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)(CH_2CHCN) (diphos = dppe (**1**), dcpe (**2**); dppe = $Ph_2PCH_2CH_2PPh_2$, dcpe = $Cy_2PCH_2CH_2PCy_2$, Cy = cyclo-C_6H_{11}) 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-$Me_3C_6H_2$, Mes* = 2,4,6-(t-Bu)$_3C_6H_2$). Acrylonitrile does not insert into the Pt−H bond of these hydrides to give cyanoethyl ligands; the putative products, the phosphido complexes Pt(diphos)(CH_2CH_2CN)(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)CH_2PRR′](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)CH_2PRR′](Me), (**14**, **15**, **18**). Similarly, treatment of Pt(dcpe)-(PHMes*)(H) (**22**) with acrylonitrile gives Pt(dcpe)[CH(CN)CH_2PHMes*](H) (**24**) as a mixture of diastereomers; the isomeric Pt(dcpe)[PMes*(CH_2CH_2CN)](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)(CH_2CHCN) (**2**) and PHMes*(CH_2CH_2CN) (**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)(CH_2CH_2CN)(PHMes*) (**11**), *trans*-Pt-(PPh_3)$_2$(CH_2CH_2CN)(Br), and $PMes_2$(CH_2CH_2CN) (**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 catalyti-

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(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992. (b) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Ed.; VCH: Weinheim, Germany, 1996.

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

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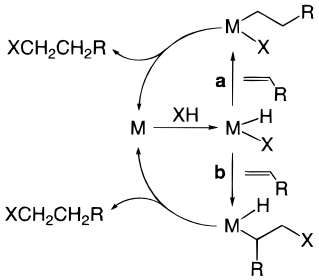
Scheme 1. Two Possible Pathways for Metal-Catalyzed Addition of X−H Bonds to Olefins[a]



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

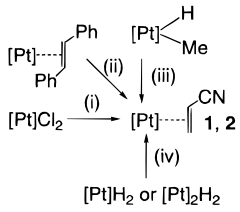
cally active one. Comparison to literature results on metal-catalyzed X−H additions shows how the nature of the X group affects the individual steps in the reaction and provides design principles for further rational development of this important class of reactions.[4]

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 PtL_2-(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 $PH(CH_2CH_2CN)_2$ to acrylonitrile.[5b]

To avoid formation of bimetallic complexes, we studied catalysis by the diphosphine complexes Pt(diphos)-(CH_2CHCN) (**1**, diphos = dppe ($Ph_2PCH_2CH_2PPh_2$); **2**, diphos = dcpe ($Cy_2PCH_2CH_2PCy_2$, Cy = *cyclo*-C_6H_{11})), prepared as shown in Scheme 2. $^{31}P\{^1H\}$ 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]

Scheme 2[a]



[a] [Pt] = Pt(diphos). For **1** (i−ii), diphos = dppe; for **2** (iii−iv), diphos = dcpe. Legend: (i) CH_2CHCN, $NaBH_4$, EtOH; (ii) CH_2CHCN; (iii) CH_2CHCN, 50 °C, 1 day; (iv) CH_2CHCN.

Complexes **1** and **2** act as catalyst precursors or catalysts for addition of the P−H bonds in the primary phosphines PH_2Ph and PH_2Mes^* (Mes* = 2,4,6-(t-$Bu)_3C_6H_2$) and in the secondary phosphines PH(Ph)(R) (R = Mes, Ph, Cy, i-Bu, Me; Mes = 2,4,6-$Me_3C_6H_2$) across the acrylonitrile C=C double bond to give the phosphines $PPh(CH_2CH_2CN)_2$, $PH(Mes^*)(CH_2CH_2CN)$ (**3a**), and $P(Ph)(R)(CH_2CH_2CN)$, respectively (Scheme 3). With PH_2Ph, the secondary phosphine[7] PH(Ph)-(CH_2CH_2CN) was observed as an intermediate, but conversion of the bulkier PH_2Mes^* to the tertiary phosphine $PMes^*(CH_2CH_2CN)_2$ 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 PH_3/CH_2CHCN 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 PH_2Mes^*) on addition of excess phosphine, even when excess acrylonitrile is present, to form Pt-

(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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(8) The new secondary phosphine $PH(Mes^*)(CH_2CH_2CN)$ (**3a**) and the tertiary phosphine $PPh(Mes)(CH_2CH_2CN)$ (**3b**) were prepared independently by base-catalyzed hydrophosphination[8c] (see the Experimental Section). For syntheses and spectroscopic data on cyanoethylphosphines, see the following. (a) $PPh(CH_2CH_2CN)_2$: 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)(CH_2CH_2CN) (R = Cy, i-Bu, Me): Wolfsberger, W. *Chem. Ztg.* **1990**, *114*, 353−354. (c) $PPh_2(CH_2CH_2CN)$: 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 $PPh(CH_2CH_2CN)_2$ (Strem) and $PPh_2(CH_2CH_2CN)$ (Organometallics) are commercially available.

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

complex	no.	$\delta(P_1)$ (J_{Pt-P})	$\delta(P_2)$ (J_{Pt-P})	$\delta(P_3)$ (J_{Pt-P})	J_{12}	J_{13}	J_{23}
Pt(dppe)(CH_2CHCN)	**1**	53.5 (3594)	51.4 (3102)		59		
Pt(dcpe)(CH_2CHCN)	**2**	74.1(3446)	70.8 (2963)		47		
Pt(dppe)($PHPh_2$)$_2$[d]	**4**	29.2 (3581)	29.2 (3581)	−16.2 (3955)		57	
Pt(dppe)(CH_2CH_2CN)(Br)	**5**	45.4 (4163)	44.8 (1744)				
Pt(dcpe)(CH_2CH_2CN)(Br)	**6**	66.1 (1793)	59.0 (4053)				
[Pt(dppe)(CH_2CH_2CN)(PH_2Mes*)][BF_4]	**7**	55.1 (2913)	50.0 (1615)	−64.5 (2621)		386	18
[Pt(dppe)(CH_2CH_2CN)($PHMes_2$)][BF_4]	**8**	52.4 (2803)	46.2 (1659)	−47.5 (2533)		369	18
Pt(dppe)(CH_2CH_2CN)(PHMes*)	**9**	46.7 (1904)	46.0 (1755)	−65.2 (827)		124	12
Pt(dppe)(CH_2CH_2CN)($PMes_2$)	**10**	44.8 (1938)	33.1 (1869)	−57.6 (1201)	6	165	
Pt(dppe)(CH_2CH_2CN)(PHMes*)	**11**	64.1 (2011)	59.8 (1787)	−83.7 (806)	3	132	9
Pt(dppe)(Me)[CH(CN)CH_2PHMes*] (minor isomer)	**14a**	49.1 (1769)	48.0 (2208)	−65.8 (195)	3	15	
Pt(dppe)(Me)[CH(CN)CH_2PHMes*] (major isomer)	**14b**	48.5 (1755)	48.3 (2246)	−72.2 (164)		12	
Pt(dppe)(Me)[CH(CN)CH_2PMes_2]	**15**	48.7 (1819)	47.0 (2260)	−17.9 (277)		31	
[Pd(dppe)(Me)(PH_2Mes*)][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_2PHMes*][e] (minor isomer)	**18a**	49.4	39.8	−66.9		20	
Pd(dppe)(Me)[CH(CN)CH_2PHMes*] (major isomer)	**18b**	49.4	39.8	−73.5		13	
[Pt(dppe)(Me)(CH_2CHCN)][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_2PHMes*](H) (major isomer)	**24a**	75.9 (2165)	65.0 (1772)	−68.5 (276)		6	
Pt(dcpe)[CH(CN)CH_2PHMes*](H) (minor isomer)	**24b**	76.1 (2190)	64.9 (1758)	−69.7 (219)		5	
Pt(dcpe)[PHMes*(CH_2CH_2CN)](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% H_3PO_4), and coupling constants are in Hz. [b] P_1 and P_2 are the diphos P nuclei; P_3 is trans to P_1. [c] Solvents: C_6D_6 for **1**, **2**, **9**, **10**, **14**, **20**−**22**, and **24**−**26**; $CDCl_3$ for **5**, **6**, and **19**; CH_2Cl_2 for **7** and **8**; CD_2Cl_2 for **11**; THF-d_8 for **15**, **28**, and **29**; THF for **4**, **16**, and **18**; toluene-d_8, (−50 °C) for **17.** [d] Tetrahedral complex: P_1 and P_2 = dppe, P_3 and P_4 = $PHPh_2$. [e] The dppe resonances for the two isomers overlapped. $^1J_{PH}$ (PHMes*): 202 (**18a**), 221 (**18b**). [f] Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125−127. [g] Data for *trans*-Pt(PPh_3)$_2$[CH(Me)(CN)](Br) (**27**) in THF-d_8: δ 25.9 (J_{Pt-P} = 3071). In CH_2Cl_2, 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).

