Terminal Platinum(II) Phosphido Complexes: Synthesis, Structure, and Thermochemistry

Denyce K. Wicht, Sara N. Paisner, Belinda M. Lew, and David S. Glueck*

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

Glenn P. A. Yap, Louise M. Liable-Sands, and Arnold L. Rheingold

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

Christopher M. Haar and Steven P. Nolan

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received October 14, 1997

A series of terminal Pt(II) phosphido complexes Pt(dppe)(Me)(PRR′) (R = H; R′ = Mes* (**1**), R′ = Mes (**2**), R′ = Ph (**3**), R′ = Cy (**4**); R = R′ = Mes (**5**); R = R′ = Ph (**6**); R = R′ = Cy (**7**); R = R′ = Et (**8**); R = Ph, R′ = i-Bu (**9**)) has been prepared by proton transfer from the appropriate phosphine to the methoxide ligand of Pt(dppe)(Me)(OMe) (**10**) (dppe = $Ph_2PCH_2CH_2PPh_2$; Mes* = 2,4,6-$(t\text{-}Bu)_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$; Cy = cyclo-C_6H_{11}). Complexes **1** and **2** were also made by deprotonation of the cations [Pt(dppe)(Me)(PH_2Ar)][BF_4] (Ar = Mes* (**13**); Ar = Mes (**14**)). For comparison to **1**, the arylthiolate and aryloxide complexes Pt(dppe)(Me)(EMes*) (E = S (**11**); E = O (**12**)) were also prepared from **10**. NMR studies of the proton-transfer equilibria between Pt(dppe)(Me)(X), Pt(dppe)(Me)(Y), and the acids HY and HX (see Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456 and Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 1441−1452) provide an approximate partial ranking of Pt−P bond strengths in this series: Pt−PHPh > Pt−PHMes > Pt−PHMes*; Pt−PPh_2 > Pt−$PMes_2$. Complementary solution calorimetry investigations probe the role of entropic effects on the equilibria. Both steric and electronic factors appear to be important in controlling relative Pt−P bond strengths. The Pt−S bonds in **11** and Pt(dppe)(Me)(SPh) are stronger than the analogous Pt−P bonds in **1** and **3**. Complexes **1** and **5**·THF were structurally characterized by X-ray crystallography.

Introduction

Phosphido complexes of the group 10 metals are important proposed intermediates in catalytic phosphination[1] and hydrophosphination[2] reactions and in P−C cleavage processes that deactivate phosphine-containing metal complex catalysts.[3] Many phosphido-bridged dinuclear complexes of these metals have been reported,[4] but the more reactive terminal phosphido ligands, which are of greater relevance to the processes mentioned above, are less common, and little is known about the structure and properties of these compounds.[5] We report here synthetic, structural, and thermodynamic studies of a series of terminal Pt(II) phosphido compounds and of some related arylthiolate and aryloxide complexes, which provide information about the relative Pt−X bond strengths in this series of anionic ligands.

---

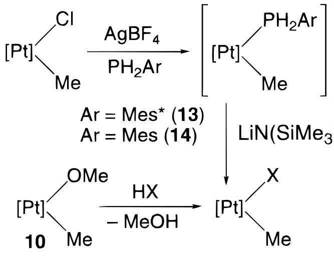
[1] (a) Hillhouse, J. H. *Abstracts of Papers*, 212th ACS National Meeting, Orlando, FL, 1996; American Chemical Society: Washington, DC, 1996; ORG329. (b) Hillhouse, J. H. U.S. Patent No. 5550295 (to Cytec), 1996. (c) Beletskaya, I. P.; Veits, Y. A.; Leksunkin, V. A.; Foss, V. L. *Bull. Russ. Acad. Sci., Div. Chem. Sci.* **1992**, *41*, 1272−1274. (d) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180−7181. (e) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*, 69−76. (f) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748−753. (g) Veits, Y. A.; Karlstedt, N. B.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1994**, *30*, 70−73. (h) Veits, Y. A.; Karlstedt, N. B.; Nasonova, N. S.; Borisenko, A. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1994**, *30*, 515−523.

[2] (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (b) Pringle, P. G.; Brewin, D.; Smith, M. B.; Worboys, K. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Kluwer: Dordrecht, 1995; Vol. 5, pp 111−122. (c) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, *74*, 269−274. (d) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701−1702. (e) Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096−1097. (f) Nagel, U.; Rieger, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223−239.

[3] (a) For a review of metal-mediated P−C cleavage reactions, see: Garrou, P. E. *Chem. Rev. (Washington, D.C.)* **1985**, *85*, 171−185. For selected recent examples involving the group 10 metals, see: (b) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794−2805. (c) Hartwig, J. F.; Richards, S.; Baranano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626−3633. (d) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313−6315. (e) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576−8581 and references therein. (f) Archambault, C.; Bender, R.; Braunstein, P.; De Cian, A.; Fischer, J. *Chem. Commun.* **1996**, 2729−2730. (g) Novak, B. M.; Wallow, T. I.; Goodson, F.; Loos, K. *Polym. Prepr.* **1995**, *36*, 693−694. (h) Wallow, T. I.; Novak, B. M. *Polym. Prepr.* **1993**, *34*, 1009−1010. (i) Wallow, T. I.; Seery, T. A. P.; Goodson, F. E., III.; Novak, B. M. *Polym. Prepr.* **1994**, *35*, 710−711. (j) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787−6795.

S0276-7333(97)00889-3 CCC: $15.00
Publication on Web 01/30/1998

Scheme 1[a]



X = PHMes* (**1**)
X = PHMes (**2**)
X = PHPh (**3**)
X = PHCy (**4**)
X = PMes$_2$ (**5**)
X = PPh$_2$ (**6**)
X = PCy$_2$ (**7**)
X = PEt$_2$ (**8**)
X = PPh(i-Bu) (**9**)
X = SMes* (**11**)
X = OMes* (**12**)

[a] [Pt] = Pt(dppe).

Results and Discussion

In connection with our studies of Pt-catalyzed hydrophosphination of acrylonitrile, we have previously communicated the synthesis of the terminal Pt(II) phosphido complexes Pt(dppe)(Me)(PRR′) (R = H; R′ = Mes* (**1**), R = R′ = Mes (**5**) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$; Mes = 2,4,6-Me$_3$C$_6$H$_2$)) as shown in Scheme 1.[2a] The two-step synthesis of **1** by complexation and deprotonation of supermesitylphosphine has been extended to mesitylphosphine to afford [Pt(dppe)(Me)(PH$_2$Mes)][BF$_4$] (**14**) and Pt(dppe)(Me)(PHMes) (**2**) (Scheme 1). A more convenient synthetic method involves treatment of the methoxide[6] Pt(dppe)(Me)(OMe) (**10**) with a phosphine to provide methanol and the phosphido complexes Pt(dppe)(Me)(PRR′) **1**–**9** (R = H; R′ = Mes (**2**), R′ = Ph (**3**), R′ = Cy (**4**); R = R′ = Ph (**6**); R = R′ = Cy (**7**); R = R′ = Et (**8**); R = Ph, R′ = i-Bu (**9**); Cy = cyclo-C$_6$H$_{11}$, Scheme 1). This approach also affords the arylthiolate and aryloxide complexes Pt(dppe)(Me)(EMes*) (E = S (**11**); E = O (**12**); Scheme 1). Significantly, the reactions of **10** with phosphines and the thiol proceed quantitatively with 1 equiv of added HX; the consequences of the position of these equilibria are considered in more detail below. Formation of aryloxide complex **12** is somewhat less clean, but again in this case the equilibrium qualitatively favors the products.

Most of the new platinum complexes were formed quantitatively from methoxide **10** and isolated in high yields as orange, yellow, or white solids after recrystallization (see the Experimental Section for details). These complexes were also stable in solution. However, reaction of **10** with diethylphosphine gave several byproducts in addition to complex **8**, which appears to be unstable in solution and could not be obtained pure. Similarly, the cyclohexylphosphido complex **4** could not be purified, and the mixed arylalkylphosphido complex **9** decomposed in solution at room temperature. The complexes were characterized by spectroscopic techniques and elemental analyses. The ^{31}P NMR spectra are particularly diagnostic and are given in Table 1. The cations **13** and **14** show $^1J_{PH}$ values much larger than those in the free phosphine (380 and 404 Hz)[7] and large trans $^2J_{P-P}$ couplings (400 and 392 Hz) similar to that in the cationic tertiary phosphine complex[8] [Pt(dppe)(Me)(PPh$_3$)]$^+$ (380 Hz). In addition, complex **13** shows a P–H stretch[9] in the IR spectrum at 2416 cm^{-1} and a PH$_2$ signal in the ^{1}H NMR spectrum (THF-d_8) at δ 6.07.

