.70 (d, ^2J(P,P) = 424 Hz, ^1J(Pt,P) = 3002 Hz). Anal. Calcd for $C_{38}H_{32}N_2P_2Pt$: C, 58.99; H, 4.17; N, 3.62. Found: C, 58.87; H, 4.32; N, 3.66. Mp: >260 °C.

$PdPtMe_2(\mu$-Cl)(μ-dpfam) (5). To a solution of **4b** (77 mg, 0.10 mmol) in benzene (4 mL) was added PdMeCl(cod) (27 mg, 0.10 mmol). The mixture was stirred at room temperature overnight. Addition of pentane to the reaction mixture led to the precipitation of a pale yellow powder, which was collected by filtration, washed with pentane, and dried. Yield: 90 mg, 97%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.66 (d, ^3J(P,H) = 1.7 Hz, 3H, Pd*Me*), 0.70 (d+br satellites, ^3J(P,H) = 2.4 Hz, 3H, Pt*Me*), 6.87−6.92 (m, 2H), 7.05−7.17 (m, 4H), 7.25−7.34 (m, 10H), 7.39−7.46 (m, 4H), 7.55−7.68 (m, 8H), 8.55 (s+br satellites, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 20.22 (^1J(Pt,P) = 5079 Hz, Pt*P*), 39.00 (Pd*P*). Anal. Calcd for $C_{39}H_{35}ClN_2P_2PdPt$: C, 50.33; H, 3.79; N, 3.01; Cl, 3.81. Found: C, 49.92; H, 3.71; N, 3.19; Cl, 3.86. Mp: >260 °C.

Treatment of **4a** (69 mg, 0.1 mmol) with PtMeCl(cod) (35 mg, 0.1 mmol) in a similar manner also afforded **5** in 100% yield (94 mg).

Reaction of 4a and $PdCl_2$(cod). To a solution of **4a** (77 mg, 0.1 mmol) in benzene (4 mL) was added $PdCl_2$(cod) (29 mg, 0.10 mmol). The mixture was stirred at room temperature overnight to give a orange precipitate of **2e**, which was collected by filtration, washed with benzene, and dried. Yield: 76 mg, 88%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.69 (d, ^3J(P,H) = 1.9 Hz, 3H, Pd*Me*), 6.97−7.04 (m, 2H), 7.09−7.20 (m, 3H), 7.20−7.26 (m, 1H), 7.35−7.65 (m, 18H), 7.71−7.78 (m, 4H), 8.13 (s, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 40.14, 46.33. Anal. Calcd for $C_{38}H_{32}Cl_2N_2P_2Pd_2$: C, 52.92; H, 3.74; N, 3.25; Cl; 8.22. Found: C, 52.83; H, 4.09; N, 3.40; Cl, 8.50. Mp: 212 °C dec.

$Pt_2Me_2(\mu$-H)(μ-dpfam) (6). To a solution of **3a** (0.31 g, 0.30 mmol) in CH_2Cl_2 (36 mL) was added $NaBH_4$ (23 mg, 0.60 mmol) and methanol (3.6 mL) at 0 °C. After the mixture was stirred for 1 h at 0 °C, the solvents were removed under reduced pressure. The solid residue was extracted with CH_2Cl_2 and passed through a Celite column. The solvent was removed under reduced pressure to give a pale yellow solid. Yield: 0.30 g, 100%. ^{1}H NMR (400 MHz, $CDCl_3$): δ −4.06 (t, ^2J(P,H) = 92 Hz, ^1J(Pt,H) = 779 Hz, Pt*H*Pt), 0.82−1.03 (m, 6H, Pt*Me*), 6.90−6.95 (m, 2H), 7.30−7.45 (m, 18H), 7.63−7.71 (m, 8H), 10.13 (s, ^3J(Pt,H) = 44 Hz, 1H, NC*H*N). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 31.10 (^1J(Pt,P) = 3863 Hz, ^2J(Pt,P) = 391 Hz, ^3J(P,P) = 68 Hz). Anal. Calcd for $C_{39}H_{36}N_2P_2Pt_2$: C, 47.56; H, 3.68; N, 2.84. Found: C, 47.69; H, 3.85; N, 2.97. Mp: >260 °C.

X-ray Structure Determinations. All X-ray measurements were made with a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å).