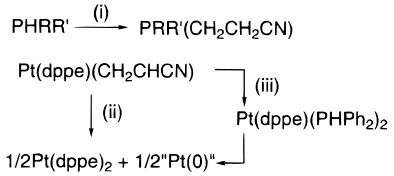
Table 2. Selected IR and ^{1}H NMR Data for Pt(diphos) Complexes[a−c]

no.	IR[d]	selected ^{1}H NMR
1	2198	2.80 (d, $^3J_{HH}$ = 9.3, $^2J_{Pt-H}$ = 68, 1H, CH_2CHCN), 2.75 (d, $^3J_{HH}$ = 4.5, $^2J_{Pt-H}$ = 54, 1H, CH_2CHCN), 2.49 (dd, $^3J_{HH}$ = 9.3, $^3J_{HH}$ = 4.5, $^2J_{Pt-H}$ = 50, 1H, CH_2C*H*CN)
2	2195	2.47 (apparent t, $^3J_{HH}$ = 9.6, 9.6, $^2J_{Pt-H}$ = 63, 1H, CH_2C*H*CN), 2.24 (dd, $^3J_{HH}$ = 9.6, $^2J_{HH}$ = 5.4, 1H, CH_2CHCN), 2.13 (dd, $^3J_{HH}$ = 9.6, $^2J_{HH}$ = 5.4, 1H, CH_2CHCN)
5	2231	1.63−1.39 (m, $^2J_{Pt-H}$ = 55, Pt−CH_2)
9	2400, 2230	5.10 (d of apparent triplets, J_{PH} = 215, 8, 8, $^2J_{Pt-H}$ = 64, PH)
10	2230	1.46−1.40 (m, $^2J_{Pt-H}$ = 50, Pt−CH_2)
11	2390, 2229	5.30 (ddd, J_{PH} = 211, 9, 2, $^2J_{Pt-H}$ = 59, PH)
14a,b	2393, 2185	4.57 (ddd, $^1J_{PH}$ = 220, $^3J_{HH}$ = 10, 7, minor PH), 4.26 (ddd, $^1J_{PH}$ = 222, $^3J_{HH}$ = 11, 5, major PH)
15	2179	3.31 (m, $^2J_{AA'}$ = 12.3, $^3J_{AB}$ = 11.9, 1H, CH_2PMes_2), 3.25 (m, $^2J_{AA'}$ = 12.3, $^3J_{A'B}$ = 3.9, 1H, CH_2PMes_2), 2.81 (m, $^3J_{AB}$ = 11.9, $^3J_{A'B}$ = 3.9, $^2J_{Pt-H}$ = 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, $^3J_{HH}$ = 11, 1H, CH_2), 6.23 (d, $^3J_{HH}$ = 17, 1H, CH_2), 6.03 (dd, $^3J_{HH}$ = 17, 11, 1H, CH)
20	2372, 2053	5.56 (d of apparent t, J_{PH} = 211, 8, 8, $^2J_{Pt-H}$ = 62, PH), −1.34 (ddd, $^2J_{PH}$ = 188, 15, 6, $^1J_{Pt-H}$ = 1151, Pt−H)
21[e]	2033	−2.13 (ddd, J_{PH} = 187, 13.5, 13.5, $^1J_{Pt-H}$ = 1107, Pt−H)
22	2375, 2024	5.87 (ddd, J_{PH} = 204, 8, 2, $^2J_{Pt-H}$ = 58, PH), −1.47 (dd, $^2J_{PH}$ = 182, 16, $^1J_{Pt-H}$ = 1063, Pt−H)
24a		5.62 (d of apparent t, $^1J_{PH}$ = 228, $^3J_{HH}$ = 9, 9, PH), −1.33 (ddd, $^2J_{PH}$ = 185, 18, 5, $^1J_{Pt-H}$ = 1106, Pt−H)
24b		4.86 (ddd, $^1J_{PH}$ = 217, $^3J_{HH}$ = 13, 5, PH), −1.27 (ddd, $^2J_{PH}$ = 188, 17, 5, $^1J_{Pt-H}$ = 1132, Pt−H)
25	2239, 2029	−2.41 (d of apparent t, $^2J_{PH}$ = 171, 17, 17, $^1J_{Pt-H}$ = 1006, Pt−H)
26	2182, 1993	−1.30 (dd, $^2J_{PH}$ = 191, 17, $^1J_{Pt-H}$ = 1121, Pt−H)
27	2199	2.02 (q, $^3J_{HH}$ = 7, CH), 0.50 (d, $^3J_{HH}$ = 7, $^3J_{Pt-H}$ = 67, Me)
29	2399, 2185	5.18 (br dd, J_{PH} = 209, 8, $^2J_{Pt-H}$ = 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. ^{31}P-decoupled spectra reported for **1**, **2**, **27**. The temperature is 22 °C except where noted. [c] Solvents: C_6D_6 for **1**, **2**, **9**, **10**, **15**, **20**−**22**, and **24**−**26**; $CDCl_3$ for **5** and **19**; THF-d_8 for **27** and **29**; CD_2Cl_2 for **11**, **14**, and **16**; toluene-d_8 (−50 °C) for **17**. [d] ν_{PH} ∼2400 cm^{-1}, ν_{CN} ∼2200 cm^{-1}, ν_{Pt-H} ∼2000 cm^{-1}. [e] Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125−127.

