Notes

Regiochemistry of Platinum-Catalyzed Hydrophosphination of a Diene. Formation of the Chiral Diphosphine $Et_2PCH(CN)CH(CH_2CH_2CN)PEt_2$ via Monophosphine Intermediates

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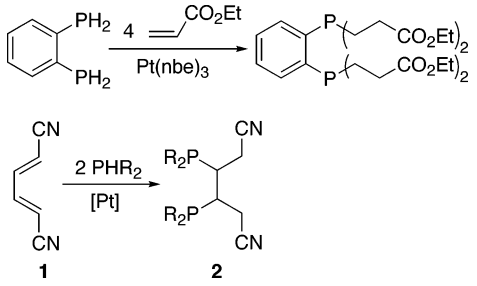
Summary: Pt-catalyzed addition of diethylphosphine to the diene cis,cis-muconononitrile gave the new diphosphine $Et_2PCH(CN)CH(CH_2CH_2CN)PEt_2$ as a 3:2 mixture of diastereomers. Two monophosphine−alkene intermediates in the hydrophosphination were characterized by NMR spectroscopy.

Introduction

Platinum-catalyzed hydrophosphination of unsaturated substrates has been used to synthesize functionalized phosphines for use in homogeneous catalysis.[1] Even chelating diphosphines can be prepared, despite the possibility of catalyst poisoning. For example, Pringle and co-workers reported Pt-catalyzed addition of di-primary phosphines to ethyl acrylate (Scheme 1).[2] An alternative approach to chelate ligands would involve addition of 2 equiv of a secondary phosphine to a diene,[3] such as commercially available muconononitrile (**1**).

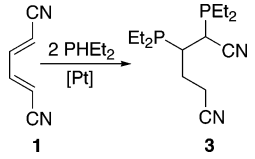
If diene **1** behaved like linked, noninteracting acrylonitriles, hydrophosphination would give diphosphine **2**, analogous to Chiraphos (Scheme 1). This 2,3-regiochemistry was reported for addition of 2 equiv of an amine to analogous muconic esters[4] and for bis-adducts of thiols with muconaldehyde.[5,6] However, anionic polymerization of **1** gave a material derived from nucleophilic attack both β and α to CN; the latter predominated.[7] More generally, the regiochemistry of nucleophilic additions to dienes is sensitive to steric effects and reaction conditions.[8] Addition of P−H bonds to dienes such as **1** has not been reported,[1] and the effect of a catalyst on regioselection is unpredictable. Experimentally, we found that Pt-catalyzed addition of diethylphosphine to **1** yielded a diphosphine regioselectively, but it was not **2**!

Scheme 1. Two Routes to Bidentate Diphosphines via Hydrophosphination: Addition of a Di-Primary Phosphine to an Alkene (Known) or Addition of Two Secondary Phosphines to a Diene (Unknown)[a]



[a] Legend: nbe = norbornene, [Pt] = Pt(0) catalyst.

Scheme 2[a]



[a] Legend: [Pt] = Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (2.5 mol %).

Results and Discussion

Hydrophosphination of muconononitrile with diethylphosphine (2 equiv) using the catalyst precursor Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene)[9] gave the unsymmetrical diphosphine **3** (as a 3:2 mixture of diastereomers in ca. 90% purity) in 77% yield (Scheme 2). No reaction occurred in the absence of the Pt catalyst.

Although diphosphine **3** could not be isolated in pure form, it was characterized spectroscopically.[10] Each diastereomer gave

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(6) Soft carbon nucleophiles formed monoadducts with diethylmuconate by attack at the 2-position, but subsequent isomerization gave a mixture of products. See ref 8, p 648, and references therein.

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Scheme 3

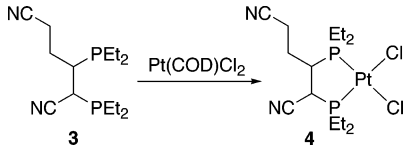
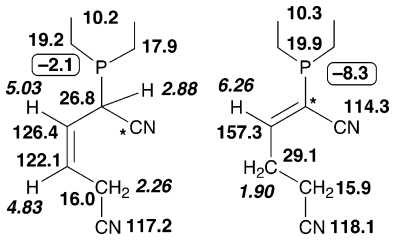


Chart 1. Intermediates in the Formation of Diphosphine 3, with Selected Multinuclear NMR Data[a]



