

Platinum-Catalyzed Acrylonitrile Hydrophosphination. P–C Bond Formation via Olefin Insertion into a Pt–P Bond

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The acrylonitrile complexes Pt(diphos)(CH₂CHCN) (diphos = dppe (**1**), dcpe (**2**); dppe = Ph₂PCH₂CH₂PPh₂, dcpe = Cy₂PCH₂CH₂PCy₂, Cy = cyclo-C₆H₁₁) are catalyst precursors and, for some substrates, resting states, during addition of P–H bonds in primary and secondary phosphines across the C=C double bond of acrylonitrile (hydrophosphination). Oxidative addition of P–H bonds to related catalyst precursors gives the phosphido hydride complexes Pt(diphos)(PRR')(H) (diphos = dppe, R = H, R' = Mes* (**20**), R = R' = Mes (**21**); diphos = dcpe, R = H, R' = Mes* (**22**); Mes = 2,4,6-Me₃C₆H₂, Mes* = 2,4,6-(*t*-Bu)₃C₆H₂). Acrylonitrile does not insert into the Pt–H bond of these hydrides to give cyanoethyl ligands; the putative products, the phosphido complexes Pt(diphos)(CH₂CH₂CN)(PRR') (diphos = dppe, R = H, R' = Mes* (**9**), R = R' = Mes (**10**); diphos = dcpe, R = H, R' = Mes* (**11**)) were prepared independently and found to be stable to P–C reductive elimination. Instead, catalysis appears to occur by selective insertion of acrylonitrile into the Pt–P bond to yield the alkyl hydrides Pt(diphos)[CH(CN)CH₂PRR'](H), followed by C–H reductive elimination and regeneration of **1** or **2**. This insertion was observed directly in model methyl phosphido complexes M(dppe)-(Me)(PRR') (M = Pt, R = H, R' = Mes* (**12**), R = R' = Mes (**13**); M = Pd, R = H, R' = Mes* (**17**)), yielding M(dppe)[CH(CN)CH₂PRR'](Me), (**14**, **15**, **18**). Similarly, treatment of Pt(dcpe)-(PHMes*)(H) (**22**) with acrylonitrile gives Pt(dcpe)[CH(CN)CH₂PHMes*](H) (**24**) as a mixture of diastereomers; the isomeric Pt(dcpe)[PMes*(CH₂CH₂CN)](H) (**25**), which was prepared independently, was also observed during this reaction. Both **24** and **25** decompose in the presence of acrylonitrile to form Pt(dcpe)(CH₂CHCN) (**2**) and PHMes*(CH₂CH₂CN) (**3a**). The C–H reductive elimination step was modeled by studies of Pt(dcpe)[CH(Me)(CN)](H) (**26**). Another isomer, Pt(dcpe)[CH(Me)(CN)](PHMes*) (**29**), which formally results from insertion of acrylonitrile into the Pt–H bond of **22**, was formed by decomposition of complex **2** during catalysis. Complex **29** is inactive in catalysis but decomposes to partially regenerate the active catalyst **2**. The cyanoethyl compounds Pt(dcpe)(CH₂CH₂CN)(PHMes*) (**11**), *trans*-Pt-(PPh₃)₂(CH₂CH₂CN)(Br), and PMes₂(CH₂CH₂CN) (**23**) were structurally characterized by X-ray crystallography.

Introduction

Metal-catalyzed addition of X–H bonds to olefins is an important industrial process for several X groups (e.g. hydrogenation, hydrosilylation, hydroboration, hydrocyanation).¹ Analogous catalyses for X = N, O, P, S are potentially useful but have been less well developed.² A common pathway for such reactions involves

oxidative addition of the X–H bond to a low-valent metal center to give a hydride complex. X–C bond formation can then proceed (Scheme 1) either (a) by olefin insertion into the M–H bond, followed by X–C reductive elimination, or (b) by olefin insertion into the M–X bond and subsequent C–H reductive elimination. Evidence has been presented for the operation of one or both of these mechanisms in a variety of catalytic and model systems.³

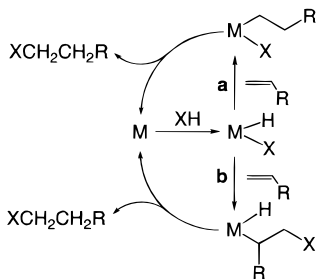
We report here a study of Pt-catalyzed addition of P–H bonds to acrylonitrile (hydrophosphination), including direct observation of the fundamental steps described above. In particular, P–C bond formation via olefin insertion into a Pt–P bond (path b) has been characterized both in a model system and in a catalytic

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(2) For a recent review, see: Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395–402.

Scheme 1. Two Possible Pathways for Metal-Catalyzed Addition of X–H Bonds to Olefins^a



^a For convenience, only one regioisomer of the product is shown.

cally active one. Comparison to literature results on metal-catalyzed X–H additions shows how the nature of the X group affects the individual steps in the reaction and provides design principles for further rational development of this important class of reactions.⁴

Results and Discussion

Hydrophosphination Catalysis. Pringle has used Pt-catalyzed hydrophosphination to prepare useful ligands for homogeneous catalysis.⁵ His previous studies provided the following information on the mechanism of these reactions. (1) As substrates, activated, Michael acceptor olefins are required. (2) Olefin complexes PtL₂–(olefin) (L = phosphine) are the catalyst resting states.^{5a–e} (3) Parallel mechanisms involving both mononuclear and dinuclear intermediates were proposed for the Pt-catalyzed addition of PH(CH₂CH₂CN)₂ to acrylonitrile.^{5b}

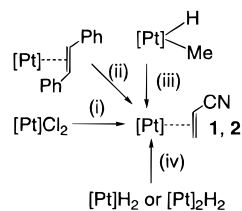
To avoid formation of bimetallic complexes, we studied catalysis by the diphosphine complexes Pt(diphos)–(CH₂CHCN) (**1**, diphos = dppe (Ph₂PCH₂CH₂PPh₂); **2**,

(3) For some recent examples and leading references, see the following. (a) X = N: Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738–6744. (b) X = O: Bennett, M. A.; Jin, H.; Li, S.; Rendina, L. M.; Willis, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 8335–8340. (c) X = B: Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367–4368. (d) X = Si: Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151–2156. (e) For analogous X–H additions with lanthanide catalysts, see: Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633–3639 and references therein.

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(5) (a) Costa, E.; Pringle, P. G.; Worboys, K. *Chem. Commun.* **1998**, 49–50. (b) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277–4282. (c) Pringle, P. G.; Brewin, D.; Smith, M. B.; Worboys, K. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., and Joo, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1995; Vol. 5, pp 111–122. (d) Hoyer, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, 74, 269–274. (e) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701–1702. (f) Harrison, K. N.; Hoyer, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096–1097. For related chemistry, see: (g) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259–3261. (h) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571–1572. (i) Nagel, U.; Rieger, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223–239. (j) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000–7001. (k) Han, L.-B.; Hua, R.; Tanaka, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 94–96. For lanthanide-catalyzed reactions, see: (l) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishita, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simoes, J. A., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; pp 35–51. (m) Groger, H.; Saida, Y.; Arai, S.; Martens, J.; Sasai, H.; Shibasaki, M. *Tetrahedron Lett.* **1996**, *37*, 9291–9292. (n) Groger, H.; Saida, Y.; Sasai, H.; Yamaguchi, K.; Martens, J.; Shibasaki, M. *J. Am. Chem. Soc.* **1998**, *120*, 3089–3103.

Scheme 2^a



^a [Pt] = Pt(diphos). For **1** (i–ii), diphos = dppe; for **2** (iii–iv), diphos = dcpe. Legend: (i) CH₂CHCN, NaBH₄, EtOH; (ii) CH₂CHCN; (iii) CH₂CHCN, 50 °C, 1 day; (iv) CH₂CHCN.

diphos = dcpe (Cy₂PCH₂CH₂PCy₂, Cy = *cyclo*-C₆H₁₁)), prepared as shown in Scheme 2. ³¹P{¹H} NMR data for these and other complexes prepared in this study are found in Table 1, and selected IR and ¹H NMR data are given in Table 2; see the Experimental Section for synthetic details and additional characterization data. We hoped that understanding the mechanism of catalysis with these bidentate ligands and screening trends in catalyst activity, selectivity, and lifetime would allow the eventual development of Pt-catalyzed *asymmetric* hydrophosphination with ligands such as Binap or Duphos.⁶

Complexes **1** and **2** act as catalyst precursors or catalysts for addition of the P–H bonds in the primary phosphines PH₂Ph and PH₂Mes* (Mes* = 2,4,6-*t*-Bu)₃C₆H₂) and in the secondary phosphines PH(Ph)(R) (R = Mes, Ph, Cy, *i*-Bu, Me; Mes = 2,4,6-Me₃C₆H₂) across the acrylonitrile C=C double bond to give the phosphines PPh(CH₂CH₂CN)₂, PH(Mes*)(CH₂CH₂CN) (**3a**), and P(Ph)(R)(CH₂CH₂CN), respectively (Scheme 3). With PH₂Ph, the secondary phosphine⁷ PH(Ph)(CH₂CH₂CN) was observed as an intermediate, but conversion of the bulkier PH₂Mes* to the tertiary phosphine PMes*(CH₂CH₂CN)₂ did not occur.⁸

The (unoptimized) catalytic reactions are summarized in Table 3. Hydrophosphination also occurs for most of the phosphine substrates in the absence of catalyst, but more slowly than in the Pt-catalyzed processes. These reactions occur more quickly for smaller phosphines, and in many cases, other phosphine products (Table 3) are formed. Pringle has proposed^{5b} that byproducts in the PH₃/CH₂CHCN system are due to reaction of more than one acrylonitrile with the starting phosphine; we assume that the phosphines formed here are similar.

The dppe complex **1** decomposes rapidly (except for the substrate PH₂Mes*) on addition of excess phosphine, even when excess acrylonitrile is present, to form Pt-

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(7) Vinokurova, G. M.; Nagaeva, K. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 414.

(8) The new secondary phosphine PH(Mes*)(CH₂CH₂CN) (**3a**) and the tertiary phosphine PPh(Mes)(CH₂CH₂CN) (**3b**) were prepared independently by base-catalyzed hydrophosphination^{8c} (see the Experimental Section). For syntheses and spectroscopic data on cyanoethylphosphines, see the following. (a) PPh(CH₂CH₂CN)₂: Mann, F. G.; Millar, I. T. *J. Chem. Soc.* **1952**, 4453–4457. Rauhut, M. M.; Hechenbleikner, I.; Currier, H. A.; Schaefer, F. C.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 1103–1107. (b) P(Ph)(R)(CH₂CH₂CN) (R = Cy, *i*-Bu, Me): Wolfsberger, W. *Chem. Ztg.* **1990**, *114*, 353–354. (c) PPh₂(CH₂CH₂CN): Habib, M.; Trujillo, H.; Alexander, C. A.; Storhoff, B. N. *Inorg. Chem.* **1985**, *24*, 2344–2349. For reviews of hydrophosphination, see: (d) Wolfsberger, W. *Chem. Ztg.* **1988**, *112*, 215–221. (e) Wolfsberger, W. *Chem. Ztg.* **1988**, *112*, 53–68. The phosphines PPh(CH₂CH₂CN)₂ (Strem) and PPh₂(CH₂CH₂CN) (Organometallics) are commercially available.

Table 1. ³¹P NMR Data for Pt(diphos) Complexes^{a-c}

complex	no.	δ(P ₁) (J _{Pt-P})	δ(P ₂) (J _{Pt-P})	δ(P ₃) (J _{Pt-P})	J ₁₂	J ₁₃	J ₂₃
Pt(dppe)(CH ₂ CHCN)	1	53.5 (3594)	51.4 (3102)		59		
Pt(dcpe)(CH ₂ CHCN)	2	74.1(3446)	70.8 (2963)		47		
Pt(dppe)(PPhPh ₂) ^d	4	29.2 (3581)	29.2 (3581)	-16.2 (3955)		57	
Pt(dppe)(CH ₂ CH ₂ CN)(Br)	5	45.4 (4163)	44.8 (1744)				
Pt(dcpe)(CH ₂ CH ₂ CN)(Br)	6	66.1 (1793)	59.0 (4053)				
[Pt(dppe)(CH ₂ CH ₂ CN)(PH ₂ Mes*)][BF ₄]	7	55.1 (2913)	50.0 (1615)	-64.5 (2621)		386	18
[Pt(dppe)(CH ₂ CH ₂ CN)(PHMes ₂ *)][BF ₄]	8	52.4 (2803)	46.2 (1659)	-47.5 (2533)		369	18
Pt(dppe)(CH ₂ CH ₂ CN)(PHMes*)	9	46.7 (1904)	46.0 (1755)	-65.2 (827)		124	12
Pt(dppe)(CH ₂ CH ₂ CN)(PMes ₂)	10	44.8 (1938)	33.1 (1869)	-57.6 (1201)	6	165	
Pt(dppe)(CH ₂ CH ₂ CN)(PHMes*)	11	64.1 (2011)	59.8 (1787)	-83.7 (806)	3	132	9
Pt(dppe)(Me)[CH(CN)CH ₂ PHMes*] (minor isomer)	14a	49.1 (1769)	48.0 (2208)	-65.8 (195)	3	15	
Pt(dppe)(Me)[CH(CN)CH ₂ PHMes*] (major isomer)	14b	48.5 (1755)	48.3 (2246)	-72.2 (164)		12	
Pt(dppe)(Me)[CH(CN)CH ₂ PMes ₂]	15	48.7 (1819)	47.0 (2260)	-17.9 (277)		31	
[Pd(dppe)(Me)(PH ₂ Mes*)][BF ₄]	16	60.0	46.3	-72.0	24	278	37
Pd(dppe)(Me)(PHMes*)	17	40.2	39.2	-51.1	21	115	
Pd(dppe)(Me)[CH(CN)CH ₂ PHMes*] ^e (minor isomer)	18a	49.4	39.8	-66.9		20	
Pd(dppe)(Me)[CH(CN)CH ₂ PHMes*] (major isomer)	18b	49.4	39.8	-73.5		13	
[Pt(dppe)(Me)(CH ₂ CHCN)][OTf]	19	50.8 (1735)	39.5 (4322)				
Pt(dppe)(PHMes*)(H)	20	53.0 (1995)	50.8 (1773)	-73.1 (882)		115	
Pt(dppe)(PMes ₂)(H) ^f	21	53.3 (2011)	44.9 (1906)	-59.0 (1212)		156	
Pt(dcpe)(PHMes*)(H)	22	80.2 (1969)	68.0 (1775)	-89.9 (868)		115	7
Pt(dcpe)[CH(CN)CH ₂ PHMes*](H) (major isomer)	24a	75.9 (2165)	65.0 (1772)	-68.5 (276)		6	
Pt(dcpe)[CH(CN)CH ₂ PHMes*](H) (minor isomer)	24b	76.1 (2190)	64.9 (1758)	-69.7 (219)		5	
Pt(dcpe)[PHMes*(CH ₂ CH ₂ CN)](H)	25	79.9 (1934)	67.5 (1953)	-4.8 (1130)		147	8
Pt(dcpe)[CH(Me)(CN)](H)	26^g	76.0 (2083)	63.8 (1759)				
Pt(dcpe)[CH(Me)(CN)](Br)	28	66.6 (2000)	60.1 (3860)				
Pt(dcpe)[CH(Me)(CN)](PHMes*)	29	60.0 (2004)	54.2 (2031)	-81.5 (broad)	7	112	
Pt(dcpe)[CH(Me)(CN)](PHMes*) (-60 °C, major isomer)	29a	61.2 (2043)	54.0 (2035)	-77.7 (720)		119	
Pt(dcpe)[CH(Me)(CN)](PHMes*) (-60 °C, minor isomer)	29b	60.9 (2033)	52.6 (2028)	-92.0 (643)		114	

^a The temperature is 22 °C except where noted. Chemical shifts are in ppm (external reference 85% H₃PO₄), and coupling constants are in Hz. ^b P₁ and P₂ are the diphos P nuclei; P₃ is trans to P₁. ^c Solvents: C₆D₆ for **1**, **2**, **9**, **10**, **14**, **20–22**, and **24–26**; CDCl₃ for **5**, **6**, and **19**; CH₂Cl₂ for **7** and **8**; CD₂Cl₂ for **11**; THF-*d*₆ for **15**, **28**, and **29**; THF for **4**, **16**, and **18**; toluene-*d*₈, (-50 °C) for **17**. ^d Tetrahedral complex: P₁ and P₂ = dppe, P₃ and P₄ = PPhPh₂. ^e The dppe resonances for the two isomers overlapped. ^f ¹J_{PH} (PHMes*): **202** (**18a**), **221** (**18b**). ^g Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125–127. ^h Data for *trans*-Pt(PPh₃)₂[CH(Me)(CN)](Br) (**27**) in THF-*d*₆: δ 25.9 (J_{Pt-P} = 3071). In CH₂Cl₂, a 1:1 ratio of *cis* and *trans* isomers was observed: *cis*, δ 20.9 (J_{Pt-P} = 1950), 20.3 (J_{Pt-P} = 4228), J_{PP} = 17; *trans*, δ 24.5 (J_{Pt-P} = 3052).