(dppe)$_2$ (Scheme 3).[9] With $PHPh_2$, a small amount of Pt(dppe)($PHPh_2$)$_2$ (**4**) was also observed.[10] The expected disproportionation byproduct,[11] Pt(L)$_n$(CH_2CHCN)$_m$ (L = phosphine), was not observed, but the ^{31}P NMR peaks due to the phosphines present were broadened, consistent with exchange processes involving such Pt(0)

Scheme 3[a]



[a] Legend: (i) CH_2CHCN, catalytic Pt(diphos)(CH_2CHCN) (**1** or **2**), 50 °C, THF, for R and R′, see Table 3; (ii) PHRR′, CH_2CHCN, 25 °C; (iii) excess $PHPh_2$, 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 PH_2Mes*, 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 ^{31}P 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 intermediates[14] were prepared as shown in Scheme 4. Treatment of Pt(dppe)(*trans*-stilbene)[6] with $BrCH_2CH_2CN$ gave Pt(dppe)(CH_2CH_2CN)(Br) (**5**).[15] The analogous dcpe complex Pt(dcpe)(CH_2CH_2CN)(Br) (**6**) was prepared by addition of dcpe to the known *trans*-$Pt(PPh_3)_2(CH_2CH_2CN)(Br)$.[15] Bromide abstraction from **5** with $AgBF_4$ in the presence of the appropriate phosphine gave the cationic complexes [Pt(dppe)(CH_2CH_2CN)(PHRR′)][BF_4] (R = H, R′ = Mes* (**7**); R = R′ = Mes (**8**)), which could be deprotonated to yield the desired phosphido complexes Pt(dppe)(CH_2CH_2CN)(PRR′) (R = H, R′ = Mes* (**9**); R = R′ = Mes (**10**)).[16] The dcpe complex Pt(dcpe)(CH_2CH_2CN)(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*-$Pt(PPh_3)_2(CH_2CH_2CN)(Br)$ 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 PH_2Mes* and acrylonitrile. Instead, complex **11** decomposed slowly under catalytic conditions to give a trace of the secondary phosphine PH(Mes*)(CH_2CH_2CN) (**3a**) and, after several days, a small amount of Pt(dcpe)(CH_2CHCN) (**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 regiospecifically to furnish the dialkyls Pt(dppe)(Me)[CH(CN)CH_2PRR′] (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−C*H* ^{1}H NMR signal (C_6D_6) is a multiplet (δ 2.81, $^2J_{Pt-H}$ = 106 Hz) with inequivalent couplings ($^3J_{HH}$ = 11.9, 3.9 Hz) to the diastereotopic CH_2 protons, whose resonances appear as multiplets at 3.31 and 3.25 ppm with $^2J_{HH}$ = 12.3 Hz. The Pt−*C*H(CN) ^{13}C 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

(9) Pt(dppe)$_2$ was identified by ^{31}P 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 $PHPh_2$. Addition of a large excess of $PHPh_2$ 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(PPh$_2$py)$_2$(H)(Cl) (PPh$_2$py = 2-pyridyldiphenylphosphine) gives a cyanoethyl group: Xie, Y.; James, B. R. *J. Organomet. Chem.* **1991**, *417*, 277−288. (b) However, *trans*-Pt(PEt$_3$)$_2$(*p*-BrC_6H_4)(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 PH_2Mes*, 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.

(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]

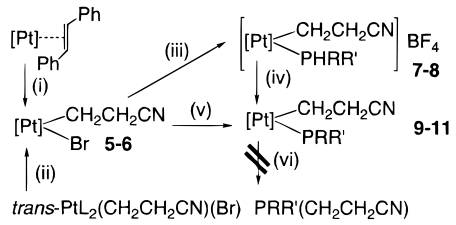
$$PHRR' \xrightarrow{\text{cat.}} PRR'(CH_2CH_2CN)$$

cat. = Pt(diphos)(CH_2CHCN)
diphos = dppe (**1**) or dcpe (**2**)

reactant	product	TOF dppe[b]	TOF dcpe[b]	TOF no Pt[c]	selectivity (dppe, dcpe), %
PH_2Ph	$P(Ph)(ce)_2$	0.5 h^{-1}	10 h^{-1}	1 day^{-1}	68, 29[d]
PH_2Mes^*	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*-Bu)	P(Ph)(*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 PH_2Ph), THF, 50 °C. ce = cyanoethyl, CH_2CH_2CN. Catalyst **1** decomposed immediately (see text) in all cases except for PH_2Mes^*. Catalyst **2** decomposed within 1 h for PH(Ph)(Me), over 7 days for PH_2Mes^* (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; $PPh_2(ce)$, −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 ^{31}P NMR (PPh_3O internal standard) until the starting phosphine was consumed (10 turnovers), except for the slow reactions of PH_2Mes^*, which were observed for ca. 1 half-life. The turnover frequency (TOF) is defined as equiv of products formed/equiv 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 ^{31}P NMR for at least as long as the corresponding catalytic ones, except for the very slow reaction of PH_2Mes^*, 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, $BrCH_2CH_2CN$; (ii) for **6**, diphos = dcpe, dcpe; (iii) $AgBF_4$, PHRR′; diphos = dppe, R = H, R′ = Mes* (**7**), R = R′ = Mes (**8**); (iv) $NaN(SiMe_3)_2$, 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 center[20] 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 ^{31}P NMR signal at δ −80 (d, $^4J_{PP}$ ≈ 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*)(CH_2CH_2CN) (**3a**).

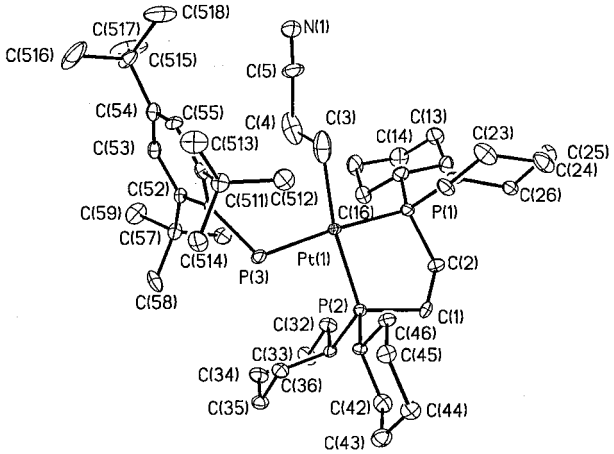


Figure 1. ORTEP diagram of Pt(dcpe)(CH_2CH_2CN)(PHMes*)·Et_2O (**11**·Et_2O) with 30% thermal ellipsoids. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) = 2.283(2), Pt(1)−P(2) = 2.304(2), Pt(1)−P(3) = 2.390-(2), Pt(1)−C(3) = 2.258(14), 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).

In analogous palladium chemistry (Scheme 5), the cationic complex [Pd(dppe)(Me)(PH_2Mes^*)][BF_4] (**16**) was prepared by treatment of Pd(dppe)(Me)(Cl) with $AgBF_4$ and PH_2Mes^*. Low-temperature deprotonation

(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−CH_2CH_2OAr 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 ^{31}P NMR spectrum of **15** was unchanged at −75 °C.

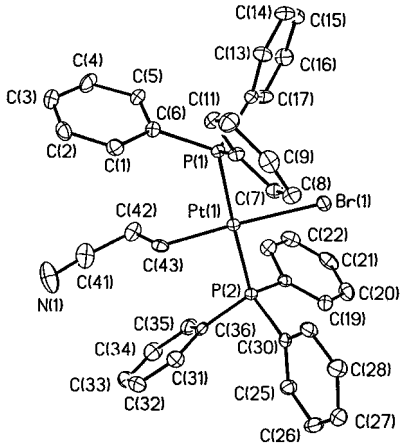


Figure 2. ORTEP diagram of [*trans*-Pt(PPh_3)$_2$(CH_2CH_2-CN)(Br)] with 30% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt−P(1) = 2.331(2), Pt−P(2) = 2.336(2), Pt−C(43) = 2.115(7), Pt−Br(1) = 2.5630(7), C(41)−C(42) = 1.489-(12), C(42)−C(43) = 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*-Pt(PPh_3)$_2$(CH_2CH_2CN)(Br) (A), Pt(dcpe)(CH_2CH_2CN)(PHMes*)·Et_2O (11·Et_2O), and $PMes_2CH_2CH_2CN$ (23)