Recrystalization of **2f** by vapor diffusion of diethyl ether into a solution of dichloromethane afforded a orange crystal (**2f**·$2CH_2Cl_2$). The collected data were solved by Patterson methods (DIRDIF92 PATTY) and refined by a full-matrix least-squares procedure using TEXSAN programs. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined. Crystal data and refinement details are summarized in Table 6.

Recrystallization of **3a** by vapor diffusion of diethyl ether into a solution of dichloromethane afforded a pale yellow crystal (**3a**·CH_2Cl_2). The collected data were solved by direct methods (SIR92) and refined by a full-matrix least-squares procedure using TEXSAN programs. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined. Crystal data and refinement details are summarized in Table 6.

Recrystallization of **4b** by slow diffusion of pentane into a solution of THF afforded a yellow crystal. The collected data were solved by Patterson methods (SAPI) and refined by a full-matrix least-squares procedure using TEXSAN programs. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined. Crystal data and refinement details are summarized in Table 6.

Recrystallization of **6** by slow diffusion of pentane into a solution of benzene afforded a pale yellow crystal (**6**·C_6H_6). The

Table 6. Crystal Data and Refinement Details for 2f, 3a, 4b, and 6

	2f·$2CH_2Cl_2$	**3a**·CH_2Cl_2	**4b**	**6**·C_6H_6
formula	$C_{39}H_{33}N_2P_2Pd_2Cl_7$	$C_{40}H_{37}Cl_3N_2P_2Pt_2$	$C_{38}H_{32}N_2P_2Pt_2$	$C_{45}H_{42}N_2P_2Pt_2$
fw	1052.62	1104.23	773.72	1062.97
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	12.247(6)	12.67(6)	11.302(5)	13.380(3)
b (Å)	18.225(5)	21.63(7)	15.529(4)	14.297(3)
c (Å)	18.541(4)	14.46(5)	9.919(3)	10.830(4)
α (deg)	101.42(2)	107.24(2)		
β (deg)	92.64(3)	91.8(3)	112.14(3)	100.54(2)
γ (deg)	81.81(3)	93.74(2)		
Z	4	4	2	2
V (Å^3)	4133(1)	3961(25)	1576.2(9)	1929.3
D_{calcd} (g cm^{-3})	1.691	1.851	1.630	1.830
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
abs coeff (cm^{-1})	14.31	73.40	45.65	73.32
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
temp (°C)	23	23	24	23
$2\theta_{max}$ (deg)	50.0	50.1	50.0	50.0
no. of data collected	7909	7427	5854	7108
no. of observns	5028	5509	4778	6039
no. of variables	469	442	388	460
R ($I > 3\sigma(I)$)	0.075	0.030	0.027	0.043 (R1)[a]
R_w ($I > 3\sigma(I)$)	0.100	0.039	0.031	0.045 (R_w)[a]

[a] The structure was refined using the reflection data within 10° < 2θ < 50° by means of the SHELX97 program. R1 is the residual value for 6039 reflections with $I > 2\sigma(I)$, and R_w is the residual value for all of the 6728 unique reflections.

collected data were solved by Patterson methods (DIRDIF92 PATTY) and finally refined by a full-matrix least-squares procedure using another program (SHELX97) in order to examine more accurately the position of the H(1) atom. After the refinement was converged for all non-hydrogen atoms anisotropically, where all hydrogen atoms except for H(1) were fixed in calculated positions, the resulting difference Fourier map showed two peaks in the central positions of two Pt atoms with densities of 1.2 and 1.0 eV/Å^3, which were assigned to H(1) and H(1′), respectively. Only these two hydrogen atoms, where occupancies of 0.6 and 0.4 are assigned, were refined using the limited reflections within 20° < 2θ < 40°. As a result, the positions and thermal temperature factors were refined reasonably as follows: Pt(1)−H(1) = 1.66(7), Pt(1)−H(1′) = 1.70(8), Pt(2)−H(1) = 1.63(8), Pt(2)−H(1′) = 1.69(8) Å; Pt(1)−H(1)−Pt(2) = 117.0(8), Pt(1)−H(1′)−Pt(2) = 111(1)°. These results show that the hydrogen atom attached to Pt(1) and Pt(2) was disordered with approximately the same Pt−H bond lengths. Finally, all non-hydrogen atoms were refined anisotropically using all unique reflections within 10° < 2θ < 50°, where the H(1) and H(1′) hydrogen atoms were again fixed.

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Supporting Information Available: Tabulations of crystallographic data, positional and thermal parameters, and bond lengths and angles for **2f**, **3a**, **4b**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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