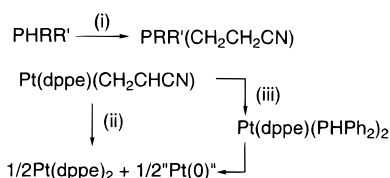
Table 2. Selected IR and ¹H NMR Data for Pt(diphos) Complexes^{a-c}

no.	IR ^d	selected ¹ H NMR
1	2198	2.80 (d, ³ J _{HH} = 9.3, ² J _{Pt-H} = 68, 1H, CH ₂ CHCN), 2.75 (d, ³ J _{HH} = 4.5, ² J _{Pt-H} = 54, 1H, CH ₂ CHCN), 2.49 (dd, ³ J _{HH} = 9.3, ³ J _{HH} = 4.5, ² J _{Pt-H} = 50, 1H, CH ₂ CHCN)
2	2195	2.47 (apparent t, ³ J _{HH} = 9.6, 9.6, ² J _{Pt-H} = 63, 1H, CH ₂ CHCN), 2.24 (dd, ³ J _{HH} = 9.6, ² J _{HH} = 5.4, 1H, CH ₂ CHCN), 2.13 (dd, ³ J _{HH} = 9.6, ² J _{HH} = 5.4, 1H, CH ₂ CHCN)
5	2231	1.63–1.39 (m, ² J _{Pt-H} = 55, Pt–CH ₂)
9	2400, 2230	5.10 (d of apparent triplets, J _{PH} = 215, 8, 8, ² J _{Pt-H} = 64, PH)
10	2230	1.46–1.40 (m, ² J _{Pt-H} = 50, Pt–CH ₂)
11	2390, 2229	5.30 (ddd, J _{PH} = 211, 9, 2, ² J _{Pt-H} = 59, PH)
14a,b	2393, 2185	4.57 (ddd, ¹ J _{PH} = 220, ³ J _{HH} = 10, 7, minor PH), 4.26 (ddd, ¹ J _{PH} = 222, ³ J _{HH} = 11, 5, major PH)
15	2179	3.31 (m, ² J _{AA'} = 12.3, ³ J _{AB} = 11.9, 1H, CH ₂ PMes ₂), 3.25 (m, ² J _{AA'} = 12.3, ³ J _{AB} = 3.9, 1H, CH ₂ PMes ₂), 2.81 (m, ³ J _{AB} = 11.9, ³ J _{AB} = 3.9, ² J _{Pt-H} = 106, CH(CN))
16	2407	5.61 (ddd, J _{PH} = 350, 6, 4, PH ₂)
17		4.83 (dm, J _{PH} = 203, PH)
19	2233	6.47 (d, ³ J _{HH} = 11, 1H, CH ₂), 6.23 (d, ³ J _{HH} = 17, 1H, CH ₂), 6.03 (dd, ³ J _{HH} = 17, 11, 1H, CH)
20	2372, 2053	5.56 (d of apparent t, J _{PH} = 211, 8, 8, ² J _{Pt-H} = 62, PH), -1.34 (ddd, ² J _{PH} = 188, 15, 6, ¹ J _{Pt-H} = 1151, Pt–H)
21^e	2033	-2.13 (ddd, J _{PH} = 187, 13.5, 13.5, ¹ J _{Pt-H} = 1107, Pt–H)
22	2375, 2024	5.87 (ddd, J _{PH} = 204, 8, 2, ² J _{Pt-H} = 58, PH), -1.47 (dd, ² J _{PH} = 182, 16, ¹ J _{Pt-H} = 1063, Pt–H)
24a		5.62 (d of apparent t, ¹ J _{PH} = 228, ³ J _{HH} = 9, 9, PH), -1.33 (ddd, ² J _{PH} = 185, 18, 5, ¹ J _{Pt-H} = 1106, Pt–H)
24b		4.86 (ddd, ¹ J _{PH} = 217, ³ J _{HH} = 13, 5, PH), -1.27 (ddd, ² J _{PH} = 188, 17, 5, ¹ J _{Pt-H} = 1132, Pt–H)
25	2239, 2029	-2.41 (d of apparent t, ² J _{PH} = 171, 17, 17, ¹ J _{Pt-H} = 1006, Pt–H)
26	2182, 1993	-1.30 (dd, ² J _{PH} = 191, 17, ¹ J _{Pt-H} = 1121, Pt–H)
27	2199	2.02 (q, ³ J _{HH} = 7, CH), 0.50 (d, ³ J _{HH} = 7, ³ J _{Pt-H} = 67, Me)
29	2399, 2185	5.18 (br dd, J _{PH} = 209, 8, ² J _{Pt-H} = 56, PH)

^a IR spectra (KBr pellets) are in cm⁻¹. Additional ν_{CN} IR data (cm⁻¹): 2222 (**6**), 2230 (**10**), 2233 (**19**), 2193 (**28**). ^b Chemical shifts are in ppm, and coupling constants are in Hz. ^c ³¹P-decoupled spectra reported for **1**, **2**, **27**. The temperature is 22 °C except where noted. ^d Solvents: C₆D₆ for **1**, **2**, **9**, **10**, **15**, **20–22**, and **24–26**; CDCl₃ for **5** and **19**; THF-*d*₆ for **27** and **29**; CD₂Cl₂ for **11**, **14**, and **16**; toluene-*d*₈ (-50 °C) for **17**. ^e ν_{PH} ~2400 cm⁻¹, ν_{CN} ~2200 cm⁻¹, ν_{Pt-H} ~2000 cm⁻¹. ^f Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125–127.

(dppe)₂ (Scheme 3).⁹ With PPhPh₂, a small amount of Pt-(dppe)(PPhPh₂)₂ (**4**) was also observed.¹⁰ The expected disproportionation byproduct,¹¹ Pt(L)_n(CH₂CHCN)_m (L

= phosphine), was not observed, but the ³¹P NMR peaks due to the phosphines present were broadened, consistent with exchange processes involving such Pt(0)

Scheme 3^a

^a Legend: (i) CH₂CHCN, catalytic Pt(diphos)(CH₂CHCN) (**1** or **2**), 50 °C, THF, for R and R', see Table 3; (ii) PHRR', CH₂CHCN, 25 °C; (iii) excess P(HPh)₂, 25 °C.

complexes. Such mixtures were active hydrophosphination catalysts. In contrast, dcpe complex **2** remains unchanged during most of the catalytic reactions examined. We assume that **2** is more stable than **1** due to increased steric protection of the metal center, as well as the difficulty of displacing the more electron-donating alkylphosphine in an associative reaction. However, for PH(Ph)(Me), decomposition occurred within 1 h, and for PH(Ph)(Cy), partial decomposition was observed after 1 day. For PH₂Mes*, the catalyst slowly decomposed over the course of 1 week; this chemistry is discussed in more detail below. In cases where catalysts **1** and **2** remained intact, no other Pt(diphos) species were observed by ³¹P NMR during the reaction.

Cyanoethyl Complexes. As mentioned in the Introduction, formation of a cyanoethyl group by insertion of acrylonitrile into a Pt–H bond,¹² followed by P–C reductive elimination,¹³ is a plausible mechanism (path a, Scheme 1) for these reactions. The putative cyanoethyl phosphido intermediates¹⁴ were prepared as shown in Scheme 4. Treatment of Pt(dppe)(*trans*-stilbene)⁶ with BrCH₂CH₂CN gave Pt(dppe)(CH₂CH₂CN)(Br) (**5**).¹⁵ The analogous dcpe complex Pt(dcpe)(CH₂CH₂CN)(Br) (**6**) was prepared by addition of dcpe to the known *trans*-Pt(PPh₃)₂(CH₂CH₂CN)(Br).¹⁵ Bromide abstraction from **5** with AgBF₄ in the presence of the appropriate phosphine gave the cationic complexes [Pt(dppe)(CH₂CH₂

(9) Pt(dppe)₂ was identified by ³¹P NMR and by comparison to an authentic sample: Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107–115.

(10) Complex **4** was generated independently, along with Pt(dppe)₂, by treatment of Pt(dppe)(stilbene)⁶ with excess P(HPh)₂. Addition of a large excess of P(HPh)₂ to Pt(dppe)₂ also generates a small amount of **4**.

(11) For examples of related disproportionations, see: (a) Bennett, M. A.; Chiraratvatana, C. *J. Organomet. Chem.* **1985**, *296*, 255–267. (b) Davies, J. A.; Eagle, C. T.; Otis, D. E.; Venkataraman, U. *Organometallics* **1989**, *8*, 1080–1088. (c) Reference 9.

(12) (a) Insertion of acrylonitrile into the Pt–H bond of *trans*-Pt(PPh₂py)₂(H)(Cl) (PPh₂py = 2-pyridyldiphenylphosphine) gives a cyanoethyl group: Xie, Y.; James, B. R. *J. Organomet. Chem.* **1991**, *417*, 277–288. (b) However, *trans*-Pt(PEt₃)₂(*p*-BrC₆H₄)(H) does not react with acrylonitrile in boiling *n*-hexane: Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110–2116.

(13) For examples of P–C reductive elimination, see: (a) Falvello, L. R.; Fornies, J.; Fortuno, C.; Martin, A.; Martinez-Sarinena, A. P. *Organometallics* **1997**, *16*, 5849–5856. (b) Archambault, C.; Bender, R.; Braunstein, P.; De Cian, A.; Fischer, J. *Chem. Commun.* **1996**, 2729–2730. (c) Shulman, P. M.; Burkhardt, E. D.; Lundquist, E. G.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 101–109. (d) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519–1521. (e) Fryzuk, M. D.; Joshi, K.; Chadha, R. K.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 8724–8736. (f) Gaumont, A.-C.; Hursthouse, M. B.; Coles, S. J.; Brown, J. M. *Chem. Commun.* **1999**, 63–64.

(14) The PHMes* phosphido ligand was chosen, since complexes **1** and **2** decompose only slowly during Pt-catalyzed reaction of acrylonitrile and PH₂Mes*, and because this reaction in the absence of catalyst is slow. Dimesitylphosphido complex **10** was prepared for comparison.

(15) For analogous oxidative additions of haloalkylnitriles to Pt(0), see: Ros, R.; Renaud, J.; Roulet, R. *Helv. Chim. Acta* **1975**, *58*, 133–139.

CN)(PHRR')][BF₄] (R = H, R' = Mes* (**7**); R = R' = Mes (**8**)), which could be deprotonated to yield the desired phosphido complexes Pt(dppe)(CH₂CH₂CN)(PRR') (R = H, R' = Mes* (**9**); R = R' = Mes (**10**)).¹⁶ The dcpe complex Pt(dcpe)(CH₂CH₂CN)(PHMes*) (**11**) was prepared directly from **6** by treatment with LiPHMes*.

The structures of cyanoethyl complex **11** (as an ether solvate, Figure 1) and its precursor *trans*-Pt(PPh₃)₂(CH₂CH₂CN)(Br) were confirmed by X-ray crystallography (see Figures 1 and 2, Table 4, the Experimental Section, and the Supporting Information for details). Both show the expected square-planar structure, with some distortion for **11** due to the constraints of the dcpe chelate (bite angle 86.45(7)°). The Pt–C bond in **11** (2.258(14) Å) is longer than that in the precursor (2.115(7) Å), consistent with the expected *trans* influence of dcpe and bromide ligands.¹⁷ The PH proton in **11** was not located, but the Pt–PHMes* bond length of 2.390(2) Å is similar to that previously reported for Pt(dppe)(Me)(PHMes*) (2.378(5) Å).¹⁶

The cyanoethyl phosphido compounds **9–11** are thermally stable in solution and show no tendency to decompose via P–C reductive elimination,¹⁸ which suggests that path a in Scheme 1 is not the mechanism of catalysis. Consistent with this conclusion, complexes **9** and **11** did not catalyze the reaction of PH₂Mes* and acrylonitrile. Instead, complex **11** decomposed slowly under catalytic conditions to give a trace of the secondary phosphine PH(Mes*)(CH₂CH₂CN) (**3a**) and, after several days, a small amount of Pt(dcpe)(CH₂CHCN) (**2**).

Acrylonitrile Insertion: Model Systems. These observations suggest that P–C bond formation might occur via insertion of acrylonitrile into a Pt–P bond (path b, Scheme 1). The model phosphido complexes Pt(dppe)(Me)(PRR') (**12**, **13**)¹⁶ undergo this reaction regioselectively to furnish the dialkyls Pt(dppe)(Me)[CH(CN)CH₂PRR'] (R = H, R' = Mes*, **14** (2:1 mixture of diastereomers); R = R' = Mes, **15**; Scheme 5). The regiochemistry of insertion was established spectroscopically. For example, in **15**, the Pt–CH ¹H NMR signal (C₆D₆) is a multiplet (δ 2.81, ²J_{Pt–H} = 106 Hz) with inequivalent couplings (³J_{HH} = 11.9, 3.9 Hz) to the diastereotopic CH₂ protons, whose resonances appear as multiplets at 3.31 and 3.25 ppm with ²J_{HH} = 12.3 Hz. The Pt–CH(CN) ¹³C NMR signal appears at δ 7.6 (d, ²J_{PC} = 90, ¹J_{Pt–C} = 585 Hz), and the CN IR signal (KBr, 2179 cm⁻¹) is at lower frequency than usual for nitrile groups, as previously observed for α-cyanoalkyl complexes, consistent with the proposed regiochemistry of insertion.¹⁹

When pure samples of **14** and **15** are redissolved, they decompose by extrusion of acrylonitrile to regenerate the phosphido starting materials **12** and **13** (Scheme 5). These reactions proceed slowly at room temperature or

(16) 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.

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

(18) The analogous methyl complexes Pt(dppe)(Me)(PRR') also do not undergo reductive elimination.¹⁶ See the Supporting Information for details of the thermolyses of **9–13**.

(19) (a) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554–558. (b) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1992**, *11*, 4285–4292. (c) Reger, D. L.; McElligott, P. J. *J. Organomet. Chem.* **1981**, *216*, C12–C14. (d) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660–664. (e) See also ref 15.