The neutral compounds show characteristically small trans $^2J_{P-P}$ and $^1J_{Pt-P}$ couplings to the phosphido ligands, as previously observed for platinum[5] and for other metal phosphido complexes[10] and rationalized in terms of low s-character in the Pt–P bond. These observations further suggest that the phosphido P is pyramidal with a stereochemically active lone pair and that a planar phosphido ligand involved in Pt–P multiple bonding is not present.[11]

In addition, the primary phosphido complexes show P–H stretches in the IR spectra from 2279 to 2232 cm^{-1}. The P–H protons in these complexes give rise to ^{1}H NMR signals ranging from 5.07 to 3.06 ppm, which show coupling to all three phosphorus nuclei and an additional Pt–H coupling of ~60 Hz. The one-bond P–H couplings of ~200 Hz are much smaller than those observed in cations **13** and **14** and similar to those in the free primary phosphines. Despite the bulky ligands employed, no restricted rotation of the Mes or Mes* groups is observed at room temperature by ^{1}H NMR. The new arylthiolate and aryloxide complexes **11** and **12** are spectroscopically similar to the previously reported Pt(dppe)(Me)(SPh),[8] Pt(dppe)(Me)(O-*p*-MeOC$_6$H$_4$),[8] and Pt(dppe)(Me)(O-*p*-Tol).[12]

Appleton and Bennett[8] have reported NMR data for a series of Pt(dppe)(Me)(X) complexes and shown that the trans influence of the X group correlates with the Pt–P coupling of the dppe phosphorus trans to X. Using this criterion, the terminal phosphido ligand in this series has a large trans influence similar to that of an alkyl group (Table 1). The relative trans influence of

---

(4) (a) Review: Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; pp 559–619. Selected recent references: (b) Sommovigo, M.; Pasquali, M.; Leoni, P.; Englert, U. *Inorg. Chem.* **1994**, *33*, 2686–2688. (c) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1994**, *13*, 4017–4025. (d) Sommovigo, M.; Pasquali, M.; Marchetti, F.; Leoni, P.; Beringhelli, T. *Inorg. Chem.* **1994**, *33*, 2651–2656. (e) Kourkine, I. V.; Chapman, M. B.; Glueck, D. S.; Eichele, K.; Wasylishen, R. E.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 1478–1485. (f) Maslennikov, S. V.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2483–2488. (g) Leoni, P.; Manetti, S.; Pasquali, M. *Inorg. Chem.* **1995**, *34*, 749–752.

(5) See ref 2a and (a) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *Inorg. Chim. Acta* **1991**, *189*, 105–110. (b) 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. (c) Handler, A.; Peringer, P.; Muller, E. P. *J. Chem. Soc., Dalton Trans.* **1990**, 3725–3727. (d) David, M.-A.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4040–4042. (e) Schafer, H.; Binder, D. *Z. Anorg. Allg. Chem.* **1988**, *560*, 65–79. For related dihydrodiphosphete and phospholene complexes, see: (f) Sillett, G.; Ricard, L.; Patois, C.; Mathey, F. *J. Am. Chem. Soc.* **1992**, *114*, 9453–9457.

(6) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603–1604.

(7) $^1J_{PH}$ in metal-coordinated primary phosphines is usually larger than in the free ligand, see: Kourkine, I. V.; Maslennikov, S. V.; Ditchfield, R.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 6708–6716 and references therein, and also ref 10.

(8) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738–747.

(9) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986.

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

(11) See refs 5 and 10. For somewhat different observations in a square-planar Rh–phosphido complex, see: Dahlenburg, L.; Hock, N.; Berke, H. *Chem. Ber.* **1988**, *121*, 2083–2093.

(12) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800–12814.

Table 1. ^{31}**P NMR Data for [Pt(dppe)Me(X)]**$^{n+}$ **(1−14)**^{a,b}

X	δ(PR$_2$)	J_{Pt-P} (PR$_2$)	J_{PP} (trans)	J_{PP} (cis)	δ(dppe) (trans)	δ(dppe) (cis)	J_{Pt-P} (trans)	J_{Pt-P} (cis)
PHMes* (**1**)^c	−71.1	863	131	12	46.5	47.4	1956	1756
PHMes (**2**)	−88.4	806	137		49.9	48.7	1978	1813
PHPh (**3**)	−53.2	819	143		49.8	51.0	2039	1842
PHCy (**4**)	−27.1	846	137		51.3	49.6	1870	1842
PMes$_2$ (**5**)	−56.4	1239	172		45.1	34.0	1993	1870
PPh$_2$ (**6**)	−7.8	1039	144	18	47.8	45.0	1932	1825
PCy$_2$ (**7**)^d	−15.6	948	108	22	46.0	39.3	1608	1836
PEt$_2$ (**8**)	−6.1	911	130	5	48.1	47.1	1643	1915
PPh(i-Bu) (**9**)	−29.9	946	134	12	48.0	45.3	1805	1871
OMe (**10**)^e					36.0	37.4	3356	1852
SMes* (**11**)					45.9	46.2	3053	1758
OMes* (**12**)					35.2	47.0	3914	1848
PH$_2$Mes* (**13**)	−66.8	2700	400	17	54.7	50.8	2979	1627
PH$_2$Mes (**14**)	−76.7	2469	392	20	57.6	52.4	2956	1724

^{a} Temperature = 22 °C. Chemical shifts in ppm, external ref 85% H_3PO_4, coupling constants in hertz. For **13** and **14**, $n = 1$; for **1**−**12**, $n = 0$. ^{b} Solvents: C_6D_6 for **1**−**9**, **11**, and **12**; THF-d_8 for **10** and **13**; MeCN for **14**. Trans and cis are with respect to the X group. ^{c} $^1J_{PH}$: 213 (**1**), 199 (**2**), 201 (**3**), 183 (**4**), 380 (**13**), 404 (**14**). ^{d} J_{PP}(cis, dppe) = 5. ^{e} Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805−4813.

the phosphido groups falls in the order X = PCy$_2$ > PEt$_2$ > PPh(i-Bu) > PHCy > PPh$_2$ > PHMes* > PHMes > PMes$_2$ > PHPh. Values for the mono- and dialkylphosphido groups are substantially lower, while the remaining mono- and diarylphosphides have similar trans influences. In the series of primary arylphosphido groups it appears that alkyl substitution slightly increases the trans influence, consistent with the presence of a more electron-rich aryl group. However, this effect is reversed in the secondary arylphosphides. The coordinated primary phosphines in **13** and **14** exhibit a trans influence slightly less than that of PPh$_3$ and P(OPh)$_3$ (J_{Pt-P} = 2743 and 2718 Hz).[8] The aryloxide and thiolate ligands are relatively low in the series and follow the trans influence order PHMes* > SMes* > OMes*. Comparison of the ^{31}P NMR data for these complexes shows that the SMes* group has a larger trans influence than the SPh ligand, but the opposite trend is observed for the aryloxides; the $^1J_{Pt-P(trans,\ dppe)}$ values are 3380 (SPh), 3053 (SMes*), 3840 (O-*p*-MeOC$_6$H$_4$), 3811 (O-*p*-Tol), and 3914 (OMes*).

X-ray Crystallographic Studies. The crystal structures of phosphido complexes **1** and **5** (as a THF solvate) have been determined (ORTEP diagrams are shown in Figures 1 and 2). Table 2 contains details of the data acquisition and solution and refinement of the structures, Table 3 contains selected bond lengths and angles, and additional information is provided in the Experimental Section and the Supporting Information.

Both complexes contain roughly square-planar Pt(II) centers, with the usual constraints imposed by the chelating dppe ligand. The dppe bite angle (85°) is the same in the two cases, and other angles at Pt are close to the ideal 90°, except for the Me−Pt−PHMes* angle of 97.2(6)°, which is a bit bigger than the corresponding 93.0(2)° angle in the PMes$_2$ case. This is balanced out by the Me−Pt−P(dppe) angles of 89.2(6)° and 92.0(2)°, respectively.

