Palladium(II) Terminal Phosphido Complexes Derived from Cyclometalated Dimesitylphosphine: Synthesis, Structure, and Low-Barrier Phosphorus Inversion

Michael A. Zhuravel and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Lev N. Zakharov and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received April 1, 2002

The cyclometalated cationic Pd(II) and Pt(II) complexes [M(diphos)($CH_2C_6H_2Me_2P$(Mes)-(H))][X] (**5**−**8**: M = Pd, Pt; diphos = dppe ($Ph_2PCH_2CH_2PPh_2$), dppen (*cis*-$Ph_2PCH{=}CHPPh_2$); Mes = 2,4,6-$Me_3C_6H_2$; X = OTf, BF_4) were prepared by thermolysis of the cations [M(diphos)-(Me)($PMes_2H$)][X]. Deprotonation of **5**−**8** gave the neutral phosphido complexes M(diphos)-($CH_2C_6H_2Me_2P$(Mes)) (**9**−**12**); the Pd(II) compounds **9** and **11** are the first examples of stable palladium terminal phosphido alkyl complexes, and their crystal structures were determined. Fluxional processes in complexes **9**−**12** were studied by variable-temperature NMR spectroscopy; the spectra are consistent with low barriers to phosphorus inversion.

Introduction

Terminal phosphido complexes of Ni, Pd, and Pt are important intermediates in metal-catalyzed hydrophosphination[1] and phosphination reactions.[2] Although several Pt and a few Ni complexes with terminal phosphido ligands have been structurally characterized,[3,4] analogous Pd complexes have been elusive.[5] We generated Pd phosphido alkyl complexes such as Pd(dppe)(Me)-(PHMes*) (dppe = $Ph_2PCH_2CH_2PPh_2$, Mes* = 2,4,6-(t-Bu)$_3C_6H_2$) in solution, but they decomposed by reductive elimination below room temperature.[3g,6] Here we report the synthesis and structure of thermally stable Pd terminal phosphido complexes derived from cyclometalated dimesitylphosphine. Low barriers to inversion at the phosphido P were established for these and analogous Pt complexes by variable-temperature NMR studies.

Results and Discussion

The complexes [Pd(dppen)(Me)($PMes_2H$)][OTf] (**1**; dppen = *cis*-$Ph_2PCH{=}CHPPh_2$, Mes = 2,4,6-$Me_3C_6H_2$) and [Pt(dppen)(Me)($PMes_2H$)][OTf] (**2**) were prepared by treatment of M(dppen)(Me)(Cl) (M = Pd, Pt) with AgOTf and $PMes_2H$ in THF in the presence of MeCN (Scheme 1). The complexes were isolated in good yields as white crystalline solids and characterized by NMR and IR spectroscopy (Table 1) and elemental analysis. The

* To whom correspondence should be addressed. E-mail: Glueck@Dartmouth.Edu.

(1) Wicht, D. K.; Glueck, D. S. In *Catalytic Heterofunctionalization: From Hydroamination to Hydrozirconation*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; pp 143−170.

(2) For selected examples of catalytic phosphination, see: (a) Lucht, B. L.; St. Onge, N. O. *Chem. Commun.* **2000**, 2097−2098. (b) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Synth.* **1999**, *76*, 6−11. (c) Herd, O.; Hessler, A.; Hingst, M.; Machnitzki, P.; Tepper, M.; Stelzer, O. *Catal. Today* **1998**, *42*, 413−420. (d) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748−753.

(3) For Pt terminal phosphido complexes, see: (a) Kovacik, I.; Wicht, D. K.; Grewal, N. S.; Glueck, D. S.; Incarvito, C. D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2000**, *19*, 950−953. (b) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381−5394. (c) Wicht, D. K.; Glueck, D. S.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5130−5140. (d) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141−5151. (e) Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125−127. (f) Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Haar, C. M.; Nolan, S. P. *Organometallics* **1998**, *17*, 652−660. (g) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (h) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *Inorg. Chim. Acta* **1991**, *189*, 105−110. (i) Handler, A.; Peringer, P.; Muller, E. P. *J. Chem. Soc., Dalton Trans.* **1990**, 3725−3727. (j) Maassarani, F.; Davidson, M. F.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, M. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1995**, *235*, 327−338. (k) Schaefer, H.; Binder, D. *Z. Anorg. Allg. Chem.* **1988**, *560*, 65−79. (l) Allen, C. W.; Ebsworth, E. A. V.; Henderson, S. G.; Rankin, D. W. H.; Robertson, H. E.; Turner, B.; Whitelock, J. D. *J. Chem. Soc., Dalton Trans.* **1986**, 1333−1338.

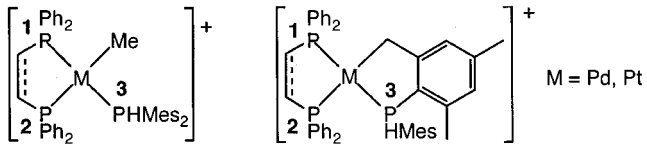
(4) For Ni terminal phosphido complexes, see: (a) Schaefer, H.; Binder, D.; Deppisch, B.; Mattern, G. *Z. Anorg. Allg. Chem.* **1987**, *546*, 79−98. (b) Schaefer, H. *Z. Anorg. Allg. Chem.* **1979**, *459*, 157−169. (c) Driess, M.; Pritzkow, H.; Winkler, U. *J. Organomet. Chem.* **1997**, *529*, 313−321. (d) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846−3847.

(5) For Pd bridging phosphido complexes, see: (a) Leoni, P.; Marchetti, P.; Papucci, S.; Pasquali, M. *J. Organomet. Chem.* **2000**, *593*−*594*, 12−18. (b) Zhuravel, M. A.; Moncarz, J. R.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 3447−3454. (c) Review: Mealli, C.; Ienco, A.; Galindo, A.; Carreño, E. P. *Inorg. Chem.* **1999**, *38*, 4620−4625. (d) See also: Belykh, L. B.; Cherenkova, T. V.; Shmidt, F. K. *Russ. J. Coord. Chem. (Engl. Transl.)* **1999**, *25*, 418−422. (e) For Pd diphosphaureylene complexes (formally, terminal phosphido complexes, with the chelating Mes*PC(O)PMes* ligand; Mes* = 2, 4, 6-(t-Bu)$_3C_6H_2$), see: David, M.-A.; Wicht, D. K.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4768−4770.

(6) (a) Zhuravel, M. A. Ph.D. Thesis, Dartmouth College, 2000. (b) Zhuravel, M. A.; Wicht, D. K.; Sweeder, R. D.; Moncarz, J. R.; Glueck, D. S.; Lam, K.-C.; Yap, G. P. A., Incarvito, C. D.; Sommer, R.; Rheingold, A. L. Manuscript in preparation.