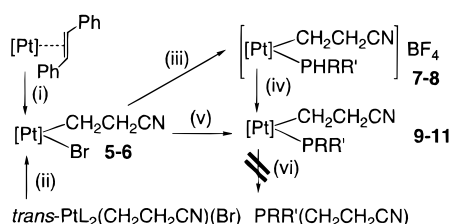
Table 3. Pt-Catalyzed Hydrophosphination of Acrylonitrile^a

$$\text{PHRR}' \xrightarrow{\text{cat.}} \text{PRR}'(\text{CH}_2\text{CH}_2\text{CN}) \quad \text{cat.} = \text{Pt}(\text{diphos})(\text{CH}_2\text{CHCN})$$

diphos = dppe (1) or dcpe (2)

reactant	product	TOF			selectivity (dppe, dcpe), %
		dppe ^b	dcpe ^b	no Pt ^c	
PH ₂ Ph	P(Ph)(ce) ₂	0.5 h ⁻¹	10 h ⁻¹	1 day ⁻¹	68, 29 ^d
PH ₂ Mes*	PH(Mes*)(ce)	1 day ⁻¹	1 day ⁻¹	0.1 day ⁻¹	>95
PHPh ₂	PPh ₂ (ce)	10 h ⁻¹	0.5 h ⁻¹	0.05 h ⁻¹	95, 88 ^e
PH(Ph)(Mes)	P(Ph)(Mes)(ce)	1 day ⁻¹	0.5 day ⁻¹	0 ^f	>95
PH(Ph)(Cy)	P(Ph)(Cy)(ce)	10 day ⁻¹	8 day ⁻¹	0.2 day ⁻¹	82, 45 ^g
PH(Ph)(<i>i</i> -Bu)	P(Ph)(<i>i</i> -Bu)(ce)	10 h ⁻¹	8 day ⁻¹	2 day ⁻¹	82, 57 ^h
PH(Ph)(Me)	P(Ph)(Me)(ce)	10 h ⁻¹	10 day ⁻¹	4 day ⁻¹	88, 55 ⁱ

^a Conditions: 10 mol % catalyst, 1.5:1 acrylonitrile to phosphine ratio (3:1 for PH₂Ph), THF, 50 °C. ce = cyanoethyl, CH₂CH₂CN. Catalyst **1** decomposed immediately (see text) in all cases except for PH₂Mes*. Catalyst **2** decomposed within 1 h for PH(Ph)(Me), over 7 days for PH₂Mes* (see text), and slowly for PH(Ph)(Cy) (partial decomposition observed after 1 day). Product chemical shifts are as follows (δ): PPh(ce)₂, -22.3; PH(Mes*)(ce), -73.0; PPh₂(ce), -15.5; PPh(Mes)(ce), -24.9; PPh(Cy)(ce), -10.6; PPh(*i*-Bu)(ce), -27.3; PPh(Me)(ce), -33.5. ^b Catalytic reactions were monitored by ³¹P NMR (PPh₃O internal standard) until the starting phosphine was consumed (10 turnovers), except for the slow reactions of PH₂Mes*, which were observed for ca. 1 half-life. The turnover frequency (TOF) is defined as equiv of products formed/quiv of catalyst per unit time. ^c The control experiments were carried out under identical conditions with the same amounts of phosphine and acrylonitrile as the catalytic ones, except that no Pt catalyst was added. TOF is defined in this case as equiv of products formed/unit time, where the amount of starting phosphine is defined as 10 equiv, to permit direct comparison of the rates of the control reactions with those catalyzed using 10 mol % (1 equiv) Pt complex. For example, 50% conversion of starting phosphine to products after 1 day would be reported as a TOF of 5 day⁻¹. The control experiments were monitored by ³¹P NMR for at least as long as the corresponding catalytic ones, except for the very slow reaction of PH₂Mes*, which was observed for 5 days. ^d The known secondary phosphine PH(Ph)(ce) (δ -53.1, d, J_{PH} = 211 Hz) was observed immediately both in the dppe system and without added Pt. For dppe, other byproduct chemical shifts are as follows: δ -12.4, -26.2, -27.5 (ca. 1:3:4 ratio). dcpe: δ -26.2, -27.6, -30.6, -31.6, -32.9 in ca. 4:6:1:2:3 ratio. Without Pt: δ -26.2, -27.5, -59.6, -61.9 (ratio ca. 1:1:1:1). ^e For both catalysts and without Pt, one byproduct (δ -20.1). ^f No reaction observed over 7 days. ^g dppe: byproducts δ -14.9, -16.6 (ca. 1:2 ratio); dcpe: δ -14.9, -15.4, -16.6 (ca. 1:1:3 ratio); no byproducts without Pt. ^h dppe: byproducts δ -31.4, -33.2 (ca. 1:2 ratio; dcpe, ca. 1:3; without Pt, ca. 1:1). ⁱ dppe: byproducts δ -37.4, -38.9, -45.6 (ca. 1:1.5:trace; dcpe, ca. 1:1:trace; without Pt, similar to dppe results).

Scheme 4^a

^a [Pt] = Pt(diphos). Legend: (i) for **5**, diphos = dppe, BrCH₂CH₂CN; (ii) for **6**, diphos = dcpe, dppe; (iii) AgBF₄, PHRR'; diphos = dppe, R = H, R' = Mes* (**7**), R = R' = Mes (**8**); (iv) NaN(SiMe₃)₂, for **9** and **10**, diphos and R, R' as in **7** and **8**; (v) for **11**, diphos = dcpe, LiPHMes*; (vi) heating in toluene or THF.

more quickly at 60 °C to reach an apparent equilibrium with **12** and **13**. Attempts to measure the equilibrium constants quantitatively were unsuccessful due to slow decomposition, but qualitatively, the equilibrium favors the insertion at room temperature. Coordination of the P lone pair in **14** and **15** to the metal center²⁰ may be important in these β-phosphido olefin eliminations and may also contribute to the observed Pt–P and P–P couplings.²¹

A similar reaction of the cyanoethyl phosphido complex **9** with acrylonitrile proceeded slowly and gave a mixture of products; a ³¹P NMR signal at δ -80 (d, ⁴J_{PP}

(20) For related examples in which the lone pair of a pendant amino or phosphido ligand coordinates to the metal center, see: (a) Reference 3a. (b) Hegedus, L. S.; Akermark, B.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122–7126. (c) Hey-Hawkins, E.; Kurz, S.; Sieler, J.; Baum, G. *J. Organomet. Chem.* **1995**, *486*, 229–235.

(21) A related β-aryloxy elimination from complexes containing the Pt–CH₂CH₂OAr group has been reported to occur on heating, see: Komiya, S.; Shindo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1672–1673. Reversible coordination of the tertiary phosphine to the metal in a four-membered ring might occur quickly in **14** and **15** on the NMR time scale at room temperature, but the ³¹P NMR spectrum of **15** was unchanged at -75 °C.

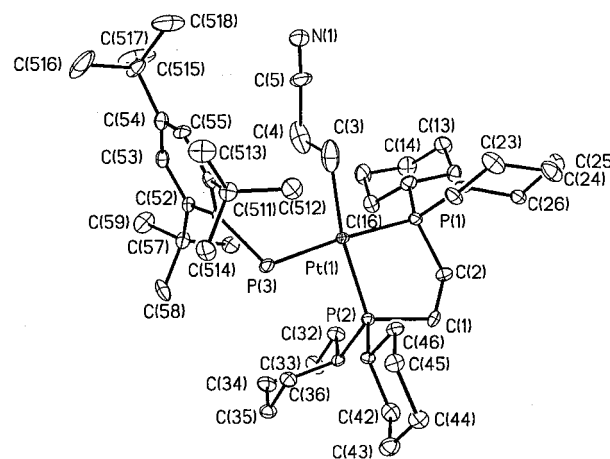


Figure 1. ORTEP diagram of Pt(dcpe)(CH₂CH₂CN)-(PHMes*)·Et₂O (**11**·Et₂O) with 30% thermal ellipsoids. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)–P(1) = 2.283(2), Pt(1)–P(2) = 2.304(2), Pt(1)–P(3) = 2.390(2), Pt(1)–C(3) = 2.258(14), C(3)–C(4) = 1.427(16), C(4)–C(5) = 1.579(19), N(1)–C(5) = 1.132(13); C(3)–Pt(1)–P(1) = 88.4(3), P(1)–Pt(1)–P(2) = 86.45(7), C(3)–Pt(1)–P(3) = 95.1(3), P(2)–Pt(1)–P(3) = 89.19(7).

≈ 10, ³J_{Pt–P} ≈ 160 Hz, THF) may be assigned to an insertion product analogous to **14**. However, this reaction appeared to be reversible and this product could not be isolated. Neither **9** nor these materials were observed during catalysis, ruling out the possibility that complex **9** is formed as an intermediate which reacts further with acrylonitrile en route to the hydrophosphination product PH(Mes*)(CH₂CH₂CN) (**3a**).

In analogous palladium chemistry (Scheme 5), the cationic complex [Pd(dppe)(Me)(PH₂Mes*)][BF₄] (**16**) was prepared by treatment of Pd(dppe)(Me)(Cl) with AgBF₄ and PH₂Mes*. Low-temperature deprotonation

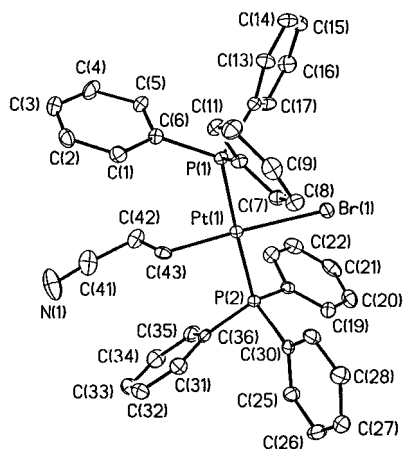


Figure 2. ORTEP diagram of $[trans\text{-Pt}(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2\text{-CN})(\text{Br})]$ with 30% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt–P(1) = 2.331(2), Pt–P(2) = 2.336(2), Pt–C(43) = 2.115(7), Pt–Br(1) = 2.5630(7), C(41)–C(42) = 1.489(12), C(42)–C(43) = 1.508(11), N(1)–C(41) = 1.167(12); C(43)–Pt(1)–P(1) = 90.8(2), C(43)–Pt(1)–P(2) = 91.1(2), P(1)–Pt(1)–Br(1) = 90.66(5), P(2)–Pt(1)–Br(1) = 87.36(4).

Table 4. Crystallographic Data for $trans\text{-Pt}(\text{PPh}_3)_2(\text{CH}_2\text{CH}_2\text{CN})(\text{Br})$ (A**), $\text{Pt}(\text{dcpe})(\text{CH}_2\text{CH}_2\text{CN})(\text{PHMe}^*)\cdot\text{Et}_2\text{O}$ (**11}\cdot\text{Et}_2\text{O}**), and $\text{PMes}_2\text{CH}_2\text{CH}_2\text{CN}$ (**23**)**

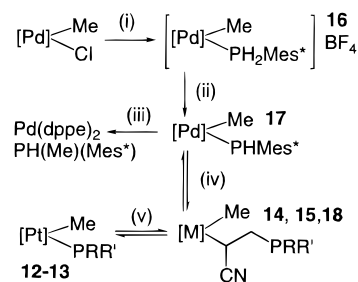
	A	11}\cdot\text{Et}_2\text{O}	23
formula	$\text{C}_{39}\text{H}_{34}\text{BrNP}_2\text{Pt}$	$\text{C}_{53}\text{H}_{92}\text{NOP}_3\text{Pt}$	$\text{C}_{21}\text{H}_{26}\text{NP}$
fw	853.61	1047.28	323.40
space group	$P2_1/n$	$P2_1/n$	$Pna2_1$
<i>a</i> , Å	12.1765(2)	11.1690(2)	20.019(5)
<i>b</i> , Å	23.7244(3)	19.5742(2)	8.843(2)
<i>c</i> , Å	13.2394(2)	24.6275(2)	21.219(5)
β , deg	114.570(2)	99.2733(3)	
<i>V</i> , Å ³	3478.30(6)	5313.76(11)	3756(1)
<i>Z</i>	4	4	8
cryst color, habit	colorless rod	pale yellow block	colorless
<i>D</i> (calcd), g cm ⁻³	1.630	1.309	1.144
μ (Mo K α), cm ⁻¹	53.03	27.66	1.460
temp, K	198(2)	173(2)	298
<i>T</i> (max)/ <i>T</i> (min)		1.000/0.796	
diffractometer	Siemens P4/CCD	Siemens P4/CCD	P4
radiation		Mo K α (λ = 0.710 73 Å)	
<i>R</i> (<i>F</i>), % ^a	4.13	5.07	4.21
<i>R</i> _w (<i>F</i> ²), % ^a	11.57	14.93	10.39

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

of **16** yields neutral $\text{Pd}(\text{dppe})(\text{Me})(\text{PHMe}^*)$ (**17**), which decomposes on warming to the known secondary phosphine $\text{PH}(\text{Me})(\text{Mes}^*)$ ²² and the fragment $\text{Pd}(\text{dppe})$, which either disproportionates to $\text{Pd}(0)$ and $\text{Pd}(\text{dppe})_2$ or can be trapped by added dppe to give only $\text{Pd}(\text{dppe})_2$.²³

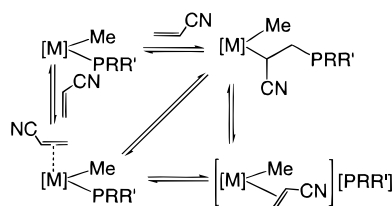
At low temperature, **17** reacts with acrylonitrile to yield $\text{Pd}(\text{dppe})(\text{Me})[\text{CH}(\text{CN})\text{CH}_2\text{PHMe}^*]$ (**18**) as a mixture of diastereomers (2:1 ratio on warming to room

Scheme 5^a



^a [M] = M(dppe); M = Pd, Pt. Legend: (i) AgBF_4 , PH_2Mes^* ; (ii) $\text{LiN}(\text{SiMe}_3)_2$, -78°C ; (iii) dppe , -78 to 25°C ; (iv) CH_2CHCN , -78°C (for **18**); (v) CH_2CHCN , $\text{R} = \text{H}$, $\text{R}' = \text{Mes}^*$ (**12**, **14**), $\text{R} = \text{R}' = \text{Mes}$ (**13**, **15**).

Scheme 6^a



^a [M] = M(dppe); M = Pd, Pt.

temperature). Low-temperature monitoring of this reaction shows that one diastereomer is initially formed selectively but eventually becomes the minor product on warming. A mixture of **18** and acrylonitrile decomposes on standing to give $\text{PH}(\text{Me})(\text{Mes}^*)$; presumably this occurs via extrusion of acrylonitrile and thermal decomposition of the palladium phosphido complex. Although such mixtures were stable at room temperature for hours, attempts to isolate **18** led to decomposition.

Related work on small-molecule insertion into metal–heteroatom bonds²⁴ suggests two possible limiting pathways for these reactions (Scheme 6). In a classical migratory insertion process, acrylonitrile could bind to the coordinatively unsaturated Pt center, followed by insertion into the Pt–P bond. Bryndza has provided evidence for such a process in the closely related insertion of tetrafluoroethylene into the Pt–O bond of $\text{Pt}(\text{dppe})(\text{Me})(\text{OMe})$ and in analogous CO insertions.²⁵ A similar reaction could occur without prior binding of the olefin. Alternatively, acrylonitrile could displace the phosphido group to form the ionic intermediate $[\text{Pt}(\text{dppe})(\text{Me})(\text{CH}_2\text{CHCN})][\text{PRR}']$, followed by attack of the phosphido anion on coordinated acrylonitrile to yield the observed products. A related intermediate, $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2][\text{OR}]$, was observed during carbonylation of $trans\text{-Ir}(\text{PPh}_3)_2(\text{CO})(\text{OR})$ by Atwood.²⁶

Since acrylonitrile reacts quickly with phosphido anions, a crossover experiment is not possible. Therefore, to test the latter possibility, the proposed intermediate cation $[\text{Pt}(\text{dppe})(\text{Me})(\text{CH}_2\text{CHCN})]^+$ (**19**) was

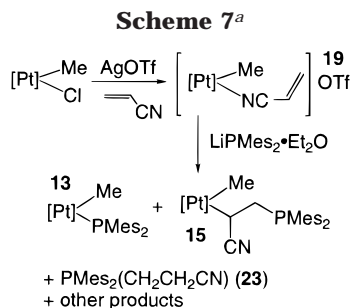
(22) Identified by ¹H, ¹³C, and ³¹P NMR: (a) Yoshifuji, M.; Shibayama, K.; Inamoto, N. *Chem. Lett.* **1984**, 115–118. (b) Brauer, D. J.; Bitterer, F.; Dorrenbach, F.; Hessler, G.; Stelzer, O.; Kruger, C.; Lutz, F. *Z. Naturforsch., B* **1996**, 51, 1183–1196.

