P−C and C−C Bond Formation by Michael Addition in Platinum-Catalyzed Hydrophosphination and in the Stoichiometric Reactions of Platinum Phosphido Complexes with Activated Alkenes

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We recently proposed a new mechanism for platinum-catalyzed hydrophosphination of activated alkenes, in which nucleophilic attack of a phosphido ligand in the intermediate hydride complex Pt(diphos)(PR_2)(H) (**1**) on the alkene $H_2C{=}CH(X)$ (X = CN or CO_2R) gave the zwitterion Pt(diphos)(H)(PR_2CH_2CHX) (**2**), containing a cationic Pt center and a phosphine ligand with a pendent stabilized carbanion. Subsequent C−H bond formation involving the Pt−H and the carbanion would yield the product $R_2PCH_2CH_2X$ (**3**) and regenerate the catalyst, while attack of the carbanion on another alkene would yield byproducts derived from more than one alkene, such as $R_2P(CH_2CH(X))_nCH_2CH_2X$ (**7**). Several tests of this mechanism and related pathways for product and byproduct formation were investigated. Attempts to trap the proposed carbanion with another electrophile led to the development of a Pt-catalyzed three-component coupling of secondary phosphines, *tert*-butyl acrylate, and benzaldehyde, yielding the functionalized phosphines $R_2PCH_2CH(CO_2t\text{-Bu})(CHPh(OH))$ (R_2P = Ph_2P (**10a**); R_2P = Me(Is)P (**10b**, Is = 2,4,6-(i-Pr)$_3C_6H_2$)). Reactions of the complexes Pt(diphos)(R′)(PR_2) (diphos = (*R*,*R*)-Me-Duphos, R′ = Me, PR_2 = PPh_2 (**11**), PPh(i-Bu) (**12**); R′ = Ph, PR_2 = PMeIs (**13**); diphos = dppe, R′ = Me, PR_2 = PPh_2 (**14**), PPh(i-Bu) (**15**)), models for **1**, with *tert*-butyl acrylate or acrylonitrile gave mixtures of products including Pt(diphos)(R′)($CH(X)CH_2PR_2$) (**A**, X = CO_2t-Bu or CN), Pt(diphos)(R′)($CH(X)CH_2CH(X)CH_2PR_2$) (**B**), $R_2PCH_2CH_2X$ (**3**), $R_2P(CH_2CH(X))_n(CH_2CH_2X)$ (**7**), and, in some cases, the dinuclear phosphido-bridged cations $[(Pt(diphos)(Me))_2(\mu\text{-}PR_2)]^+$ (**17**). When *tert*-butanol or water was added to these reactions, more of the phosphines **3** and **7**, and less of the intermediates **A** and **B**, were formed. Decomposition of **A** and **B** gave unidentified platinum dialkyls (**C**), tentatively formulated as Pt(diphos)(R′)(CH(X)R″). The complex Pt(dppe)(Me)($CH(Me)CO_2t$-Bu) (**21**), a model for **A**, **B**, and **C**, was generated either from Pt(dppe)(Cl)($CH(Me)CO_2t$-Bu) (**20**) and $ZnMe_2$ or from Pt(dppe)(Me)(Cl) (**19**) and ZnBr($CH(Me)CO_2t$-Bu)·THF; complexes **20** and **21** did not react with *tert*-butyl acrylate. These observations are consistent with the proposed nucleophilic mechanism for P−C and C−C bond formation.

Introduction

Recently, we proposed a new mechanism for Pt-catalyzed hydrophosphination of activated alkenes (Scheme 1).[1] P−H oxidative addition to yield hydride **1** followed by attack of the nucleophilic phosphido group at the alkene would give zwitterion **2**, which might form phosphine **3** via two complementary pathways. Carbanion attack at the cationic platinum hydride would yield **3**, complexed to Pt(0). Subsequent displacement of **3** by a secondary phosphine, followed by oxidative addition, would regenerate **1**. Alternatively, carbanion attack at platinum, along with Pt−P dissociation, could generate alkyl hydride **4**, perhaps via five-coordinate **5**. The intermediates **4**, which might also form from **1** by coordination/migratory insertion, have been observed in stoichiometric reactions; they decomposed, presumably by C−H reductive elimination, to yield **3**.[2]

Carbanion attack on additional alkene, as in anionic polymerization, might also occur (**2** → **6**, Scheme 2). C−H bond formation via **6** or its neutral isomer **8** would then yield phosphines derived from more than one alkene (**7**), which are commonly observed as byproducts in such reactions.[3] Alternatively, **7** could be formed by single or repeated alkene insertion into the Pt−C bond of **4**, followed by reductive elimination from **8**.[4]

We hypothesized that protonation of zwitterion **2** with a weak acid HY would yield cationic phosphine complex **9**. Pt−H deprotonation by the conjugate base Y^- would yield **3** and regenerate **1** (Scheme 3). If intermediate **2** reacted more quickly with acid than with the alkene, then adding HY might suppress

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(1) Scriban, C.; Kovacik, I.; Glueck, D. S. *Organometallics* **2005**, *24*, 4871−4874.

(2) (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (b) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381−5394. (c) Kovacik, I.; Wicht, D. K.; Grewal, N. S.; Glueck, D. S.; Incarvito, C. D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2000**, *19*, 950−953.

(3) Wicht, D. K.; Glueck, D. S. Hydrophosphination and Related Reactions. In *Catalytic Heterofunctionalization. From Hydroamination to Hydrozirconation*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; pp 143−170.

(4) Costa, E.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4277−4282.

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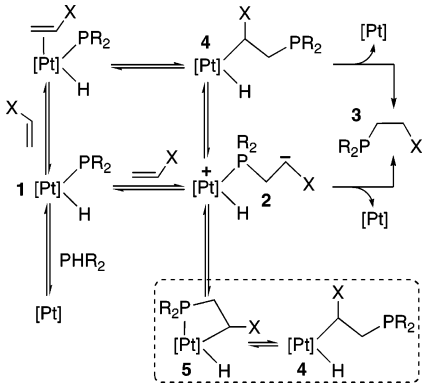
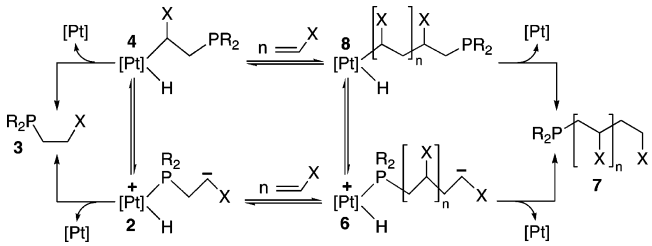
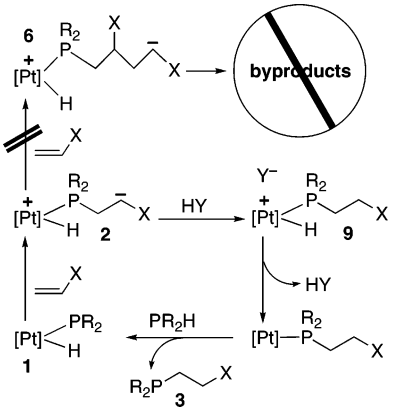
Scheme 1. Possible Mechanisms for Product Formation in Pt-Catalyzed Hydrophosphination of Activated Alkenes ([Pt] = Pt(diphos), X = CN or CO_2R)