10.1021/om020249k CCC: $22.00
Publication on Web 06/19/2002

Table 1. ^{31}P NMR and Selected ^{1}H NMR and IR Data for Cationic Complexes 1−8[a]

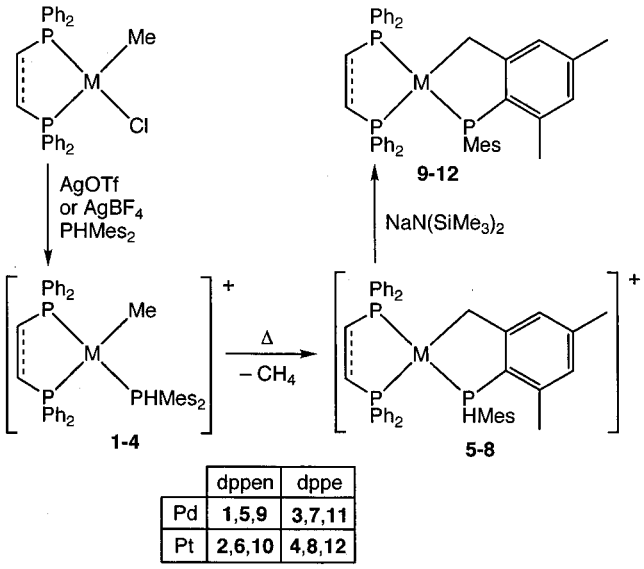


1-4 5-8

compd	$\delta(P_1)$ (J_{PtP})	$\delta(P_2)$ (J_{PtP})	$\delta(P_3)$ (J_{PtP})	J_{13}	J_{12}	J_{23}	δ(PH)	$^{1}J_{PH}$	ν_{PH}
1	64.6	54.4	−47.6	373	12	33	6.61	360	2389
2	59.1 (2852)	55.9 (1711)	−50.0 (2597)	387	8	16	6.95	366	2372
3	59.5	42.7	−47.2	367	33	26	6.52	357	2318
4	54.9 (2846)	49.6 (1692)	−42.8 (2553)	379	4	17	7.01	378	*b*
5	56.9	50.7	−19.7	344	16	29	*b*	*b*	2384
6	61.5 (2757)	59.3 (1786)	−16.7 (2681)	358	8	13	6.51	*b*	2391
7	54.7	43.8	−14.8	339	29	30	6.53	364	2381
8	50.1 (2767)	44.2 (1788)	−17.7 (2632)	352	7	15	*b*	362[c]	2390

[a] Legend and conditions: M = Pd (**1**, **3**, **5**, **7**), Pt (**2**, **4**, **6**, **8**); diphos = dppen (**1**, **2**, **5**, **6**), dppe (**3**, **4**, **7**, **8**); solvent CD_2Cl_2; ^{31}P NMR chemical shift reference external H_3PO_4 (85%); coupling constants in Hz. [b] Not observed. [c] From the ^{31}P NMR spectrum.

Scheme 1



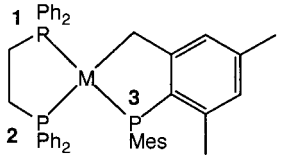
	dppen	dppe
Pd	1,5,9	3,7,11
Pt	2,6,10	4,8,12

spectroscopic data agree well with those for the analogous dppe complexes $[M(dppe)(Me)(PMes_2H)]^+$ (M = Pd (**3**), Pt (**4**)).[7]

As previously reported for **3** and **4**, thermolysis of **1** and **2** (Scheme 1) produced the cyclometalated complexes $[M(dppen)(CH_2C_6H_2Me_2P(Mes)(H))][OTf]$ (M = Pd (**5**), Pt (**6**)) as white solids (Table 1).[7] In the $^{1}H\{^{31}P\}$ NMR spectra (CD_2Cl_2) of **5** and **6** the cyclometalated CH_2 protons appear as AB patterns at δ 3.68−3.57 ($^{2}J_{HH}$ = 15 Hz) and 3.98−3.56 ($^{2}J_{HH}$ = 18 Hz), respectively. In the $^{13}C\{^{1}H\}$ NMR spectra (CD_2Cl_2) of **5** and **6** the M−CH_2 groups gave rise to doublets at δ 40.8 ($^{2}J_{PC}$ = 84 Hz) and 34.8 ($^{2}J_{PC}$ = 78 Hz), respectively. This is consistent with the observations for the dppe complexes $[M(dppe)(CH_2C_6H_2Me_2P(Mes)(H))][OTf]$ (M = Pd (**7**), Pt (**8**)).[7]

Deprotonation of **5**−**8** with $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, or other bases gave the neutral phosphido compounds M(diphos)($CH_2C_6H_2Me_2P$(Mes)) (diphos = dppen, M = Pd (**9**), M = Pt (**10**); diphos = dppe, M = Pd (**11**), M = Pt (**12**)) (Scheme 1). Since these neutral complexes tended to cocrystallize with LiOTf or NaOTf, we prepared and deprotonated the analogous BF_4 salts of **5**−**8** (see the Experimental section). The less soluble $NaBF_4$ could be separated from **9**−**12** by recrystallization. The ^{31}P NMR spectra of salt-free **9**−**12** were identical with those of samples which contained triflate or BF_4 salts. As previously observed for terminal Pt and Pd phosphido complexes, **9**−**12** display reduced trans J_{PP} and J_{PtP} values (Table 2) in comparison to cationic precursors **5**−**8**.[3,5]

Table 2. ^{31}P NMR Data for Terminal Phosphido Complexes 9−12[a]



diphos = dppen
M = Pd (**9**)
M = Pt (**10**)

diphos = dppe
M = Pd (**11**)
M = Pt (**12**)

compd	$\delta(P_1)$ (J_{PtP})	$\delta(P_2)$ (J_{PtP})	$\delta(P_3)$ (J_{PtP})	J_{13}	J_{12}	J_{23}
9	47.3	47.0	30.5	124	3	7
10	56.9 (1895)	58.0 (1935)	10.6 (1102)	140	13	*b*
11	36.4	34.4	24.7	124	21	8
12	47.9 (1922)	45.9 (1933)	8.8 (1112)	143	*b*	*b*

[a] Conditions: solvent toluene-d_8; ^{31}P NMR chemical shift reference external H_3PO_4 (85%); coupling constants in Hz. [b] Not observed.

We reported previously that the terminal phosphido alkyl complex Pd(dppe)(Me)(PHMes*) decomposed by P−C reductive elimination below room temperature, and this reactivity appears to be general for such complexes.[3g,6] However, Pd complexes **9** and **11** are thermally stable, and **9** showed no traces of decomposition on heating at 60 °C for 3 days or heating to 100 °C for 30 min. The chelate may prevent reductive elimination by restricting approach of the P and C atoms, or ring strain in the putative product might make P−C bond formation thermodynamically unfavorable.