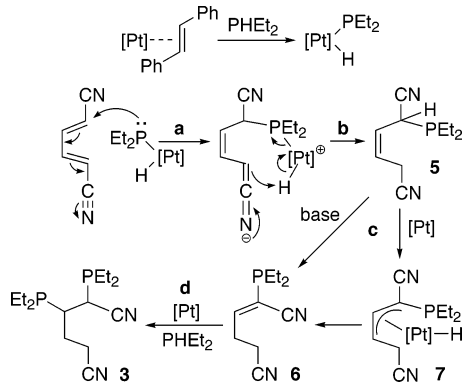
[a] Legend for NMR chemical shifts: in the box, ^{31}P; boldface type, ^{13}C; italic type, ^{1}H. The solvent was C_6D_6. An asterisk indicates ^{13}C nuclei for which assignments were not possible. *E*/*Z* isomerism is possible in phosphines **5** and **6** (see the Experimental Section for NMR data), and these structures were drawn arbitrarily.

rise to a pair of doublets in the ^{31}P NMR spectrum, with significantly different J_{PP} values (13 and 44 Hz). The inequivalent cyano groups were observed by IR (CH_2Cl_2, 2248 and 2224 cm^{-1}) and ^{13}C NMR spectroscopy (C_6D_6, four peaks between δ 118.9 and 118.1). The ^{13}C NMR spectrum also contained signals for four inequivalent Et groups, two CH carbons, with distinctive P−C coupling, and one cyanoethyl group per isomer. Reaction of impure **3**, a viscous oil, with Pt(COD)Cl_2 (COD = cyclooctadiene) gave Pt(Muconophos)Cl_2 (**4**) as white crystals which could be isolated in analytically pure form (Scheme 3). The ^{31}P NMR spectrum of **4** (CD_2Cl_2, diastereomer **a**, AB quartet, δ 62.2 (d, J = 8 Hz, J_{Pt-P} = 3412 Hz), 61.3 (d, J = 8 Hz, J_{Pt-P} = 3563 Hz); diastereomer **b**, AB quartet, δ 67.0 (d, J = 6 Hz, J_{Pt-P} = 3485 Hz), 61.1 (d, J = 6 Hz, J_{Pt-P} = 3585 Hz)) showed chemical shifts and coupling constants similar to those reported for Pt(depe)Cl_2 (depe = $Et_2PCH_2CH_2PEt_2$; in $CDCl_3$, δ 57.5 (J_{Pt-P} = 3546 Hz)),[11] consistent with the proposed structure of ligand **3**.

How does diphosphine **3** form? According to monitoring by ^{31}P NMR spectroscopy, a multistep reaction occurred. Initially, phosphine **5** (δ −2.1, C_6D_6) was formed; it was soon partially replaced by a longer-lived intermediate (**6**, δ −8.3) (Chart 1). Neither could be isolated because conversion from the starting materials was incomplete, and formation of product **3** and other unidentified compounds was also observed, but both intermediates were identified (Chart 1) by ^{1}H and ^{13}C NMR spectra of the reaction mixtures and by mass spectroscopy of the mixture. The results were similar with 2:1 or 1:1 PEt_2H/muconononitrile mixtures; the latter was convenient to maximize the concentrations of the intermediates.

These intermediates displayed characteristic multiplet ^{1}H NMR signals for the alkene protons, with accompanying ^{13}C NMR resonances.[12] The presence of a chiral center in **5** rendered the P−Et groups and the CH_2CN protons diastereotopic,

Scheme 4[a]



[a] Legend: [Pt] = Pt((*R*,*R*)-Me-Duphos).

although this effect was only observed directly for the P−CH_2 ^{13}C NMR signals. In contrast, spectra of phosphine **6** were simplified by its higher symmetry.

On the basis of this information, a potential mechanism for formation of diphosphine **3** is shown in Scheme 4. P−H oxidative addition is generally accepted as the first step in Pt-catalyzed hydrophosphination.[1] In this case, treatment of Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) with an excess of diethylphosphine gave a mixture of Pt((*R*,*R*)-Me-Duphos)$(PEt_2H)_2$ and the phosphido hydride Pt((*R*,*R*)-Me-Duphos)(PEt_2)(H). We have recently proposed a new mechanism for P−C bond formation in Pt-catalyzed hydrophosphination, based on Michael addition of the nucleophilic Pt−PR_2 group to the activated alkene.[13] With muconononitrile, after attack at the cyano-bearing carbon, charge may be delocalized to the other CN group (step **a**).[8,14] Proton transfer from Pt then yields alkene **5** (step **b**).