Scheme 2. Possible Mechanisms for Byproduct Formation in Pt-Catalyzed Hydrophosphination of Activated Alkenes ([Pt] = Pt(diphos), X = CN or CO_2R)



Scheme 3. A Protic Additive HY Suppressed Formation of Byproducts in Pt-Catalyzed Hydrophosphination of Activated Alkenes ([Pt] = Pt(diphos), X = CN or CO_2R)

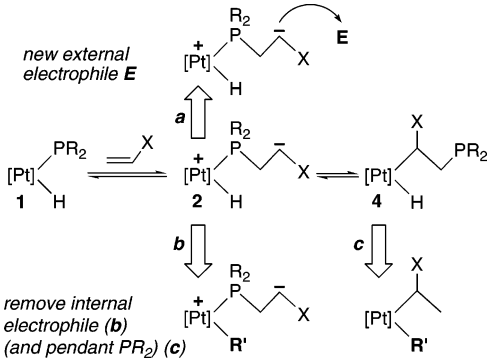


byproduct formation, and indeed this was observed with the weak acids *tert*-butanol and water.[1]

We devised three additional probes of the intermediacy of proposed zwitterion **2** (Chart 1): (a) trapping **2** with a new external electrophile, instead of *t*-BuOH or water; (b) replacing the acidic Pt−H in **2** with an alkyl group to promote carbanion attack on an alkene, yielding analogues of **6**;[5] (c) preparing analogues of Pt−alkyl **4** to test the proposed insertion of an alkene into the Pt−C bond (intermediate **4** → **8**, Scheme 2). These probes provided additional evidence for the nucleophilic attack/zwitterion mechanism of Schemes 1−3.

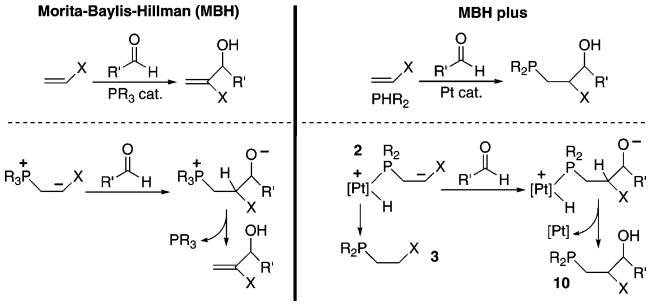
(5) C−C reductive elimination from **4**-**R′** is expected to be slower than C−H reductive elimination from **4**. See: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396−3403.

Chart 1. Three Probes of the Mechanisms in Schemes 1−3[a]



[a] (a) Trapping zwitterion **2** with a new external electrophile **E**; (b) hydride-free models of **2**; (c) models of **4** without Pt−H and pendent PR_2 groups ([Pt] = Pt(diphos), X = CN or CO_2R).

Scheme 4. Proposed Mechanism of Reaction of Zwitterion 2 with Benzaldehyde, by Analogy with the Phosphine-Catalyzed Morita−Baylis−Hillman Reaction ([Pt] = Pt(diphos), X = CN or CO_2R)



Results and Discussion

(a) Trapping Zwitterion 2 with a New External Electrophile. The proposed mechanism for nucleophilic catalysis of the Morita−Baylis−Hillman (MBH) reaction[6] (Scheme 4) suggested trapping **2** with benzaldehyde.

In a MBH mechanism, Michael addition of the phosphine catalyst to an alkene yields a zwitterion, which is trapped by the aldehyde. Proton transfer and loss of the phosphine then gives the product.[7] Similarly, reaction of zwitterion **2** with an aldehyde ("MBH plus"), followed by proton transfer, would yield phosphine **10**. Because this reaction would compete with "normal" hydrophosphination, the product ratio **3**/**10** would reflect the selectivity of zwitterion **2** for reaction with the internal (Pt−H) and external (PhCHO) electrophiles.[8]

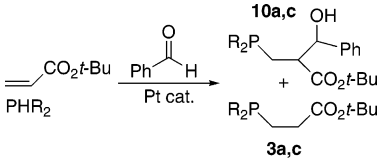
Indeed, Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) was a catalyst precursor for the three-component reaction of secondary phosphines ($PHPh_2$ or PHMe(Is), Is = 2,4,6-(*i*-Pr)$_3C_6H_2$) with *tert*-butyl acrylate and benzaldehyde to yield ∼1:1 mixtures of

(6) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811−891.

(7) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035−1050.

(8) Formation of **10** and **3** could also be explained without invoking zwitterion **2**. Alkyl hydride intermediate **4** could undergo either reductive elimination, yielding hydrophosphination product **3**, or insertion of benzaldehyde into the Pt−C bond to yield an alkoxy hydride, which would afford **10** by O−H reductive elimination. Although we cannot distinguish these mechanisms, the proposed insertion of an aldehyde into a Pt−C bond does not appear to be known; see: Krug, C.; Hartwig, J. F. *Organometallics* **2004**, *23*, 4594−4607, and references therein.

Scheme 5. Pt-Catalyzed Three-Component "MBH Plus" Coupling (Pt catalyst precursor = Pt((*R,R*)-Me-Duphos)(*trans*-stilbene), PR_2 = PPh_2 (a) or PMeIs (c))[10]



phosphines **10** and **3** (Scheme 5). As expected, the ratio **10**/**3** increased when excess benzaldehyde was used.[9]

Although neat $PHPh_2$ and PhCHO reacted quickly[11] and Pt-catalyzed addition of PH_3 to formaldehyde is known,[12] we found that secondary phosphines reacted very slowly with benzaldehyde in toluene even in the presence of a Pt(Me-Duphos) catalyst, and the reaction of $PHPh_2$ and PhCHO appeared to be reversible under these conditions. Subsequent addition of *tert*-butyl acrylate to these reaction mixtures yielded **10** and **3**. The PPh_2 derivative **10a** was separated from **3a**, obtained as a mixture highly enriched in one diastereomer, and characterized by X-ray crystallography (see Figure 1, Table 1, and the Supporting Information). Although the Pt catalyst is chiral, neither of the diastereomers of **10a** were enantiomerically enriched (see the Experimental Section for details).