(23) $\text{Pd}(\text{dppe})_2$ was identified by ³¹P NMR and comparison to an authentic sample. Further results on this and related reductive eliminations in palladium phosphido complexes will be reported separately: Zhuravel, M. A.; Wicht, D. K.; Nthenge, J. M.; Sweeder, R. D.; Glueck, D. S. Manuscript in preparation.

(24) For a review, see: Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, 88, 1163–1188.

(25) (a) Bryndza, H. E. *Organometallics* **1985**, 4, 406–408. (b) Bryndza, H. E. *Organometallics* **1985**, 4, 1686–1687. (c) For related work implicating a migratory insertion mechanism for carbonylation of $[\text{Pt}(\text{triphos})(\text{OAr})]^+$, see: Dockert, D. W.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1996**, 118, 4846–4852. (d) See also ref 3b.

(26) Rees, W. M.; Churchill, M. R.; Fettingner, J. C.; Atwood, J. D. *Organometallics* **1985**, 4, 2179–2185.



prepared as a triflate salt by treatment of Pt(dppe)(Me)-(Cl) with AgOTf and an excess of acrylonitrile (Scheme 7).²⁷ The ³¹P NMR spectrum of **19** (Table 1) is very similar to that of [Pt(dppe)(Me)(NCMe)][BF₄],²⁸ which suggests that acrylonitrile in **19** is bound to Pt via the nitrile nitrogen, not by the C=C bond.²⁹ Consistent with this conclusion, no Pt satellites are observed on the ¹H (Table 2) or ¹³C NMR signals due to coordinated acrylonitrile, which appear at chemical shifts similar to those in the free ligand.

Freshly prepared **19** was treated with LiPMes₂·Et₂O in THF-*d*₈ at -78 °C;³⁰ the ³¹P NMR spectrum of the reaction mixture at -50 °C showed that a mixture of products was formed (Scheme 7). The major species present were Pt(dppe)(Me)(PMes₂) (**13**) and Pt(dppe)(Me)[CH(CN)CH₂PMes₂] (**15**) in a ratio of approximately 2:1. A small amount of PMes₂(CH₂CH₂CN) (**23**, see below) was also observed by ³¹P NMR, along with several other unidentified products.

These results suggest that the phosphido anion displaces acrylonitrile from Pt to give **13** and that alkyl complex **15** is formed by reaction between **13** and acrylonitrile, while phosphine **23** could be formed from reaction of lithium phosphide with acrylonitrile followed by quenching of the resulting anion with adventitious water. It is possible that the reaction of **13** with acrylonitrile does proceed via displacement of the phosphido ligand to form the cation of **19** but that the lithium salt of dimesitylphosphide is not a good model for the resulting anion. Nonetheless, the simplest explanation of the observed chemistry involves a migratory insertion with neutral intermediates.

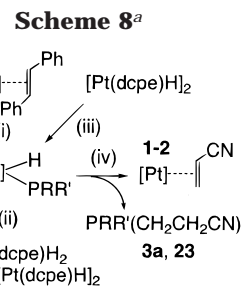
Acrylonitrile Insertion: Catalyst System. These model studies suggested that P-C bond formation in

(27) Although **19** could be isolated as a white solid in good yield, we were unable to obtain analytically pure samples of the triflate or BF₄ salts, as indicated by peaks due to minor impurities in the ³¹P NMR spectrum and by irreproducible results of IR spectra, which showed a variety of CN stretches depending on sample history and anion. Complex **19** decomposed over a period of days in methylene chloride solution under nitrogen.

(28) In CDCl₃, δ 49.1 (¹J_{Pt-P} = 1809 Hz), 38.9 (¹J_{Pt-P} = 4370 Hz): Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738–747.

(29) (a) A similar coordination mode was reported for *trans*-[Pt(PMe₂-Ph)₂(Me)(CH₂CHCN)][BF₄]; see: Clark, H. C.; Ruddick, J. D.; *Inorg. Chem.* **1970**, *9*, 1226–1229. For *trans*-[Pt(PtEt₃)₂(R)(CH₂CHCN)][BF₄] (R = Me, H), see: Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *202*, 107–114. (b) For a review of acrylonitrile coordination chemistry, see: Bryan, S. J.; Huggett, P. G.; Wade, K.; Daniels, J. A.; Jennings, J. R. *Coord. Chem. Rev.* **1982**, *44*, 149–189. (c) For a recent report of an analogous cationic Pt diazabutadiene complex with π-bound acrylonitrile, see: Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **1998**, *17*, 5102–5113. However, this complex has recently been reformulated as N-bound. See: Albietz, P. J., Jr.; Yang, K.; Eisenberg, R. *Organometallics* **1999**, *18*, 2747–2749.

(30) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941–1946.



^a [Pt] = Pt(diphos). Legend: (i) diphos = dppe, PH₂Mes* (for **20**), PHMes₂ (for **21**); (ii) PH₂Mes* (for **22**); (iii) 2 PH(Mes*)(CH₂CH₂CN) (for **25**); (iv) 2 CH₂CHCN, **20** and **25** yield **3a**, **21** yields **23**. For reaction of **22** with acrylonitrile, see Scheme 9.

the Pt-catalyzed hydrophosphinations studied here proceeds via acrylonitrile insertion into the Pt-P bond of a phosphido hydride complex.³¹ We next sought evidence for the insertion step in a catalytically active system by the synthesis of phosphido hydride complexes.

Oxidative addition of P-H bonds to Pt(dppe)(*trans*-stilbene) generates Pt(dppe)(PRR')(H) (R = H, R' = Mes* (**20**); R = R' = Mes (**21**); Scheme 8). Pt(dcppe)-(PHMes*)(H) (**22**) was prepared by treatment of Pt-(dcppe)H₂ and/or [Pt(dcppe)H]₂ with PH₂Mes*.³² These complexes were characterized spectroscopically but could not all be isolated in analytically pure form. As previously described, dimesitylphosphido complex **21** is formed in an equilibrium with the precursor stilbene complex and decomposes in solution.³³ The high solubility of supermesitylphosphido complexes **20** and **22** made them difficult to purify.

Treatment of the dppe hydrides **20** and **21** with 2 equiv of acrylonitrile affords the acrylonitrile complex **1** and the cyanoethylphosphines PH(Mes*)(CH₂CH₂CN) (**3a**) and PMes₂(CH₂CH₂CN) (**23**), respectively (Scheme 8). The regiochemistry of this P-C bond-forming step was confirmed by NMR data and by the crystal structure of **23** (see Figure 3, Table 4, the Experimental Section, and the Supporting Information). No intermediates were observed when these reactions were monitored by NMR at low temperature in toluene-*d*₈; formation of **3a** and **23** was observed above -40 and -30 °C, respectively.

However, on addition of 1 equiv of acrylonitrile to dcppe complex **22** at low temperature, the diastereomeric

(31) A closely related sequence of selective insertion of acrylonitrile into a Pt-N, not a Pt-H, bond was reported in *trans*-Pt(PtEt₃)₂(NHPh)-(H). Notably, the isolable product *trans*-Pt(PtEt₃)₂[CH(CN)CH₂NHPh]-(H) undergoes reductive elimination on heating to form 3-anilinopropionitrile, while the related reaction of *trans*-Pt(PtEt₃)₂(OPh)(H) with acrylonitrile leads directly to PhOCH₂CH₂CN without isolation of an intermediate. See: Cowan, R. L.; Troglor, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750–4761.

(32) In previous work, these hydrides were prepared by reduction of Pt(dcppe)Cl₂ under H₂; the monomer could be converted to the dinuclear complex by heating in toluene in an open system. See: (a) Clark, H. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 3829–3830. (b) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554–1556. (c) Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014–4025. We found that treatment of Pt(dcppe)Cl₂ with 2 equiv of LiEt₃H in THF or toluene also provided Pt(dcppe)H₂, sometimes contaminated with the known cation [Pt₂(dcppe)₂H₃]⁺ formed from traces of water. Surprisingly, stirring a slurry of Pt(dcppe)H₂ in petroleum ether overnight caused almost complete conversion to [Pt(dcppe)H]₂. For a similar synthesis of [Pt(dppe)H]₂ (dppe = *i*-Pr)₂PCH₂CH₂P(*i*-Pr)₂), see: Edelbach, B. L.; Vivic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784–4794.

(33) Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125–127.

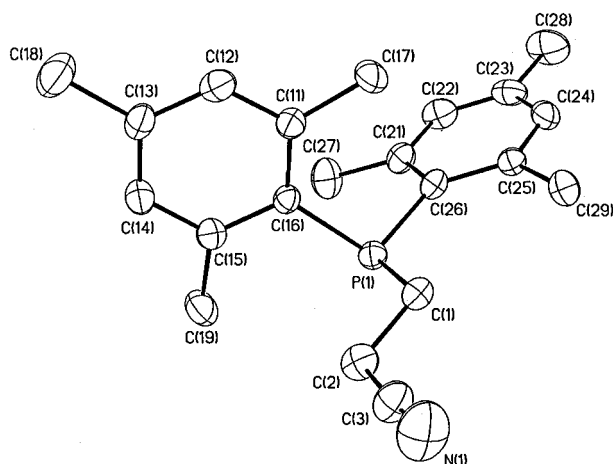
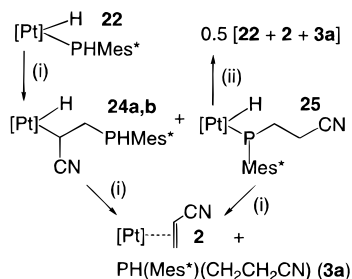


Figure 3. ORTEP diagram of one of the two independent but chemically equivalent molecules of $\text{PMes}_2(\text{CH}_2\text{CH}_2\text{CN})$ (**23**) in the asymmetric unit. Selected bond lengths (Å) and angles (deg) for one of these: $\text{P}(1)-\text{C}(26) = 1.842(6)$, $\text{P}(1)-\text{C}(16) = 1.853(5)$, $\text{P}(1)-\text{C}(1) = 1.835(5)$, $\text{C}(1)-\text{C}(2) = 1.524(8)$, $\text{C}(2)-\text{C}(3) = 1.454(8)$, $\text{N}(1)-\text{C}(3) = 1.119(7)$; $\text{C}(26)-\text{P}(1)-\text{C}(16) = 105.7(2)$, $\text{C}(26)-\text{P}(1)-\text{C}(1) = 111.4(2)$, $\text{C}(16)-\text{P}(1)-\text{C}(1) = 99.3(2)$.

Scheme 9^a

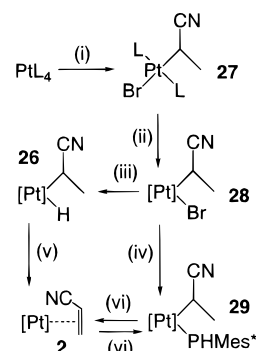


^a $[\text{Pt}] = \text{Pt}(\text{dcpe})$. Legend: (i) CH_2CHCN ; (ii) 50 °C, days.

insertion products $\text{Pt}(\text{dcpe})[\text{CH}(\text{CN})\text{CH}_2\text{PHMes}^*](\text{H})$ (**24a**, ca. 12% of the mixture, and **24b**, ca. 4%) were observed at -40 °C, along with unreacted **22** (84%, Scheme 9). Warming to -20 °C caused further conversion of **22** (64%) to **24a,b** (26, 10%); in addition, a trace of $\text{Pt}(\text{dcpe})[\text{PMes}^*(\text{CH}_2\text{CH}_2\text{CN})](\text{H})$ (**25**, see below) was observed. Warming to room temperature caused further reaction; after 90 min at 20 °C, the mixture consisted of starting material **22** (32%), diastereomers **24a,b** (14 and 14%), **25** (33%), and $\text{PHMes}^*(\text{CH}_2\text{CH}_2\text{CN})$ (**3a**, 7%). Similar results were observed when complex **22** was treated with acrylonitrile at room temperature (Supporting Information). On further reaction (room temperature, 1 day) complexes **24a,b** in such mixtures decompose. The resulting mixture contains starting material **22** (ca. 13% of the Pt in the mixture), $\text{Pt}(\text{dcpe})(\text{CH}_2\text{CHCN})$ (**2**; ca. 39%), and phosphido hydride **25** (ca. 48%), plus phosphine **3a**, formed along with **2**. Addition of 2 equiv more of CH_2CHCN causes, after 1 day, complete conversion of hydrides **22** and **25** to phosphine **3a** and acrylonitrile complex **2**.

Complex **25** was prepared independently (Scheme 8) from $[\text{Pt}(\text{dcpe})\text{H}]_2$ and $\text{PH}(\text{Mes}^*)(\text{CH}_2\text{CH}_2\text{CN})$ (**3a**). A similar reaction of **3a** with $\text{Pt}(\text{dcpe})\text{H}_2$, generated from $\text{Pt}(\text{dcpe})\text{Cl}_2$ and LiEt_3H , is slower; **25** is the initial product under these conditions, but surprisingly, $\text{Pt}(\text{dcpe})(\text{PHMes}^*)(\text{H})$ (**22**) and $\text{Pt}(\text{dcpe})(\text{CH}_2\text{CHCN})$ (**2**) are also formed.

Scheme 10^a



^a $\text{L} = \text{PPh}_3$, $[\text{Pt}] = \text{Pt}(\text{dcpe})$. Legend: (i) $\text{CH}(\text{Me})(\text{Br})(\text{CN})$; (ii) dcpe ; (iii) $\text{NaBH}(\text{OMe})_3$; (iv) LiPHMes^* ; (v) CH_2CHCN ; (vi) excess PH_2Mes^* , excess CH_2CHCN , THF, 50 °C.

Remarkably, heating a sample of isolated **25** (containing a trace of phosphine **3a**) in C_6D_6 at 50 °C caused it to decompose slowly, over several days, to a mixture of $\text{Pt}(\text{dcpe})(\text{PHMes}^*)(\text{H})$ (**22**), $\text{Pt}(\text{dcpe})(\text{CH}_2\text{CHCN})$ (**2**), and $\text{PH}(\text{Mes}^*)(\text{CH}_2\text{CHCN})$ (**3a**) in a 1:1:1 ratio (Scheme 9). This reversible hydrophosphination might occur via conversion of **25** to the isomeric alkyl hydrides **24a,b**, followed by extrusion of acrylonitrile to form **22**. The liberated acrylonitrile could then react with another 1 equiv of **25** to form phosphine **3a** and acrylonitrile complex **2**. This last proposed step was confirmed by independent treatment of **25** with acrylonitrile, which gave **2** and **3a** slowly over 1 day at room temperature (Scheme 9). No intermediates were observed in this reaction by ^{31}P NMR.