Isomerization of **5** to **6**, which was observed, might occur by two different pathways (step **c**). Complexation of Pt to the double bond and C−H activation of the α-cyano proton would then give the allyl hydride complex **7**. Isomerization[15] would afford alkene **6**. Alternatively, base-catalyzed isomerization might occur by deprotonation of the acidic CH(CN)(PEt_2) proton in **5**, with diethylphosphine or the other phosphines formed acting as a base.[16] Further hydrophosphination of **6**, now with the "usual" regiochemistry, would yield the observed product, diphosphine **3** (step **d**).[17]

Conclusion

Pt-catalyzed hydrophosphination of a diene provided a selective route to a chiral diphosphine as a result of a novel

(10) Since diphosphine **3** was not obtained pure, we could not accurately assess its enantiomeric excess (ee). We observed, however, that the catalyst precursor Pt(dcpe)(CH_2=CH(CN)) (dcpe = $Cy_2PCH_2CH_2PCy_2$, Cy = cyclohexyl[13c]) also gave **3** in a 3:2 diastereomeric ratio; displacement of Me-Duphos during the reaction is plausible, or the product ratio may be under thermodynamic control.[16]

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(12) For ^{13}C NMR data for an analogous cyano-substituted vinylphosphine oxide, see: Kostyuk, A. N.; Svyaschenko, Y. V.; Volochnyuk, D. M.; Lysenko, N. V.; Tolmachev, A. A.; Pinchuk, A. M. *Tetrahedron Lett.* **2003**, *44*, 6487−6491. See also: Odinets, I. L.; Artyushin, O. I.; Kalyanova, R. M.; Matveeva, A. G.; Petrovskii, P. V.; Lysenko, K. A.; Antipin, M. Y.; Mastryukova, T. A.; Kabachnik, M. I. *Russ. J. Gen. Chem.* **1997**, *67*, 862−871.

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(16) Similarly, reversible deprotonation of the CH(CN)(PEt_2) group in diphosphine **3** could result in racemization of this stereocenter to yield a thermodynamic mixture of diastereomers.[10]

1,2-addition. On the basis of observation of monophosphine intermediates **5** and **6**, we propose the mechanism in Scheme 4. Further investigation of P−C bond formation in related systems may result in rational syntheses of unsymmetrical diphosphines such as **3**.

Experimental Section

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, toluene, and CH_2Cl_2 were dried using columns of activated alumina.[18] Deuterated solvents used for NMR spectroscopy were dried over molecular sieves and degassed. NMR spectra were recorded using Varian 300 or 500 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz, as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. IR spectra are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Mass spectra were recorded at the University of Illinois Urbana-Champaign. Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature procedures: Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene)[19] and $Pt(COD)Cl_2$.[20]

Synthesis of the Diphosphine $Et_2PCH(CN)CH(CH_2CH_2CN)$-$PEt_2$ (3, Muconophos). Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (16.4 mg, 0.024 mmol, 2.5 mol %) was dissolved in ca. 1 mL of toluene, and the orange solution was treated with 220 μL (1.92 mmol) of PEt_2H. The orange solution turned to wine red after addition of 100 mg (0.96 mmol) of *cis*,*cis*-muconononitrile in 10 mL of toluene. The mixture was stirred for 2 h (a brown-red solid precipitated), and then it was left to stand at room temperature for 1 week. The orange solution, which contained brown-red solid, was filtered through Celite, and the orange filtrate was passed down a column of silica gel. The toluene was removed under reduced pressure. The viscous orange residue was suspended in ether, and the suspension was again passed through silica gel. Evaporation of the solvent provided 210 mg (0.74 mmol, 77% yield) of a viscous pale yellow oil of the diphosphine in ca. 90% purity. Alternatively, a simpler workup procedure gave comparable results. The reaction mixture was pumped down under vacuum, and the resulting residue was extracted with a 7:3 petroleum ether−THF mixture and loaded onto a silica column (5 cm height, 0.6 cm diameter). The phosphine product was obtained by elution with this solvent mixture; the catalyst did not elute.