(b) Hydride-Free Models of Zwitterion 2. Several complexes Pt(diphos)(R′)(PR_2) are known;[13] we also prepared Pt((*R,R*)-Me-Duphos)(Me)(PPh_2) (**11**). Its structure (Figure 2, Table 1, and the Supporting Information) was similar to that of the PPh(*i*-Bu) analogue **12**.[13c]

The reactions of Pt hydrocarbyl phosphido complexes **11**−**15** with *tert*-butyl acrylate or acrylonitrile are summarized in Scheme 6 and Table S1 (Supporting Information). Complicated product mixtures, which depended on the Pt precursor and the reaction conditions, were formed (see the Experimental Section and the Supporting Information for details).

The complexes Pt(diphos)(Me)(PR_2) and Pt((*R,R*)-Me-Duphos)(H)(PPhIs) reacted with acrylonitrile to give olefin "insertion" products **A**.[2,14] Similar products were formed from **11**−**15**, but **A** was not stable under the reaction conditions (in some cases, it decomposed even at low temperature). Mixtures of diastereomers of the "double-insertion" products **B** also formed, and **A** was often converted to **B**, especially in the presence of excess alkene. Both **A** and **B** decomposed to yield **C**, which could not be identified; its tentative formulation in Scheme 6 is discussed in more detail below. The organic products included phosphines **3** and **7** ($n \geq 1$)[15] and alkene **16**,[16] whose formation from *tert*-butyl acrylate is catalyzed by nucleophilic phosphines.[16,17] With excess alkene, **3** was converted to **7**.[1] In some cases, the dinuclear cations **17**, known to form on decomposition of **14** and **15**, were also observed.[13c]

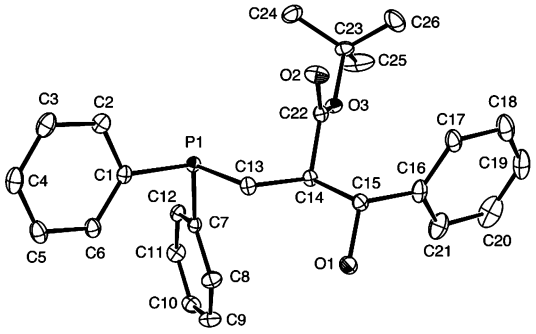


Figure 1. ORTEP diagram of $Ph_2PCH_2CH(CO_2t\text{-Bu})(CHPh(OH))$ (**10a**).

Intermediates **A** were identified by their ^{31}P NMR spectra (Table 2 and Supporting Information), which were similar to those of the previously reported analogues.[2,14]

Table 3 summarizes ^{31}P NMR spectral data for intermediates **B**, whose PR_2 chemical shifts were similar to those of the structurally related phosphines **7**; as expected, $^5J_{Pt-P}$ was not observed. The $J_{Pt-P(diphos)}$ values were similar to those of intermediates **A** and the related Pt dialkyl **21** (see below).

The lifetime of intermediates **A** depended on the substituents of the Pt complex and the alkene (Table S1 and Supporting Information). For example, treatment of Pt(dppe)(Me)($PMes_2$) (**18**, Mes = 2,4,6-$Me_3C_6H_2$) with acrylonitrile cleanly gave the "insertion" product **A-18′** (Scheme 7),[2a,b] but the PPh_2 analogue **14** formed **A-14′**, **B-14′**, and phosphine **3a′**. With excess acrylonitrile, **A-14′** was converted to **B-14′**.

In most cases, decomposition of **A** in the presence of alkene gave the longer-lived **B**. Over time, and especially in the presence of excess alkene, both **A** and **B** were converted to complexes **C**. The nature of these products did not depend on the original phosphido group; both Pt(dppe)(Me)(PPh_2) (**14**) and Pt(dppe)(Me)(PPh(*i*-Bu)) (**15**), for example, gave the same product **C** on reaction with *tert*-butyl acrylate. These compounds could not be isolated, but the J_{Pt-P} values (Table 4) suggested that they retain the Pt(diphos)(R′) fragment and that the unidentified fourth ligand has a large trans influence, similar to that of the functionalized alkyl group in intermediates **A** and **B**.[18] A possible structure for **C** (Scheme 6) is discussed in more detail below.

(c) Model Compounds without Pt−H and Pendent PR_2 Groups. We prepared the complexes Pt(dppe)(R)(CHMe(CO_2t-Bu)) (R = Cl (**20**) or Me (**21**), Scheme 8) to test the importance of the pendent PR_2 group in their reactions with alkenes.

Carbene insertion into the Pt−Me bond of **19** gave **20**, as

(9) For a related fluoride-catalyzed coupling of silylphosphines, see: (a) Hayashi, M.; Matsuura, Y.; Watanabe, Y. *Tetrahedron Lett.* **2005**, *46*, 5135−5138. (b) Hayashi, M.; Matsuura, Y.; Watanabe, Y. *Tetrahedron Lett.* **2004**, *45*, 9167−9169.

(10) Several phosphines $R_2PCH_2CH_2X$ (**3**) were prepared, differing in X and PR_2. Numbering scheme: for X = CO_2t-Bu, PPh_2 = **a**, PPh(*i*-Bu) = **b**, PMeIs = **c**. Numbering for X = CN is similar but with an additional ′. For example, $Ph_2PCH_2CH_2CO_2t$-Bu is **3a**, MeIsP$CH_2CH_2CO_2t$-Bu is **3c**, and $Ph_2PCH_2CH_2CN$ is **3a′**. A similar scheme applies to compounds **10a** and **10c**.

(11) Muller, G.; Sainz, D. *J. Organomet. Chem.* **1995**, *495*, 103−111.

(12) (a) Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1096−1097. (b) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Chem. Soc., Dalton Trans.* **1993**, 269−274.

(13) (a) For Pt(dppe)(Me)(PR_2) (PR_2 = PPh_2 (**14**) or PPh(*i*-Bu) (**15**)), see: 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. (b) For Pt((*R,R*)-Me-Duphos)(Ph)(PMeIs) (**13**), see: Scriban, C.; Glueck, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 2788−2789. (c) For Pt((*R,R*)-Me-Duphos)(Me)(PPh(*i*-Bu)) (**12**), see: Scriban, C.; Wicht, D. K.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2006**, *25*, 3370−3378.

(14) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141−5151.

(15) Several phosphines $R_2P(CH_2CH(X))_nCH_2CH_2X$ (**7**) were prepared, differing in *n*, X, and PR_2. Numbering scheme: for X = CO_2t-Bu, PPh_2 = **a**, PPh(*i*-Bu) = **b**, PMeIs = **c**; *n* = **1** or **2**. Numbering for X = CN is similar but with an additional ′. For example, $Ph_2P(CH_2CH(CO_2t\text{-Bu})CH_2\text{-}CH_2CO_2t$-Bu) is **7a1**, MeIsP$(CH_2CH(CO_2t\text{-Bu}))_2CH_2CH_2CO_2t$-Bu is **7c2**, and $Ph_2P(CH_2CH(CN))_2CH_2CH_2CN$ is **7a1′**.

(16) (a) Amri, H.; Rambaud, M.; Villieras, J. *Tetrahedron Lett.* **1989**, *30*, 7381−7382. (b) Amri, H. Personal communication.