The fact that reductive elimination of the C–H bond in alkyl hydrides **24** occurs at room temperature is surprising in view of literature reports of the stability of the related $\text{Pt}(\text{dcpe})(\text{Me})(\text{H})$ ³⁴ and the stabilizing effects of the CH_2CN group³⁵ on $\text{Pt}(\text{II})$ alkyl hydrides. To investigate this reaction, the model hydride $\text{Pt}(\text{dcpe})[\text{CH}(\text{Me})(\text{CN})](\text{H})$ (**26**) was prepared as shown in Scheme 10. Oxidative addition of $\text{CH}(\text{Me})(\text{CN})(\text{Br})$ to $\text{Pt}(\text{PPh}_3)_4$ gave *trans*- $\text{Pt}(\text{PPh}_3)_2[\text{CH}(\text{Me})(\text{CN})](\text{Br})$ (**27**), which yielded $\text{Pt}(\text{dcpe})[\text{CH}(\text{Me})(\text{CN})](\text{Br})$ (**28**) on treatment with *dcpe* in CH_2Cl_2 . Reaction of bromide **28** with $\text{NaBH}(\text{OMe})_3$ gave the hydride **26**, which was thermally stable and decomposed slowly at 50 °C in toluene. Addition of PH_2Mes^* did not induce reductive elimination, even on heating to 50 °C for 1 day. However, addition of 2 equiv of acrylonitrile in toluene caused smooth formation of acrylonitrile complex **2** at room temperature over 3 days (Scheme 10). The analogous methyl complex $\text{Pt}(\text{dcpe})(\text{Me})(\text{H})$ also reacts with acrylonitrile at room temperature to give **2** (Scheme 2), but this reaction is slower and unidentified byproducts are formed. It is difficult to compare the rate for acrylonitrile-induced decomposition of **26** directly to that for decomposition of the analogous alkyl hydrides **24** due to the formation of phosphido hydride **25** in the latter case; qualitatively, however, the rates are similar and it appears that acrylonitrile is required for reductive elimination to occur.

There is literature precedent for such associative reductive elimination pathways in four-coordinate group

(34) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449–1462.

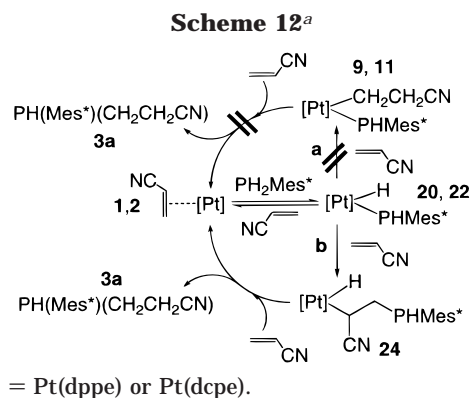
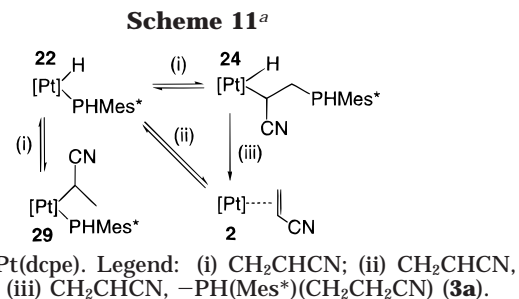
(35) (a) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1977**, *139*, 355–359. (b) Reference 11b.

10 M(II) complexes.³⁶ It is also possible that intramolecular phosphorus coordination³⁷ of the CH(CN)CH₂-PHMes* side chain in **24a,b** promotes reductive elimination; a similar five-coordinate species could also be involved in acrylonitrile extrusion. Although the lack of reaction of model complex **26** with PH₂Mes* argues against this, the chelate effect would favor the formation of such an intermediate for **24**.

The slow decomposition of Pt(dcpe)(CH₂CHCN) (**2**) during the catalytic reaction of PH₂Mes* with acrylonitrile (THF, 50 °C, ca. 1 week), mentioned briefly above, provides additional information on the mechanism of catalysis. This reaction yields another isomer of **24** and **25**, the phosphido alkyl complex Pt(dcpe)[CH(Me)(CN)]-(PHMes*) (**29**), which was confirmed by independent synthesis via treatment of bromide **28** with LiPHMes* (Scheme 10).³⁸

We examined the chemistry of **29** to test its role in the catalytic hydrophosphination. Heating to 50 °C in THF caused slow decomposition. Acrylonitrile did not react with **29** at room temperature, in striking contrast to the low-temperature insertion observed with the hydride analogue Pt(dcpe)(PHMes*)(H) (**22**), but consistent with the sluggish reaction observed for Pt(dppe)-(CH₂CH₂CN)(PHMes*) (**9**). Heating this mixture to 50 °C for several days led to slow decomposition; a trace of the acrylonitrile complex Pt(dcpe)(CH₂CHCN) (**2**) was observed by ³¹P NMR. Finally, when **29** (10 mol %) was treated with PH₂Mes* and acrylonitrile under the standard catalytic conditions, the secondary phosphine PH(Mes*)(CH₂CH₂CN) (**3a**) was formed faster than in the Pt-free system, but slower than if catalyst **2** was used. Under these conditions, significant amounts of complex **2** are formed (ca. 20% of **29** is converted to **2** after 2 days at 55 °C) and additional unidentified products are also observed. It is not clear how phosphido alkyl complex **29** could be formed cleanly from acrylonitrile complex **2** in the original catalytic reaction and yet decompose to form some of **2** under similar conditions. Presumably these interconversions depend on the concentrations of PH₂Mes* and acrylonitrile; since decomposition of **29** was not clean, we did not investigate this chemistry further.

These observations are consistent with the mechanism shown in Scheme 11. Complex **29** could be formed in the original catalysis by insertion of acrylonitrile into the Pt–H bond of Pt(dcpe)(PHMes*)(H) (**22**). However, as described above, treatment of pure **22** with acrylonitrile leads instead to the alkyl hydride Pt(dcpe)[CH(CN)-CH₂PHMes*](H) (**24**) by insertion into the Pt–P bond. If, as seems likely from the model studies, the kineti-



cally favored Pt–P insertion is reversible, a competing, but slower, insertion into the Pt–H bond could eventually lead to the formation of **29**. Formation of **2** from **29** under catalysis conditions could occur by acrylonitrile extrusion to regenerate phosphido hydride **22**, which we have shown reacts with excess acrylonitrile to form **2**. Thus, although Pt–H insertion may occur, *productive* P–C bond formation appears to operate via acrylonitrile insertion into the Pt–P bond of phosphido hydride **22**.

Conclusions

We conclude that, in these systems, Pt-catalyzed acrylonitrile hydrophosphination proceeds by the general mechanism illustrated in path b of Scheme 1: P–H oxidative addition, selective acrylonitrile insertion into the M–P rather than the M–H bond, and acrylonitrile-induced C–H reductive elimination of the resulting alkyl hydride complex. As shown in Scheme 12, all the species in this pathway, as well as in alternative path a, have been prepared independently and isolated or observed spectroscopically. While the product-forming reductive elimination appears to be irreversible, both oxidative addition and insertion steps are reversible, in some cases. The key P–C bond-forming step was observed both in a model system and in a catalytically active one; the rate and reversibility of this reaction are very sensitive to the nature of the ligands in the Pt(II) phosphido complex. The insertion does not appear to proceed by displacement of phosphide by the olefin; instead, a classical insertion pathway, involving either acrylonitrile precoordination or a concerted insertion, is plausible.

These observations provide valuable information on fundamental mechanistic steps in hydrophosphination and, by analogy, in other metal-catalyzed additions of X–H bonds to olefins.

Oxidative Addition. Catalytic hydrophosphination is faster for smaller phosphines, probably because the position of the equilibrium between acrylonitrile com-

(36) For examples, see: (a) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466–1468. (b) McKinney, R. J.; Roe, C. D. *J. Am. Chem. Soc.* **1985**, *107*, 262–264 and references therein. (c) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265–274. For theoretical discussion, see: (d) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181–8188. (e) See also ref 31 and: Seligson, A. L.; Cowan, R. L.; Troglor, W. C. *Inorg. Chem.* **1991**, *30*, 3371–3381.

(37) Four-membered metallacycles have been observed in olefin hydroamination. For examples, see ref 20a,b.

(38) At room temperature, the ³¹P NMR phosphido resonance of **29** (δ –81.5) is broad and unresolved as the result of a fluxional process, inversion at the phosphido P, which interconverts the diastereomers of **29** on the NMR time scale. These diastereomers (7:3 ratio) were observed under slow-exchange conditions at low temperature by ³¹P NMR (Table 1) and ¹H NMR. Full details will be reported separately.

plexes such as **1** and **2** and phosphido hydrides such as **20–22** and **25** depends on phosphine bulk. In general, the rate of X–H oxidative addition will depend on such competition between the substrate and the olefin for binding to the metal center. Using electron-rich metal complexes to promote oxidative addition will not solve this problem, since π -acceptor olefin ligands will then bind more tightly to the metal. Rapid turnover may therefore require electronic or steric destabilization of the olefin complex and/or the use of smaller X–H substrates. However, these approaches may favor higher oxidation state metal species, thus slowing product-forming reductive elimination. In this study, for example, reaction of Pt(dppe)(PHMes*)(H) (**20**) with acrylonitrile gave the product PH(Mes*)(CH₂CH₂CN) (**3a**) much faster than in the analogous dcpe system, where insertion product **24** could be observed. Further, such reductive eliminations may require additional olefin, as suggested by the chemistry of hydrides **24** and **26**.

Insertion. Once formed by X–H oxidative addition, metal hydride complexes ML_n(H)(X) can react with olefins either by insertion, leading to product formation (as observed with **22**), or by undesired reductive elimination (seen with **25**).³⁹ The reactions of **22** and **25** may have different outcomes due to steric effects, but in general the factors that control this competition, or the one between insertion into M–X and M–H bonds, are not well-understood. Further, it is not clear why Pt-catalyzed hydrophosphination requires Michael-acceptor olefin substrates, but other catalytic X–H additions will proceed with less reactive olefins. Further mechanistic study of the insertion step may help to answer these questions.

Reductive Elimination. P–C reductive elimination is not involved in the Pt-catalyzed hydrophosphination studied here. However, the observation of this reaction in a model Pd complex suggests path a (Scheme 1) might operate in related reactions with different catalysts or substrates.

Ancillary Ligand. Pt-catalyzed asymmetric hydrophosphination will require a chiral bidentate ligand that binds tightly to the metal and cannot be displaced as readily as dppe. Hydrophosphination is unusual among X–H addition reactions in that both substrate and product phosphines are good ligands for the metal center; thus, this requirement is not likely to be general.

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 from Na/benzophenone. CH₂Cl₂ was distilled from CaH₂. Methanol and ethanol were dried over Mg(OMe)₂ and Mg(OEt)₂, respectively. Silica gel 60 (EM Science) was used for chromatography.

NMR spectra were recorded on Varian 300 or 500 MHz spectrometers. ¹H and ¹³C NMR chemical shifts are reported relative to Me₄Si and were determined by reference to the residual ¹H or ¹³C solvent peaks. ³¹P NMR chemical shifts are reported relative to H₃PO₄ (85%) used as an external reference.

(39) For other examples of olefin-induced X–H reductive elimination, see: (a) Glueck, D. S.; Newman Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462–1479. (b) Hauger, B.; Caulton, K. G. *J. Organomet. Chem.* **1993**, *450*, 253–261. (c) Reference 36e.

Unless otherwise noted, peaks in NMR spectra are singlets; coupling constants are reported in Hz. Infrared spectra, recorded as KBr pellets on a Perkin-Elmer 1600 series FTIR instrument, are reported in cm⁻¹. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Unless otherwise noted, reagents were from commercial suppliers. The Pt(diphos)Cl₂ compounds were made from Pt(COD)Cl₂ and the diphos ligand in CH₂Cl₂. The following were made by the literature methods: *trans*-Pt(PPh₃)₂(CH₂CH₂CN)(Br),¹⁵ Pt(dppe)(*trans*-stilbene),⁶ Pt(dppe)(Me)(PHMes*) (**12**) and Pt(dppe)(Me)(PMes₂) (**13**),¹⁶ PH₂-Mes*,⁴⁰ PHMes₂,⁴¹ Pd(dppe)(Me)(Cl),⁴² Pt(dppe)(Me)(Cl),⁴³ Pt(dcpe)(Me)(H).³⁴ ³¹P NMR and selected ¹H NMR and IR data for the new metal complexes are in Tables 1 and 2; more ¹H NMR and ¹³C NMR data and synthetic details are given below. For additional experimental details and complete IR data, see the Supporting Information.

Pt(dppe)(CH₂CHCN) (1). To a suspension of Pt(dppe)Cl₂ (110 mg, 0.165 mmol) in 5 mL of ethanol was added acrylonitrile (22 μ L, 0.33 mmol). A solution of NaBH₄ (25 mg, 0.66 mmol) in 5 mL of ethanol was added via cannula with stirring. A new white precipitate formed, and evolution of gas was observed. After 1 h, the precipitate was allowed to settle, and the solution above it was removed via filter cannula. The crude product was washed with ethanol (2 \times 2 mL), water (2 \times 1 mL), and ether (2 \times 1 mL) and then dried under vacuum to give a white solid (58 mg, 54%), which can be recrystallized from THF/petroleum ether or further purified by chromatography on silica gel with toluene eluent. Anal. Calcd for C₂₉H₂₇NPt: C, 53.87; H, 4.22; N, 2.17. Found: C, 53.61; H, 4.59; N, 1.95. ¹H NMR (C₆D₆): δ 7.92 (m, 2H, Ar), 7.58–7.46 (m, 6H, Ar), 7.20 (m, 2H, Ar), 6.96 (m, 10H, Ar), 2.83–2.66 (m, 2H, CH₂CHCN), 2.54–2.38 (m, 1H, CH₂CHCN), 2.08–1.70 (m, 4H, dppe CH₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 135.0–134.3 (m, quat Ar), 133.2–132.7 (m, Ar), 130.8–130.6 (m, Ar), 129.3–128.9 (m, Ar), 126.8 (dd, ³J_{PC} = 8, 3, CN), 30.3 (dd, ²J_{PC} = 44, 4, ¹J_{Pt-C} = 246, CH₂CHCN), 29.2 (dd, J_{PC} = 35, 15, dppe CH₂), 28.7 (dd, J_{PC} = 34, 14, dppe CH₂), 13.6 (dd, ²J_{PC} = 39, 7, ¹J_{Pt-C} = 229, CH₂CHCN).

Pt(dcpe)(CH₂CHCN) (2). A solution of 200 mg (0.32 mmol) of Pt(dcpe)(Me)(H) in 5 mL of toluene was treated with 62 μ L (0.96 mmol) of acrylonitrile. The solution was heated at 50 °C for 24 h. The solvent was then evaporated to give a viscous yellow residue, which was treated with ca. 5 mL of ethanol to precipitate a white solid that was washed with two 3 mL portions of ethanol and finally dried in vacuo (yield 110 mg, 52%).