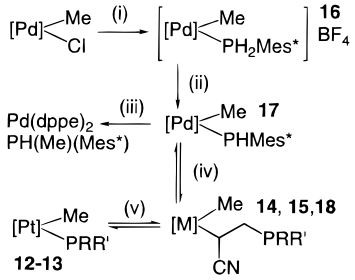
	A	11·Et_2O	23
formula	$C_{39}H_{34}BrNP_2Pt$	$C_{53}H_{92}NOP_3Pt$	$C_{21}H_{26}NP$
fw	853.61	1047.28	323.40
space group	$P2_1/n$	$P2_1/n$	$Pna2_1$
a, Å	12.1765(2)	11.1690(2)	20.019(5)
b, Å	23.7244(3)	19.5742(2)	8.843(2)
c, Å	13.2394(2)	24.6275(2)	21.219(5)
β, deg	114.570(2)	99.2733(3)	
V, Å^3	3478.30(6)	5313.76(11)	3756(1)
Z	4	4	8
cryst color, habit	colorless rod	pale yellow block	colorless
D(calcd), g cm^{-3}	1.630	1.309	1.144
μ(Mo Kα), cm^{-1}	53.03	27.66	1.460
temp, K	198(2)	173(2)	298
T(max)/*T*(min)		1.000/0.796	
diffractometer	Siemens P4/CCD	Siemens P4/CCD	P4
radiation	Mo Kα (*λ* = 0.710 73 Å)		
R(*F*), %[a]	4.13	5.07	4.21
$R_w(F^2)$, %[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 Pd(dppe)(Me)(PHMes*) (**17**), which decomposes on warming to the known secondary phosphine PH(Me)(Mes*)[22] and the fragment Pd(dppe), which either disproportionates to Pd(0) and Pd(dppe)$_2$ or can be trapped by added dppe to give only Pd-(dppe)$_2$.[23]

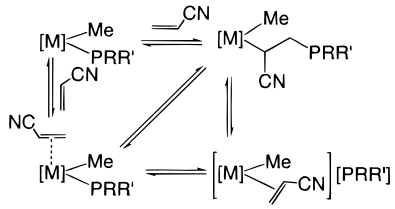
At low temperature, **17** reacts with acrylonitrile to yield Pd(dppe)(Me)[CH(CN)CH_2PHMes*] (**18**) as a mixture of diastereomers (2:1 ratio on warming to room temperature). Low-temperature monitoring of this reaction shows that one diastereomer is initially formed selectively but eventually becomes the minor product on warming. A mixture of **18** and acrylonitrile decomposes on standing to give PH(Me)(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.

Scheme 5[a]



[a] [M] = M(dppe); M = Pd, Pt. Legend: (i) $AgBF_4$, PH_2Mes*; (ii) $LiN(SiMe_3)_2$, −78 °C; (iii) dppe, −78 to 25 °C; (iv) CH_2CHCN, -78 °C (for **18**); (v) CH_2CHCN, R = H, R′ = Mes* (**12**, **14**), R = R′ = Mes (**13**, **15**).

Scheme 6[a]



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

Related work on small-molecule insertion into metal−heteroatom bonds[24] 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 Pt(dppe)(Me)(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 [Pt-(dppe)(Me)(CH_2CHCN)][PRR′], followed by attack of the phosphido anion on coordinated acrylonitrile to yield the observed products. A related intermediate, [Ir(CO)$_3$-(PPh_3)$_2$][OR], was observed during carbonylation of *trans*-Ir(PPh_3)$_2$(CO)(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 [Pt(dppe)(Me)(CH_2CHCN)]$^+$ (**19**) was

(22) Identified by ^{1}H, ^{13}C, and ^{31}P 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.

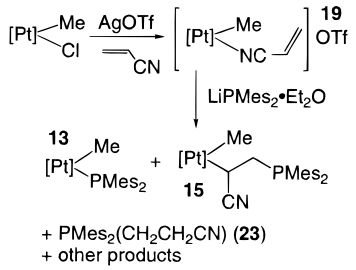
(23) Pd(dppe)$_2$ was identified by ^{31}P NMR and comparison to an authentic sample. Further results on this and related reductive eliminations in palladium phosphido complexes will be reported separately: Zhuravel, M. A.; Wicht, D. K.; Nthenge, J. M.; Sweeder, R. D.; Glueck, D. S. Manuscript in preparation.

(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 [Pt(triphos)(OAr)]$^+$, see: Dockter, 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.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179−2185.

Scheme 7[a]



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

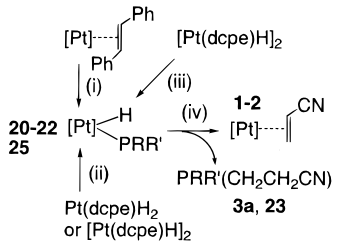
prepared as a triflate salt by treatment of Pt(dppe)(Me)(Cl) with AgOTf and an excess of acrylonitrile (Scheme 7).[27] The ^{31}P NMR spectrum of **19** (Table 1) is very similar to that of [Pt(dppe)(Me)(NCMe)][BF_4],[28] which suggests that acrylonitrile in **19** is bound to Pt via the nitrile nitrogen, not by the C=C bond.[29] Consistent with this conclusion, no Pt satellites are observed on the ^{1}H (Table 2) or ^{13}C NMR signals due to coordinated acrylonitrile, which appear at chemical shifts similar to those in the free ligand.

Freshly prepared **19** was treated with $LiPMes_2 \cdot Et_2O$ in THF-d_8 at −78 °C;[30] the ^{31}P 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)($PMes_2$) (**13**) and Pt(dppe)(Me)[$CH(CN)CH_2PMes_2$] (**15**) in a ratio of approximately 2:1. A small amount of $PMes_2(CH_2CH_2CN)$ (**23**, see below) was also observed by ^{31}P 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 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.

Scheme 8[a]



[a] [Pt] = Pt(diphos). Legend: (i) diphos = dppe, PH_2Mes^* (for **20**), $PHMes_2$ (for **21**); (ii) PH_2Mes^* (for **22**); (iii) 2 PH(Mes*)(CH_2CH_2CN) (for **25**); (iv) 2 CH_2CHCN, **20** and **25** yield **3a**, **21** yields **23**. For reaction of **22** with acrylonitrile, see Scheme 9.

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(dcpe)(PHMes*)(H) (**22**) was prepared by treatment of Pt(dcpe)H_2 and/or [Pt(dcpe)H]$_2$ with PH_2Mes^*.[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*)(CH_2CH_2CN) (**3a**) and $PMes_2(CH_2CH_2CN)$ (**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 dcpe complex **22** at low temperature, the diastereomeric

(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 BF_4 salts, as indicated by peaks due to minor impurities in the ^{31}P 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 $CDCl_3$, 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(PMe_2Ph)$_2$(Me)(CH_2CHCN)][BF_4]; see: Clark, H. C.; Ruddick, J. D.; *Inorg. Chem.* **1970**, *9*, 1226−1229. For *trans*-[Pt(PEt_3)$_2$(R)(CH_2CHCN)][BF_4] (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.

(31) A closely related sequence of selective insertion of acrylonitrile into a Pt−N, not a Pt−H, bond was reported in *trans*-Pt(PEt_3)$_2$(NHPh)(H). Notably, the isolable product *trans*-Pt(PEt_3)$_2$[$CH(CN)CH_2NHPh$](H) undergoes reductive elimination on heating to form 3-anilinopropionitrile, while the related reaction of *trans*-Pt(PEt_3)$_2$(OPh)(H) with acrylonitrile leads directly to $PhOCH_2CH_2CN$ without isolation of an intermediate. See: Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750−4761.

(32) In previous work, these hydrides were prepared by reduction of Pt(dcpe)Cl_2 under H_2; 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(dcpe)Cl_2 with 2 equiv of $LiBEt_3H$ in THF or toluene also provided Pt(dcpe)H_2, sometimes contaminated with the known cation [Pt_2(dcpe)$_2H_3$]$^+$ formed from traces of water. Surprisingly, stirring a slurry of Pt(dcpe)H_2 in petroleum ether overnight caused almost complete conversion to [Pt(dcpe)H]$_2$. For a similar synthesis of [Pt(dippe)H]$_2$ (dippe = (*i*-Pr)$_2$$PCH_2CH_2P$(*i*-Pr)$_2$), see: Edelbach, B. L.; Vicic, 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.