(17) McClure, J. D. *J. Org. Chem.* **1970**, *35*, 3045−3048.

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

Table 1. Crystallographic Data for $Ph_2PCH_2CH(CO_2t\text{-}Bu)(CH(Ph)(OH))$ (10a), Pt((*R*,*R*)-Me-Duphos)(Me)(PPh_2) (11), Pt(dppe)(Cl)(CH(Me)(CO_2t-Bu))·CH_2Cl_2 (20·CH_2Cl_2), and Pt(dppe)(Me)(CH(Me)(CO_2t-Bu))·THF (21·THF)

	10a	11	20·CH_2Cl_2	21·THF
formula	$C_{26}H_{29}O_3P$	$C_{31}H_{41}P_3Pt$	$C_{34}H_{39}Cl_3O_2P_2Pt$	$C_{38}H_{48}O_3P_2Pt$
fw	420.46	701.64	843.03	809.79
space group	*P*2(1)	*P*2(1)	*Pna*2(1)	*P*2(1)/*n*
a, Å	10.7290(11)	9.7369(14)	17.3082(10)	10.2780(4)
b, Å	9.6080(10)	19.017(3)	10.2818(6)	17.6054(7)
c, Å	11.2870(11)	15.778(2)	19.0494(11)	20.0000(8)
α, deg	90	90	90	90
β, deg	92.169(2)	91.064(3)	90	99.7550(10)
γ, deg	90	90	90	90
V, Å^3	1162.7(2)	2921.0(7)	3390.0(3)	3566.6(2)
Z	2	4	4	4
D(calc), g/cm^3	1.201	1.595	1.652	1.508
μ(Mo Kα), mm^{-1}	0.142	4.986	4.500	4.058
temp, K	100(2)	213(2)	213(2)	100(2)
R(*F*), %[a]	4.14	2.87	4.22	2.79
$R_w(F^2)$, %[a]	10.03	6.40	10.37	6.50

[a] Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$. A Bruker CCD diffractometer was used in all cases.

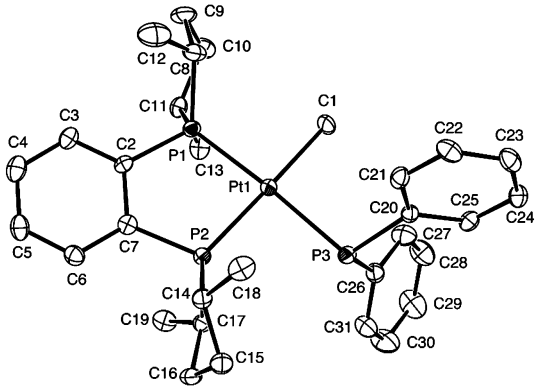
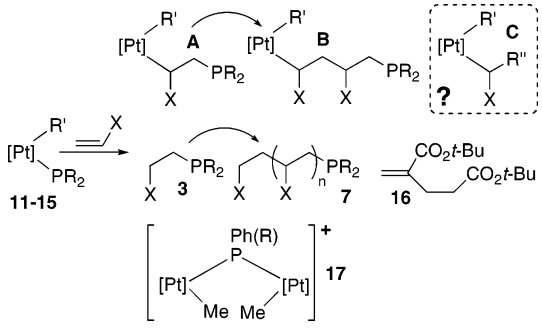


Figure 2. ORTEP diagram of Pt((*R*,*R*)-Me-Duphos)(Me)(PPh_2) (**11**), showing one of the two molecules in the unit cell.

Scheme 6 [a]



[a] Reactions of Pt(diphos)(R′)(PR_2) complexes with *tert*-butyl acrylate and acrylonitrile. [Pt] = Pt((*R*,*R*)-Me-Duphos), R′ = Me, PR_2 = PPh_2 (**11**), PPh(*i*-Bu) (**12**); R′ = Ph, PR_2 = PMeIs (**13**); [Pt] = Pt(dppe), R′ = Me, PR_2 = PPh_2 (**14**), PPh(*i*-Bu) (**15**), X = CN or CO_2t-Bu. Complex **C** could not be identified; a tentative formulation is shown (see the text for discussion). For **17**, [Pt] = Pt(dppe), R = Ph (**17a**) or *i*-Bu (**17b**); [Pt] = Pt((*R*,*R*)-Me-Duphos), R = *i*-Bu.

previously described for related complexes.[19] Treatment of **20** with dimethylzinc generated dialkyl **21**. This reaction seemed to be an equilibrium, but addition of excess $ZnMe_2$ led to formation of Pt(dppe)Me_2, which was difficult to separate from the desired product. Complex **21** could also be generated cleanly by reaction of **19** with the Reformatsky reagent ZnBr($CHMeCO_2t$-Bu)·THF, but attempts to isolate the pure compound were unsuccessful; Pt(dppe)Me_2 and Pt(dppe)(Me)(Cl) were the major impurities.[20] Nevertheless, **21** was characterized by multinuclear NMR spectroscopy. Its ^{31}P NMR spectrum was similar to that of intermediates **A** and **B**, consistent with their proposed structures, and also to that of the unidentified Pt complex **C** (Table 5).

Complexes **20** and **21** were crystallographically characterized (see Figures 3 and 4, Table 1, and the Supporting Information). The structures were similar to that of Pt((*S*,*S*)-Diop)(Cl)(CH(Me)CO_2Et)) (**20-Diop-Et**),[19] with the expected significant bite angle differences between Diop (∼100°) and dppe (∼86°).[21]

No reaction occurred after addition of excess *t*-Bu acrylate to **20-Diop-Et**,[19] **20**, or impure **21**, even after several days at room temperature.[22] In contrast, the unstable intermediate **A-14**, which, unlike model **21**, contains a pendent PPh_2 group, was observed only at low temperature on treatment of **14** with *t*-Bu acrylate.

Mechanism of P−C and C−C Bond Formation in the Reaction of Pt−Phosphido Complexes with Activated Alkenes. The reactions of Scheme 6 resulted in P−C and C−C bond formation, yielding intermediates **A** and **B** and phosphines **3** and **7**. How do these compounds form and interconvert? Scheme 9 shows the proposed mechanism. After formation of zwitterion **2-R′**, carbanion attack at the Pt center would yield **A**, while attack on another alkene would give **B**, via **6-R′**. Reversibility of these steps would explain the observed conversion of **A** to **B**.

Formation of phosphines **3** and **7** would require an acid, perhaps adventitious water, to protonate the carbanion in zwitterions **2-R′** and **6-R′**.[23] Deliberately adding a weak acid should promote this reaction, in preference to formation of **A** and **B** (Scheme 9). As predicted, when **14** or **15** was treated with 5 equiv of *tert*-butyl acrylate in 1:1 toluene/*t*-BuOH,

(19) Bergamini, P.; Costa, E.; Cramer, P.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1994**, *13*, 1058−1060.