Pd complexes **9** (as a pentane hemisolvate) and **11** were further characterized by X-ray crystallography (see Figures 1 and 2 for ORTEP diagrams and Table 3 and the Supporting Information for details of data collection and refinement). As observed in analogous Pt complexes, the phosphido P atoms are pyramidal (sum of angles 319.6 and 324.6°, respectively).[3]

The structures of **9**·0.5C_5H_{12} and **11**, which are very similar, may be compared to that of the previously

(7) Zhuravel, M. A.; Grewal, N. S.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2882−2890.

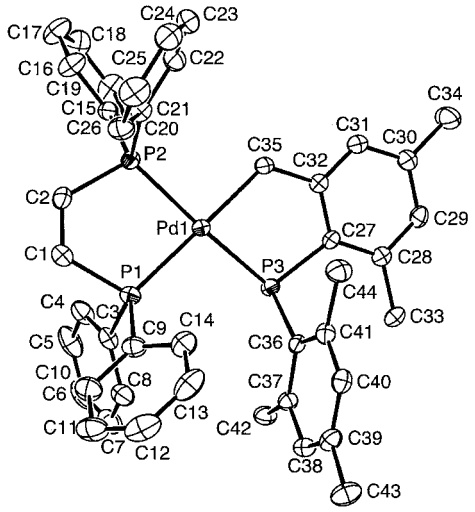


Figure 1. ORTEP diagram of Pd(dppen)($CH_2C_6H_2Me_2P$-(Mes))·$0.5C_5H_{12}$ (**9**·$0.5C_5H_{12}$) with thermal ellipsoids at 30% probability. Hydrogen atoms and the disordered solvent molecule are not shown.

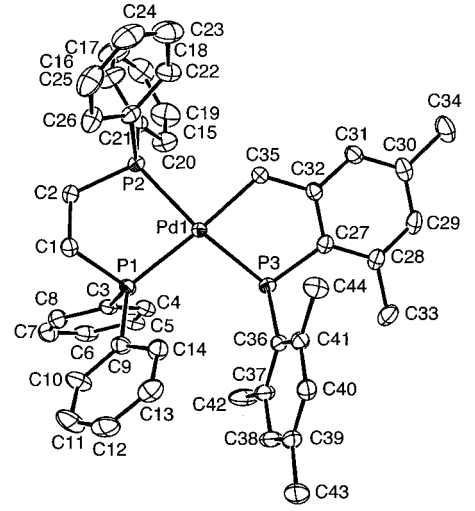


Figure 2. ORTEP diagram of Pd(dppe)($CH_2C_6H_2Me_2P$-(Mes)) (**11**) with thermal ellipsoids at 30% probability. Hydrogen atoms are not shown.

reported [Pd(dppe)($CH_2C_6H_2Me_2P$(Mes)(H))][OTf] (**7**·$0.5C_7H_8$);[7] for selected bond lengths and angles, see Table 4. Interestingly, all three Pd−P bonds, as well as the Pd−C bond, are shorter in neutral **9** and **11** than in the related cationic precursor **7**. In contrast, conversion of *trans,mer*-[$IrCl_2(PH_3)(PMe_2Ph)_3$]$^+$ to neutral *trans,-mer*-[$IrCl_2(PH_2)(PMe_2Ph)_3$] led to an increase in the Ir−P(phosphido) bond length.[8] Perhaps the structural changes in the Pd complexes may be ascribed to reduced steric hindrance at the crowded P atom upon deprotonation.

Variable-Temperature NMR Behavior. The observation of five separate signals due to methyl groups in the ^{1}H NMR spectrum of **8** (CD_2Cl_2, 21 °C) prompted a variable-temperature study of rotation about the P−C(Mes) bond in cations **5**−**8** (Table 5). In the low-temperature limit, when rotation is slow on the NMR time scale, the *o*-Me protons give rise to two resonances; two more are observed for the *m*-Mes protons. At high temperature, these signals coalesce separately to give an averaged spectrum with equivalent ortho and meta groups. The rotational barriers thus measured range from 14.4 to 15.4 kcal/mol, with good agreement between the results obtained from coalescence of the two groups of signals.[9]

Similar coalescence behavior was observed for the *o*-Me and *m*-Mes resonances in the variable-temperature ^{1}H{^{31}P} NMR spectra of neutral phosphido complexes **9**−**12** (Table 6). Moreover, the signals due to the diastereotopic CH_2 protons also show dynamic behavior. In the low-temperature limit, AB patterns were observed, while at high temperature these protons are equivalent, yielding singlet signals. Measurement of the coalescence temperatures for the three separate groups

Table 3. Crystallographic Data for Pd(dppen)($CH_2C_6H_2Me_2P$(Mes))·$0.5C_5H_{12}$ (9**·$0.5C_5H_{12}$) and Pd(dppe)($CH_2C_6H_2Me_2P$(Mes)) (11)**

	9·$0.5C_5H_{12}$	**11**
formula	$C_{46.5}H_{49}P_3Pd$	$C_{44}H_{45}P_3Pd$
fw	807.17	773.11
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.4352(17)	9.6982(7)
b, Å	23.389(4)	11.7577(8)
c, Å	18.249(3)	16.9489(12)
α, deg	90	79.3180(10)
β, deg	90.213(4)	80.2990(10)
γ, deg	90	88.0510(10)
V, Å^3	4027.2(12)	1872.0(2)
Z	4	2
D(calcd), g/cm^3	1.331	1.372
μ(Mo Kα), mm^{-1}	0.611	0.654
temp, K	223(2)	221(2)
diffractometer	Siemens P4 CCD	Siemens P4 CCD
radiation	MoKα (0.710 73 Å)	MoKα (0.710 73 Å)
$R(F)$, %[a]	4.02	3.83
$R_w(F^2)$, %[a]	9.87	13.49

[a] Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Cyclometalated Complexes [Pd(dppe)($CH_2C_6H_2Me_2P$(Mes)(H))][OTf]·$0.5C_7H_8$ (7**·$0.5C_7H_8$),[a] Pd(dppe)($CH_2C_6H_2Me_2P$(Mes)) (11), and Pd(dppen)($CH_2C_6H_2Me_2P$(Mes))·$0.5C_5H_{12}$ (**9**·$0.5C_5H_{12}$)**