The Pt−PMes$_2$ bond distance (2.351(2) Å) is significantly shorter than the Pt−PHMes* one (2.378(5) Å), although the absolute difference is small. These bond lengths are similar to those previously found for terminal Pt(II) phosphido complexes.[13] Consistent with the ^{31}P NMR data, these phosphido ligands have a similar trans influence; the Pt−P$_{(trans,dppe)}$ bond lengths of 2.273(5) (**1**) and 2.287(2) Å (**5**·THF) are the same within experimental error. The Pt−P(dppe) bond lengths in **1** (2.273(5) Å trans to PHMes* and 2.273(4) trans to Me) are the same, although the NMR data suggest Me has a slightly larger trans influence in this case. The data for **5**·THF are more consistent with the NMR results, since the Pt−P(dppe) bond distance trans to PMes$_2$ (2.287(2) Å) is significantly shorter than the one trans to Me (2.308(2) Å). The Pt−P(dppe) bond length (trans to Me) in **5**·THF (2.308(2) Å) is significantly longer than that in **1** (2.273(4) Å); this may be a steric effect to avoid destabilizing interactions of the PMes$_2$ and dppe PPh$_2$ groups. The Pt−C(Me) bond lengths in the two structures (2.13(2) (**1**) and 2.122(9) Å (**5**·THF)) are the same within experimental error.

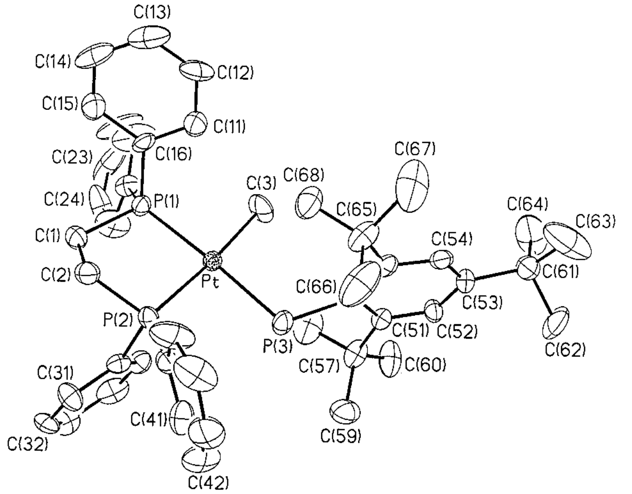


Figure 1. ORTEP diagram of Pt(dppe)(Me)(PHMes*) (**1**) showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Consistent with the conclusions from the ^{31}P NMR data, the PMes$_2$ phosphorus in **5** is pyramidal (the sum of the angles at P is 333.9°; compare with 328.5° for a tetrahedral and 360° for a planar atom). The P−H atom in **1** was not located, but the Pt−P−C(Ar) angle of 116.8(6)° in this complex is similar to that in **5** and consistent with a similar structure in the two cases. Similarly, large angles have been observed in related metal−

---

[13] Compare Pt(PPh$_3$)(CO)[Mes*PC(O)PMes*] (ref 5d), 2.321(7) and 2.337(7) Å, and the related dihydrodiphosphete complex Pt(PPh$_3$)$_2$-[PPhCPh=CPhPPh] (ref 5f), 2.288(2) and 2.282(2) Å.

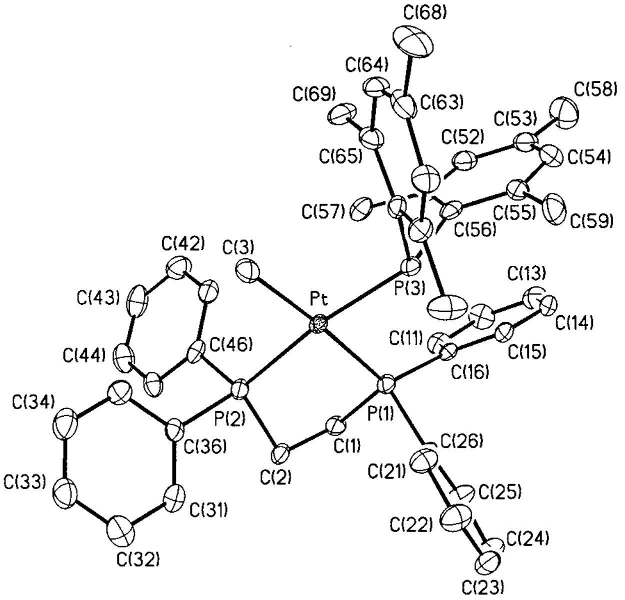


Figure 2. ORTEP diagram of Pt(dppe)(Me)(PMes$_2$)·THF (**5**·THF) showing 30% probability thermal ellipsoids. The THF solvent molecule and hydrogen atoms are omitted for clarity.

Table 2. Crystallographic Data for Pt(dppe)(Me)(PHMes*) (1) and Pt(dppe)(Me)(PMes$_2$) (5·THF)

	1	**5**·THF
formula	$C_{45}H_{57}P_3Pt$	$C_{49}H_{57}OP_3Pt$
fw	885.90	949.95
space group	$P2_12_12_1$	$P2_1/c$
a, Å	14.1610(10)	20.591(3)
b, Å	14.502(3)	11.295(3)
c, Å	22.634(6)	18.851(4)
β, deg		99.23(1)
V, Å^3	4648(2)	4328(2)
Z	4	4
cryst color, habit	yellow rod	orange block
D(calc), g cm^{-3}	1.265	1.458
μ(Mo Kα), cm^{-1}	31.48	33.90
temp, K	298(2)	238(2)
2θ scan range, deg	4.0–45.0	4.0–45.0
data collected (*h*, *k*, *l*)	−15, +15, +24	±22, −12, +19
no. of rflns collected	4240	6978
no. of indpt obsd rflns (4σ(F_o))	3180	4321
R(*F*), %^{a}	4.78	4.46
R (wF^2), %^{a}	11.80	10.29

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

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Terminal Platinum Phosphido Complexes 1 and 5·THF

	1	**5**·THF
Pt−PR$_2$	2.378(5)	2.351(2)
Pt−P (dppe, trans)	2.273(5)	2.287(2)
Pt−P (dppe, cis)	2.273(4)	2.308(2)
Pt−Me	2.13(2)	2.122(9)
P−C(Ar)	1.90(2)	1.846(8) 1.854(9)
P−Pt−PR$_2$	88.9(2)	90.04(8)
C−Pt−PR$_2$	97.2(6)	93.0(2)
P−Pt−P	85.0(2)	84.80(8)
C−Pt−P	89.2(6)	92.0(2)
Pt−P−Ar	116.8(6)	116.2(3) 116.9(2)
C(Ar)−P−C(Ar)		100.8(4)

phosphido complexes.[14] Comparison of the structure of **5** with those of PHMes$_2$ (sum of angles at P = 323°)[15] and PMes$_3$ (sum of angles at P = 329.1°)[16] suggests that the distortion of the PMes$_2$ pyramid observed in **5**·THF is mainly a consequence of steric effects. The P−C(Mes) bond lengths in these three structures are not significantly different, so coordination to Pt does not significantly perturb the P−C bonds, as might be expected if the phosphido ligand were acting as a π-acceptor.[17]

NMR and Calorimetric Studies of Proton-Transfer Reactions. Bryndza, Bercaw and co-workers have reported extensive solution NMR studies of the equilibria in eq 1.[18] A brief summary of their results follows.

$$\mathrm{Pt(dppe)(Me)(OMe)} + \mathrm{HX} \rightleftharpoons \mathrm{Pt(dppe)(Me)(X)} + \mathrm{MeOH} \quad (1)$$

(1) For a range of X groups, this reaction was approximately thermoneutral; assuming that entropy effects can be neglected, the measured equilibrium constant, along with literature values for the H−X and H−OMe bond strengths, provides information on relative Pt−OMe and Pt−X bond strengths. (2) For several weak acids HX, a remarkable correlation is found between Pt−X and H−X bond strengths. (3) Some X groups do not obey the correlation; in these cases (X = SH, CN) the Pt−X bond is stronger than predicted, and these observations were rationalized as involving either π-bonding (to cyanide) or particularly favorable soft−soft interactions with the second-row substituent sulfur.

As mentioned above, methoxide **10** is consumed on reaction with 1 equiv of phosphine or thiol in the formation of the phosphido complexes **1**−**9** and the thiolate **11**, as well as the known Pt(dppe)(Me)(SPh)[8] (eq 1). Thus, the phosphido and thiolate groups do not obey the Pt−X/H−X bond strength correlation previously established for bonds between the Pt(dppe)(Me) fragment and the first-row atoms C, N, and O. As for SH and CN, these Pt−X bonds to second-row atoms are *stronger* than predicted.

