Platinum-Catalyzed Acrylonitrile Hydrophosphination via Olefin Insertion into a Pt−P Bond

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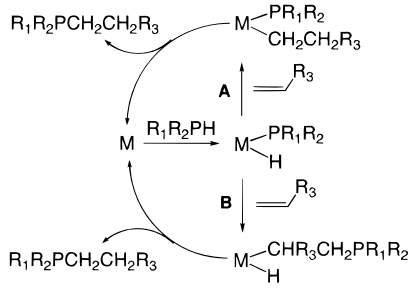
Catalytic addition of P−H bonds to unsaturated substrates mediated by platinum group metal complexes offers a regiocontrolled way to prepare biologically active substances and useful ligands for homogeneous catalysis.[1] Further rational development of these reactions requires mechanistic understanding, which so far is limited; Scheme 1 shows possible mechanisms for an olefin substrate as an example. After oxidative addition of the P−H bond,[2] it is not known whether catalytic P−C bond formation occurs by reductive elimination[3] (path A) after insertion of the unsaturated substrate into the M−H bond or by insertion into the M−P bond[4] (path B), followed by C−H reductive elimination. We report evidence for the latter pathway in Pt-catalyzed hydrophosphination of acrylonitrile and direct observation of both proposed P−C bond-forming steps in model systems.

The complex Pt(dppe)(CH_2CHCN) (**1**) catalyzes hydrophosphination of acrylonitrile with PH_2Mes^*, which yields $PHMes^*(CH_2CH_2CN)$ (**2**) (dppe = $Ph_2PCH_2CH_2PPh_2$, Mes* = 2,4,6-(t-Bu)$_3C_6H_2$, Scheme 2). The reaction proceeds slowly (10 mol % **1**, THF, 55 °C, one turnover per 24 h), and no intermediates are observed by ^{31}P NMR during catalysis. However, oxidative addition of P−H bonds to the catalyst precursor Pt(dppe)(*trans*-stilbene) (**3**) generates the phosphido hydride complexes Pt(dppe)(PR_1R_2)H [$R_1 = R_2$ = Mes (**4**); R_1 = H, R_2 = Mes* (**5**), Mes = 2,4,6-$Me_3C_6H_2$]. Treatment of these hydrides with 2 equiv of acrylonitrile affords the phosphines $PMes_2CH_2CH_2CN$ (**6**) and **2**, respectively, and Pt complex **1**.

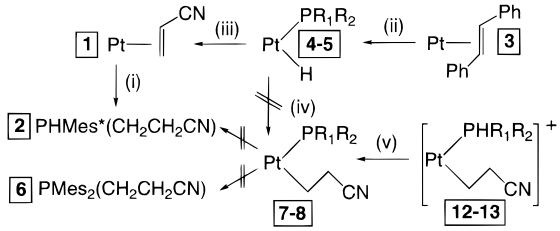
The putative intermediates in this transformation, Pt(dppe)(PR_1R_2)CH_2CH_2CN [$R_1 = R_2$ = Mes (**7**); R_1 = H, R_2 = Mes* (**8**)] were prepared by deprotonation of the cationic phosphine complex precursors **12** and **13**,[5] while the analogous methyl compounds M(dppe)(PR_1R_2)Me [$R_1 = R_2$ = Mes, M = Pt (**9**); R_1 = H, R_2 = Mes*, M = Pt (**10**), Pd (**11**)] could be synthesized by this method from **14** and **15** or by direct proton transfer to a Pt−OMe group (Scheme 3).[6] The Pt phosphido alkyls **7**−**10** are readily isolated and stable to reductive elimination in solution, even on heating; as expected from these observations, complexes **7** and **8** are inactive in catalytic hydrophosphination. In contrast, Pd complex **11** must be generated at −78 °C, since it decomposes at room temperature to yield PH(Me)Mes*.[7] In the absence of trapping reagents, the Pd products are Pd(dppe)$_2$ and Pd(0); adding dppe avoids this disproportionation and gives only Pd(dppe)$_2$ (Scheme 3).[8]

These results suggest that catalysis operates by insertion of acrylonitrile into the Pt−P bond of phosphido hydride **5**, followed by C−H reductive elimination from an unobserved

Scheme 1

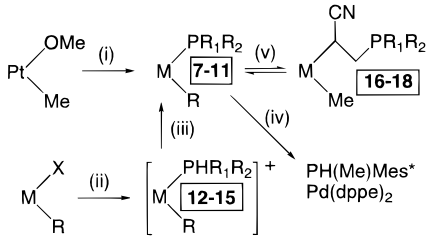


Scheme 2[a] Platinum Phosphido Hydrides and Alkyls in Catalytic Acrylonitrile Hydrophosphination



[a] Pt = Pt(dppe), $R_1 = R_2$ = Mes (**4**, **7**, **12**); R_1 = H, R_2 = Mes* (**5**, **8**, **13**). Reagents: (i) CH_2CHCN, PH_2Mes^*, catalytic in Pt; (ii) PHR_1R_2, −stilbene; (iii) $2CH_2CHCN$, $-PR_1R_2CH_2CH_2CN$ (**2**, **6**); (iv) CH_2CHCN; (v) $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$.