	7·$0.5C_7H_8$	**11**	**9**·$0.5C_5H_{12}$
	Bond Lengths		
Pd−C(35)	2.137(13)	2.080(3)	2.091(4)
Pd−P(1)	2.415(3)	2.3266(8)	2.3104(11)
Pd−P(2)	2.381(3)	2.3143(8)	2.3025(12)
Pd−P(3)	2.380(3)	2.3270(8)	2.3292(12)
P(3)−C(27)	1.909(11)	1.816(4)	1.837(4)
P(3)−C(36)	1.904(10)	1.844(3)	1.855(4)
	Bond Angles		
C(35)−Pd−P(1)	174.1(3)	173.71(10)	175.00(13)
C(35)−Pd−P(2)	90.0(3)	90.60(9)	92.51(12)
P(2)−Pd−P(1)	84.54(9)	85.93(3)	85.44(4)
C(35)−Pd−P(3)	82.7(3)	83.34(9)	83.49(12)
P(2)−Pd−P(3)	172.72(9)	164.03(3)	170.19(4)
P(1)−Pd−P(3)	102.74(10)	101.34(3)	99.24(4)
Pd−P(3)−C(27)	104.7(4)	102.44(10)	102.35(13)
Pd−P(3)−C(36)	121.1(3)	114.51(10)	112.30(14)
C(27)−P(3)−C(36)	110.7(5)	107.60(14)	104.92(18)

[a] Zhuravel, M. A.; Grewal, N. S.; Glueck, D. S.; Lam, K.-C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2882−2890.

(8) Deeming, A. J.; Doherty, S.; Marshall, J. E.; Powell, J. L.; Senior, A. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1093−1100.

(9) Friebolin, H. In *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: New York, 1993; pp 287−314.

Table 5. Variable-Temperature $^1H\{^{31}P\}$ NMR Data for Cationic Complexes of Cyclometalated Dimesitylphosphine[a]

complex (M(diphos))	resonance	δ (ppm)	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_c^{\ddagger}$ (kcal/mol)
5 (Pd(dppen))	Me	2.12, 1.68	217	319	14.8
	Ar	6.81, 6.48	162	314	14.8
6 Pt(dppen))	Me	2.11, 1.71	203	319	14.9
	Ar	6.78, 6.45	162	319	15.0
7 Pd(dppe))	Me	1.95, 1.86	48	294	14.5
	Ar	6.72, 6.62	53	294	14.4
8 (Pt(dppe))	Me	1.99, 1.87	57	314	15.4
	Ar	6.71, 6.60	58	314	15.4

[a] Legend and conditions: anion BF_4; solvent CD_2Cl_2 for **7**, $CDCl_3$ for **5**, **6**, and **8**; chemical shifts and $\Delta\nu$ values from slow-exchange spectra at −40 °C for **5**, −20 °C for **6**, 0 °C for **7**, and 21 °C for **8**; estimated errors are different for each resonance, "typical" errors are 5 Hz in $\Delta\nu$, 10 °C in T_c, and 0.5 kcal/mol in $\Delta G_c^{\ddagger}$.

Table 6. Variable-Temperature $^1H\{^{31}P\}$ NMR Data for Terminal Phosphido Complexes Derived from Cyclometalated Dimesitylphosphine[a]

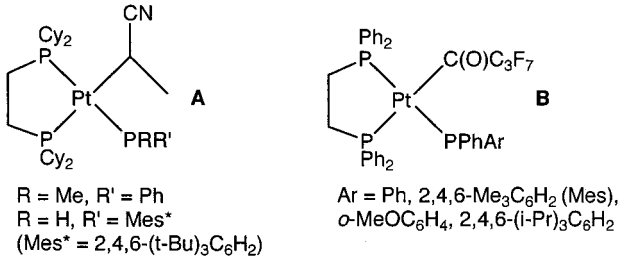
complex (M(diphos))	resonance	δ (ppm)	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_c^{\ddagger}$ (kcal/mol)
9 (Pd(dppen))	CH_2	4.30, 3.63[b]	332	321	14.6
	Me	2.76, 2.00	380	323	14.6
	Ar	6.62, 6.34	140	306	14.4
10 (Pt(dppen))	CH_2	4.39, 4.34[c]	21	270	13.3
	Me				*f*
	Ar	6.55, 6.18	183	286	13.3
11 (Pd(dppe))	CH_2	3.91, 3.58[d]	163	309	14.5
	Me	2.46, 2.31	164	297	14.4
	Ar	6.62, 6.49	61	292	14.2
12 (Pt(dppe))	CH_2	4.17, 3.73[e]	217	281	13.0
	Me	2.46, 2.41	27	271	13.6
	Ar	6.50, 6.31	97	276	13.2

[a] Legend and conditions: solvent toluene-d_8; chemical shifts, $\Delta\nu$ values, and coupling constants from slow-exchange spectra at −40 °C (**9**), −75 °C (**10**), −20 °C (**11**), and −60 °C (**12**); estimated errors are different for each resonance, "typical" errors are 5 Hz in $\Delta\nu$, 10 °C in T_c, and 0.5 kcal/mol in $\Delta G_c^{\ddagger}$. [b] J_{HH} = 14 Hz. [c] J_{HH} = 18 Hz; J_{PtH} = 83 Hz (δ 4.39), 55 Hz (δ 4.34). [d] J_{HH} = 14 Hz. [e] J_{HH} = 17.5 Hz, J_{PtH} = 85 Hz (δ 4.17), 50 Hz (δ 3.73). [f] Not observed.

of signals in these spectra provides approximate free energies of activation for the dynamic processes (Table 6).[9] The good agreement between the data obtained for the three different groups suggests that the same process(es) are responsible in each case. The similarity of the barriers for the dppe and dppen complexes indicates that conformational changes in the dppe ring are not involved. The observed barriers are similar for Pd and Pt complexes.

Dynamic Processes. Pyramidal inversion at phosphorus in metal phosphido complexes is rapid on the NMR time scale.[10] Variable-temperature NMR observations provide barriers to a composite process, which includes both P inversion and rotation about the M−P bond. For the Pt phosphido complexes Pt(diphos)(X)[P(R)(R′)] (diphos = diphosphine, X = alkyl (**A**), C(O)C_3F_7 (**B**); Chart 1), such barriers range from 11 to 16 kcal/mol, similar in magnitude to the barriers described above for **9**−**12**.[3c,d]

Chart 1



The M−CH_2 protons in phosphido complexes **9**−**12** were intended to serve as ^1H NMR spectroscopic probes of phosphorus inversion. As for the diastereotopic CF_2 fluorines in **B**, the diastereotopic protons in a CH_2 group are expected to have different chemical shifts if inversion is slow on the NMR time scale, while rapid phosphorus inversion via a planar transition state makes them equivalent. As foreseen, the ^1H NMR signals due to the CH_2 groups are singlets in the high-temperature limit, consistent with rapid P inversion. In the low-temperature spectra, AB patterns are observed, consistent with slow inversion on the NMR time scale. Since rotation about the M−P bond is prevented by the chelate, the measured barriers are those for a pure inversion process.