The following NMR spectra are reported as a mixture of diastereomers **a** and **b** (in the ratio 3:2) unless otherwise indicated. $^{31}P\{^1H\}$ NMR (C_6D_6): diastereomer **a**, AB quartet, δ −4.0 (d, J = 13), −4.6 (d, J = 13); diastereomer **b**, AB quartet, δ −7.4 (d, J = 44), −9.3 (d, J = 44). ^1H NMR (C_6D_6): δ 2.59 (dd, 1H of **a**, J_{PH} = 6.0, J_{HH} = 3.0), 2.44 (ddd, 1H of **b**, J_{PH} = 17.7, J_{PH} = 1.5, J_{HH} = 6.3), 2.12−2.02 (m, 2H of **a**), 1.96−0.70 (m, 23H of **a** + 25H of **b**). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 118.9 (CN of **a**), 118.6 (CN of **b**), 118.4 (dd, J = 4, 2, CN of **a**), 118.1 (dd, J = 4, 2, CN of **b**), 34.2 (dd, J = 23, 16, CH of **b**), 32.5 (dd, J = 25, 12, CH of **a**), 29.9 (dd, J = 33, 15, CH of **b**), 29.3 (dd, J = 31, 9, CH of **a**), 26.2 (dd, J = 11, 5, CH_2 of **a**), 25.7 (dd, J = 10, 4, CH_2 of **b**); the following 10 resonances are due to cyanoethyl and P−CH_2 groups, 18.9 (dd, J = 17, 7), 18.6 (dd, J = 16, 2), 18.1 (d, J = 19), 17.9 (d, J = 18), 17.3 (dd, J = 15, 2), 16.6 (dd, J = 11, 5), 16.5 (dd, J = 13, 1), 16.4 (dd, J = 12, 1), 15.9 (dd, J = 16, 2), 15.7 (dd, J = 5, 2); the following 8 resonances are due to P−Et *Me* carbons, 10.8 (d, J = 19), 10.6 (d, J = 17), 10.5 (d, J = 18), 10.3 (d, J = 16), 10.0 (dd, J = 18, 1), 9.7 (d, J = 15), 9.4 (d, J = 15), 9.2 (d, J = 13). IR (CH_2Cl_2): 2966, 2935, 2908, 2877, 2248, 2224, 1497, 1455, 1424, 1381. The protonated bis-phosphine oxide was observed by mass spectroscopy. HRMS (*m*/*z*): calcd for $C_{14}H_{27}N_2O_2P_2^+$ (MO_2H^+), 317.1548; found, 317.1536.

Synthesis of Pt(Muconophos)Cl_2 (4). The diphosphine **3** (210 mg, 0.74 mmol) was dissolved in 6 mL of CH_2Cl_2. Four milliliters of this solution (0.49 mmol) was treated with a CH_2Cl_2 solution (10 mL) of 120 mg (0.32 mmol) of $Pt(COD)Cl_2$. The solution was stirred for 1 h and then concentrated by partial removal (to ca. 3 mL) of CH_2Cl_2 and cooled to −30 °C. After one night, a white solid crystallized; this was isolated, washed twice with ca. 0.5 mL of petroleum ether, and finally dried in vacuo (yield 80 mg, 45%). The sample consisted of the two diastereomers **a** and **b** in the ratio 4:1.

Anal. Calcd for $C_{14}H_{26}N_2Cl_2P_2Pt$: C, 30.56; H, 4.76. Found: C, 30.68; H, 4.89. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): diastereomer **a**, AB quartet, δ 62.2 (d, J = 8, J_{Pt-P} = 3412), 61.3 (d, J = 8, J_{Pt-P} = 3563); diastereomer **b**, AB quartet, δ 67.0 (d, J = 6, J_{Pt-P} = 3485), 61.1 (d, J = 6, J_{Pt-P} = 3585). ^1H NMR (CD_2Cl_2): δ 3.07−1.80 (m, 14 H, 4 CH_2 + 2 CH + 8 P−CH_2), 1.47−1.26 (m, 12H, P−CH_2CH_3). IR (KBr): 2971, 2937, 2908, 2877, 2245−2216 (broad), 1453, 1408, 1381, 1265, 1248, 1190, 1156, 1050, 1022, 903, 762, 701, 677, 663, 557, 506.