Scheme 3[a] Synthesis and P−C Bond-Forming Reactions of Platinum and Palladium Phosphido Alkyl Complexes



[a] M = Pt(dppe), except M = Pd(dppe) for **11**, **15**, and **18**, X = halide. $R_1 = R_2$ = Mes: R = Me (**9**, **16**), R = CH_2CH_2CN (**7**, **12**). R_1 = H, R_2 = Mes*: R = Me (**10**, **11**, **14**, **15**, **17**, **18**), R = CH_2CH_2CN (**8**, **13**). Reagents: (i) PHR_1R_2, −MeOH; (ii) $AgBF_4$, PHR_1R_2; (iii) $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$; (iv) dppe; (v) CH_2CHCN.

(1) (a) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701−1702. (b) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, *74*, 269−74. (c) Pringle, P. G.; Brewin, D.; Smith, M. B.; Worboys, K. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Kluwer: Dordrecht, 1995; Vol. 5, pp 111−122. (d) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259−3261. (e) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571−1572. (f) Nagel, U.; Rieger, B.; Bublewitz, A. *J. Organomet. Chem.* **1989**, *370*, 223−239. See also: (g) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000−7001. For lanthanide-catalyzed reactions, see: Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simoes, J. A., Ed.; Kluwer: Dordrecht, 1992; pp 35−51.

(2) For examples, see: (a) Ebsworth, E. A. V.; Gould, R. O.; Mayo, R. A.; Walkinshaw, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2831−2838. (b) Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* **1990**, *9*, 387−393. (c) Reference 1e.

(3) See refs 1a−c. For previous examples of P−C reductive elimination, see: (a) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519−1521. (b) Fryzuk, M. D.; Joshi, K.; Chadha, R. K.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 8724−8736.

(4) For insertion of alkynes,[4a,b] CO,[4c] CO_2,[4d] diazoalkanes,[4e] isonitriles,[4f] and carbodiimides[4f] into M−P bonds, see: (a) Barnett, B. L.; Krueger, C. *Cryst. Struct. Commun.* **1973**, *2*, 347−354. (b) Hey-Hawkins, E.; Lindenberg, F. *Chem. Ber.* **1992**, *125*, 1815−1819. (c) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670−4678. (d) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1987**, *26*, 3087−3088. (e) Hey, E.; Muller, U. *Z. Naturforsch. B* **1989**, *44*, 1538−1544. (f) Lindenberg, F.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **1996**, *15*, 1459−1464.

(5) Prepared (Scheme 3) from the precursor Pt(dppe)(CH_2CH_2CN)Br, which was synthesized from **3** and $BrCH_2CH_2CN$.

(6) The thermodynamics of the reactions with Pt(dppe)Me(OMe) (see: Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 1441−52) are under investigation (Wicht, D. K.; Paisner, S. N.; Glueck, D. S.; Li, C.; Nolan, S. P. Unpublished results).

(7) See: Brauer, D. J.; Bitterer, F.; Dorrenbach, F.; Hessler, G.; Stelzer, O.; Kruger, C.; Lutz, F. *Z. Naturforsch. B* **1996**, *51*, 1183−1196 and ref 5b therein.

(8) Such apparent reductive eliminations from Pd(II) phosphido alkyl complexes, which have been previously proposed to occur in Pd-catalyzed P−C coupling reactions (see for example: Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748−753), appear to be general. Details and related mechanistic studies will be reported separately.

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alkyl hydride intermediate (path B above). In support of this hypothesis, the phosphido alkyls **9**−**11** undergo regiospecific insertion of acrylonitrile into the M−P bonds to give M(dppe)-[CH(CN)$CH_2PR_1R_2$]Me [$R_1 = R_2$ = Mes, M = Pt (**16**); R_1 = H, R_2 = Mes*, M = Pt (**17**), Pd (**18**)] (Scheme 3). Platinum complexes **16** and **17** were isolated as stable pale yellow solids, while Pd complex **18** decomposes on attempted workup. For **10** and **11**, which contain a chiral phosphido group, the insertion is diastereoselective; **17** and **18** exist as ∼2:1 mixtures of diastereomers. This is probably a thermodynamic ratio, since insertion is reversible. Isolated, acrylonitrile-free **16** and **17** de-insert acrylonitrile slowly in THF solution to reach an equilibrium with **9** and **10**, while **18**, generated in solution, decomposes to PH(Me)Mes*, via phosphido complex **11**.[9]

In conclusion, our results suggest that, in this system, Pt-catalyzed acrylonitrile hydrophosphination proceeds by selective insertion into the M−P bond in preference to the M−H bond.[10] However, the observed P−C bond formation from a palladium phosphido alkyl suggests that path A may also be important in Pd-catalyzed additions of P−H bonds to unsaturated substrates. The effects of metal, ancillary ligands, and substrates on these and related catalyses are currently under investigation.

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Supporting Information Available: Analytical and spectroscopic data for complexes **1**−**18** (9 pages). See any current masthead page for ordering and Internet access instructions.

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(9) These equilibria lie to the right, favoring insertion. Decomposition during the long reaction times required to reach equilibrium prevented precise measurement of $K_{eq.}$

(10) Related pathways are possible in metal-catalyzed hydroamination and hydroxylation of unsaturated substrates. (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750−4761. (b) Bennett, M. A.; Jin, H.; Li, S.; Rendina, L. M.; Willis, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 8335−8340.