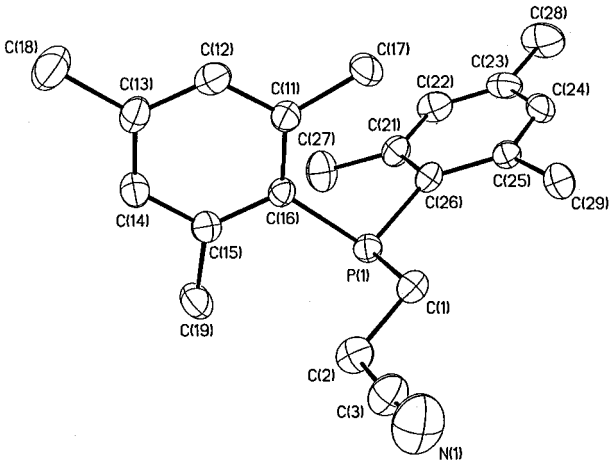
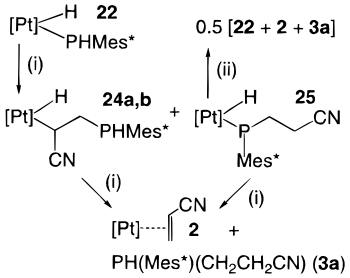


Figure 3. ORTEP diagram of one of the two independent but chemically equivalent molecules of $PMes_2(CH_2CH_2CN)$ (**23**) in the asymmetric unit. Selected bond lengths (Å) and angles (deg) for one of these: P(1)−C(26) = 1.842(6), P(1)−C(16) = 1.853(5), P(1)−C(1) = 1.835(5), C(1)−C(2) = 1.524(8), C(2)−C(3) = 1.454(8), N(1)−C(3) = 1.119(7); C(26)−P(1)−C(16) = 105.7(2), C(26)−P(1)−C(1) = 111.4(2), C(16)−P(1)−C(1) = 99.3(2).

Scheme 9[a]

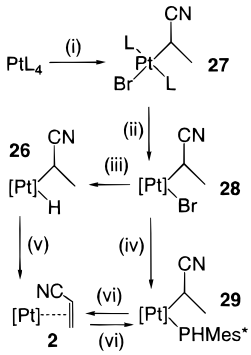


[a] [Pt] = Pt(dcpe). Legend: (i) CH_2CHCN; (ii) 50 °C, days.

insertion products Pt(dcpe)[CH(CN)CH_2PHMes*](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 Pt(dcpe)[PMes*(CH_2CH_2CN)](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 PHMes*(CH_2CH_2CN) (**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), Pt(dcpe)-(CH_2CHCN) (**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 $[Pt(dcpe)H]_2$ and PH(Mes*)(CH_2CH_2CN) (**3a**). A similar reaction of **3a** with Pt(dcpe)H_2, generated from Pt(dcpe)Cl_2 and $LiBEt_3H$, is slower; **25** is the initial product under these conditions, but surprisingly, Pt-(dcpe)(PHMes*)(H) (**22**) and Pt(dcpe)(CH_2CHCN) (**2**) are also formed.

Scheme 10[a]



[a] L = PPh_3, [Pt] = Pt(dcpe). Legend: (i) CH(Me)(Br)(CN); (ii) dcpe; (iii) $NaBH(OMe)_3$; (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 Pt(dcpe)(PHMes*)(H) (**22**), Pt(dcpe)(CH_2CHCN) (**2**), and PH(Mes*)(CH_2CHCN) (**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 Pt(dcpe)(Me)(H)[34] and the stabilizing effects of the CH_2CN group[35] on Pt(II) alkyl hydrides. To investigate this reaction, the model hydride Pt(dcpe)-[CH(Me)(CN)](H) (**26**) was prepared as shown in Scheme 10. Oxidative addition of CH(Me)(CN)(Br) to $Pt(PPh_3)_4$ gave *trans*-$Pt(PPh_3)_2$[CH(Me)(CN)](Br) (**27**), which yielded Pt(dcpe)[CH(Me)(CN)](Br) (**28**) on treatment with dcpe in CH_2Cl_2. Reaction of bromide **28** with $NaBH(OMe)_3$ 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 Pt(dcpe)-(Me)(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.

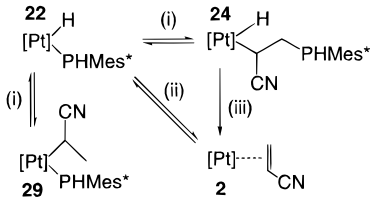
10 M(II) complexes.[36] It is also possible that intramolecular phosphorus coordination[37] of the $CH(CN)CH_2$-PHMes* side chain in **24a**,**b** promotes reductive elimination; a similar five-coordinate species could also be involved in acrylonitrile extrusion. Although the lack of reaction of model complex **26** with PH_2Mes^* argues against this, the chelate effect would favor the formation of such an intermediate for **24**.

The slow decomposition of Pt(dcpe)(CH_2CHCN) (**2**) during the catalytic reaction of PH_2Mes^* 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)-(CH_2CH_2CN)(PHMes*) (**9**). Heating this mixture to 50 °C for several days led to slow decomposition; a trace of the acrylonitrile complex Pt(dcpe)(CH_2CHCN) (**2**) was observed by ^{31}P NMR. Finally, when **29** (10 mol %) was treated with PH_2Mes^* and acrylonitrile under the standard catalytic conditions, the secondary phosphine PH(Mes*)(CH_2CH_2CN) (**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 PH_2Mes^* and acrylonitrile; since decomposition of **29** was not clean, we did not investigate this chemistry further.

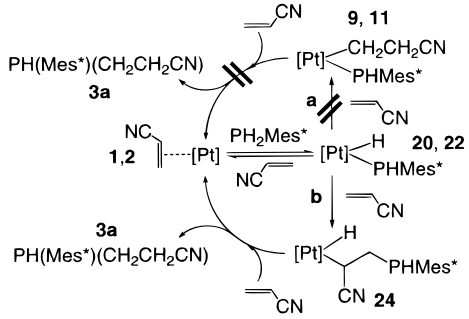
These observations are consistent with the mechanism shown in Scheme 11. Complex **29** could be formed in the original catalysis by insertion of acrylonitrile into the Pt−H bond of Pt(dcpe)(PHMes*)(H) (**22**). However, as described above, treatment of pure **22** with acrylonitrile leads instead to the alkyl hydride Pt(dcpe)[CH(CN)-CH_2PHMes*)](H) (**24**) by insertion into the Pt−P bond. If, as seems likely from the model studies, the kinetically 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**.

Scheme 11[a]



[a] [Pt] = Pt(dcpe). Legend: (i) CH_2CHCN; (ii) CH_2CHCN, $-PH_2Mes^*$; (iii) CH_2CHCN, $-PH(Mes^*)(CH_2CH_2CN)$ (**3a**).

Scheme 12[a]



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

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.; Trogler, 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 ^{31}P 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 ^{31}P NMR (Table 1) and ^{1}H 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*)(CH_2CH_2CN) (**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. CH_2Cl_2 was distilled from CaH_2. 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. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported relative to H_3PO_4 (85%) used as an external reference.