The following alternative synthesis gave purer material. A white slurry of Pt(dcpe)Cl₂ (200 mg, 0.29 mmol) in 20 mL of toluene was treated with 581 μ L of LiBEt₃H (1 M solution in THF, 0.58 mmol). The mixture was stirred for 30 min and then filtered through Celite. According to ³¹P{¹H} NMR, the yellowish filtrate contained Pt(dcpe)H₂ in ca. 95–98% purity (the rest was [Pt₂(dcpe)₂H₃]⁺). The filtrate was then treated with 80 μ L (1.2 mmol) of CH₂CHCN, which gave a colorless solution. The solvent and the excess of acrylonitrile were removed in vacuo, and the viscous residue was redissolved in ca. 3 mL of toluene and passed down a short (ca. 1 cm long, 0.5 cm in diameter) column of silica gel. The complex Pt(dcpe)(CH₂CHCN) was eluted with ca. 10–20 mL of toluene, while the [Pt₂(dcpe)₂H₃]⁺ stayed on the column. Removal of toluene from the eluate provided a viscous colorless residue which turned into a white solid upon addition of ca. 3 mL of ether. This solid

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was separated, washed twice with 2 mL of ether and then twice with 2 mL of petroleum ether, and finally dried in vacuo (yield 50 mg, 26%). The low yield is likely due to losses in the final washing step. Anal. Calcd for $C_{29}H_{51}NP_2Pt$: C, 51.93; H, 7.66; N, 2.09. Found: C, 51.78; H, 7.94; N, 2.10. 1H NMR (C_6D_6): δ 2.47 (dddd, 1 H, $^3J_{PH} = 9.6$, $^3J_{PH} = 3.3$, $^3J_{HH} = 9.6$, $^3J_{HH} = 9.6$, $^2J_{Pt-H} = 63$, $CHCNCH_2$), 2.27–0.95 (m, 50H, $CHCNCH_2$ + dcpe). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.9 (dd, $^3J_{PC} = 8$, 3, $^2J_{Pt-C} = 58$, CN), 35.7–35.1 (m, Cy CH), 35.6 (dd, $^2J_{PC} = 24$, 4, CH_2-CHCN), 30.1–26.1 (m, Cy CH_2), 24.5 (dd, $J_{PC} = 28$, 15, dcpe CH_2), 23.5 (dd, $J_{PC} = 26$, 13, dcpe CH_2), 10.4 (dd, $^2J_{PC} = 40$, 7, $^1J_{Pt-C} = 221$, CH_2CHCN).

General Procedure for Catalytic Hydrophosphination. Catalytic reactions were carried out in NMR tubes, which were charged with 10 mol % catalyst, 0.13 mmol of phosphine, 0.20 mmol of acrylonitrile (0.40 mmol for PH_2Ph), 0.13 mmol of PPh_3O (internal standard), and ca. 0.8 mL of THF. Reaction mixtures were heated at 50 °C and monitored by ^{31}P NMR spectroscopy. For all substrates, control experiments with identical amounts of reagents, but without Pt catalyst, were also carried out. See Table 3 for results.

PH(Mes*)(CH_2CH_2CN) (3a). In the air, acrylonitrile (143 mg, 170 μ L, 2.5 mmol) was added via microliter syringe to a mixture of PH_2Mes^* (235 mg, 0.84 mmol), 10 mL of acetonitrile, and 1 mL of a 50% aqueous NaOH solution. The reaction mixture was placed under slight vacuum and heated at 65 °C for 3 h. The clear solution was cooled to room temperature, and the product crystallized as a white solid: 220 mg, 79% yield. Anal. Calcd for $C_{21}H_{34}NP$: C, 76.07; H, 10.36; N, 4.23. Found: C, 75.80; H, 10.47; N, 4.27. 1H NMR ($CDCl_3$): δ 7.35 (d, $^4J_{PH} = 2$, 2H, Ar), 4.93 (ddd, $^1J_{PH} = 221$, $^3J_{HH} = 9$, $^3J_{HH} = 7$, 1H, PH), 2.35–2.21 (m, 1H, CH_2), 2.18–2.03 (m, 1H, CH_2), 1.99–1.86 (m, 1H, CH_2), 1.65–1.56 (m, 1H, CH_2), 1.53 (18H, *o*- $CMes_3$), 1.28 (9H, *p*- $CMes_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.0 (d, $^2J_{PC} = 7$, quat Ar), 150.0 (quat Ar), 130.3 (d, $^1J_{PC} = 28$, quat Ar), 122.5 (d, $^3J_{PC} = 4$, Ar), 119.5 (d, $^3J_{PC} = 10$, CN), 38.5 (*o*- $CMes_3$), 35.1 (*p*- $CMes_3$), 33.7 (d, $^4J_{PC} = 6$, *o*- $CMes_3$), 31.4 (*p*- $CMes_3$), 23.2 (d, $J_{PC} = 17$, CH_2), 15.2 (d, $J_{PC} = 17$, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -73.0. ^{31}P NMR ($CDCl_3$): δ -73.0 (dd, $^1J_{PH} = 221$, $^2J_{PH} = 7$). IR: 2392 (PH), 2240 (CN). GCMS: *m/z* (relative intensity) 331 (25%), 330 (100%), 277 (30%).

P(Ph)(Mes)(CH_2CH_2CN) (3b). The synthesis of $P(Ph)(Mes)$ from $PPhCl_2$ will be described elsewhere. To a solution of $P(Ph)(Mes)$ (1.0 g, 4.4 mmol) and acrylonitrile (ca. 0.5 mL, ca. 400 mg, ca. 7.5 mmol) in acetonitrile (10 mL) was added ca. 0.5 mL of an aqueous 50% KOH solution. The flask was heated at 50 °C for 2 h, and the resulting yellow solution was concentrated under vacuum to give a yellow solid. Extraction with ether separated yellow insoluble material and gave a clear solution, which upon cooling to -25 °C gave white crystals of the product (630 mg), which were washed with a small amount of petroleum ether. An additional crop (227 mg) was obtained from the mother liquor; total yield 857 mg (70%). An analytical sample was obtained by a second recrystallization from ether. Anal. Calcd for $C_{18}H_{20}NP$: C, 76.83; H, 7.18; N, 4.98. Found: C, 76.55; H, 7.08; N, 4.88. 1H NMR (C_6D_6): δ 7.05–6.94 (m, 5H, Ph), 6.71–6.70 (m, 2H, Mes), 2.21 (6H, *o*-Me), 2.07 (3H, *p*-Me), 2.06–1.98 (m, 2H, CH_2), 1.85–1.74 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.0 (d, $J_{PC} = 16$, quat Mes), 141.0 (d, $J_{PC} = 14$, quat Ar), 140.7 (d, $J_{PC} = 1$, quat Ar), 130.7 (d, $J_{PC} = 4$, Ar), 129.6 (d, $J_{PC} = 15$, Ar), 129.1 (d, $J_{PC} = 4$, Ar), 128.6 (d, $J_{PC} = 18$, quat Ar), 127.3 (d, $J_{PC} = 2$, Ar), 119.8 (d, $J_{PC} = 15$, CN), 23.7 (d, $J_{PC} = 19$, *o*-Me), 22.9 (d, $J_{PC} = 18$, CH_2), 21.4 (*p*-Me), 15.4 (d, $J_{PC} = 30$, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -24.9. IR (KBr): 2918, 2249, 1604, 1433, 1376, 1025, 933, 856, 747, 699, 557.

Pt(dppe)(CH_2CH_2CN)(Br) (5). An orange slurry of $Pt(dppe)(trans\text{-stilbene})$ (707 mg, 0.91 mmol) and $BrCH_2CH_2CN$ (160 mg, 1.19 mmol) in toluene (25 mL) was stirred for 2 days, during which time the color of the suspended solid turned to beige. The reaction mixture was filtered in air to give 280 mg

of beige solid, which contained only traces of impurities. Removing the solvent from the orange filtrate gave an additional 266 mg of product (total yield 546 mg, 82%) which was less pure but could also be used in subsequent reactions. 1H NMR ($CDCl_3$): δ 7.84–7.76 (m, 4H, Ar), 7.69–7.61 (m, 4H, Ar), 7.58–7.43 (m, 12H, Ar), 2.5–2.1 (m, 6H, dppe + CH_2CN), 1.63–1.39 (m, 2H, $^2J_{Pt-H} = 55$, $Pt-CH_2$).

Pt(dcpe)(CH_2CH_2CN)(Br) (6). A solution of 1.0 g (1.2 mmol) of $trans\text{-}[Pt(PPh_3)_2(CH_2CH_2CN)(Br)]$ in 80 mL of THF was treated with a THF solution (20 mL) of dcpe (0.50 g, 1.2 mmol). The reaction mixture was stirred for 90 min and then filtered through Celite. The filtrate was concentrated to ca. 10 mL by partial removal of THF in vacuo and cooled to -20 °C. After 7 days, the resulting white solid was separated from the mother liquor, washed twice with cold THF (5 mL), and finally dried in vacuo (yield 0.60 g, 68%). Anal. Calcd for $C_{29}H_{52}BrNP_2Pt$: C, 46.33; H, 6.99; N, 1.86; Br, 10.63. Found: C, 46.91; H, 7.22; N, 1.69; Br, 10.80. 1H NMR ($CDCl_3$): δ 2.87–2.80 (m, 2H), 2.36–1.92 (m, 8H), 1.90–1.62 (m, 18H), 1.60–1.10 (m, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 125.3 (d, $^4J_{PC} = 12$, $^3J_{Pt-C} = 72$ CN), 35.1–34.5 (m, CH), 29.4–28.6 (m, CH_2), 27.2–26.8 (m, CH_2), 26.1 (broad, CH_2), 20.7 (dd, $^3J_{PC} = 26$, 6, $^2J_{Pt-C} = 84$ CH_2CN), 18.3 (m, CH_2), 12.0 (dd, $^2J_{PC} = 98$, 7, $^1J_{Pt-C} = 720$, $Pt-CH_2$).

Pt(dppe)(CH_2CH_2CN)($PHMes^*$) (9). This was prepared as for the $PMes_2$ analogue **10** (see below) in 76% yield. As for **10**, the intermediate $[Pt(dppe)(CH_2CH_2CN)(PH_2Mes^*)][BF_4]$ (**7**) was not isolated. Anal. Calcd for $C_{47}H_{58}NP_3Pt$: C, 61.02; H, 6.33; N, 1.51. Found: C, 60.94; H, 6.76; N, 1.53. 1H NMR (C_6D_6): δ 7.74–7.66 (m, 6H, Ar), 7.39–7.32 (m, 4H, Ar), 7.13–7.00 (m, 12H, Ar), 5.10 (d of apparent triplets, $^1J_{PH} = 215$, $^2J_{PH} = ^2J_{PH} = 8$, $^2J_{Pt-H} = 64$, 1H, PH), 1.82 (18H, *o*-*t*-Bu), 1.80–1.76 (m, 6H, dppe + CH_2CN), 1.54 (9H, *p*-*t*-Bu), 1.50–1.30 (m, 2H, $^2J_{Pt-H} = 55$, $Pt-CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 154.8 (d, $^2J_{PC} = 6$, quat *o*- Mes^*), 147.8 (quat *p*- Mes^*), 134.3 (d, $J_{PC} = 6$, Ar), 133.8–133.4 (m, Ar), 131.8 (d, $J_{PC} = 27$, Ar), 131.2 (d, $J_{PC} = 15$, Ar), 129.3 (d, $J_{PC} = 10$, Ar), 128.9 (d, $J_{PC} = 10$, Ar), 123.5 (d, $J_{PC} = 12$, $^3J_{Pt-C} = 107$, CN), 121.6 (broad, Ar), 39.1 (quat $CMes_3$), 35.4 (quat $CMes_3$), 33.8 (d, $J_{PC} = 8$, *o*- $CMes_3$), 32.3 (*p*- $CMes_3$), 29.4–28.5 (m, dppe CH_2), 19.1 (broad, CH_2CN), 12.9 (dd, $^2J_{PC} = 87$, 7, $^1J_{Pt-C} = 655$, $Pt-CH_2$).

Pt(dppe)(CH_2CH_2CN)($PMes_2$) (10). A solution of $Pt(dppe)(CH_2CH_2CN)(Br)$ (**5**; 130 mg, 0.18 mmol) in CH_2Cl_2 (~5 mL) was added to a solid mixture of $AgBF_4$ (36 mg, 0.18 mmol) and $PHMes_2$ (52 mg, 0.19 mmol) to give a brown slurry. After 1 h, the reaction mixture was filtered through Celite to give a yellow-orange solution containing $[Pt(dppe)(CH_2CH_2CN)(PHMes_2)][BF_4]$ (**8**) (^{31}P NMR). The solvent was removed in vacuo, and the resulting brown oil was taken up in 3 mL of THF and added to solid $NaN(SiMe_3)_2$ (34 mg, 0.19 mmol), yielding a yellow-brown solution. The THF was pumped off, and the residue was extracted with three 1 mL portions of toluene. The orange-red toluene extract was filtered through Celite, layered with petroleum ether, and cooled to -20 °C to give yellow crystalline product (112 mg in two crops, 68%). A sample was recrystallized from THF/petroleum ether for analysis. Anal. Calcd for $C_{47}H_{50}NP_3Pt$: C, 61.56; H, 5.51; N, 1.53. Found: C, 61.12; H, 5.54; N, 1.38. 1H NMR (C_6D_6): δ 7.57–7.43 (m, 8H, Ar), 7.10–7.07 (m, 6H, Ar), 6.96–6.94 (m, 6H, Ar), 6.69 (4H, Ar), 2.63 (12H, *o*-Me), 2.14 (6H, *p*-Me), 1.84–1.62 (br m, 6H, dppe + CH_2CN), 1.46–1.40 (m, 2H, $^2J_{Pt-H} = 50$, $Pt-CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 143.6 (d, $J_{PC} = 15$, quat *o*- Mes), 134.9 (Ar), 134.2 (d, $J_{PC} = 6$, Ar), 133.7 (d, $J_{PC} = 11$, Ar), 132.8, 132.2, 131.4, 130.6, 129.6–129.4 (m), 128.2 (observed by solvent), 123.1 (d, $J_{PC} = 13$, CN), 28.3–27.5 (ddd, $J_{PC} = 30$, 15, 6, dppe CH_2), 27.4–26.8 (dd, $J_{PC} = 30$, 14, dppe CH_2), 26.0 (d, $J_{PC} = 15$, *o*-Me), 21.3 (*p*-Me), 17.9 (d, $J_{PC} = 8$, CH_2CN), 9.9 (dd, $^2J_{PC} = 93$, 5, $Pt-CH_2$, Pt satellites not resolved).

Pt(dcpe)(CH_2CH_2CN)($PHMes^*$) (11). A solution of 150 mg (0.2 mmol) of $Pt(dcpe)(CH_2CH_2CN)(Br)$ (**6**) in 10 mL of THF

was treated with 10 mL of a THF solution of LiPHMes* (0.6 mmol, freshly prepared from 374 μ L of 1.6 M *n*-BuLi in THF and 167 mg (0.6 mmol) of PH₂Mes*). The reaction mixture was stirred at room temperature for 30 min. The solvent was then removed in vacuo, and the yellow-orange solid residue was extracted with ca. 20 mL of toluene. The extract was filtered through Celite, and the solvent was removed in vacuo. Addition of an excess of ether to the fluffy residue gave a yellow solid, which was washed three times with ca. 5 mL of ether and finally dried in vacuo (yield 70 mg, 37%). Anal. Calcd for C₄₇H₈₂NP₃Pt: C, 59.46; H, 8.72; N, 1.48. Found: C, 59.03; H, 8.64; N, 1.42. ¹H NMR (CD₂Cl₂): δ 7.41 (2H, Ar), 5.30 (ddd, ²J_{PH} = 211, ³J_{PH} = 9, 2, ²J_{Pt-H} = 59, 1H, PH), 2.40–0.95 (br m, 52H, dcpe + C₂H₄CN), 1.72 (18H, *o*-t-Bu), 1.41 (9H, *p*-t-Bu). ¹³C{¹H} NMR (CD₂Cl₂): δ 154.0 (dd, J_{PC} = 7, 2, *o*-Mes*), 146.5 (d, J_{PC} = 2, *p*-Mes*), 138.1–137.0 (br m, *ipso* Mes*), 124.7 (d, J_{PC} = 11, *m*-Mes*), 121.5–121.0 (m, CN), 38.8 (br, *o*-CMe₃), 35.3–34.2 (m, Cy CH), 34.9 (*p*-CMe₃), 33.1 (d, J_{PC} = 8, *o*-CMe₃), 31.7 (br, *p*-CMe₃), 30.0–26.0 (m, dcpe CH₂), 24.6–23.5 (m, dcpe CH₂), 18.5–18.2 (m, CH₂CH₂CN), 7.0 (dd, ²J_{PC} = 88, 8, CH₂CH₂CN).