This analysis assumes that both chelate rings can access a conformation in which the square plane of the molecule is a plane of symmetry. Further, the P−Mes group must be able to occupy the square plane or be perpendicular to it. The latter conformation, with a pyramidal P, is similar to that observed in the solid-state structure of **9**. If this conformation is maintained in solution, then the *o*-Me and *m*-H positions of the P−Mes group could be made equivalent at high temperature either by rotation about the P−C(Mes) bond or by P inversion via a planar transition state. The low-temperature NMR observations of these inequivalent Mes signals then require *both* these processes to be slow on the NMR time scale.[11]

Since the coalescence behavior of the CH_2 proton signals and those from the P−Mes group leads to the same barriers, this analysis suggests that the barrier to P−C(Mes) rotation is greater than or equal to the inversion barrier. This is consistent with the measured rotation barriers in cations **5**−**8**, which should be a good model for those in neutral complexes **9**−**12**; barriers to rotation and inversion are probably similar in magnitude.

The variable-temperature NMR behavior of samples of **9**−**12** which contained LiOTf was identical with that of salt-free material, which suggests that inversion does not occur via heterolytic cleavage of the M−P bonds to give an ionic intermediate. Instead, as commonly as-

(10) (a) Rogers, J. R.; Wagner, T. P. S.; Marynick, D. S. *Inorg. Chem.* **1994**, *33*, 3104−3110. (b) Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1985**, *24*, 3505−3507. (c) Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 3980−3993. (d) Crisp, G. T.; Salem, G.; Wild, S. B.; Stephan, F. S. *Organometallics* **1989**, *8*, 2360−2367. (e) Malisch, W.; Maisch, R.; Meyer, A.; Greissinger, D.; Gross, E.; Colquhoun, E. J.; McFarlane, W. *Phosphorus Sulfur Relat. Elem.* **1983**, *18*, 299−302. (f) Baker, R. T.; Whitney, J. G.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049−1051. (g) Bonnet, G.; Kubicki, M. M.; Moise, C.; Lazzaroni, R.; Salvadori, P.; Vitulli, G. *Organometallics* **1992**, *11*, 964−967. (h) Fryzuk, M. D.; Joshi, K.; Chadha, R. K.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 8724−8736. (i) References 3a−d.

(11) If the P(Mes) group adopts a low-temperature conformation which is unsymmetrical with respect to the square plane (i.e., neither parallel nor perpendicular to it), then the CH_2 protons as well as the *o*-Me groups and *m*-H protons would be inequivalent. In this case, the measured barriers would reflect only P−C(Mes) rotation. We favor the simpler explanation in the text, however.

sumed, we believe that inversion proceeds via a planar-P transition state.

Conclusion

Deprotonation of cationic Pd(II) and Pt(II) complexes derived from cyclometalated dimesitylphosphine gave neutral terminal phosphido compounds, including unusual stable Pd phosphido alkyls. As in closely related complexes, the variable-temperature NMR behavior is consistent with low barriers (13−15 kcal/mol) to phosphorus inversion, which are similar for Pd and Pt compounds. In contrast to previous work, incorporating the phosphido group in a chelate ring enabled measurement of pure inversion barriers by stopping rotation about the M−P bond.

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_2Cl_2 was distilled from CaH_2. Acetone and acetonitrile were degassed by purging with N_2 and stored over molecular sieves.

NMR spectra were recorded with Varian 300 and 500 MHz spectrometers. ^1H and ^{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 otherwise noted, peaks in NMR spectra are singlets. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory.

Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature procedures: Pd(cod)(Me)(Cl),[12] Pt(cod)(Me)(Cl),[13] $PMes_2H$,[14] and cyclometalated cations **7** and **8**.[7]

Pd(dppen)(Me)(Cl). To a slurry of Pd(cod)(Me)(Cl) (376 mg, 1.42 mmol) in 10 mL of toluene was added dppen (565 mg, 1.42 mmol), and the mixture was stirred for 2 days. The solution was decanted, and the solid residue was washed with 3 × 10 mL of ether and dried in vacuo to give the product as 735 mg (94% yield) of off-white solid. Anal. Calcd for $C_{27}H_{25}P_2ClPd$: C, 58.61; H, 4.55. Found: C, 58.23; H, 4.65.

^1H NMR (CD_2Cl_2): δ 7.77−7.71 (m, 4H, Ph), 7.65−7.57 (m, 4H, Ph), 7.56−7.40 (m, 13H), 7.25 (ddd, 1H, J = 9, 11, 55, CH), 0.76 (dd, 3H, J = 8, 3, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 66.6 (d, J = 14), 50.2 (d, J = 14). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.7 (dd, J = 44, 43, CH), 144.9 (dd, J = 34, 25, CH), 133.5−133.2 (m), 132.1, 131.8 (d, J = 3), 131.1 (d, J = 2), 130.3−129.9 (m), 129.5−129.2 (m), 128.6, 9.4 (d, J = 106, Me). IR: 3048, 2977, 2884, 1584, 1571, 1481, 1434, 1307, 1184, 1135, 1101, 1069, 1026, 998, 848, 741, 695 cm^{-1}.

Pt(dppen)(Me)(Cl). To a slurry of Pt(cod)(Me)(Cl) (99 mg, 0.28 mmol) in 4 mL of toluene was added dppen (120 mg, 0.31 mmol). After 2 h of stirring the solution was decanted, and the solid residue was washed with 3 × 10 mL of ether and dried in vacuo to give the product as 155 mg (86% yield) of white solid. Anal. Calcd for $C_{27}H_{25}P_2ClPt$: C, 50.51; H, 3.93. Found: C, 50.37; H, 3.79.

^1H NMR (CD_2Cl_2): δ 7.85−7.71 (m, 4H, Ph), 7.67−7.59 (m, 4H, Ph), 7.56−7.41 (m, 12H, Ph), 7.36−7.06 (m, 2H, CH), 0.64 (dd, 3H, J = 4, 6, J_{PtH} = 56). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.9 (d, J = 11, J_{PtP} = 1745), 46.7 (d, J = 11, J_{PtP} = 4221). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.4 (dd, J = 34, 55, CH), 146.0 (dd, J = 19, 43, CH), 133.5−133.2 (m), 131.9 (d, J = 3), 131.4, 131.2 (d, J = 3), 129.3−129.1 (m), 128.7, 6.1 (dd, J = 98, 6, Me, Pt satellites not observed). IR: 3050, 2989, 2932, 2876, 2793, 1586, 1482, 1435, 1307, 1184, 1159, 1103, 1069, 1026, 998, 848, 739, 720, 699 cm^{-1}.