Information on the *relative* Pt−X bond strengths for second-row substituents was obtained from ^{31}P NMR studies of the equilibria shown in eq 2 in THF solvent.

$$\mathrm{Pt(dppe)(Me)(PRR')} + \mathrm{HX} \rightleftharpoons \mathrm{Pt(dppe)(Me)(X)} + \mathrm{PHRR'} \quad (2)$$

$$\mathrm{X} = \text{phosphide or thiolate}$$

Some such reactions were approximately thermoneutral, allowing measurement of the equilibrium constants at room temperature (Chart 1). Details of the experimental measurements and estimation of error limits are described in the Experimental Section. In most cases, the equilibria could be approached from either side and

---

[14] For example, the sum of the bond angles at the di-*tert*-butylphosphido group in CpRe(NO)(PPh$_3$)[P(t-Bu)$_2$] is 332.1°, see: Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427−2439.

[15] Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941−1946.

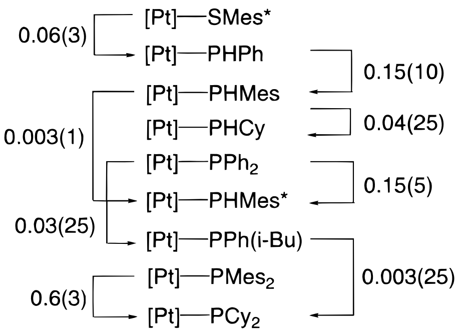
[16] Blount, J. F.; Maryanoff, C. A.; Mislow, K. *Tetrahedron Lett.* **1975**, *11*, 913−916.

[17] (a) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653−661. (b) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206−1210. (c) Reference 7.

[18] (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456. (b) Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 1441−1452.

Chart 1. Equilibrium Constants for Proton Transfer Reactions[a]

$$\mathrm{Pt(dppe)(Me)(X) + HY \rightleftharpoons Pt(dppe)(Me)(Y) + HX}$$



[a] THF, 22 °C, from ^{31}P NMR.

Table 4. Free Energy and Enthalpy Changes (kcal/mol) for the Reaction[a]

$$\mathrm{Pt(dppe)(Me)(PMes_2) + HX \rightleftharpoons Pt(dppe)(Me)(X) + PHMes_2}$$

X	NMR[b]	calorimetry[c]
PHMes*	−4.2(8)	−4.0(1)
PPh_2	−5.3(8)	−4.6(1)
PHPh	−8.8(9)	−6.0(2)
SMes*	−10.5(9)	−10.2(1)

[a] In THF. [b] ^{31}P NMR, 22 °C. [c] Solution calorimetry, 30 °C.

gave reproducible results for the equilibrium constants. Equilibria were established quickly, and a relatively narrow concentration range was required for reasons of solubility and ^{31}P NMR detection limits. Measurements involving alkylphosphido complexes **4** and **9** were hampered by decomposition (see Experimental Section), but the results obtained are internally consistent and also agree with the results from complementary solution calorimetry studies (see below).

In other cases, the position of the equilibria was far to one side, preventing direct NMR measurement of K_{eq}. Estimates of the equilibrium constants for such "irreversible" reactions were obtained from the products of individual equilibrium constants in a ladder (Chart 1). Such transformations were also studied directly by solution calorimetry in THF at 30 °C starting with the dimesitylphosphido complex **5**. Comparison of the results obtained with these complementary techniques (Table 4) shows relatively good agreement, despite the slightly different temperatures employed, and is considered in detail below. Although the reactions described above reach equilibrium in minutes to hours, the aryloxide complex **12** reacted much more slowly. For example, **12** did not react with $PHMes_2$ in THF at room temperature in 1 day; after 6 days at 50 °C, **12** was consumed and **5** formed. However, under these conditions, some decomposition occurs. Complex **12** also reacted quantitatively with PH_2Mes^* and Mes*SH upon heating under similar conditions to give **1** and **11**, again with some decomposition.

Further quantitative analysis of these results requires several assumptions, some necessary because of the limited data available on organophosphorus thermochemistry. Very few P−H bond strengths have been reported; in fact, only those for PH_3 (83.9 ± 0.5 kcal/mol),[19] PH_2Me (two separate studies have reported either between 74 and 79.5 kcal/mol[20] or 79.3 kcal/mol),[21] and $PHMe_2$ (77.3 kcal/mol)[21] are known. Assuming that P−H bond strengths in mono- and diarylphosphines follow trends similar to those observed for E−H bonds[19,22,23] (E = C, H, N, O, S), it is likely that they decrease in the order H−PHPh > H−PHMes > H−PHMes* for the primary arylphosphines, and $H{-}PPh_2 > H{-}PMes_2$ for the secondary ones. The relative P−H bond strengths in alkyl-, aryl-, and mixed alkylarylphosphines are difficult to predict, but the P−H bonds in the primary phosphines are probably stronger than those in the secondary phosphines in this series; this assumption is supported by data for the methylphosphines and by analogy to amines. Similarly, although S−H BDE's in a variety of substituted thiophenols have been reported,[23] that for Mes*SH is unknown; it is likely to be significantly lower than the PhSH value of 79.1 kcal/mol.

In general, the reaction of a secondary phosphido complex $[Pt]{-}PR_2$ ([Pt] = Pt(dppe)(Me)) with a primary phosphine to give a primary phosphido complex and a secondary phosphine (eq 3) favors the products, despite the energetic cost associated with making a secondary P−H bond at the expense of a primary one. This

$$\mathrm{Pt(dppe)(Me)(PR_2) + PH_2R' \rightleftharpoons Pt(dppe)(Me)(PHR') + PHR_2} \quad (3)$$

suggests that these reactions are controlled by the relative Pt−P bond strengths. These in turn clearly depend on steric effects, with bonds to smaller phosphido ligands being thermodynamically favored. Relevant cone angles reported by Tolman[24] and others include those for PH_2Ph (101°), PH_2Mes (110°),[7] PH_2Mes^* (132°),[25] PH_2Cy (115°),[26] $PHPh_2$ (128°), $PHCy_2$ (143°),[27] and $PHMes_2$ (170°).[27] For primary arylphosphido complexes, the Pt−P bond strengths follow the order Pt−PHPh > Pt−PHMes > Pt−PHMes*; a similar steric trend is seen for diarylphosphides ($Pt{-}PPh_2 > Pt{-}PMes_2$). In these cases, the predicted decrease in P−H bond energies with increasing substitution on the aryl group(s) is apparently outweighed by effects on the Pt−P bonds. Similarly, dicyclohexylphosphido complex **7** is consumed on reaction with diethylphosphine to give mainly diethylphosphido complex **8** plus decomposition products; this reaction is presumably controlled mostly by steric effects.

---

[19] Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.

[20] Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 4737−4743.

[21] McKean, D. C.; Torto, I.; Morrisson, A. R. *J. Phys. Chem.* **1982**, *86*, 307−309.

[22] (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532. (b) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795. (c) Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410−6416. (d) Bordwell, F. G.; Zhang, X. M. *J. Phys. Org. Chem.* **1995**, *8*, 529−535. (e) Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 10819−10823.

[23] Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 6605−6610.

[24] Tolman, C. A. *Chem. Rev. (Washington, D.C.)* **1977**, *77*, 313−348.

[25] Kourkine, I. V.; Chapman, M. B.; Glueck, D. S.; Eichele, K.; Wasylishen, R. E.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 1478−1485.

[26] Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286−1294.

[27] McFarlane, W.; Regius, C. T. *Polyhedron* **1997**, *16*, 1855−1861.

In proton-transfer reactions involving the secondary phosphines $PHPh_2$, PHPh(i-Bu), and $PHCy_2$, increasing aryl substitution on the Pt−phosphido group is energetically preferred. This trend could be due to hard−soft considerations (soft arylphosphides are expected to bind more strongly to soft Pt(II) than hard alkylphosphides). Differences in relative Pt−P bond strengths could also be described by an electrostatic model in which phenyl substituents on phosphorus are preferred because they stabilize partial negative charge on the phosphido ligand.[12] However, differences in P−H bond strengths surely also contribute to the values of these equilibrium constants and may be more important than Pt−P bonding. The position of the equilibria between **2**, **4**, and the phosphines PH_2Mes and PH_2Cy also appears to reflect these factors, given the similar steric demands of these ligands, while the PHPh substituent may be favored in comparison to both of them for steric reasons.