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)Cl_2 compounds were made from Pt(COD)Cl_2 and the diphos ligand in CH_2Cl_2. The following were made by the literature methods: *trans*-Pt(PPh_3)$_2$(CH_2CH_2CN)(Br),[15] Pt(dppe)(*trans*-stilbene),[6] Pt(dppe)(Me)(PHMes*) (**12**) and Pt(dppe)(Me)($PMes_2$) (**13**),[16] PH_2Mes*,[40] $PHMes_2$,[41] Pd(dppe)(Me)(Cl),[42] Pt(dppe)(Me)(Cl),[43] Pt(dcpe)(Me)(H).[34] ^{31}P NMR and selected ^{1}H NMR and IR data for the new metal complexes are in Tables 1 and 2; more ^{1}H NMR and ^{13}C NMR data and synthetic details are given below. For additional experimental details and complete IR data, see the Supporting Information.

Pt(dppe)(CH_2CHCN) (1). To a suspension of Pt(dppe)Cl_2 (110 mg, 0.165 mmol) in 5 mL of ethanol was added acrylonitrile (22 μL, 0.33 mmol). A solution of $NaBH_4$ (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 × 2 mL), water (2 × 1 mL), and ether (2 × 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 $C_{29}H_{27}NP_2Pt$: C, 53.87; H, 4.22; N, 2.17. Found: C, 53.61; H, 4.59; N, 1.95. ^{1}H NMR (C_6D_6): 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, CH_2CHCN), 2.54−2.38 (m, 1H, CH_2CHCN), 2.08−1.70 (m, 4H, dppe CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): 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, *C*N), 30.3 (dd, $^2J_{PC}$ = 44, 4, $^1J_{Pt-C}$ = 246, *C*H_2CHCN), 29.2 (dd, J_{PC} = 35, 15, dppe *C*H_2), 28.7 (dd, J_{PC} = 34, 14, dppe *C*H_2), 13.6 (dd, $^2J_{PC}$ = 39, 7, $^1J_{Pt-C}$ = 229, CH_2*C*HCN).

Pt(dcpe)(CH_2CHCN) (2). A solution of 200 mg (0.32 mmol) of Pt(dcpe)(Me)(H) in 5 mL of toluene was treated with 62 μL (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)Cl_2 (200 mg, 0.29 mmol) in 20 mL of toluene was treated with 581 μL of $LiBEt_3H$ (1 M solution in THF, 0.58 mmol). The mixture was stirred for 30 min and then filtered through Celite. According to ^{31}P{^{1}H} NMR, the yellowish filtrate contained Pt(dcpe)H_2 in ca. 95−98% purity (the rest was $[Pt_2(dcpe)_2H_3]^+$). The filtrate was then treated with 80 μL (1.2 mmol) of CH_2CHCN, 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)(CH_2-CHCN) was eluted with ca. 10−20 mL of toluene, while the $[Pt_2(dcpe)_2H_3]^+$ 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

(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.

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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. ^{1}H NMR (C_6D_6): δ 2.47 (dddd, 1 H, $^3J_{PH} = 9.6$, $^3J_{PH} = 3.3$, $^3J_{HH} = 9.6$, $^3J_{HH} = 9.6$, $^2J_{Pt-H} = 63$, C*H*CNCH$_2$), 2.27−0.95 (m, 50H, CHCNCH_2 + dcpe). ^{13}C{^{1}H} NMR (C_6D_6): δ 126.9 (dd, $^3J_{PC} = 8$, 3, $^2J_{Pt-C} = 58$, *C*N), 35.7−35.1 (m, Cy *C*H), 35.6 (dd, $^2J_{PC} = 24$, 4, *C*H$_2$-CHCN), 30.1−26.1 (m, Cy *C*H$_2$), 24.5 (dd, $J_{PC} = 28$, 15, dcpe *C*H$_2$), 23.5 (dd, $J_{PC} = 26$, 13, dcpe *C*H$_2$), 10.4 (dd, $^2J_{PC} = 40$, 7, $^1J_{Pt-C} = 221$, CH$_2$*C*HCN).

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$_2$CH$_2$CN) (3a). In the air, acrylonitrile (143 mg, 170 μL, 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. ^{1}H 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*-CMe$_3$), 1.28 (9H, *p*-CMe$_3$). ^{13}C{^{1}H} 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*-*C*Me$_3$), 35.1 (*p*-*C*Me$_3$) 33.7 (d, $^4J_{PC} = 6$, *o*-C*Me$_3$*), 31.4 (*p*-C*Me$_3$*), 23.2 (d, $J_{PC} = 17$, CH$_2$), 15.2 (d, $J_{PC} = 17$, CH$_2$). ^{31}P-{^{1}H} 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$_2$CH$_2$CN) (3b). The synthesis of PH(Ph)-(Mes) from $PPhCl_2$ will be described elsewhere. To a solution of PH(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. ^{1}H 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-{^{1}H} 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{^{1}H} NMR (C_6D_6): δ −24.9. IR (KBr): 2918, 2249, 1604, 1433, 1376, 1025, 933, 856, 747, 699, 557.

Pt(dppe)(CH$_2$CH$_2$CN)(Br) (5). An orange slurry of Pt-(dppe)(*trans*-stilbene) (707 mg, 0.91 mmol) and BrCH$_2$CH$_2$CN (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. ^{1}H 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$_2$CN), 1.63−1.39 (m, 2H, $^2J_{Pt-H} = 55$, Pt−CH$_2$).

Pt(dcpe)(CH$_2$CH$_2$CN)(Br) (6). A solution of 1.0 g (1.2 mmol) of *trans*-[Pt(PPh$_3$)$_2$(CH$_2$CH$_2$CN)(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. ^{1}H 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{^{1}H} 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, $^2J_{Pt-C} = 84$ *C*H$_2$CN), 18.3 (m, CH$_2$), 12.0 (dd, $^2J_{PC} = 98$, 7, $^1J_{Pt-C} = 720$, Pt-*C*H$_2$).

Pt(dppe)(CH$_2$CH$_2$CN)(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$_2$CH$_2$CN)(PH$_2$Mes*)][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. ^{1}H 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$_2$CN), 1.54 (9H, *p*-*t*-Bu), 1.50−1.30 (m, 2H, $^2J_{Pt-H} = 55$, Pt−CH$_2$). ^{13}C{^{1}H} 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 *C*Me$_3$), 35.4 (quat *C*Me$_3$), 33.8 (d, $J_{PC} = 8$, *o*-C*Me$_3$*), 32.3 (*p*-C*Me$_3$*), 29.4−28.5 (m, dppe CH$_2$), 19.1 (broad, *C*H$_2$CN), 12.9 (dd, $^2J_{PC} = 87$, 7, $^1J_{Pt-C} = 655$, Pt−CH$_2$).

Pt(dppe)(CH$_2$CH$_2$CN)(PMes$_2$) (10). A solution of Pt(dppe)-(CH$_2$CH$_2$CN)(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$_2$CH$_2$CN)-(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. ^{1}H 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$_2$CN), 1.46−1.40 (m, 2H, $^2J_{Pt-H} = 50$, Pt−CH$_2$). ^{13}C{^{1}H} 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 (obscured 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, $J_{PC} = 8$, *C*H$_2$CN), 9.9 (dd, $^2J_{PC} = 93$, 5, Pt−CH$_2$, Pt satellites not resolved).