[Pd(dppen)(Me)($PMes_2H$)][OTf] (1). To a slurry of Pd(dppen)(Me)(Cl) (213 mg, 0.39 mmol) in 3 mL of a THF/MeCN mixture (10:1) was added AgOTf (99 mg, 0.39 mmol) and $PMes_2H$ (104 mg, 0.39 mmol). Grey precipitate formed instantly, and the reaction mixture was allowed to stand for 15 min. The solution was filtered, and the solvent was removed under vacuum. The resulting crude product was washed with 3 × 10 mL of petroleum ether and dried in vacuo to give the final product as 336 mg (93% yield) of white solid. Anal. Calcd for $C_{46}H_{48}P_3SO_3F_3Pd$: C, 58.95; H, 5.16. Found: C, 58.59; H, 5.25.

^1H NMR (CD_2Cl_2): δ 7.68−7.16 (m, 22H), 6.79 (d, J = 3, 4H, Mes), 6.61 (dd, J = 360, 12, 1H, P−H), 2.25 (6H, Me), 2.09 (12H, Me), 0.52−0.45 (m, 3H, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64.6 (dd, J = 12, 373), 54.4 (dd, J = 12, 33), −47.6 (dd, J = 373, 33). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.0−145.8 (m), 142.2 (d, J = 8), 141.8, 133.2 (d, J = 11), 132.6 (d, J = 4), 132.4 (d, J = 12), 132.1 (d, J = 2), 130.7 (d, J = 7), 130.0 (d, J = 11), 129.7 (d, J = 9), 128.7 (d, J = 40), 128.2 (d, J = 51), 120.7−120.0 (m), 23.3 (d, J = 10, Me), 21.0 (d, J = 1, Me), 5.2 (d, J = 81, Me). IR: 3054, 2967, 2919, 2389, 1603, 1557, 1437, 1379, 1268, 1223, 1150, 1101, 1030, 853, 749, 697 cm^{-1}.

[Pt(dppen)(Me)($PMes_2H$)][OTf] (2). To a slurry of Pt(dppen)(Me)(Cl) (82 mg, 0.13 mmol) in 2 mL of THF was added 0.1 mL of MeCN, AgOTf (33 mg, 0.13 mmol), and $PMes_2H$ (35 mg, 0.13 mmol), and the resulting gray slurry was stirred for 5 min. The solution was filtered, petroleum ether was added, and cooling to −25 °C gave the product as 115 mg (88% yield) of white solid. Anal. Calcd for $C_{46}H_{48}P_3SO_3F_3Pt$: C, 53.85; H, 4.72. Found: C, 54.07; H, 4.95.

^1H NMR (CD_2Cl_2): δ 7.70−7.42 (m, 13H), 7.38−7.26 (m, 9H), 6.79 (d, J = 3, 4H, Mes), 6.95 (dm, $^1J_{PH}$ = 366, 1H, PH), 2.26 (6H, Me), 2.13 (12H, Me), 0.64−0.37 (m, $^2J_{PtH}$ = 60, 3H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 59.1 (dd, J = 8, 387, J_{PtP} = 2852), 55.9 (dd, J = 8, 16, J_{PtP} = 1711), −50.0 (dd, J = 16, 387, J_{PtP} = 3377). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.3−145.5 (m), 142.5−142.1 (m), 133.4−133.1 (m), 132.7−132.2 (m), 130.7 (d, J = 9), 129.9 (d, J = 11), 129.5 (d, J = 10), 128.4, 128.0, 127.6, 127.1, 119 (m), 23.3 (m), 21.0, −2.5 (dm, J = 74, J_{PtC} = 529, Me). IR: 3054, 2967, 2920, 2372, 1603, 1557, 1437, 1272, 1223, 1151, 1101, 1030, 852, 749, 697 cm^{-1}.

[Pd(dppen)($CH_2C_6H_2Me_2P$(Mes)(H))][OTf] (5). A solution of **1** (72 mg, 0.08 mmol) in 1 mL of THF was placed in an NMR tube and heated at 60−65 °C for 3 days. The resulting orange solution was filtered, petroleum ether was added, and cooling to −30 °C gave the product as 45 mg (63% yield) of orange solid. Anal. Calcd for $C_{45}H_{44}P_3SO_3F_3Pd$: C, 58.67; H, 4.81. Found: C, 58.48; H, 4.81.

^1H NMR (CD_2Cl_2): δ 7.70−7.26 (m, 18H), 7.06−6.98 (m, 3H), 6.83−6.65 (m, 5H), 3.63 (br, 2H, Pd−CH_2), 2.27 (6H), 2.10 (br, 3H), 1.91 (3H), 1.78 (br, 3H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 56.9 (dd, J = 344, 16), 50.7 (dd, J = 29, 16), −19.7 (dd, J = 344, 29). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.2−156.9 (m), 147.6−147.0 (m), 145.4−144.8 (m), 143.9 (m), 142.7, 142.3 (m), 134.0 (d, J = 14), 133.2−133.1 (m), 132.7 (d, J = 3), 132.6 (d, J = 2), 131.1, 131.0 (m), 130.3−130.0 (m), 129.8, 129.7, 129.4 (d, J = 10), 129.2, 128.9, 128.8−128.6 (m), 128.5, 128.2, 128.1, 127.7, 125.2−124.8 (m), 122.6, 122.1, 121.7, 120.1, 117.5, 40.8 (d, J = 84), 23.0−22.2 (br m), 21.2−21.1 (m), 20.1−20.0 (m). IR: 2918, 2384 (PH), 1601, 1563, 1436, 1070, 893, 852, 745, 696.

(12) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937−1948.
(13) Clark, H. C.; Manzer, L. E. *Inorg. Chem*. **1974**, *13*, 1291−1297.
(14) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem*. **1987**, *26*, 1941−1946.

[Pt(dppen)($CH_2C_6H_2Me_2$P(Mes)(H))][OTf] (6). In air, a 25 mL ampule was charged with a solution of [Pt(dppen)(Me)-(PHMes$_2$)][Tf] (**2**; 480 mg, 0.47 mmol) in $Cl_2HCCHCl_2$ (6 mL). The ampule was evacuated, and the solution was heated at 95−100 °C for 3 days. The solvent was then removed under reduced pressure to give the crude product as a yellow oil, which was washed with 5 × 20 mL of petroleum ether and dried in vacuo to give the final product as 412 mg (87% yield) of white solid. Anal. Calcd for $C_{45}H_{44}SO_3F_3P_3Pt$: C, 53.52; H, 4.39. Found: C, 53.82; H, 4.65.