Related experimental observations suggest that Pt−S bond strengths in this system are stronger than the analogous Pt−P ones. Treatment of the primary arylphosphido complexes **1** and **3** with stoichiometric amounts of the arylthiols Mes*SH and PhSH led to quantitative formation of the thiolates **11** and Pt(dppe)(Me)(SPh), respectively, along with PH_2Mes^* and PH_2Ph. Even on addition of excess phosphine to these thiolate complexes, formation of **1** and **3** was not observed. However, an equilibrium between **3**, **11**, PH_2Ph, and Mes*SH could be accessed from either side (Chart 1). The reaction of **3** with PhSH (eq 4) allows estimation of relative Pt−SPh and Pt−PHPh bond strengths in this system. Given that the PhS−H BDE

$$\mathrm{Pt(dppe)(Me)(PHPh)} + \mathrm{PhSH} \rightleftharpoons \mathrm{Pt(dppe)(Me)(SPh)} + \mathrm{PH_2Ph} \quad (5)$$

is 79.1 kcal/mol and assuming conservative upper bounds for the energy of this reaction (−4 kcal/mol) and for the H−PHPh BDE (82 kcal/mol) suggests that the Pt−SPh bond is at least 1 kcal/mol stronger than the Pt−PHPh one. As above, this difference can be rationalized either on hard−soft or on electrostatic grounds (the more electronegative S can stabilize negative charge better than P).

A similar comparison of Pt−O and Pt−X bond strengths is complicated by the sluggish reactivity of aryloxide complex **12**, which precluded measurements of equilibrium constants involving this compound. Complex **12** reacts with PH_2Mes^* and Mes*SH to afford **1** and **11** respectively, suggesting that for these ligands of comparable steric demand, Pt−S and Pt−P bonds are stronger than the Pt−O one. However, the E−H bonds involved in these reactions may have equal or greater importance, since the H−OMes* BDE of 82.3 kcal/mol[28] is likely to be significantly greater than the analogous P−H and S−H bond strengths.

Since the NMR equilibrium studies measure the free energy of reaction and the calorimetric ones only the reaction enthalpy, differences between the two sets of results evident in Table 4 may be ascribed to the entropy term. The best agreement between the two types of measurements is for the bulkiest ligands (conversion of dimesitylphosphido complex **5** to PHMes* complex **1** or SMes* complex **11**), and the smaller PHPh and PPh_2 complexes are thermodynamically favored *more* than would be expected from the reaction enthalpy results; the discrepancy is largest for the smallest ligand, PHPh. The order of magnitude of the presumed entropic effects is similar to that observed by Bryndza and co-workers[18] in the equilibrium between $RuCp^*(PMe_3)_2(OH)$, diphenylamine, $RuCp^*(PMe_3)_2(NPh_2)$, and water, where the entropic contribution to the equilibrium free energy at 25 °C was −1.8 kcal/mol.

As described above, the Pt−PHMes* bond is slightly longer than the $Pt{-}PMes_2$ one in the solid state. For Pt(II) complexes of tertiary phosphines, $^1J_{Pt-P}$ correlates with the Pt−P distance,[29] and the same effect is observed here ($^1J_{Pt-P} = 863$ Hz for **1** and 1239 Hz for **5**). Because the appropriate P−H BDE's are not known, however, our data do not provide information on relative Pt−P bond strengths in these compounds for possible correlation with the bond lengths.[30]

Conclusions

Data for the series of phosphido complexes **1**−**9** show that the terminal phosphido ligand contains a pyramidal phosphorus, that the Pt−P bond has low s character, and that the phosphido ligand has a large trans influence, comparable to that of an alkyl group; the strongest trans-influence ligands in the phosphido series are those with electron-releasing alkyl groups. Complementary NMR and calorimetry studies of proton-transfer equilibria suggest that the Pt−P bonds in **1**−**9** are weaker than analogous Pt−S bonds and also provide some information on entropic contributions to the equilibria. Stronger Pt−P bonds are formed by smaller ligands. For ligands of comparable steric bulk, in equilibria between alkyl- and arylphosphido complexes and the analogous phosphines, arylphosphides are energetically favored; this effect may reflect changes in the Pt−P bond as well as P−H BDE differences. Because current knowledge of organophosphorus thermochemistry is limited, more work in this field is required to separate these effects.

Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere using either standard Schlenk apparatus or a glovebox. Solvents were distilled from sodium benzophenone (toluene, THF, ether, petroleum ether) or from CaH_2 (methylene chloride) and stored under nitrogen. NMR spectra were obtained at the following frequencies (MHz) ^{31}P, 121.4; ^{13}C, 75.4; ^{1}H, 299.9 and are referenced either via internal solvent peaks to TMS or to an external standard of 85% H_3PO_4. Coupling constants are reported in hertz. IR spectra were recorded in KBr pellets, and peaks are reported in cm^{-1}. Elemental analyses were done by Schwarzkopf Labs, Woodside, NY. The following were prepared by literature procedures: PH_2Mes^*,[31] Mes*SH,[32] PH_2Mes,[15] $PHMes_2$,[15] Pt(dppe)-

---

[28] Bordwell, F. G.; Zhang, X. M. *J. Phys. Org. Chem.* **1995**, *8*, 529−535.

[29] Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095−2099.

[30] Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Nuber, B.; Ziegler, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 5075−5081.

[31] Cowley, A. H.; Norman, N. C.; Pakulski, M. *Inorg. Synth.* **1990**, *27*, 235−240.

[32] Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467−3474.

(Me)(Cl),[33] Pt(dppe)(Me)(OMe),[6] and Pt(dppe)(Me)(SPh).[8] PH(Ph)(i-Bu) was a gift from Cytec Canada and was prepared by Hillhouse's method.[1a,b]

[Pt(dppe)(Me)(PH_2Mes*)][BF_4] (13). To a solution of Pt(dppe)(Me)(Cl) (505 mg, 0.78 mmol) in CH_2Cl_2 (15 mL) was added a slurry of $AgBF_4$ (151 mg, 0.78 mmol) in CH_3CN (3 mL). Immediate reaction occurred, as indicated by the formation of a white precipitate. PH_2Mes* (239 mg, 0.86 mmol) dissolved in CH_2Cl_2 (3 mL) was then added to the solution. The reaction mixture was allowed to stir overnight in the dark at room temperature. The yellow solution was filtered, and the solvent was removed in vacuo to give a pale yellow solid. The solid was dissolved in a minimal amount of THF, and petroleum ether was added to the THF solution. Cooling of this solution to −25 °C yielded 702 mg (92%) of pale yellow [Pt(dppe)(Me)(PH_2Mes*)][BF_4].

^{1}H NMR (THF-d_8): δ 7.77−7.52 (br m, 22H, Ar), 6.07 (d, $^{1}J_{PH}$ = 380, 2H, PH_2), 2.84−2.74 (m, 4H, CH_2), 1.45 (18H, *o*-CMe_3), 1.28 (9H, *p*-CMe_3), 0.28−0.21 (m, $^{2}J_{Pt-H}$ = 60, 3H, Pt−Me). ^{13}C{^{1}H} NMR (THF-d_8): δ 156.5 (quat Ar), 154.0 (quat Ar), 134.6−134.2 (m, Ar), 132.9 (Ar), 130.7−130.2 (m, Ar), 129.8 (quat Ar), 129.1 (quat Ar), 128.3 (quat Ar), 124.4 (d, $^{3}J_{C-P}$ = 10, Ar), 39.1 (*o*-*C*Me$_3$), 36.0 (*p*-*C*Me$_3$), 33.6 (*o*-C*Me$_3$*), 31.4 (*p*-C*Me$_3$*), 30.8−29.1 (m, dppe CH_2), 2.5 (dm, $^{2}J_{C-P(trans)}$ = 72, $^{1}J_{C-Pt}$ = 510, Pt−Me). IR: 2416 (PH), 1054 (BF_4). Anal. Calcd for $C_{45}H_{58}BF_4P_3Pt$: C, 55.51; H, 6.00. Found: C, 55.29; H, 6.19.

[Pt(dppe)(Me)(PH_2Mes)][BF_4] (14) was prepared similarly and identified by ^{31}P NMR (Table 1) but not isolated or further characterized.