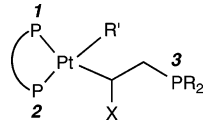
(20) Hama, T.; Liu, X.; Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 11176−11177. For Pt(dppe)Me_2 and Pt(dppe)(Me)(Cl), see: Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439−446.

(21) Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1529.

(22) Complex **21** was prepared by the Me_2Zn route (Experimental Section) and isolated in ca. 90% purity; the major impurities were precursor **20** and Pt(dppe)Me_2. Neither **21** nor these impurities reacted with *tert*-butyl acrylate in C_6D_6 at room temperature.

(23) Although solvents were dried by standard methods and reactions were carried out under nitrogen in dry glassware, acrylonitrile and *tert*-butyl acrylate were not dried or distilled. Some of the dependence of the results in Table S1 (Supporting Information) on the scale and stoichiometry might be due to differing amounts of adventitious water.

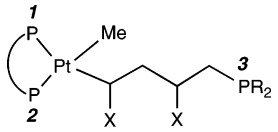
Table 2. Selected ^{31}P NMR Data for the "Insertion" Intermediates Pt(diphos)(R′)(CH(X)CH$_2$PR$_2$) (A)



number, Diphos	R′	X	PR_2	δ P$_3$ (J_{Pt-P}, J_{PP})
A-11, (*R*,*R*)-Me-Duphos[a]	Me	CO_2t-Bu	PPh_2	−10.5 (296, 34), −11.6 (265, 34)
A-12, (*R*,*R*)-Me-Duphos[b,c]	Me	CO_2t-Bu	PPh(*i*-Bu)	−21.4 (196, 21), −23.6 (158, *d*)
A-13, (*R*,*R*)-Me-Duphos[b,e]	Ph	CO_2t-Bu	PMeIs	−40.2 (280, 32), −43.0 (*d*, 29), −42.1 (*d*, 40)
A-14, dppe[f]	Me	CO_2t-Bu	PPh_2	−16.8 (159, *d*)
A-14′, dppe[e]	Me	CN	PPh_2	−15.2 (153, 11)

[a] In toluene-d_8, −75 °C. [b]Not all of the expected diastereomers were observed. [c]In toluene-d_8, −50 °C. [d]Not resolved. [e]In toluene-d_8, 21 °C. [f]In toluene-d_8, −40 °C.

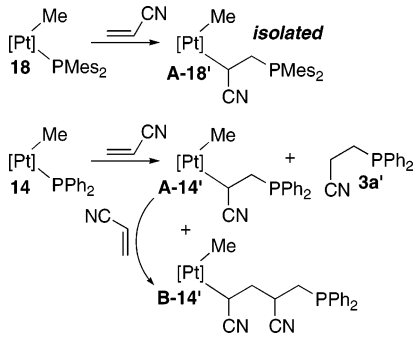
Table 3. ^{31}P NMR Data for "Double-Insertion" Products Observed in the Reaction of *tert*-Butyl Acrylate and Acrylonitrile with Pt(diphos)(Me)(PR$_2$) (B)



number, Diphos	X	PR_2	δ P$_1$ (J_{Pt-P})	δ P$_2$ (J_{Pt-P})	δ P$_3$
B-14′, dppe	CN	PPh_2[a]	46.6 (2295)	48.9 (1772)	−19.4
			47.6 (2307)	48.7 (1769)	−19.6
B-14, dppe	CO_2t-Bu	PPh_2[a,b]	49.3 (2173)	46.4 (1770)	−18.4
			46.3 (2167)	48.9 (1781)	−17.8
B-15, dppe	CO_2t-Bu	PPh(*i*-Bu)[a,c,d]	49.5 (2191)	46.0 (1762)	−32.3
			46.6 (2179)	49.0 (1877)	−31.7
			49.3 (2165)	46.2 (1760)	−31.3
			46.4 (*e*)	48.5 (*e*)	−31.0
B-11, (R,R)-Me-Duphos	CO_2t-Bu	PPh_2[f,c]	66.1 (2142)	68.1 (1756)	−18.1
			65.8 (2133)	67.2 (1773)	−19.7
			66.4 (2145)	68.9 (1764)	−19.0
			65.5 (2127)	65.7 (1764)	−18.7
B-12, (*R*,*R*)-Me-Duphos	CO_2t-Bu	PPh(*i*-Bu)[f,g]	66.5 (2139)	68.9 (1765)	−31.0
			65.5 (2122)	65.6 (1769)	−31.3
			66.2 (2146)	68.0 (1752)	−31.5
			65.9 (2138)	66.1 (1756)	−32.2
			66.4 (2136)	67.3 (1769)	−32.3
					−32.4
					−32.8
					−33.3

[a] In toluene-d_8. [b]J_{12} values for the two diastereomers were 6 and 5 Hz, respectively. [c]The assignment of the P3 peaks to the four diastereomers was based on integration of the P1−P3 peaks. [d]J_{12} values for all four diastereomers were 5 Hz. [e]Not observed. [f]In C_6D_6. [g]The assignment of the P3 peaks to the various diastereomers and observation of all the expected Duphos signals were not possible due to the complexity of the Duphos region.

Scheme 7 [a]



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

intermediates **A** and **B** were not observed. Instead, phosphines **3** and **7** (for **14**) or **7** (for **15**) and the dinuclear cations [(Pt(dppe)(Me))$_2$(μ-PPhR)]$^+$ (R = Ph (**17a**), R = *i*-Bu, (**17b**)) formed (Scheme 10),[13c] perhaps by trapping the [Pt(dppe)(Me)]$^+$ fragment with the phosphido starting material.

Similarly, adding 1 equiv of water to the reactions of Pt(dppe)(Me)(PPh_2) (**14**) with 10 equiv of *tert*-butyl acrylate or acrylonitrile promoted the formation of phosphines **3** and **7** (see Scheme 11 for results with the acrylate and the Supporting Information for more details). With both alkenes, the "dry" reactions gave small amounts of phosphines **3** and **7**; most of the PPh_2 moiety was in intermediates **B-14** and **B-14′**. With added water, phosphines **3a** and **7a1** (for acrylate) or **3a′** (for acrylonitrile) formed more quickly; they were the major PPh_2-containing compounds in the mixture.

Table 4. ^{31}P NMR Data for Compounds C, Formed in the Reaction of Pt(diphos)(R′)(PR$_2$) with CH$_2$=CH(X)[a]

diphos	R′	X	δ (P$_1$) (J_{Pt-P})	δ (P$_2$) (J_{Pt-P})	J_{12}
dppe	Me	CN	45.5[b]	48.5[b]	3
dppe	Me	CO_2t-Bu	47.1 (2289)	48.3 (1778)	3
(*R*,*R*)-Me-Duphos	Me	CO_2t-Bu	66.6 (2249)	66.1 (1758)	3
(*R*,*R*)-Me-Duphos	Ph	CO_2t-Bu	59.6 (2200)	62.4 (1677)	3

[a] Solvent = toluene-d_8, J in Hz. [b]J_{Pt-P} was not detected.