Pt(dcpe)(CH$_2$CH$_2$CN)(PHMes*) (11). A solution of 150 mg (0.2 mmol) of Pt(dcpe)(CH$_2$CH$_2$CN)(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 μL of 1.6 M *n*-BuLi in THF and 167 mg (0.6 mmol) of PH_2Mes^*). 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 $C_{47}H_{82}NP_3Pt$: C, 59.46; H, 8.72; N, 1.48. Found: C, 59.03; H, 8.64; N, 1.42. ^{1}H NMR (CD_2Cl_2): 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 + C_2H_4CN), 1.72 (18H, *o*-*t*-Bu), 1.41 (9H, *p*-*t*-Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2): 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*-*C*Me$_3$), 35.3−34.2 (m, Cy CH), 34.9 (*p*-*C*Me$_3$), 33.1 (d, J_{PC} = 8, *o*-C*Me*$_3$), 31.7 (br, *p*-C*Me*$_3$), 30.0−26.0 (m, dcpe CH_2), 24.6−23.5 (m, dcpe CH_2), 18.5−18.2 (m, CH_2*C*H_2CN), 7.0 (dd, $^2J_{PC}$ = 88, 8, *C*H_2CH$_2$CN).

Pt(dppe)(Me)[CH(CN)CH$_2$PHMes*] (14). Pt(dppe)(Me)(PHMes*) was generated in situ by treatment of Pt(dppe)(Me)(OMe) (245 mg, 0.38 mmol) with PH_2Mes^* (117 mg, 0.42 mmol) in 20 mL of THF. The solution was concentrated under vacuum to 10 mL. Acrylonitrile (41 mg, 50 μL, 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 ^{31}P{^{1}H} 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 $C_{48}H_{60}NP_3Pt$: C, 61.40; H, 6.44; N, 1.49. Found: C, 61.64; H, 6.47; N, 1.60. ^{1}H NMR (500 MHz, CD_2Cl_2; 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 CH_2), 2.36−2.06 (broad m, 4H, major dppe CH_2), 2.06−1.74 (broad m, 2H, major C*H*$_2$PHMes*), 1.91−1.63 (broad m, 2H, minor C*H*$_2$-PHMes*), 1.41 (broad, 9H, *p*-CMe$_3$), 1.27 (broad, 18H, *o*-CMe$_3$), 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). ^{13}C{^{1}H} NMR (CD_2Cl_2, 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*-*C*Me$_3$), 35.1 (*o*-*C*Me$_3$), 33.7 (*p*-C*Me*$_3$), 31.8−31.2 (m, *C*H$_2$PMes*), 31.3 (*o*-C*Me*$_3$), 30.0−28.7 (broad m, dppe CH_2), 7.14 (d, $^2J_{PC}$ = 99, minor Me), 5.0 (d, $^2J_{PC}$ = 95, $^1J_{Pt-C}$ = 570, *C*H(CN)), 3.5 (d, $^2J_{PC}$ = 90, $^1J_{Pt-C}$ = 604, major Me).

Pt(dppe)(Me)[CH(CN)CH$_2$PMes$_2$] (15). Pt(dppe)(Me)(PMes$_2$) was generated in situ by treatment of Pt(dppe)(Me)(OMe) (254 mg, 0.40 mmol) with $PHMes_2$ (118 mg, 0.44 mmol). An excess of acrylonitrile (approximately 500 μL, 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)-CH_2PMes_2]. Anal. Calcd for $C_{48}H_{52}NP_3Pt$: C, 61.92; H, 5.64; N, 1.50. Found: C, 61.99; H, 6.04; N, 1.32. ^{1}H NMR (500 MHz, C_6D_6; labeling Pt−CH$_B$(CN)CH$_A$H$_{A'}$PMes$_2$): 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, CH_2-PMes$_2$), 3.25 (m, $^2J_{AA'}$ = 12.3, $^3J_{A'B}$ = 3.9, 1H, CH_2PMes_2), 2.81 (m, $^3J_{AB}$ = 11.9, $^3J_{A'B}$ = 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, CH_2), 1.29 (dd, $^3J_{PH}$ = 6.5, 6.5, $^2J_{Pt-H}$ = 60, 3H, Pt-Me). ^{13}C{^{1}H} NMR (THF-d_8): 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, CH_2PMes_2), 30.9−29.5 (broad m, dppe CH_2), 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, *C*H(CN)), 3.4 (dd, $^2J_{PC}$ = 92, 7, $^1J_{Pt-C}$ = 600, Me) (the nitrile carbon was not resolved).

[Pd(dppe)(Me)(PH$_2$Mes*)][BF$_4$] (16). To a stirred suspension of Pd(dppe)(Me)(Cl) (297 mg, 0.53 mmol) in THF (10 mL) was added a solution of $AgBF_4$ (104 mg, 0.53 mmol) dissolved in CH_3CN (3 mL). A white precipitate formed immediately. PH_2Mes^* (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 $C_{45}H_{58}BF_4P_3Pd$: C, 61.06; H, 6.61. Found: C, 60.13; H, 6.25 (results for carbon were consistently low). ^{1}H NMR (CD_2Cl_2): δ 7.63−7.50 (broad m, 22H, Ar), 5.61 (ddd, $^1J_{PH}$ = 350, $^3J_{PH}$ = 6, 4, 2H, PH_2), 2.64−2.42 (m, 4H, CH_2), 1.42 (18H, *o*-CMe$_3$), 1.28 (9H, *p*-CMe$_3$), 0.35−0.28 (m, 3H, Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): 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*-*C*Me$_3$), 35.4 (*p*-*C*Me$_3$), 33.1 (*o*-C*Me*$_3$), 31.0 (*p*-C*Me*$_3$), 29.4−28.7 (m, dppe CH_2), 27.4−26.9 (m, dppe CH_2), 8.2 (d, $^2J_{PC}$ = 80, Me).

Generation of Pd(dppe)(Me)[CH(CN)CH$_2$PHMes*] (18). [Pd(dppe)(Me)(PH_2Mes^*)][BF_4] (**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 μL, 10.6 mmol) was added to the cooled solution via cannula. LiN(SiMe$_3$)$_2$ (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 ^{31}P 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)(CH$_2$CHCN)][OTf] (19). To a white slurry of Pt(dppe)(Me)(Cl) (525 mg, 0.82 mmol) and acrylonitrile (3 mL, 0.05 mol) in CH_2Cl_2 (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 CH_2Cl_2 (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 CH_2Cl_2/petroleum ether at −25 °C gave an off-white oil. The compound decomposes to a mixture of unknown products in $CDCl_3$ after 2 days. ^{1}H NMR ($CDCl_3$): δ 7.62−7.45 (broad m, 20H, Ar), 6.47 (d, $^3J_{HH}$ = 11, 1H, NCCHC*H*$_2$ trans to CN), 6.23 (d, $^3J_{HH}$ = 17, 1H, NCCHC*H*$_2$ cis to CN), 6.03 (dd, $^3J_{HH}$ = 17, 11, 1H, NCC*H*CH$_2$), 2.60−2.27 (m, 4H, dppe CH_2), 0.53 (dd, $^3J_{PH}$ = 7, 3, $^2J_{Pt-H}$ = 50, 3H, Pt−Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.8 (NCCHCH$_2$), 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 (NC*C*HCH$_2$), 30.5 (dd, $^1J_{PC}$ = 44, $^2J_{PC}$ = 16, dppe CH_2), 24.9 (dd, $^1J_{PC}$ = 35, $^2J_{PC}$ = 5, dppe CH_2), 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 PH_2Mes^* (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 $C_{44}H_{55}P_3Pt$: C, 60.61; H, 6.36. Found: C, 59.43; H, 6.43. ^{1}H NMR (C_6D_6): 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). ^{13}C{^{1}H} NMR (C_6D_6): 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 (*C*Me$_3$), 35.3 (broad, *C*Me$_3$), 34.8 (d, J_{PC} = 9, *o*-Me), 32.3 (*p*-Me), 30−29 (m, CH_2).