Pt(dppe)(Me)(PHMes*) (1). To a solution of [Pt(dppe)(Me)(PH_2Mes*)][BF_4] (**13**) (133 mg, 0.14 mmol) in THF (8 mL) was added LiN($SiMe_3$)$_2$ (23 mg, 0.14 mmol) dissolved in THF (3 mL). The reaction mixture immediately turned bright yellow. The solvent was removed in vacuo, and the yellow residue was washed with 3 1 mL portions of petroleum ether. The solid was dried under vacuum to yield 112 mg (93%) of yellow Pt(dppe)(Me)(PHMes*). Alternatively, to a solution of Pt(dppe)(Me)(OMe) (200 mg, 0.31 mmol) dissolved in THF (10 mL) was added a solution of PH_2Mes* (96 mg, 0.34 mmol) dissolved in THF (5 mL). The solution immediately became bright yellow and was allowed to stir at room temperature for 1 h. The solvent was removed under vacuum and the yellow residue was washed with 3 1 mL portions of petroleum ether. The solid was redissolved in a minimal amount of THF and filtered. Petroleum ether was added to the THF solution, and cooling of the solution to −25 °C yielded 144 mg (50%) of product. Crystals for X-ray crystallography were grown from THF/petroleum ether at −25 °C.

^{1}H NMR (C_6D_6): δ 7.77 (br, 4H, Ar), 7.71 (2H, Ar), 7.48 (br, 4H, Ar), 7.17−7.08 (m, 6H, Ar), 6.97−6.94 (m, 6H, Ar), 5.07 (ddd, $^{1}J_{P-H}$ = 213, $^{3}J_{P-H}$ = 9, $^{3}J_{P-H}$ = 6, $^{2}J_{Pt-H}$ = 66, 1H, PH), 1.96 (9H, *p*-CMe_3), 1.90−1.76 (br m, 4H, CH_2), 1.39 (18H, *o*-CMe_3), 0.56−0.50 (m, $^{2}J_{Pt-H}$ = 68, 3H, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.8 (quat Ar), 146.2 (quat Ar), 138.8−138.6 (m, quat Ar), 138.1−137.9 (m, quat Ar), 134.4−134.1 (br m, Ar), 133.9 (Ar), 133.8 (Ar), 132.6−131.8 (m, Ar), 130.8 (Ar), 129.0 (Ar), 128.9 (Ar), 121.2 (Ar), 39.3 (*o*-*C*Me$_3$), 35.3 (*p*-*C*Me$_3$), 33.9 (d, $^{4}J_{CP}$ = 7, *o*-C*Me$_3$*), 32.1 (*p*-C*Me$_3$*), 29.9−28.9 (m, dppe CH_2), 0.8 (dd, $^{2}J_{CP(trans)}$ = 83, $^{2}J_{CP(cis)}$ = 7, $^{1}J_{CPt}$ = 600, Me). IR: 2265 (PH). Anal. Calcd for $C_{45}H_{57}P_3Pt$: C, 61.00; H, 6.50. Found: C, 60.64; H, 6.67.

Pt(dppe)(Me)(PHMes) (2). Pt(dppe)(Me)(OMe) (300 mg, 0.47 mmol) was suspended in THF (10 mL), and mesitylphosphine (90 mg, 0.59 mmol) was added by syringe. On addition, the suspended solid immediately solubilized to give a yellow solution, which was filtered through Celite and layered with petroleum ether. Light yellow crystals formed at room temperature over 2 days. These crystals were washed with petroleum ether and vacuum-dried to give 254 mg of a light yellow solid (71% yield). A second recrystallization from benzene/THF/petroleum ether at room temperature gave analytically pure light yellow crystals. Alternatively, addition of LiN($SiMe_3$)$_2$ to a THF solution of cation **14** also gave **2**, according to ^{31}P NMR.

^{1}H NMR (∼5:1 C_6D_6/THF-d_8): δ 7.7−7.5 (br, 8H, Ar), 7.11−7.08 (m, 12H, Ar), 6.72 (2H, Mes), 3.77 (ddd, $^{1}J_{PH}$ = 199, $^{3}J_{PH}$ = 13, 8, $^{2}J_{Pt-H}$ = 64, 1H, PH), 2.50 (6H, *o*-Me), 2.12 (3H, *p*-Me), 2.1−1.8 (br, 4H, CH_2), 0.59 (m, J_{Pt-H} = 68, 3H, Pt−Me). Since the complex is sparingly soluble, the ^{13}C NMR spectrum was not recorded. IR: 2915, 2279, 1434, 1102, 1028, 998, 878, 852, 823, 744, 692, 531, 485. Anal. Calcd for $C_{36}H_{39}P_3Pt$: C, 56.91; H, 5.18. Found: C, 56.78; H, 5.06.

Pt(dppe)(Me)(PHPh) (3). Pt(dppe)(Me)(OMe) (100 mg, 0.156 mmol) was suspended in C_6D_6 (1 mL), and phenylphosphine (17 μL, 0.16 mmol) was added by syringe. The suspension turned red at the solid−solution interface on addition then yellow as all the solid dissolved. The ^{31}P and ^{1}H NMR spectra showed complete conversion to **3**. The solution was decanted, filtered through Celite, and crystallized by addition of petroleum ether. White solid (65 mg, 58%) formed over 2 days at room temperature; it was washed with petroleum ether and dried in a vacuum. A second recrystallization from THF/petroleum ether at −20 °C gave yellow crystals for analysis.

^{1}H NMR (C_6D_6): δ 7.70−7.64 (m, 6H, Ar), 7.55−7.49 (m, 4H, Ar), 7.06−6.94 (m, 15H, Ar), 4.42 (ddd, $^{1}J_{PH}$ = 201, $^{3}J_{PH}$ = 15, 6, $^{2}J_{Pt-H}$ = 57, 1H, PH), 1.90−1.72 (m, 4H, CH_2), 1.28 (m, J_{Pt-H} = 67, 3H, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 145.3−145.0 (m, Ar), 135.5 (dd, J = 3, 14, Ar), 134.4−133.7 (m, Ar), 132.0 (d, J = 44, Ar), 130.9 (Ar), 129.0 (m, Ar), 127.5 (d, J = 5, Ar), 125.1 (Ar), 31.5−30.8 (m, CH_2), 1.2 (dm, J_{PC} = 86, Pt−Me). IR: 3050, 2919, 2873, 2256, 1579, 1482, 1435, 1411, 1308, 1185, 1159, 1102, 1068, 1026, 998, 877, 820, 742, 692, 652, 531, 484. Anal. Calcd for $C_{33}H_{33}P_3Pt$: C, 55.23; H, 4.64. Found: C, 54.96; H, 4.75.

Pt(dppe)(Me)(PHCy) (4). PH_2Cy (19 mg, 0.16 mmol) was added to a slurry of Pt(dppe)(Me)(OMe) (100 mg, 0.16 mmol) in C_6D_6 (1 mL). The reaction mixture immediately became a homogeneous yellow solution, and NMR confirmed formation of **4** and methanol, along with unidentified impurities. The solution was filtered through Celite, layered with petroleum ether, and cooled to −25 °C to give a light yellow powder, 45 mg (40%). Recrystallization from THF/petroleum ether or toluene/ether was not successful in purifying this material.

^{1}H NMR (C_6D_6): δ 7.77−7.71 (m, 4H, Ph), 7.63−7.57 (m, 4H, Ph), 7.10−7.01 (m, 12H, Ph), 3.06 (dddd, J_{PH} = 6, 18, 183, J_{HH} = 9, J_{Pt-H} = 54, 1H, PH), 2.42−2.38 (m, 2H), 2.04−1.78 (m, 4H), 1.76−1.0 (m, 9H, Cy), 1.32 (m, J_{Pt-H} = 55, 3H, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 134.4−134.3 (m, Ph), 134.0−133.7 (m, Ph), 133.6−133.3 (m, Ph), 132.9−132.3 (m, Ph), 130.8 (Ph), 129.2−128.8 (m, Ph), 34.1 (m), 31.6−30.9 (m), 29.9−29.5 (m), 29.3−29.2 (m), 27.2, −3.2 (dd, J_{PC} = 8, 88, J_{Pt-C} = 583, Pt−Me). IR: 3050, 2916, 2842, 2232, 1483, 1434, 1102, 819, 745, 693, 531, 484.

Pt(dppe)(Me)($PMes_2$) (5). $PHMes_2$ (49 mg, 0.18 mmol) dissolved in THF (2 mL) was added to a solution of Pt(dppe)(Me)(OMe) (115 mg, 0.18 mmol) dissolved in THF (10 mL). The reaction mixture immediately became bright orange. The solvent was removed under vacuum, and the orange solid was washed 3 times with 1 mL portions of petroleum ether. The solid was redissolved in a minimal amount of THF and filtered. Petroleum ether was added to the THF solution, and the solution was cooled to −25 °C to yield 133 mg (84%) of orange Pt(dppe)(Me)($PMes_2$), isolated as a THF solvate. Successive recrystallization from THF/petroleum ether as described yielded X-ray quality crystals.