We next sought to explain the conversion of **3** into **7** in the presence of alkene, as well as the formation of the Pt product **C**. If protonation of **2-R′** to give **3** were *reversible*, then subsequent formation and protonation of **6-R′** would complete the conversion of **3** to **7**. This reaction would require 1 equiv

Scheme 8. Synthesis of α-Functionalized Pt Alkyl Complexes ([Pt] = Pt(dppe))

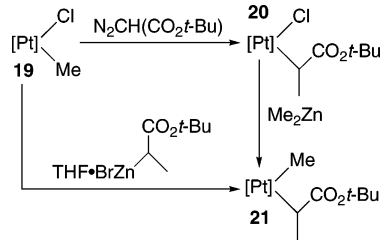
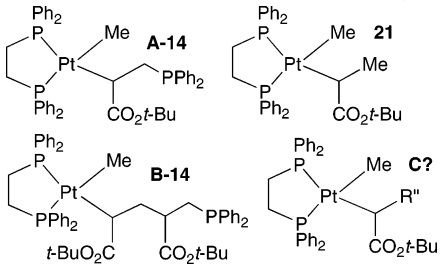


Table 5. Selected ^{31}P NMR Data for the Intermediates Pt(dppe)(Me)(CH(CO$_2$*t*-Bu)CH$_2$PPh$_2$) (A-14), Pt(dppe)(Me)(CH(CO$_2$*t*-Bu)CH$_2$CH(CO$_2$*t*-Bu)CH$_2$PPh$_2$) (B-14), the Model Compound Pt(dppe)(Me)(CHMe(CO$_2$*t*-Bu)) (21), and Product C (for which a tentative structure is shown)[a]



complex	δ (P$_1$) (J_{Pt-P})	δ (P$_2$) (J_{Pt-P})	J_{PP} (dppe)
A-14[b]	44.4 (2211)	47.6 (1849)	4
B-14[c]	49.3 (2173)	46.4 (1770)	6
	46.3 (2167)	48.9 (1781)	5
21[d]	47.3 (2094)	48.9 (1794)	5
C[c]	47.1 (2289)	48.3 (1778)	3

[a] Labeling: P1 is trans to the functionalized alkyl, P2 is trans to Me, P3 is the pendent PPh$_2$ group. [b] In toluene-d_8, −20 °C. Additional couplings to the PPh$_2$ group (P3) were also observed in the dppe signals (J_{13} = 13, J_{23} = 10), but the PPh$_2$ peak was broad. [c] In toluene-d_8. [d] In C_6D_6.

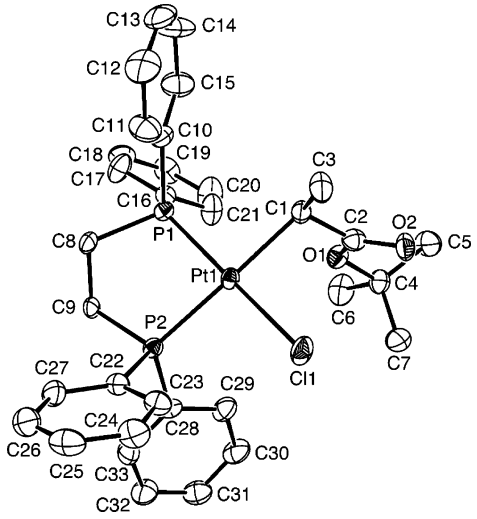


Figure 3. ORTEP diagram of Pt(dppe)(Cl)(CH(Me)CO$_2$*t*-Bu)·CH$_2$Cl$_2$ (**20**·CH$_2$Cl$_2$), with the solvent molecule omitted.

of the acid HY and might reversibly produce the Pt complex Pt(diphos)(R′)(Y) (Scheme 9). If HY was water, then Pt(diphos)(R′)(OH) should act as a base toward phosphine **3**, yielding intermediate **2-R′** and, from it, complexes **A** and **B**.[24]

To test this hypothesis, we treated the known hydroxide Pt(dppe)(Me)(OH) (**22**)[24] with the phosphine PPh$_2$CH$_2$CH$_2$CN (**3a′**) (Scheme 12). The initial major product was **A-14′**. Small amounts of the phosphido complex Pt(dppe)(Me)(PPh$_2$) (**14**)

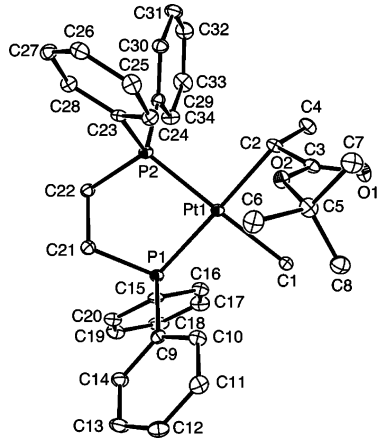
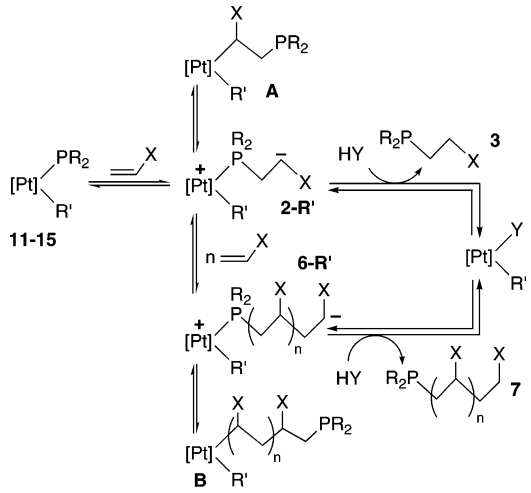
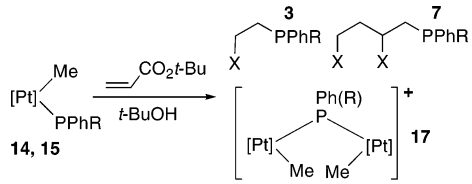


Figure 4. ORTEP diagram of Pt(dppe)(Me)(CH(Me)CO$_2$*t*-Bu)·THF (**21**·THF); the solvent molecule is not shown.