Catalytic Hydrophosphination of *cis*,*cis*-Muconononitrile with $PHEt_2$. Generation of $(PEt_2)(CN)CHCH{=}CHCH_2CN$ (5) and $(PEt_2)(CN)C{=}CHCH_2CH_2CN$ (6). To Pt((*R*,*R*)-Me-Duphos)-(*trans*-stilbene) (17 mg, 0.025 mmol) as the catalyst precursor (5 mol %) in THF (0.5 mL) was added $PHEt_2$ (45.2 mg, 0.5 mmol) via microliter syringe. The solution turned dark orange. The mixture was added to a solution of *cis*,*cis*-muconononitrile (52 mg, 0.5 mmol) in THF (0.5 mL). This mixture turned dark red immediately, and formation of a red precipitate was observed. The reaction mixture was transferred to an NMR tube and monitored by ^{31}P NMR spectroscopy. After 15 h two major monophosphine species, **5** and **6**, were observed at δ −2.1 ppm (**5**) and −8.6 ppm (**6**) (ratio **5**:**6** = 2.1:1, 66% of the mixture). Peaks belonging to the diastereomeric diphosphines **3** (ratio **a**:**b** = 1.6:1, 15% of the mixture) could be observed at δ −6.6 (d, J = 15, **a**), −6.9 (d, J = 15, **a**), −8.8 (d, J = 44, **b**), −11.2 (d, J = 44, **b**). Other peaks were observed at δ −8.0, −10.2, −10.7, −13.7, −17.2, −32.1, and −34.1 ($PHEt_2$).

The catalyst was removed from the reaction mixture on a silica column (5 cm height, 0.6 cm diameter), using a 7:3 petroleum ether−THF mixture as eluent. The catalyst did not elute. A 66 mg portion (68% yield) of a colorless oil was obtained. The solvent was removed under vacuum, and the color of the viscous residue turned to light orange after a few minutes. The residue was dissolved in C_6D_6 for further spectroscopic characterization. Two major products, the isomeric monophosphines **5** and **6** (∼57% of the mixture), were observed in the ratio ∼1.5:1. The two diastereomeric diphosphines **3** were observed in the ratio **a**:**b** = 1.3:1 (24% of the mixture). Other peaks were observed at δ −8.2, −10.5, −10.7, −12.6, −18.0, −32.3, and −34.1 ($PHEt_2$). After 6 h, the ratio **5**:**6** changed to 1.4:1, and further isomerization occurred over time. After 5 days, the ratio became 1:5.2, and after 6 days, 1:8.6.

Mass spectroscopic analysis of the mixture showed the presence of the monophosphines **5** and **6**, as well as the diphosphine **3**.

(17) A similar mechanism, involving initial 1,6-addition (by nucleophilic attack at the terminal CH_2), base-catalyzed isomerization to the conjugated alkene, and 1,4-addition, was proposed for the addition of 2 equiv of a secondary amine to 2,4-pentadienenitrile (1-cyano-1,3-butadiene) to give 2,4-diaminopentane-1-nitrile. See: (a) Frankel, M.; Mosher, H. S.; Whitmore, F. C. *J. Am. Chem. Soc.* **1950**, *72*, 81−83. (b) Stewart, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 3228−3230.

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HRMS (*m*/*z*): calcd for $C_{10}H_{16}N_2P^+$ (MH^+, monophosphines **5** and **6**), 195.1051; found, 195.1054. HRMS (*m*/*z*): calcd for $C_{14}H_{27}N_2P_2$ (MH^+, diphosphine **3**), 285.1649; found, 285.1649. The protonated mono-oxide of **3** was also observed. HRMS (*m*/*z*): calcd for $C_{14}H_{27}N_2OP_2^+$, 301.1599; found, 301.1588.

NMR analysis of the mixture enabled assignment of most of the resonances due to **5** and **6** (see Chart 1). These compounds were observed as mixtures of *E* and *Z* isomers (**a** (major) and **b** (minor)), and data are reported for the mixture unless otherwise indicated.