^{1}H NMR (CD_2Cl_2): δ 7.80−7.12 (m, 19H), 7.08−6.98 (m, 3H), 6.80−6.69 (m, 4H), 6.51 (br, 1H), 3.98−3.56 (m, 2H, $^2J_{HH}$ = 17.5, CH_2), 2.27 (6H, Me), 2.14 (br, 3H, Me), 1.92 (br, 3H, Me), 1.76 (br, 3H, Me). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 61.5 (dd, J = 358, 8, J_{PtP} = 2757), 59.3 (dd, J = 13, 8, J_{PtP} = 1786), −16.7 (dd, J = 358, 13, J_{PtP} = 2681). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 157.7−157.3 (m), 149.0−148.4 (m), 147.1 (m), 145.1−144.2 (m), 143.0−142.3 (m), 140.0 (br), 134.4−134.1 (m), 133.5−133.0 (m), 133.0−132.7 (m), 131.1−130.9 (m), 130.2−129.9 (m), 129.7−129.5 (m), 129.2 (d, J = 11), 128.7, 128.3, 128.0, 127.8, 127.6, 127.4, 125.3−124.7 (m), 122.6, 121.5, 121.1, 120.1, 34.8 (dm, J = 78), 22.9−22.6 (m), 22.2−21.9 (m), 21.1 (m), 20.2 (m). IR: 3054, 3006, 2920, 2391, 1603, 1564, 1483, 1437, 1379, 1278, 1223, 1148, 1103, 1071, 1031, 895, 853, 819, 743, 722 cm^{-1}.

M(diphos)($CH_2C_6H_2Me_2$P(Mes)) (9−12: M = Pd, Pt; diphos = dppen, dppe). Treatment of cations **5**−**8** with LiN(SiMe$_3$)$_2$, NaN(SiMe$_3$)$_2$, or other bases gave neutral complexes **9**−**12** in quantitative yields, according to ^{31}P NMR. However, we could not separate LiOTf from the metal complexes, and NaOTf could be removed only after repeated recrystallizations. Therefore, BF_4 salts of cations **5**−**8** were prepared using $AgBF_4$ instead of AgOTf; their NMR spectra were identical with those of the triflate salts. Deprotonation of **5(BF_4)**−**8(BF_4)** with NaN(SiMe$_3$)$_2$ enabled separation of the less soluble $NaBF_4$ to give pure **9**−**12** after recrystallization. These complexes are yellow or orange solids which are sparingly soluble in toluene, once pure. Details of the synthesis of **10** are provided below; preparations of the other complexes were very similar.

Pd(dppen)($CH_2C_6H_2Me_2$P(Mes)) (9). 9 was obtained in 82% yield; several recrystallizations from toluene/petroleum ether gave orange-yellow crystals suitable for X-ray crystallography and for elemental analysis. Both techniques showed the presence of 0.5 equiv of cocrystallized pentane. Anal. Calcd for $C_{44}H_{43}P_3Pd\cdot0.5C_5H_{12}$: C, 69.19; H, 6.12. Found: C, 68.94; H, 5.81.

^{1}H{^{31}P} NMR (toluene-d_8, 70 °C): δ 7.67−7.65 (m, 5H), 7.15−7.02 (m, 18H, obscured by toluene-d_8), 6.74 (1 H), 6.60 (2H), 3.85 (br, 2H), 2.42 (very br, 3H, Me), 2.33 (3H, Me), 2.21 (6H, obscured by toluene-d_8, Me), 2.13 (3H, Me). ^{1}H{^{31}P} NMR (toluene-d_8, 21 °C): δ 7.97 (br, 2H), 7.55 (br, 4H), 7.12−6.66 (m, 18H, obscured by toluene-d_8), 6.61 (br, 1H), 6.41 (br, 1H), 4.11 (br, 1H, CH_2), 3.50 (br, 1H, CH_2), 2.68 (br, 3H, Me), 2.28 (3H, Me), 2.13 (6H, Me), 2.00 (br, 3H, Me). ^{1}H{^{31}P} NMR (toluene-d_8, −40 °C): δ 7.97 (m, 2H), 7.54 (d, J = 7, 2H), 7.47 (m, 2H), 7.18−6.66 (m, 18H, obscured by toluene-d_8), 6.62 (1H), 6.34 (1H), 4.30 (AB pattern, J = 14, 1H), 3.63 (AB, J = 14, 1H), 2.76 (3H, Me), 2.33 (3H, Me), 2.18 (3H, Me), 2.13 (3H, Me), 2.00 (3H, Me). ^{31}P{^{1}H} NMR (toluene-d_8): δ 51.0 (dd, J = 124, 3), 50.7 (dd, J = 7, 3), 34.1 (dd, J = 124, 7). IR: 3051, 2914, 1599, 1435, 1262, 1159, 1100, 1031, 848, 736 cm^{-1}.

Pt(dppen)($CH_2C_6H_2Me_2$P(Mes)) (10). A solution of **6(BF_4)** (150 mg, 0.165 mmol) in 3 mL of THF was treated with NaN(SiMe$_3$)$_2$ (30 mg, 0.17 mmol) to give a deep red solution, which was filtered through Celite. Adding petroleum ether gave a cloudy orange solution, which was cooled to −25 °C to give an orange solid. The mother liquor was decanted, and the orange powder was washed with petroleum ether and then extracted with toluene (15 × 1 mL). The combined toluene extracts were filtered through Celite to give an orange solution. The toluene was removed in vacuo to give an orange powder (95 mg, 67% yield). Recrystallization from toluene/petroleum ether gave light orange chunks. Anal. Calcd for $C_{44}H_{43}P_3Pt$: C, 61.46; H, 5.04. Found: C, 61.45; H, 5.13.

^{1}H{^{31}P} NMR (toluene-d_8, 55 °C): δ 7.58 (m, 5H), 7.08−6.92 (m, 15H, obscured by toluene-d_8), 6.87−6.75 (m, 3H), 6.56 (1H), 6.42 (2H), 4.11 (J_{PtH} = 71, 2H), 2.37 (very br, 3H), 2.22 (3H), 2.11−2.08 (br, 6H, obscured by toluene-d_8), 2.03 (3H). ^{1}H{^{31}P} NMR (toluene-d_8, 21 °C): δ 7.58 (br, 5H), 7.14−6.98 (m, 15H, obscured by toluene-d_8), 6.82−6.69 (m, 3H), 6.61 (1H), 6.44 (very br, 2H), 4.16 (br, J_{PtH} = 70, 2H), 2.60 (very br, 3H), 2.25 (3H), 2.13−2.12 (br, 6H), 2.10 (3H, obscured by toluene-d_8). ^{1}H{^{31}P} NMR (toluene-d_8, −75 °C): δ 8.11 (d, J = 7, 2H), 7.64 (d, J = 7, 2H), 7.34 (d, J = 8, 2H), 7.29 (2H), 7.20−6.78 (m, 12H, obscured by toluene-d_8), 6.70−6.63 (m, 3H), 6.55 (1H), 6.49 (m, 1H), 6.18 (1H), 4.39 (br, AB, J = 18, J_{PtH} = 83, 1H), 4.34 (br, AB, J = 18, J_{PtH} = 55, 1H), 2.87 (3H), 2.35 (3H), 2.22 (6H), 2.15 (3H). ^{31}P{^{1}H} NMR (toluene-d_8, 21 °C): δ 58.0 (d, J = 13, J_{PtP} = 1935), 56.9 (dd, J = 140, 13, J_{PtP} = 1895), 10.6 (d, J = 140, J_{PtP} = 1102). IR: 3053, 2916, 1599, 1553, 1436, 1260, 1169, 1102, 1032, 849 cm^{-1}.