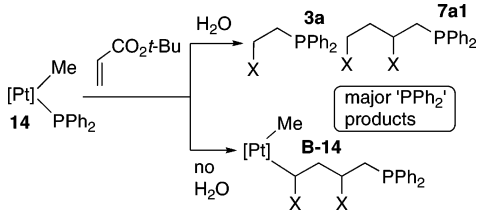
Scheme 9. Proposed Mechanism of P−C and C−C Bond Formation in the Reaction of Pt−Phosphido Complexes with Activated Alkenes ([Pt] = Pt(diphos), X = CN or CO$_2$*t*-Bu, HY = weak acid)



Scheme 10. *t*-BuOH-Promoted Phosphine Formation in the Reactions of 14 and 15 with *tert*-Butyl Acrylate ([Pt] = Pt(dppe), R = Ph (14) or *i*-Bu (15), X = CO$_2$*t*-Bu)

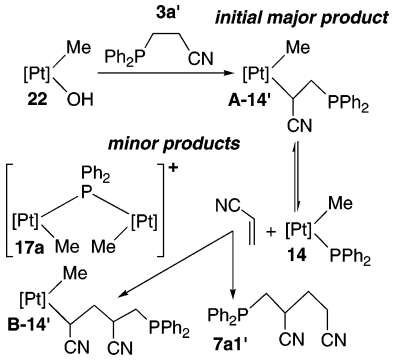


Scheme 11. Water-Promoted Phosphine Formation in the Reaction of Pt(dppe)(Me)(PPh$_2$) (14) with *tert*-Butyl Acrylate ([Pt] = Pt(dppe), X = CO$_2$*t*-Bu)



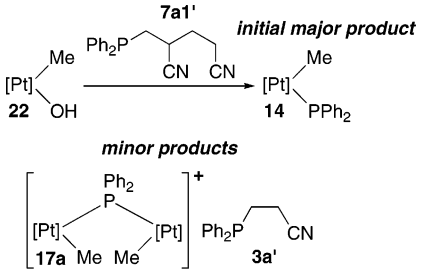
and the dinuclear cation **17a**, known to arise from decomposition of **14**,[13c] were also observed. The minor products **B-14′** and **7a1′** might arise from acrylonitrile formed in the precedented **A-14′** → **14** conversion.[2] More **14** was formed from **A-14′** over

Scheme 12. Reaction of a Platinum Hydroxide Complex with a Cyanoethylphosphine ([Pt] = Pt(dppe))[a]



[a] Although acrylonitrile was not observed directly, its formation in the proposed **A-14′**/**14** equilibrium is consistent with the products **14, 7a1′**, and **B-14′**.

Scheme 13. Reaction of a Platinum Hydroxide Complex with a Cyanoethylphosphine Derived from 2 equiv of Acrylonitrile ([Pt] = Pt(dppe))



time, consistent with a shift in the equilibrium between them driven by consumption of acrylonitrile. Similar observations with Pt((*R*,*R*)-Me-Duphos)(Ph)(OH) (**23**)[25] are described in the Experimental Section.

These experiments showed that Pt-mediated conversion of phosphine **3** into **7** via the reversible proton-transfer chemistry of Scheme 9 is plausible. The reverse process occurred on treatment of **22** with **7a1′** (Scheme 13). The major initial product was phosphido complex **14**, along with a little cation **17a**, and the phosphine **3a′**, whose concentration increased over time.

Thus, the mechanism proposed in Scheme 9 is consistent with a number of experimental observations, including the formation and interconversion of intermediates **A** and **B** and phosphines **3** and **7**. It is also consistent with the substituent effects observed. Intermediate **A** was less reactive for Me-Duphos complexes than for dppe, perhaps because five-coordinate intermediates (such as **5** in Scheme 1) required for the **A** → zwitterion **2**-R′ conversion are less readily accessible for the more sterically demanding diphosphine.[26] This idea is also consistent with the comparison between isolable Pt(dppe)(Me)(CH(CN)CH_2PMes_2) (**A-18′**) and the more reactive PPh_2 analogue **A-14′** (Scheme 7). Moreover, the lack of reactivity of **A-18′** and the model complexes Pt(dppe)(X)(CH(Me)CO_2*t*-Bu) (X = Cl or Me, **20** and **21**) with acrylonitrile and *tert*-butyl acrylate, respectively, suggests that byproduct formation does not occur by classical migratory insertion of an alkene into the Pt−C bond of intermediates like **A**.

(24) The basic nature of Pt−hydroxides has been studied in detail. For example, Pt(dppe)(Me)(OH) reacted with acetonitrile to give Pt(dppe)(Me)-(CH_2CN) (Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738−747).

(25) Scriban, C.; Glueck, D. S.; Golen, J. A.; Rheingold, A. L., manuscript in preparation.

(26) See Table S1 (Supporting Information) for details.

However, several questions remain unanswered. Although Pt hydroxides appear to be competent intermediates, they were not observed during the stoichiometric reactions, and the eventual Pt products, **C**, have not been identified. The ^{31}P NMR data are consistent with formulation of these complexes as Pt(diphos)(R′)(CH(X)CH_2OH) (**24**), which might be formed by "insertion" of alkene into the Pt−O bond of a hydroxide species.[27] However, platinum hydroxides **22** and **23** did not react with acrylonitrile or *tert*-butyl acrylate, and the reaction of Pt(dppe)(Me)(OH) (**22**) with $HOCH_2CH_2CN$ did not give **C**. We also considered the possibility that the acid HY in Scheme 9 might be the alkene itself, but no ^1H NMR vinyl signals expected for the resulting Pt complexes were observed in the mixtures.

Conclusions

We conclude that formation of a zwitterion by nucleophilic attack of a Pt−PR_2 group on an activated alkene is involved in P−C and C−C bond formation in Pt-catalyzed hydrophosphination. This hypothesis is consistent with the reactivity of the model compounds Pt(diphos)(R′)(PR_2) summarized in Scheme 9. The mechanism also has predictive value, exemplified in the effect of protic additives in Pt-catalyzed hydrophosphination (Scheme 3)[1] and related stoichiometric reactions (Schemes 10 and 11) and in the new Pt-catalyzed three-component coupling ("MBH plus" reaction, Schemes 4 and 5).

Related mechanisms may be important in the chemistry of other metal−heteroatom bonds. For example, formation of a zwitterion via nucleophilic attack of the amido group in Cu(IPr)(NHPh) on acrylonitrile was recently proposed,[28] and such pathways may also be relevant in the reactions of activated alkenes with Pt−anilide and −phenoxide complexes.[29]

Experimental Section

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a dry box 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.[30] NMR spectra were recorded using Varian 300 or 500 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported versus H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz, as absolute values. Unless indicated, peaks in NMR spectra are singlets. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory or Quantitative Technologies Inc. Reagents were from commercial suppliers, except for the following compounds, which were made by the literature procedures: Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene),[31] PHMe(Is),[32] (*S*)-[Pd(NMe_2CH(Me)C_6H_4)Cl]$_2$,[33] Pt(dppe)(Me)(P-

(27) (a) Bennett, M. A.; Jin, H.; Li, S.; Rendina, L. M.; Willis, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 8335−8340. (b) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603−1604.

(28) Munro-Leighton, C.; Blue, E. D.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2006**, *128*, 1446−1447.

(29) (a) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451−2453. (b) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750−4761.

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(31) Wicht, D. K.; Zhuravel, M. A.; Gregush, R. V.; Glueck, D. S.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1998**, *17*, 1412−1419.