(PEt_2)(CN)CHCH═CHCH_2CN (5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.1. Selected ^1H NMR (C_6D_6): δ 5.35−5.29 (m, 1H, **b**), 5.21−5.14 (m, 1H, **b**), 5.06−5.00 (m, $J_{PH} = 4$, $J_{HH} = 11, 9, 1.5, 1.5$, 1H, CH vinyl), 4.87−4.80 (m, $J_{PH} = 4$, $J_{HH} = 11, 7, 6.5, 1$, 1H, CH vinyl), 2.88 (broad dd, $J_{PH} = 3$, $J_{HH} = 9$, 1H, CHCN), 2.26 (dd, $J_{HH} = 7, 2$, 2H, CH_2), 0.80 (m, $J_{PH} = 16$, 6H, CH_3). $^1H\{^{31}P\}$ NMR (C_6D_6): δ 5.35−5.29 (m, 1H, **b**), 5.21−5.14 (m, 1H, **b**), 5.03 (m, $J = 11, 9, 1.5, 1.5$, 1H, CH vinyl), 4.83 (m, $J = 11, 7, 6.5, 1$, 1H, CH vinyl), 2.88 (d, $J = 9$, 1H, CHCN), 2.26 (dd, $J = 7, 2$, 2H, CH_2), 0.80 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.5 (d, $J =$ 12, CH vinyl, **b**), 126.4 (d, $J = 7$, CH vinyl, **a**), 122.1 (d, $J = 6$, CH vinyl, **a**), 121.9 (d, $J = 8$, CH vinyl, **b**), 117.2 (*C*N), 26.8 (d, $J = 31$, CH), 19.2 (d, $J = 18$, *C*H_2CH_3, **a**), 19.1 (d, $J = 16$, *C*H_2-CH_3, **b**), 17.9 (d, $J = 17$, *C*H_2CH_3, **a**), 17.5 (d, $J = 17$, *C*H_2CH_3, **b**), 16.0 (d, $J = 4$, *C*H_2CN), 10.2 (d, $J = 15$, CH_3, **a**), 10.0 (d, $J =$ 16, CH_3, **b**). The ratio **a**:**b** (estimated from the ^1H and $^{13}C\{^1H\}$ NMR spectra) was ca. 3:1.

(PEt_2)(CN)C═CHCH_2CH_2CN (6). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −8.3. Selected ^1H NMR (C_6D_6): δ 6.26 (dt, $J_{PH} = 11$, $J_{HH} = 8$, 1H, CH vinyl, **a**), 6.21 (dt, $J_{PH} = 16$, $J_{HH} = 8$, 1H, CH vinyl, **b**), 1.90 (apparent q, $J = 7$, 2H, *C*H_2CH_2CN), 0.88 (dtd, $J_{PH} = 16$, $J_{HH} = 8, 1$, 6H, CH_3). $^1H\{^{31}P\}$ NMR (C_6D_6): δ 6.26 (t, $J = 8$, 1H, CH vinyl, **a**), 6.21 (t, $J = 8$, 1H, CH vinyl, **b**), 1.90 (apparent q, $J = 7$, 2H, *C*H_2CH_2CN), 0.88 (td, $J = 8, 1$, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.3 (d, $J = 41$, CH vinyl, **a**), 118.1 (CN), 114.3 (d, $J = 6$, CN), 29.1 (d, $J = 10$, CH_2), 19.9 (d, $J = 11$, *C*H_2CH_3, **a**), 19.7 (d, $J = 11$, *C*H_2CH_3, **b**), 15.9 (*C*H_2CN), 10.3 (d, $J = 15$, CH_3). The ratio **a**:**b** (estimated from the $^1H\{^{31}P\}$ NMR spectrum) was 6:1.

Stoichiometric Reaction of Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) with $PHEt_2$. Generation of Pt((*R*,*R*)-Me-Duphos)(H)(PEt_2) and Pt((*R*,*R*)-Me-Duphos)($PHEt_2$)$_2$. To an orange solution of Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (34 mg, 0.05 mmol) in toluene-d_8 (0.2 mL) was added $PHEt_2$ (4.5 mg, 0.05 mmol) in toluene-d_8 (0.3 mL) via microliter syringe. The solution turned dark red. The following species could be observed in the $^{31}P\{^1H\}$ NMR spectrum: unreacted Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (as a mixture of two diastereomers), Pt((*R*,*R*)-Me-Duphos)(H)(PEt_2), and Pt((*R*,*R*)-Me-Duphos)($PHEt_2$)$_2$. The ratio of the bis-phosphine complex to the phosphido hydride was ca. 5:1.

Pt((*R*,*R*)-Me-Duphos)(H)(PEt_2). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 79.1 (dd, $J = 108, 9$, $J_{Pt-P} = 1602$), 71.3 (dd, $J = 9, 5$, $J_{Pt-P} \sim$ 1860), −6.4 (dd, $J = 108, 5$, $J_{Pt-P} = 905$).

Pt((*R*,*R*)-Me-Duphos)($PHEt_2$)$_2$. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 45.3 (apparent t with additional fine structure on the central peak, $J = 50$, $J_{Pt-P} = 3430$), −35.9 (apparent t with additional fine structure on the central peak, $J = 50$, $J_{Pt-P} = 3867$).

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