Pt(dppe)(Me)[CH(CN)CH₂PHMes*] (14). Pt(dppe)(Me)-(PHMes*) was generated in situ by treatment of Pt(dppe)(Me)-(OMe) (245 mg, 0.38 mmol) with PH₂Mes* (117 mg, 0.42 mmol) in 20 mL of THF. The solution was concentrated under vacuum to 10 mL. Acrylonitrile (41 mg, 50 μ L, 0.77 mmol) was added by microliter syringe, and the reaction mixture was stirred at room temperature for 2 days, during which time the reaction was monitored by ³¹P{¹H} NMR. The solvent was removed under vacuum, and the resulting pale yellow solid was transferred to a frit, washed with petroleum ether, and dried in vacuo to yield a 2:1 mixture of diastereomers (214 mg, 59%). Anal. Calcd for C₄₈H₆₀NP₃Pt: C, 61.40; H, 6.44; N, 1.49. Found: C, 61.64; H, 6.47; N, 1.60. ¹H NMR (500 MHz, CD₂-Cl₂; chemical shifts and relative integrals are reported for the mixture of isomers unless specified): δ 7.89–7.84 (m, 3H, Ar), 7.79–7.75 (m, 3H, Ar), 7.68–7.57 (m, 2H, Ar), 7.54–7.42 (broad m, 12H, Ar), 7.29 (2H, Ar), 4.57 (ddd, ¹J_{PH} = 220, ³J_{HH} = 10, 7, 1H, minor PH), 4.26 (ddd, ¹J_{PH} = 222, ³J_{HH} = 11, 5, 1H, major PH), 2.55–2.52 (m, ³J_{HH} = 9, 8, ²J_{Pt-H} = 104, 1H, CH(CN)), 2.42–2.18 (broad m, 4H, minor dppe CH₂), 2.36–2.06 (broad m, 4H, major dppe CH₂), 2.06–1.74 (broad m, 2H, major CH₂PHMes*), 1.91–1.63 (broad m, 2H, minor CH₂-PHMes*), 1.41 (broad, 9H, *p*-CMe₃), 1.27 (broad, 18H, *o*-CMe₃), 0.57 (dd, ³J_{PH} = 7, 7, ²J_{Pt-H} = 66, 3H, major Me), 0.55 (dd, ³J_{PH} = 7, 7, ²J_{Pt-H} = 66, 3H, minor Me). ¹³C{¹H} NMR (CD₂-Cl₂; chemical shifts are reported for the mixture of isomers unless specified): δ 154.6 (quat Ar), 149.0 (quat Ar), 134.4–134.3 (m, Ar), 133.7–132.9 (m, Ar), 132.0–131.8 (broad m, Ar), 131.3–130.8 (m, Ar), 129.1 (Ar), 122.1 (Ar), 120.7–118.7 (broad m, CN), 38.4 (*p*-CMe₃), 35.1 (*o*-CMe₃), 33.7 (*p*-CMe₃), 31.8–31.2 (m, CH₂PHMes*), 31.3 (*o*-CMe₃), 30.0–28.7 (broad m, dppe CH₂), 7.14 (d, ²J_{PC} = 99, minor Me), 5.0 (d, ²J_{PC} = 95, ¹J_{Pt-C} = 570, CH(CN)), 3.5 (d, ²J_{PC} = 90, ¹J_{Pt-C} = 604, major Me).

Pt(dppe)(Me)[CH(CN)CH₂PMes₂] (15). Pt(dppe)(Me)-(PMes₂) was generated in situ by treatment of Pt(dppe)(Me)-(OMe) (254 mg, 0.40 mmol) with PHMes₂ (118 mg, 0.44 mmol). An excess of acrylonitrile (approximately 500 μ L, 7.6 mmol) was added to the stirring solution via cannula. The reaction mixture was stirred overnight, during which time the solution turned from bright orange to yellow. The solvent was removed under vacuum, and the yellow residue was washed with three 1 mL portions of petroleum ether. The solid was dissolved 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 278 mg (75%) of pale yellow Pt(dppe)(Me)[CH(CN)-CH₂PMes₂]. Anal. Calcd for C₄₈H₅₂NP₃Pt: C, 61.92; H, 5.64; N, 1.50. Found: C, 61.99; H, 6.04; N, 1.32. ¹H NMR (500 MHz, C₆D₆; labeling Pt-CH₂(CN)CH₂PHMes₂): δ 7.87–7.83 (m, 2H, Ar), 7.68–7.62 (m, 5H, Ar), 7.51–7.47 (m, 2H, Ar), 7.27–7.15 (broad m, 8H, Ar), 7.08–7.02 (m, 3H, Ar), 6.73 (2H, Ar),

6.70 (2H, Ar), 3.31 (m, ²J_{AA'} = 12.3, ³J_{AB} = 11.9, 1H, CH₂-PMes₂), 3.25 (m, ²J_{AA'} = 12.3, ³J_{AB} = 3.9, 1H, CH₂PMes₂), 2.81 (m, ³J_{AB} = 11.9, ³J_{AB} = 3.9, ²J_{Pt-H} = 106, 1H, CH(CN)), 2.54 (6H, *o*-Me), 2.30 (6H, *o*-Me), 2.17 (3H, *p*-Me), 2.08 (3H, *p*-Me), 2.08–1.94 (broad m, 4H, CH₂), 1.29 (dd, ³J_{PH} = 6.5, 6.5, ²J_{Pt-H} = 60, 3H, Pt-Me). ¹³C{¹H} NMR (THF-*d*₆): δ 144.4 (d, ²J_{PC} = 13, quat Ar), 141.1 (d, ²J_{PC} = 13, quat Ar), 138.0 (quat Ar), 136.9 (quat Ar), 136.5 (quat Ar), 135.2–134.9 (broad m, Ar), 134.7 (quat Ar), 134.5 (quat Ar), 133.9–133.7 (broad m, Ar), 132.8 (quat Ar), 132.2 (quat Ar), 131.8–131.1 (broad m, Ar), 130.6–130.3 (Ar), 129.7–129.3 (broad m, Ar), 31.6 (d, ¹J_{PC} = 22, CH₂PMes₂), 30.9–29.5 (broad m, dppe CH₂), 24.2 (d, ²J_{PC} = 11, *o*-Me), 23.4 (d, ²J_{PC} = 14, *o*-Me), 21.2 (*p*-Me), 21.0 (*p*-Me), 7.6 (d, ²J_{PC} = 90, ¹J_{Pt-C} = 585, CH(CN)), 3.4 (dd, ²J_{PC} = 92, 7, ¹J_{Pt-C} = 600, Me) (the nitrile carbon was not resolved).

[Pd(dppe)(Me)(PH₂Mes*)][BF₄] (16). To a stirred suspension of Pd(dppe)(Me)(Cl) (297 mg, 0.53 mmol) in THF (10 mL) was added a solution of AgBF₄ (104 mg, 0.53 mmol) dissolved in CH₃CN (3 mL). A white precipitate formed immediately. PH₂Mes* (164 mg, 0.59 mmol) dissolved in THF (2 mL) was added to the reaction mixture, and the solution immediately turned orange-brown. The reaction mixture was stirred in the dark for 2 h and then filtered through a glass frit. The filtrate was concentrated under vacuum to a volume of approximately 10 mL. Petroleum ether was added, and cooling to –25 °C yielded 343 mg (73%) of orange solid. Anal. Calcd for C₄₅H₅₈-BF₄P₃Pd: C, 61.06; H, 6.61. Found: C, 60.13; H, 6.25 (results for carbon were consistently low). ¹H NMR (CD₂Cl₂): δ 7.63–7.50 (broad m, 22H, Ar), 5.61 (ddd, ¹J_{PH} = 350, ³J_{PH} = 6, 4, 2H, PH₂), 2.64–2.42 (m, 4H, CH₂), 1.42 (18H, *o*-CMe₃), 1.28 (9H, *p*-CMe₃), 0.35–0.28 (m, 3H, Me). ¹³C{¹H} NMR (CD₂Cl₂): δ 155.2 (quat Ar), 153.4 (quat Ar), 133.5–132.9 (m, Ar), 132.5 (Ar), 130.2–129.7 (m, Ar), 129.3 (quat Ar), 128.8 (quat Ar), 128.2 (quat Ar), 127.5 (quat Ar), 124.0 (d, ³J_{PC} = 9, Ar), 38.4 (*o*-CMe₃), 35.4 (*p*-CMe₃), 33.1 (*o*-CMe₃), 31.0 (*p*-CMe₃), 29.4–28.7 (m, dppe CH₂), 27.4–26.9 (m, dppe CH₂), 8.2 (d, ²J_{PC} = 80, Me).

Generation of Pd(dppe)(Me)[CH(CN)CH₂PHMes*] (18). [Pd(dppe)(Me)(PH₂Mes*)][BF₄] (16; 265 mg, 0.30 mmol) in THF (15 mL) was cooled to –78 °C in a dry ice/acetone bath. An excess of acrylonitrile (approximately 700 μ L, 10.6 mmol) was added to the cooled solution via cannula. LiN(SiMe₃)₂ (50 mg, 0.30 mmol) in THF (2 mL) was also cooled to –78 °C and transferred to the reaction mixture via cannula. The solution was stirred at –78 °C, warmed, and monitored by ³¹P NMR at room temperature. After 4 h, a 2:1 ratio of diastereomers of 18 and a small amount of PH(Me)(Mes*) were observed.

[Pt(dppe)(Me)(CH₂CHCN)][OTf] (19). To a white slurry of Pt(dppe)(Me)(Cl) (525 mg, 0.82 mmol) and acrylonitrile (3 mL, 0.05 mol) in CH₂Cl₂ (20 mL) was added AgOTf (209 mg, 0.82 mmol). Immediate formation of AgCl was observed. The reaction mixture was stirred vigorously at room temperature overnight. The solution was filtered, and the gray-purple AgCl residue was washed with CH₂Cl₂ (10 mL). The filtrates were combined, and the solvent was removed under vacuum. The white residue was washed with ether and dried to give 552 mg (84%) of crude product. Attempts to obtain the product analytically pure were unsuccessful; attempted recrystallization from CH₂Cl₂/petroleum ether at –25 °C gave an off-white oil. The compound decomposes to a mixture of unknown products in CDCl₃ after 2 days. ¹H NMR (CDCl₃): δ 7.62–7.45 (broad m, 20H, Ar), 6.47 (d, ³J_{HH} = 11, 1H, NCCHCH₂ trans to CN), 6.23 (d, ³J_{HH} = 17, 1H, NCCHCH₂ cis to CN), 6.03 (dd, ³J_{HH} = 17, 11, 1H, NCCHCH₂), 2.60–2.27 (m, 4H, dppe CH₂), 0.53 (dd, ³J_{PH} = 7, 3, ²J_{Pt-H} = 50, 3H, Pt-Me). ¹³C{¹H} NMR (CDCl₃): δ 144.8 (NCCHCH₂), 133.3–133.1 (m, Ar), 132.8–132.6 (m, Ar), 132.4–132.3 (m, Ar), 132.0–131.9 (m, Ar), 129.7–129.3 (m, Ar), 128.9 (quat Ar), 126.4 (quat Ar), 125.5 (quat Ar), 122.7 (d, ³J_{PC} = 17, CN), 105.3 (NCCHCH₂), 30.5 (dd, ¹J_{PC} = 44, ²J_{PC} = 16, dppe CH₂), 24.9 (dd, ¹J_{PC} = 35, ²J_{PC} = 5, dppe CH₂), 2.8 (dd, ²J_{PC} = 79, 5, Pt-Me).

Pt(dppe)(H)(PHMes*) (20). To a slurry of Pt(dppe)(*trans*-stilbene) (50 mg, 0.06 mmol) in THF (1 mL) was added a solution of PH₂Mes* (50 mg, 0.18 mmol) in THF (1 mL) to afford a yellow solution. The solvent was removed, and the residue was washed with petroleum ether (3 × 2 mL) to afford 50 mg (90% yield) of the crude yellow solid, which was recrystallized from ether for analysis. Anal. Calcd for C₄₄H₅₅P₃: Pt: C, 60.61; H, 6.36. Found: C, 59.43; H, 6.43. ¹H NMR (C₆D₆): δ 7.80–6.90 (m, 22H, Ar), 5.56 (d of apparent t, ¹J_{PH} = 211, ³J_{PH} = 8, 8, ²J_{Pt-H} = 62, 1H, PH), 1.80 (4H, broad, dppe), 1.40 (9H, *p*-*t*-Bu), 1.35 (18H, *o*-*t*-Bu), -1.34 (ddd, ²J_{PH} = 188, 15, 6, ¹J_{Pt-H} = 1151, 1H, Pt-H). ¹³C{¹H} NMR (C₆D₆): δ 153.2 (m, Ar), 146.4 (Ar), 138.2 (Ar), 134.0 (m, Ar), 133.8 (m, Ar), 130.8 (Ar), 129.2 (Ar), 129.0 (Ar), 128.9 (Ar), 127.3 (Ar), 122.0 (Ar), 39.4 (CMe₃), 35.3 (broad, CMe₃), 34.8 (d, J_{PC} = 9, *o*-Me), 32.3 (*p*-Me), 30–29 (m, CH₂).

Pt(dcpe)(PHMes*)(H) (22). To a slurry of Pt(dcpe)Cl₂ (500 mg, 0.73 mmol) in THF (2 mL) was added LiBHET₃ (1.45 mL of 1 M THF solution, 1.45 mmol) followed by a solution of PH₂-Mes* (213 mg, 0.76 mmol) in THF (4 mL). The resulting yellow solution was heated at 55 °C for 2 days. The solvent was removed, the residue was extracted with Et₂O (3 × 5 mL), and the extracts were concentrated and cooled to -20 °C to give 300 mg (43% yield) of air-sensitive yellow solid. The analytical sample was recrystallized from Et₂O. NaBH(OMe)₃ can be substituted for LiBHET₃ with similar yields. Anal. Calcd for C₄₄H₇₉P₃Pt: C, 59.04; H, 8.78. Found: C, 58.42; H, 9.06. ¹H NMR (C₆D₆): δ 7.74 (2H, Ar), 5.87 (1H, ddd, ¹J_{PH} = 204, ³J_{PH} = 8, 2, ²J_{Pt-H} = 58, PH), 2.17 (18H, *o*-*t*-Bu), 2.08–1.00 (48H, broad, dcpe + Cy), 1.38 (9H, *p*-*t*-Bu), -1.47 (1H, dd, ²J_{PH} = 182, 16, ¹J_{Pt-H} = 1063, Pt-H). ¹³C{¹H} NMR (C₆D₆): δ 152.7 (d, J_{PC} = 8, Ar), 145.8 (Ar), 121.9 (Ar), 39.4 (*p*-CMe₃), 36.1–34.7 (m, CH₂ + CMe₃), 32.4 (*o*-*t*-Bu), 29.8–28.9 (m, CH₂), 25.0–24.0 (m, CH). The fourth expected Ar peak is not observed.

Low-Temperature Reaction of 22 with CH₂CHCN. To a cold (-78 °C) solution of **22** (20 mg, 0.022 mmol) in toluene-*d*₈ (ca. 0.4 mL) in an NMR tube was added CH₂CHCN (1.5 μL, 0.022 mmol), and the tube was inserted into the cold (-40 °C) NMR probe. The reaction mixture was slowly warmed, during which time the progress of the reaction was monitored by ³¹P NMR spectroscopy. A separate experiment was carried out on a larger scale (75 mg, 0.084 mmol of **22**; 5 μL, 0.08 mmol of acrylonitrile). In these experiments, the same products were observed, with slightly different product ratios; therefore, average product ratios from the two runs are described in the text.