Pt(dcpe)(PHMes*)(H) (22). To a slurry of Pt(dcpe)Cl_2 (500 mg, 0.73 mmol) in THF (2 mL) was added $LiBHEt_3$ (1.45 mL of 1 M THF solution, 1.45 mmol) followed by a solution of PH_2-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 Et_2O (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 Et_2O. $NaBH(OMe)_3$ can be substituted for $LiBHEt_3$ with similar yields. Anal. Calcd for $C_{44}H_{79}P_3Pt$: C, 59.04; H, 8.78. Found: C, 58.42; H, 9.06. ^{1}H NMR (C_6D_6): 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). ^{13}C{^{1}H} NMR (C_6D_6): δ 152.7 (d, J_{PC} = 8, Ar), 145.8 (Ar), 121.9 (Ar), 39.4 (*p*-C*Me*$_3$), 36.1−34.7 (m, CH_2 + *C*Me$_3$), 32.4 (*o*-*t*-Bu), 29.8−28.9 (m, CH_2), 25.0−24.0 (m, *C*H). The fourth expected Ar peak is not observed.

Low-Temperature Reaction of 22 with CH_2CHCN. 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 CH_2CHCN (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 ^{31}P 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)CH$_2$PHMes*](H) (24a,b). ^{1}H NMR (500 MHz, C_6D_6, 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. ^{1}H NMR (500 MHz, C_6D_6): 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).

PMes$_2$(CH$_2$CH$_2$CN) (23). In the air, acrylonitrile (204 mg, 3.8 mmol) was added to a mixture of $PHMes_2$ (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 $PMes_2(CH_2CH_2CN)$, mp 157 °C. The product was recrystallized again from acetonitrile to yield X-ray-quality crystals. Anal. Calcd for $C_{21}H_{26}NP$: C, 77.99; H, 8.10; N, 4.33. Found: C, 78.11; H, 8.21; N, 4.37. ^{1}H NMR ($CDCl_3$): δ 6.78 (d, $^4J_{PH}$ = 2, 4H, Ar), 2.79 (td, $^3J_{HH}$ = 8, $^2J_{PH}$ = 3, 2H, CH_2CH$_2$CN), 2.25 (12H, *o*-Me), 2.22 (6H, *p*-Me), 2.19 (t, $^3J_{HH}$ = 8, 2H, CH$_2$CH_2-CN). ^{13}C{^{1}H} NMR ($CDCl_3$): 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, CH_2CH_2-CN), 23.3 (d, $^3J_{PC}$ = 14, *o*-Me), 20.9 (*p*-Me), 15.2 (d, $^1J_{PC}$ = 30, *C*H$_2$CH$_2$CN). ^{31}P{^{1}H} NMR ($CDCl_3$): 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(PPh_3)$_2$(CH_2CH_2CN)-(Br) (**A**) and **11**·Et_2O, 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*2$_1$ 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**·Et_2O;[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**·Et_2O 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*(CH$_2$CH$_2$CN)](H) (25). A slurry of Pt-(dcpe)Cl_2 (150 mg, 0.22 mmol) in toluene (15 mL) was treated with 440 μL (0.44 mmol) of a 1 M THF solution of $LiBHEt_3$. The resulting light yellow slurry was stirred for 30 min and then filtered through Celite. The ^{31}P NMR spectrum of the filtrate showed mostly Pt(dcpe)H_2 and a trace of [Pt$_2$-(dcpe)$_2$H$_3$]$^+$. 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 ^{31}P{^{1}H} NMR in toluene) mostly [Pt(dcpe)(H)]$_2$ with traces of Pt(dcpe)H_2 and [Pt$_2$(dcpe)$_2$H$_3$]$^+$. This material was treated with PH(Mes*)(CH_2CH_2CN) (72 mg, 0.22 mmol) in toluene (10 mL) and stirred for 24 h, when ^{31}P NMR showed that **25** had formed, with a trace of [Pt$_2$(dcpe)$_2$H$_3$]$^+$ 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 $C_{47}H_{82}NP_3Pt$: C, 59.47; H, 8.71; N, 1.47. Found: C, 57.42; H, 8.84; N, 1.38. ^{1}H NMR (C_6D_6): δ 7.60 (2H, Ar), 2.06 (18H, *o*-*t*-Bu), 2.22−0.96 (br m, 52H, dcpe + *CH$_2$CH$_2$*CN), 1.41 (9H, *p*-*t*-Bu), −2.41 (d of apparent t, $^2J_{PH}$ = 171, 17, 17, $^1J_{Pt-H}$ = 1006, Pt−H). ^{13}C{^{1}H} NMR (C_6D_6): 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*-*C*Me$_3$), 36.5−35.3 (m, Cy CH), 35.1 (d, $^4J_{PC}$ = 7, *o*-C*Me*$_3$), 34.7 (*p*-*C*Me$_3$), 31.7 (*p*-C*Me*$_3$), 30.2−25.0 (dcpe CH_2), 23.2 (dd, J_{PC} = 21, 14, CH_2 of CH_2CH_2CN), 18.2 (dd, J_{PC} = 26, 11, CH_2 of CH_2CH_2CN).

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

***trans*-Pt(PPh$_3$)$_2$[CH(Me)(CN)](Br) (27).** Pt(PPh$_3$)$_4$ (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 μL (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 $C_{39}H_{34}BrNP_2Pt$: 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. ^{1}H 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 CH_2Cl_2 solution of 260 mg (0.30 mmol) of **27** was added an equimolar amount (129 mg) of dcpe dissolved in 5 mL of CH_2Cl_2. 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 $C_{29}H_{52}NBrP_2Pt$: 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 $C_{29}H_{52}NBrP_2Pt\cdot C_4H_8O$: C, 48.11; H, 7.34; N, 1.70; Br, 9.70. The ^{31}P{^{1}H} 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. ^{1}H 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 $C_{29}H_{53}NP_2Pt$: C, 51.77; H, 7.94; N, 2.08. Found: C, 51.92; H, 7.89; N, 2.05. ^{1}H NMR (C_6D_6): 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). ^{13}C{^{1}H} NMR (C_6D_6): 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, *C*H$_3$CHCN), 30.1−26.1 (m, dcpe CH$_2$), 23.8 (dd, J_{PC} = 26, 15, dcpe CH$_2$), 23.1 (dd, J_{PC} = 24, 15, dcpe CH$_2$), −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 μL of 1.6 M n-BuLi in THF and 167 mg (0.6 mmol) of PH$_2$Mes*). 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 ^{1}H NMR and elemental analysis. Anal. Calcd for $C_{47}H_{82}NP_3Pt\cdot 0.75C_7H_8$: C, 61.62; H, 8.73; N, 1.38. Found: C, 61.56; H, 8.73; N, 1.20. ^{1}H 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). ^{13}C{^{1}H} NMR (THF-d_8, 22 °C): δ 156.0 (dd, J_{PC} = 11, J_{PC} = 3, *o*-Mes*), 154.4 (m, *o*-Mes*), 146.9 (d, J_{PC} = 2, *p*-Mes*), 136.8 (m, *ipso*-Mes*), 133.2 (m, CH(Me)*C*N), 121.5 and 121.1 (overlapping m, *m*-Mes*), 39.6 (br, *o*-*C*Me$_3$), 39.1 (br, *o*-*C*Me$_3$), 37.4−35.8 (m, Cy CH), 35.4 (br, *p*-*C*Me$_3$), 33.9 (d, J_{PC} = 6, *o*-C*Me*$_3$), 33.5 (d, J_{PC} = 10, *o*-C*Me*$_3$), 32.2 (br, *p*−*C*Me$_3$), 31.3−27.0 (m, dcpe CH$_2$), 20.7 (d, $^3J_{PC}$ = 6, CH(*Me*)CN), 1.2 (dd, $^2J_{PC}$ = 84, 5, *C*H(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(PPh$_3$)$_2$(CH$_2$CH$_2$CN)(Br), **11**·Et$_2$O, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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