^{1}H NMR (C_6D_6): δ 7.66−7.58 (br m, 8H, Ar), 7.03−6.91 (m, 12H, Ar), 6.71 (4H, Ar), 2.70 (12H, *o*-Me), 2.13 (6H, *p*-Me), 1.83−1.78 (br m, 4H, CH_2), 0.90−0.83 (m, $^{2}J_{Pt-H}$ = 69, 3H, Me).

---

(33) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* **1975**, *14*, 1518−1526.

^{13}C{^{1}H} NMR (C_6D_6): δ 143.8 (d, $^2J_{CP} = 13$, quat Ar), 141.0 (quat Ar), 140.5 (quat Ar), 133.9 (br, Ar), 133.8 (Ar), 130.9 (Ar), 130.2 (Ar), 129.2 (Ar), 129.1 (Ar), 128.2 (Ar), 128.0 (Ar), 28.4−27.9 (m, dppe CH$_2$), 26.1 (d, $^3J_{CP} = 14$, *o*-Me), 21.4 (*p*-Me), −0.3 (dd, $^2J_{CP(trans)} = 85$, $^2J_{CP(cis)} = 5$, Me, Pt satellites were not resolved). IR: 2923, 1952, 1892, 1814, 1598, 1430, 1184, 1058, 999, 873, 843, 741, 693, 639, 531. Anal. Calcd for $C_{45}H_{49}P_3$Pt: C, 61.56; H, 5.63. Found: C, 61.43; H, 5.95.

Pt(dppe)(Me)(PPh$_2$) (6). A solution of diphenylphosphine (30 mg, 0.16 mmol) in 1 mL of THF was added to a slurry of Pt(dppe)(Me)(OMe) (88 mg, 0.14 mmol) in 2 mL of THF. The mixture immediately became lemon-yellow and homogeneous. The solution was filtered through Celite, layered with petroleum ether, and cooled to −20 °C to give yellow powder, which was washed with petroleum ether and dried in a vacuum (84 mg, 76% yield). A second recrystallization from THF/petroleum ether at −20 °C gave yellow needles, which rapidly desolvated to an analytically pure yellow powder.

^{1}H NMR (C_6D_6): δ 7.77−7.52 (m, 12H), 7.07−6.95 (m, 18H), 1.88−1.77 (m, 4H, CH$_2$), 1.22 (m, 3H, $J_{Pt-H} = 68$, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 136.3 (dd, J = 4, 18, Ar), 134.7−133.8 (m, Ar), 132.4 (d, J = 10, Ar), 131.1−130.6 (m, Ar), 129.3−129.1 (m, Ar), 127.8−127.5 (m, Ar), 125.6 (Ar), 30.6−28.4 (m, CH$_2$, dppe), 4.9−3.7 (m, Pt−Me. Due to the low solubility of this complex in C_6D_6, no Pt satellites were observed for this peak). IR: 3050, 1578, 1482, 1435, 1186, 1102, 1025, 998, 877, 819, 744, 693, 531, 483. Anal. Calcd for $C_{39}H_{37}P_3$Pt: C, 59.01; H, 4.71. Found: C, 58.74; H, 4.52.

Pt(dppe)(Me)(PCy$_2$) (7). A solution of dicyclohexylphosphine (55 mg, 0.28 mmol) in 1 mL of THF was added to a slurry of Pt(dppe)(Me)(OMe) (160 mg, 0.25 mmol) in 2 mL of THF. The mixture immediately became orange and homogeneous. The solution was filtered through Celite, layered with petroleum ether, and cooled to −20 °C to give yellow chunks, which were washed with petroleum ether and dried in a vacuum. Several crops of a yellow crystalline solid were obtained; although a yellow oil initially forms, crystals grow slowly over several days (total 145 mg, 72% yield). Two more recrystallizations from THF/petroleum ether at −20 °C gave yellow needles, which rapidly desolvated to analytically pure yellow powder.

^{1}H NMR (C_6D_6): δ 7.81−7.74 (m, 4H, Ar), 7.63−7.57 (m, 4H, Ar), 7.16−7.02 (m, 12H, Ar), 2.6−2.1 (br, 4H), 2.0−1.7 (br, 11H), 1.6−1.2 (br, 11H), 1.46 (m, $J_{Pt-H} = 71$, 3H, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 134.8−134.6 (m, Ar), 134.0−133.7 (m, Ar), 133.2−133.0 (m, Ar), 132.6−132.5 (m, Ar), 130.8−130.5 (m, Ar), 129.2−129.0 (m, Ar), 128.5 (obscured by C_6D_6, Ar), 35.9−35.5 (m, Cy/dppe), 28.0 (Cy), −1.0 (d, $J_{PC} = 91$, $J_{Pt-C} = 629$, Pt−Me). IR: 2920, 2844, 1435, 1102, 1065, 819, 747, 698, 531. Anal. Calcd for $C_{39}H_{49}P_3$Pt: C, 58.12; H, 6.14. Found: C, 58.05; H, 6.27.

Pt(dppe)(Me)(PEt$_2$) (8) was generated as the major component of a mixture from Pt(dppe)(Me)(OMe) and PHEt$_2$ as described above in C_6D_6 or THF and characterized by ^{31}P NMR (Table 1). This material could not be isolated in pure form.

Pt(dppe)(Me)[P(Ph)(i-Bu)] (9). PH(Ph)(i-Bu) (187 mg, 1.13 mmol) was added to a stirring slurry of Pt(dppe)(Me)(OMe) (480 mg, 0.750 mmol) in THF (10 mL). The reaction mixture immediately became a bright yellow homogeneous solution and was concentrated in vacuo to approximately 5 mL. Petroleum ether (5 mL) was added, and the solution was cooled to −25 °C overnight to give 462 mg (80%) of a bright yellow product. ^{1}H NMR (THF-*d*$_8$): δ 7.82−7.76 (m, 2H, Ar), 7.67−7.61 (m, 3H, Ar), 7.39−7.21 (br m, 15H, Ar), 6.92−6.78 (m, 5H, Ar), 2.32−2.20 (m, 4H, dppe CH$_2$), 1.80−1.74 (m, 2H, *CH$_2$*-CH), 1.42−1.30 (m, 1H, CH$_2$*CH*), 0.72 (d, $^3J_{HH} = 6$, 6H, CH*Me$_2$*), 0.47−0.40 (m, $^2J_{Pt-H} = 69$, 3H, Pt−Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 149.6 (apparent dt, $^1J_{CP} = 34$, $J_{Pt-C} = 5$, quat Ar), 134.8 (Ar), 134.7 (Ar), 134.5 (Ar), 134.5−134.2 (m, Ar), 134.1−133.7 (m, Ar), 132.5 (d, $^1J_{CP} = 41$, quat Ar), 132.2 (d, $^1J_{CP} = 41$, quat Ar), 130.85 (Ar), 129.2−128.8 (m, Ar), 127.3−127.2 (m, Ar), 125.0−124.9 (m, Ar), 37.2 (d, $^1J_{CP} = 22$, *C*H$_2$-CH), 31.5−30.8 (m, dppe CH$_2$), 29.8 (dd, $^2J_{CP} = 13$, $^4J_{CP} = 7$, CH$_2$*C*H), 29.6−29.1 (m, dppe, CH$_2$), 25.2−25.1 (CH*Me$_2$*), 3.3 (dm, $^2J_{C-P(trans)} = 87$, $^1J_{C-Pt} = 603$, Pt−Me). Anal. Calcd for $C_{37}H_{41}P_3$Pt: C, 57.43; H, 5.35. Found: C, 56.95; H, 5.41.

Pt(dppe)(Me)(SMes*) (11). A solid mixture of Pt(dppe)(Me)(OMe) (100 mg, 0.156 mmol) and Mes*SH (60 mg, 0.22 mmol) was dissolved in a mixture of 12 mL of THF and 3 mL of petroleum ether. The resulting light orange solution was filtered through Celite, and the solvents were removed under vacuum from the filtrate. Recrystallization from THF/petroleum ether at −20 °C gave 100 mg of a beige solid (72% yield). A second recrystallization from THF/petroleum ether gave analytically pure white needles.