Pt(dcpe)[CH(CN)CH₂PHMes*](H) (24a,b). ¹H NMR (500 MHz, C₆D₆, dcpe signals could not be assigned for **24a** and **24b**): δ 7.60 (2H, m, Ar), 5.62 (1H, d of apparent t, ¹J_{PH} = 228, ³J_{HH} = 9, 9, PH), 1.76 (18H, *o*-*t*-Bu), 1.35 (9H, *p*-*t*-Bu), -1.33 (1H, ddd, ²J_{PH} = 185, 18, 5, ¹J_{Pt-H} = 1106, Pt-H).

24b. ¹H NMR (500 MHz, C₆D₆): δ 7.48 (2H, m, Ar), 4.86 (1H, ddd, ¹J_{PH} = 217, ³J_{HH} = 13, 5, PH), 1.57 (18H, *o*-*t*-Bu), 1.34 (9H, *p*-*t*-Bu), -1.27 (1H, ddd, ²J_{PH} = 188, 17, 5, ¹J_{Pt-H} = 1132, Pt-H).

PMes₂(CH₂CH₂CN) (23). In the air, acrylonitrile (204 mg, 3.8 mmol) was added to a mixture of PHMes₂ (617 mg, 2.3 mmol), 10 mL of acetonitrile, and 1 mL of a 50% aqueous sodium hydroxide solution. The mixture was cooled to -78 °C and placed under slight vacuum. The reaction mixture was heated at 55 °C for 3 h, during which time the product crystallized out of solution. The clear, colorless crystals were recrystallized from warm methanol to yield 519 mg (70%) of PMes₂(CH₂CH₂CN), mp 157 °C. The product was recrystallized again from acetonitrile to yield X-ray-quality crystals. Anal. Calcd for C₂₁H₂₆NP: C, 77.99; H, 8.10; N, 4.33. Found: C, 78.11; H, 8.21; N, 4.37. ¹H NMR (CDCl₃): δ 6.78 (d, ⁴J_{PH} = 2, 4H, Ar), 2.79 (td, ³J_{HH} = 8, ²J_{PH} = 3, 2H, CH₂CH₂CN), 2.25 (12H, *o*-Me), 2.22 (6H, *p*-Me), 2.19 (t, ³J_{HH} = 8, 2H, CH₂CH₂-CN). ¹³C{¹H} NMR (CDCl₃): δ 142.0 (d, ²J_{PC} = 14, quat Ar), 138.4 (quat Ar), 131.2 (d, ¹J_{PC} = 20, quat Ar), 130.4 (d, ³J_{PC} =

3, Ar), 120.1 (d, ³J_{PC} = 18, CN), 24.2 (d, ²J_{PC} = 18, CH₂CH₂-CN), 23.3 (d, ³J_{PC} = 14, *o*-Me), 20.9 (*p*-Me), 15.2 (d, ¹J_{PC} = 30, CH₂CH₂CN). ³¹P{¹H} NMR (CDCl₃): δ -22.2. IR: 2242 (CN). GCMS: M⁺/Z 323 (8%), 308 (100%).

Crystal Structure Determinations. Crystal data and data collection and refinement parameters are given in Table 4. For the platinum complexes *trans*-Pt(PPh₃)₂(CH₂CH₂CN)-(Br) (**A**) and **11**·Et₂O, the systematic absences in the diffraction data are uniquely consistent for the reported space groups. For phosphine **23**, the systematic absences in the diffraction data are consistent for *Pna*2₁ and *Pnam* (*Pnma*). Attempts to solve the structure in the centric option yielded bizarre results and were abandoned. The noncentric space group yielded chemically reasonable and computationally stable results with no significant correlation between independent atomic parameters. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Empirical absorption corrections were applied using SADABS for **A** and DIFABS for **11**·Et₂O;⁴⁴ semiempirical absorption corrections were not required for **23** (μ = 1.46 cm⁻¹). For **23**, two symmetry independent but chemically equivalent molecules are found in the asymmetric unit. Refinement of the absolute structure parameter yielded 0.0(1), indicating that the true hand of the structure had been determined. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on the phosphorus atom of the PHMes* ligand of **11**·Et₂O could not be located from the difference map and was ignored in the refinement, but not in the intensive properties. All other hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL version 5.03 or 5.10 program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Pt(dcpe)[PMes*(CH₂CH₂CN)](H) (25). A slurry of Pt-(dcpe)Cl₂ (150 mg, 0.22 mmol) in toluene (15 mL) was treated with 440 μL (0.44 mmol) of a 1 M THF solution of LiBHET₃. The resulting light yellow slurry was stirred for 30 min and then filtered through Celite. The ³¹P NMR spectrum of the filtrate showed mostly Pt(dcpe)H₂ and a trace of [Pt₂-(dcpe)₂H₃]⁺. Evaporation of the solvent provided a viscous residue. Petroleum ether (15 mL) was added, and the resulting yellow-white slurry was stirred overnight. The solvent was removed under vacuum to give 110 mg of a yellowish solid, which was (by ³¹P{¹H} NMR in toluene) mostly [Pt(dcpe)(H)]₂ with traces of Pt(dcpe)H₂ and [Pt₂(dcpe)₂H₃]⁺. This material was treated with PH(Mes*)(CH₂CH₂CN) (72 mg, 0.22 mmol) in toluene (10 mL) and stirred for 24 h, when ³¹P NMR showed that **25** had formed, with a trace of [Pt₂(dcpe)₂H₃]⁺ remaining. The solvent was removed under vacuum, and the orange-yellow residue was extracted with petroleum ether (3 × 5 mL) to remove the cation. The extract was filtered and concentrated (to ca. 2 mL) to provide an orange precipitate. This was washed with cold petroleum ether (2 × 2 mL) and finally dried in vacuo (yield 80 mg, 39%). This compound could not be obtained in spectroscopically pure form free from traces of phosphine **3a**, and attempts at recrystallization from petroleum ether gave only a very fine powder. The compound also appeared to decompose on storage in the solid state in the glovebox. Anal. Calcd for C₄₇H₈₂NP₃Pt: C, 59.47; H, 8.71; N, 1.47. Found: C, 57.42; H, 8.84; N, 1.38. ¹H NMR (C₆D₆): δ 7.60 (2H, Ar), 2.06 (18H, *o*-*t*-Bu), 2.22–0.96 (br m, 52H, dcpe + CH₂CH₂CN), 1.41 (9H, *p*-*t*-Bu), -2.41 (d of apparent t, ²J_{PH} = 171, 17, 17, ¹J_{Pt-H} = 1006, Pt-H). ¹³C{¹H} NMR (C₆D₆): δ 157.1 (dd, J_{PC} = 9, 3, J_{Pt-C} = 34, *o*-Mes*), 147.0 (d, J_{PC} = 2, *p*-Mes*), 146.6 (ddd, J_{PC} = 44, 7, 2, *ipso*-Mes*), 121.8 (d, J_{PC} = 5, *m*-Mes*), 121.4 (dd, J_{PC} = 14, 2, CN), 39.9 (d, ³J_{PC} = 3, *o*-CMe₃), 36.5–35.3 (m, Cy CH), 35.1 (d, ⁴J_{PC} = 7, *o*-CMe₃), 34.7 (*p*-CMe₃), 31.7 (*p*-CMe₃), 30.2–25.0 (dcpe CH₂), 23.2 (dd, J_{PC} = 21, 14, CH₂ of CH₂CH₂CN), 18.2 (dd, J_{PC} = 26, 11, CH₂ of CH₂CH₂CN).

(44) For DIFABS, see: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

trans-Pt(PPh₃)₂[CH(Me)(CN)](Br) (27). Pt(PPh₃)₄ (0.4 g, 0.32 mmol) was dissolved in 20 mL of toluene. The orange solution soon turned to pale yellow after treatment with 150 μ L (1.73 mmol, 5.4-fold excess) of CH(Me)(Br)(CN); simultaneously, a white solid started to precipitate out from the solution. The mixture was stirred at room temperature for 2 h. Then the solvent and excess of 2-bromopropionitrile were removed in vacuo. The crude pale yellow residue was washed four times with 5 mL portions of petroleum ether and then dried in vacuo to give a white solid (0.26 g, 94%). A sample for elemental analysis was recrystallized from THF. Anal. Calcd for C₃₉H₃₄BrNPt: C, 54.87; H, 4.02; N, 1.64; Br, 9.36. Found: C, 55.64; H, 4.23; N, 1.28; Br, 10.29. ¹H NMR (THF-*d*₈): δ 7.88–7.77 (m, 12H, Ar), 7.46–7.35 (m, 18H, Ar), 2.02 (m, 1H, CH), 0.50 (d, 3H, ³J_{HH} = 7, ³J_{Pt-H} = 67, Me).

Pt(dcpe)[CH(Me)(CN)](Br) (28). To 15 mL of a CH₂Cl₂ solution of 260 mg (0.30 mmol) of **27** was added an equimolar amount (129 mg) of dcpe dissolved in 5 mL of CH₂Cl₂. The pale yellow reaction mixture was stirred at room temperature for 1 day. Removal of the solvent in vacuo provided a yellowish viscous residue which turned into a white solid upon addition of ca. 5 mL of petroleum ether. The white solid was washed three times with 5 mL portions of petroleum ether and finally dried in vacuo (yield 200 mg, 87%). A sample for elemental analysis was recrystallized from THF. Anal. Calcd for C₂₉H₅₂NBrP₂Pt: C, 46.33; H, 6.99; N, 1.86; Br, 10.63. Found: C, 48.26; H, 7.53; N, 1.99; Br, 10.63. Results for C and H were consistently high; the average of four separate analyses, including the one reported above, is as follows: C, 48.23; H, 7.57; N, 1.59; Br, 8.68. A possible explanation for these results is cocrystallization with THF. Anal. Calcd for C₂₉H₅₂NBrP₂Pt·C₄H₈O: C, 48.11; H, 7.34; N, 1.70; Br, 9.70. The ³¹P{¹H} NMR spectrum (THF-*d*₈), in addition to the signals in Table 1, included impurity peaks at δ 67.7 (¹J_{Pt-P} = 2021), 58.8 (¹J_{Pt-P} = 3852), 84.6, and 68.3. ¹H NMR (THF-*d*₈): δ 2.64–1.00 (m, 52H, dcpe + CH(Me)CN). This material was pure enough for successful preparation of complexes **26** and **29**.

Pt(dcpe)[CH(Me)(CN)](H) (26). A suspension of 150 mg (0.2 mmol) of bromide **28** in 10 mL of THF was treated with a solution of NaBH(OMe)₃ (38 mg, 0.3 mmol) in 5 mL of THF. The reaction mixture was stirred at room temperature for 1 day. The solvent was then removed in vacuo, and the pale yellow residue was extracted with ca. 10 mL of toluene. The toluene extract was passed down a column (ca. 0.5 cm high, 0.5 cm in diameter) of silica gel 60. The column was then washed with an additional 5 mL of toluene. Toluene was removed in vacuo, and addition of an excess of petroleum ether to the viscous residue precipitated a white solid. This was separated, washed three times with ca. 3 mL of petroleum ether, and finally dried in vacuo (yield 80 mg, 59%). The product was recrystallized from toluene at –30 °C for analysis. Anal. Calcd for C₂₉H₅₃NPt: C, 51.77; H, 7.94; N, 2.08. Found: C, 51.92; H, 7.89; N, 2.05. ¹H NMR (C₆D₆): δ 3.03 (m, 1H, ³J_{HH} = 7, ³J_{PH} = 10, 7, ²J_{Pt-H} = 106, CH), 2.38 (m, 3H, ³J_{HH} = 7, ⁴J_{PH} = 6, 1, ³J_{Pt-H} = 70, Me), 2.20–0.90 (m, 48H, dcpe), –1.30 (dd, 1H, ²J_{PH} = 191, 17, ¹J_{Pt-H} = 1121, Pt–H). ¹³C{¹H} NMR (C₆D₆): δ 132.6 (dd, ³J_{PC} = 6, 3, ²J_{Pt-C} = 64, CN), 35.4 (br d, ¹J_{PC} = 30, ²J_{Pt-C} = 35, Cy CH), 34.1 (dd, ³J_{PC}

= 23, 21, ²J_{Pt-C} = 17, CH₃CHCN), 30.1–26.1 (m, dcpe CH₂), 23.8 (dd, ²J_{PC} = 26, 15, dcpe CH₂), 23.1 (dd, ²J_{PC} = 24, 15, dcpe CH₂), –4.1 (dd, ²J_{PC} = 83, 5, ¹J_{Pt-C} = 552, Pt–CH). FAB-MS (3-nitrobenzyl alcohol) *m/z* 672 (M⁺), 617 (Pt(dcpe)).

Pt(dcpe)[CH(Me)(CN)](PHMes*) (29). A solution of 150 mg (0.2 mmol) of bromide **28** in 10 mL of THF was treated with 10 mL of THF solution of LiPHMes* (0.6 mmol, freshly prepared from 374 μ L of 1.6 M *n*-BuLi in THF and 167 mg (0.6 mmol) of PH₂Mes*). The reaction mixture was stirred at room temperature for 2 h. The solvent was then removed in vacuo, and the yellow-orange residue was extracted with ca. 20 mL of toluene. The toluene extract was filtered through Celite, and toluene was removed under vacuum. Addition of an excess of petroleum ether to the viscous residue precipitated a yellow solid. This was separated, washed three times with ca. 5 mL of petroleum ether, and finally dried in vacuo (yield 60 mg, 32%). A sample for analysis, recrystallized from toluene, was found to be a toluene solvate by ¹H NMR and elemental analysis. Anal. Calcd for C₄₇H₈₂NPt·0.75C₇H₈: C, 61.62; H, 8.73; N, 1.38. Found: C, 61.56; H, 8.73; N, 1.20. ¹H NMR (THF-*d*₈, 22 °C, 500 MHz): δ 7.35 (1H, Ar), 7.25 (1H, Ar), 5.18 (br dd, 1H, ²J_{PH} = 209, ³J_{PH} = 8, ²J_{Pt-H} = 56, PH), 2.67 (br m, 1H, CH), 2.50–1.00 (br m, 48H, dcpe), 1.67 (9H, *o*-*t*-Bu), 1.66 (9H, *o*-*t*-Bu), 1.31 (9H, *p*-*t*-Bu), 0.80 (apparent t, 3H, ³J_{HH} = 7, ⁴J_{PH} = 7, ³J_{Pt-H} = 50, Me). ¹³C{¹H} NMR (THF-*d*₈, 22 °C): δ 156.0 (dd, ²J_{PC} = 11, ¹J_{PC} = 3, *o*-Mes*), 154.4 (m, *o*-Mes*), 146.9 (d, ¹J_{PC} = 2, *p*-Mes*), 136.8 (m, *ipso*-Mes*), 133.2 (m, CH(Me)CN), 121.5 and 121.1 (overlapping m, *m*-Mes*), 39.6 (br, *o*-CMe₃), 39.1 (br, *o*-CMe₃), 37.4–35.8 (m, Cy CH), 35.4 (br, *p*-CMe₃), 33.9 (d, ¹J_{PC} = 6, *o*-CMe₃), 33.5 (d, ¹J_{PC} = 10, *o*-CMe₃), 32.2 (br, *p*-CMe₃), 31.3–27.0 (m, dcpe CH₂), 20.7 (d, ³J_{PC} = 6, CH(Me)CN), 1.2 (dd, ²J_{PC} = 84, 5, CH(Me)CN). FAB-MS (3-nitrobenzyl alcohol): *m/z* 948 (M⁺), 894 (M – CH(Me)CN)⁺, 671 (M – PHMes*), 617 (Pt(dcpe)).

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Supporting Information Available: Text giving additional experimental information and NMR and IR spectroscopic data and tables giving details of the crystal structure determinations for *trans*-Pt(PPh₃)₂(CH₂CH₂CN)(Br), **11**·Et₂O, and **23**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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