Pd(dppe)($CH_2C_6H_2Me_2$P(Mes)) (11). 11 was obtained in 55% yield; recrystallization from toluene/petroleum ether gave orange blocks suitable for X-ray crystallography. Anal. Calcd for $C_{44}H_{45}P_3Pd$: C, 68.35; H, 5.87. Found: C, 68.36; H, 5.76.

^{1}H{^{31}P} NMR (toluene-d_8, −20 °C): δ 7.89 (m, 2H), 7.54 (m, 2H), 7.45 (m, 2H), 7.13−6.81 (m, 15H), 6.69 (1H), 6.62 (1H), 6.49 (1H), 3.91 (AB, J = 14, 1H), 3.58 (AB, J = 14, 1H), 2.46 (3H), 2.31 (3H), 2.27 (3H), 2.16 (3H), 2.13 (3H), 1.88−1.81 (br, 3H), 1.72−1.66 (br, 1H). ^{1}H{^{31}P} NMR (toluene-d_8, 21 °C): δ 7.91 (br, 2H), 7.55 (br, 4H), 7.19−6.78 (br m, 15H), 6.68 (1H), 6.64−6.46 (m, 2H), 3.88 (br, 1H), 3.57 (br, 1H), 2.48−2.25 (very br, 6H), 2.25 (3H), 2.12 (3H), 2.10 (3H), 1.94−1.80 (very br, 4H). ^{1}H{^{31}P} NMR (toluene-d_8, 60 °C): δ 7.58 (m, 4H), 7.10−6.92 (m, 17H), 6.65 (1H), 6.53 (2H), 3.69 (br, 2H), 2.34 (br, 6H), 2.23 (3H), 2.10 (3H), 2.06 (3H), 1.97−1.94 (m, 2H), 1.92−1.89 (m, 2H). ^{31}P{^{1}H} NMR (toluene-d_8, 21 °C): δ 36.4 (dd, J = 124, 21), 34.4 (dd, J = 21, 8), 24.7 (dd, J = 124, 8). ^{13}C{^{1}H} NMR (toluene-d_8, 21 °C): δ 153.9−153.6 (m), 144.8−144.6 (m), 141.7 (m), 141.4 (m), 140.0−139.9 (m), 137.8, 135.5, 134.5, 134.8−131.8 (very br m), 130.3 (br), 129.1−128.2 (m), 127.2, 125.4, 36.8 (dm, J = 85, Pd−CH_2), 30.0−29.7 (m, PCH_2), 27.9−27.6 (m, PCH_2), 24.8 (br, Me), 21.2 (Me), 21.1 (Me), 21.0 (Me).

Pt(dppe)($CH_2C_6H_2Me_2$P(Mes)) (12). 12 was obtained in 37% yield; repeated recrystallization from toluene/petroleum ether gave orange chunks. Anal. Calcd for $C_{44}H_{45}P_3Pt$: C, 61.32; H, 5.26. Found: C, 61.34; H, 5.28.

^{1}H{^{31}P} NMR (toluene-d_8, 40 °C): δ 7.58 (5H), 7.09−6.95 (m, 16H, obscured by toluene-d_8), 6.57 (1H), 6.44 (2H), 3.94 (J_{PtH} = 70, 2H), 2.37 (6H), 2.20 (3H), 2.11 (3H), 2.05 (3H), 1.89−1.78 (br m, 4H). ^{1}H{^{31}P} NMR (toluene-d_8, 21 °C): δ 7.68 (5H), 7.19−7.06 (m, 16H, obscured by toluene-d_8), 6.70 (1H), 6.56 (2H), 4.07 (br, 2H), 2.50 (br, 6H), 2.32 (3H), 2.22 (3H), 2.21 (3H), 2.04−1.84 (br, 4H). ^{1}H{^{31}P} NMR (toluene-d_8, −60 °C): δ 8.08 (m, 2H), 7.54 (m, 2H), 7.21 (m, 2H), 7.08−6.74 (m, 13H, obscured by toluene-d_8), 6.65−6.62 (m, 2H), 6.54 (1H), 6.50 (1H), 6.31 (1H), 4.17 (br, AB, J = 17.5, J_{PtH} = 85, 1H), 3.73 (br, AB, J = 17.5, J_{PtH} = 50, 1H), 2.46 (3H), 2.41 (3H), 2.18 (3H), 2.12 (3H), 2.09 (3H), 1.84−1.82 (br, 2H), 1.55−1.35 (br, 2H). ^{31}P{^{1}H} NMR (toluene-d_8, 21 °C): δ 47.9 (d, J = 143, J_{PtP} = 1922), 45.9 (J_{PtP} = 1933), 8.8 (d, J = 143, J_{PtP} = 1112).

Crystallographic Structural Determination. Suitable crystals of **9**·0.5C_5H_{12} and **11** were obtained from toluene/petroleum ether at −25 °C. Crystal data and data collection and refinement parameters are given in Table 3. A Siemens P4 diffractometer equipped with a CCD detector was used. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were treated as idealized contributions. The pentane solvent molecule in **9**·

$0.5C_5H_{12}$ is disordered over two inversion centers and was refined with isotropic thermal parameters. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Variable-Temperature NMR Data. Spectra were obtained on a Varian 500 MHz NMR spectrometer. The reported temperatures were calibrated from the chemical shift difference of the signals in the ^{1}H NMR spectrum of a standard sample of methanol (temperatures <20 °C) or ethylene glycol (temperatures >20 °C). The uncertainty in the $\Delta G^{\ddagger}(T_c)$ values was estimated on the basis of the assumption that there is an error of ±10 °C in the determination of the coalescence temperature.

Acknowledgment. We thank the NSF, DuPont, and Union Carbide (Innovation Recognition Award) for support and the Department of Education for a GAANN fellowship for M.A.Z. The University of Delaware acknowledges the NSF (Grant No. CHE-9628768) for their support of the purchase of the CCD-based diffractometer.

Supporting Information Available: Tables giving details of the X-ray crystal structure determinations for **9**·$0.5C_5H_{12}$ and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020249K