^{1}H NMR (C_6D_6): δ 8.06−8.00 (m, 4H, Ar), 7.74 (2H, Ar), 7.50−7.42 (m, 4H, Ar), 7.22−7.08 (m, 6H, Ar), 6.95−6.92 (m, 6H, Ar), 2.11 (18H, *o*-t-Bu), 1.9−1.7 (br m, 4H, CH$_2$), 1.40 (9H, *p*-t-Bu), 0.32 (dd, $^3J_{PH} = 7.2$, $^3J_{PH} = 5.4$, $^1J_{Pt-H} = 62$, 3H, Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.5 (d, J = 2.3, *o*-Ar), 145.8 (*p*-Ar), 138.5 (d, J = 4.5, Ar), 138.3 (d, J = 4.5, Ar), 134.3 (d, J = 11.9, Ar), 133.9 (d, J = 11.4, Ar), 132.6 (d, J = 41, Ar), 131.0 (d, J = 9.1, Ar), 130.6 (d, J = 51, Ar), 129.0 (d, J = 4.1, Ar), 128.9 (d, J = 4.5, Ar), 121.8 (*m*-Ar), 39.6 (*C*Me$_3$), 35.3 (*C*Me$_3$), 32.9 (C*Me$_3$*), 32.3 (C*Me$_3$*), 31.6 (m, CH$_2$), 27.6 (m, CH$_2$), 4.8 (dd, $^2J_{PC} = 86$, $^2J_{PC} = 7.2$, $^1J_{PtC} = 570$, Pt−Me). IR: 3052, 2947, 1589, 1483, 1435, 1385, 1352, 1239, 1208, 1103, 1041, 876, 818, 745, 692, 532, 487. Anal. Calcd for $C_{45}H_{56}SP_2$Pt: C, 60.99; H, 6.38. Found: C, 60.64; H, 6.46.

Pt(dppe)(Me)(OMes*) (12). Addition of Mes*OH (170 mg, 0.65 mmol) to a slurry of Pt(dppe)(Me)(OMe) (200 mg, 0.31 mmol) in 8 mL of THF gave a light yellow solution with a little suspended white solid. After 3 days, ^{31}P NMR showed that **12** was the major species present, with several minor impurities. The reaction mixture was filtered through Celite. The solvent was removed from the light yellow filtrate, and the residue was recrystallized from THF/petroleum ether at −20 °C to give a yellow solid, which was washed with petroleum ether and dried under vacuum to give 222 mg (82% yield) of a free-flowing yellow powder. White crystals suitable for elemental analysis were obtained by slow evaporation of a C_6D_6 solution.

^{1}H NMR (C_6D_6): δ 7.86−7.80 (m, 3H, Ar), 7.60−7.42 (m, 6H, Ar), 7.16−6.99 (m, 13H, Ar), 1.86 (18H, *o*-t-Bu), 1.8−1.6 (br m, 4H, CH$_2$), 1.49 (9H, *p*-t-Bu), 0.46 (dd, $^3J_{PH} = 3$, $^3J_{PH} = 7.8$, $^1J_{Pt-H} = 51$, 3H, Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 139.9 (d, J = 1.4, Ar), 136.4 (d, J = 1.9, Ar), 134.5 (d, J = 11.6, Ar), 133.9 (d, J = 2.8, Ar), 133.7 (d, J = 11.2, Ar), 133.4 (d, J = 36.7, Ar), 131.3 (d, J = 2.3, Ar), 131.0 (d, J = 1.9, Ar), 130.3 (d, J = 61.4, Ar), 129.1 (d, J = 8.4, Ar), 129.0 (d, J = 10.7, Ar), 121.6 (Ar), 37.0 (*o*-*C*Me$_3$), 34.9 (*p*-*C*Me$_3$), 32.9 (*p*-C*Me$_3$*), 32.8 (*o*-C*Me$_3$*), 30.9−30.1 (m, CH$_2$), 27.1−26.6 (m, CH$_2$), 10.4 (dd, $^2J_{PC} = 90$, $^2J_{PC} = 7.5$, Pt−Me, Pt satellites were not observed due to low concentration of the sample). IR: 2945, 1436, 1418, 1253, 1104, 878, 745, 692, 532, 492. Anal. Calcd for $C_{45}H_{56}OP_2$Pt: C, 62.12; H, 6.50. Found: C, 62.00; H, 6.25.

X-ray Crystallographic Studies. For **1**, crystal, data collection, and refinement parameters are given in Table 2. A suitable crystal was selected and mounted on the tip of a glass fiber with epoxy cement. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°).

The systematic absences in the diffraction data are uniquely consistent for orthorhombic space group $P2_12_12_1$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted beam paths, and was used to model an absorption surface for the difference between the observed and calculated structure factors.[34] The absolute configuration of the structure has been determined (Flack parameter = −0.02(2)). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on the phosphido phosphorus atom could not be located from the difference map and was ignored. All other hydrogen atoms were treated as idealized contributions.

For **5**·THF, the procedure was similar (Table 2), except the systematic absences in the diffraction data are uniquely consistent for the reported space group $P2_1/c$. A semiempirical absorption correction was applied to the data set. A tetrahydrofuran solvent molecule was located in the asymmetric unit. Two peaks remaining in the difference map (max = 2.7 e $Å^{-3}$) were located 1.1 Å from the platinum atom and were considered as noise peaks. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

NMR Equilibrium Studies. Typical Procedure. At ambient temperature, to a solution of Pt(dppe)(Me)(PHPh) (**3**, 22 mg, 0.031 mmol) in ~0.8 mL of THF in an NMR tube was added PH_2Mes (20 mg, 0.13 mmol) via syringe. Integrated intensities from the ^{31}P NMR spectra of the dppe region were used to calculate the relative amounts of **3** and the product **2** present, while the amounts of the phosphines PH_2Ph and PH_2-Mes were calculated from the mass balance; these quantities were used to obtain the equilibrium constant. The phosphines were also observed by ^{31}P NMR, but integration of these resonances was usually unreliable due to the large excess of phosphine present. Generally, equilibria could be approached from either side, giving consistent results. Equilibria were usually reached soon after mixing, and the position of equilibrium did not change over a period of days, although minor decomposition was frequently observed on standing for an extended period. Control experiments using known amounts of **2** and **3** (or the other complexes as appropriate) showed that the ^{31}P NMR integrals gave a reliable measure of the ratios of Pt complexes present, and controls using an internal standard (PPh_3O) showed that the reactions were quantitative. The equilibrium constants listed in Chart 1 are the average of at least three independent determinations. Error limits have been estimated from the deviation of these measurements, as well as from estimates of errors in weighing and integration. The equilibrium constants involving phenyl(isobutyl)phosphido complex **9** are the least reliable quantitatively, since some decomposition in these reaction mixtures was consistently observed; a similar problem was observed with cyclohexylphosphido complex **4**.

Solution Calorimetric Studies. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Monitoring of the reactions of **5** in THF by ^{31}P NMR showed clean, rapid, and quantitative formation of the products, usually within minutes, under the experimental calorimetric conditions. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[35] or the enthalpy of solution of KCl in water.[36] This calorimeter has been previously described,[37] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

In a representative experimental trial, the mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A sample of Pt(dppe)(Me)($PMes_2$) (**5**, 21.0 mg, 23.9 μmol) was charged into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A solution of Mes*SH (11.1 mg, 39.9 μmol) in THF (4.0 mL) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no platinum complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (ca. 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium (ca. 2 h). Control reactions with Hg and protonating reagents show no reaction. The enthalpy of proton exchange (−10.2 ± 0.1 kcal/mol) listed in Table 4 represents the average of at least three individual calorimetric determinations with all species in solution. The enthalpy of solution of Pt(dppe)(Me)($PMes_2$) (−3.2 ± 0.1 kcal/mol) in neat THF was determined using an identical methodology.

Acknowledgment. We thank Dartmouth College, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the NSF CAREER program, the Exxon Education Foundation, and DuPont for support. B.M.L. acknowledges an NSF-REU fellowship. We thank Johnson Matthey/Alfa/Aesar for loans of platinum salts, Dr. John Hillhouse (Cytec Canada) for gifts of phosphines, and Drs. Henry Bryndza, Robert G. Bergman, and Patrick Holland for helpful discussions and sharing results before publication. The work in New Orleans was supported by NSF Grant No. CHE-963116.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H-atom coordinates for **1** and **5**·THF (19 pages). Ordering information is given on any current masthead page.

OM9708891

---

(34) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(35) Ojelund, G.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1691−1699.

(36) Kilday, M. V. *J. Res. Natl. Bur. Stand. (U.S.)* **1980**, *85*, 467−481.

(37) (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357−362. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 4446−4448.