(32) Brauer, D. J.; Bitterer, F.; Dorrenbach, F.; Hessler, G.; Stelzer, O.; Kruger, C.; Lutz, F. *Z. Naturforsch. B* **1996**, *51*, 1183−1196.

(33) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301−4303.

PhR) (R = Ph or *i*-Bu),[13a,c] Pt(dppe)(Me)(OH),[34] Pt((*R*,*R*)-Me-Duphos)(Ph)(PMeIs),[13b] Pt((*R*,*R*)-Me-Duphos)(Ph)(OH),[25] Pt(dppe)-(Me)(Cl),[35] Pt((*S*,*S*)-Diop)(Me)(CH(Me)CO_2Et),[19] Pt((*R*,*R*)-Me-Duphos)(Me)(Cl),[13c] and MeCH(ZnBr)(CO_2*t*-Bu)·THF.[20]

Reaction of Benzaldehyde and $PHPh_2$ in the Absence of a Catalyst. A solution of $PHPh_2$ (45 mg, 0.24 mmol) in toluene-d_8 (0.3 mL) was transferred to an NMR tube, which was fitted with a septum. Benzaldehyde (25.5 mg, 24.4 μL, 0.24 mmol) was added via microliter syringe, and the reaction mixture was monitored by ^{31}P NMR spectroscopy. After 10 min, unreacted $PHPh_2$ and a small new peak at δ 5.6 (ratio 16:1) were observed in the mixture. This peak could be assigned to $Ph_2PCH(Ph)(OH)$ (lit. ^{31}P NMR (CH_2Cl_2): δ 4.2).[11] Adding 5 mol % Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) did not promote further formation of this phosphine.

Catalytic Reaction of *tert*-Butyl Acrylate with 5 equiv of Benzaldehyde and $PHPh_2$. Synthesis of Three-Component Coupling Product 10a. To Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (8.2 mg, 0.012 mmol, 5 mol %) in toluene (0.2 mL) was added $PHPh_2$ (45 mg, 0.24 mmol) in toluene (0.3 mL). The mixture was transferred to an NMR tube, which was fitted with a septum. Benzaldehyde (127 mg, 122 μL, 4.8 mmol) was added via microliter syringe, and the reaction mixture was monitored by ^{31}P NMR spectroscopy. After 20 min, unreacted $PHPh_2$ and $Ph_2PCH(Ph)$-(OH), in an approximate ratio 2:1, were observed. *tert*-Butyl acrylate (35 μL, 0.24 mmol) was added via microliter syringe. After 10 min, $PPh_2CH_2CH_2CO_2$*t*-Bu (**3a**, δ −14.2) and the two diastereomers of the hydroxyphosphine product **10a** (δ −18.1, −18.7, in an approximate ratio 3:1) were observed; all the $PHPh_2$ had been consumed. The ratio **3a**:**10a** was 1:3.0, and the ratio between the two diastereomers of **10a** was 2.9:1.

The catalyst was removed from the reaction mixture on a silica column (5 cm height, 0.6 cm diameter), using a 9:1 petroleum ether/THF mixture as eluent. The catalyst did not elute. After removing the solvent under vacuum, 100 mg of a mixture of a white solid and a colorless oil was obtained. Proton and sodium adducts of the oxidized phosphine **10a** were observed by mass spectroscopy.[1] HRMS: *m*/*z* calcd for $C_{26}H_{30}O_4P^+$ (MOH^+) 437.1882, found 437.1869. HRMS: *m*/*z* calcd for $C_{26}H_{29}O_4NaP^+$ ($MONa^+$) 459.1701, found 459.1689.

The mixture was washed with petroleum ether (3 portions of 0.5 mL) to give white crystals suitable for X-ray crystallography. The washings were collected, and the solvent was removed under vacuum, yielding a colorless oil. ^{31}P{^{1}H} NMR (C_6D_6) of the white crystals (**10a**): δ −18.9 (**a**), −19.3 (**b**) (ratio **a**:**b** = 8.5:1). ^{31}P-{^{1}H} NMR (C_6D_6) of the washings (a mixture of **10a** and **3a**): δ −14.7 (**3a**), −18.9 (**a**), −19.3 (**b**). Ratio **3a**:**10a** = 1.7:1, ratio **a**:**b** = 1:2.4. The white solid was washed further with petroleum ether (3 portions of 0.5 mL), and 60 mg (60% yield) of white crystals of **10a** was obtained (ratio **a**:**b** = 12.6:1).

A sample of this mixture of **10a** was added to a slight excess of (*S*)-[Pd($NMe_2CH(Me)C_6H_4$)Cl]$_2$ (^{31}P NMR (C_6D_6): δ 38.4, 37.6, 33.5, 31.5; ratio 14.8:12.8:1:1). The ratio between the two major species was ∼1:1, the ratio between the two minor ones was also ∼1:1, and the ratio between the major and the minor peaks was 13.8:1, similar to the ratio **a**:**b** = 12.6:1, within the experimental error, so no ee was observed.

The following NMR data for **10a** are reported as a mixture of two diastereomers **a**:**b** = 12.6:1, unless otherwise indicated. ^{1}H NMR (C_6D_6): δ 7.39−7.32 (m, 4H, Ar), 7.18−7.14 (m, 2H, Ar), 7.10−6.96 (m, 9H, Ar), 4.89 (dd, *J* = 6, 3, 1H, **a**), 4.85 (t, *J* = 7, 1H, **b**), 3.03 (d, *J* = 7, 1H, **b**), 2.91−2.87 (m, 1H, **b**), 2.81−2.74 (m, 1H, **a**), 2.68−2.53 (m, 3H), 2.34−2.29 (m, 1H, **b**), 1.33 (9H, Me, **b**), 1.30 (9H, Me, **a**). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.3 (CO_2*t*-Bu), 142.3 (quat), 140.5 (d, *J* = 13, quat), 138.3 (d, *J* = 15, quat), 134.1 (d, *J* = 20, Ar, **a**), 134.0 (d, *J* = 20, Ar, **b**), 133.0 (d, *J* = 18, **b**), 132.8 (d, *J* = 18, **a**), 129.4 (Ar), 129.2 (d, *J* = 7, Ar), 129.0 (d, *J* = 6, Ar), 128.68 (Ar), 128.67 (Ar), 128.0 (Ar), 127.3 (Ar, **a**), 127.1 (Ar, **b**), 81.5 (CO_2CMe_3), 76.6 (d, *J* = 11, CH, **b**), 75.6 (d, *J* = 10, CH, **a**), 51.6 (d, *J* = 11, CH, **a**), 51.2 (d, *J* = 17, CH, **b**), 29.7 (d, *J* = 15, CH_2, **b**), 28.4 (CMe_3, **b**), 28.3 (CMe_3, **a**), 27.1 (d, *J* = 14, CH_2, **a**).

Reaction of PHMe(Is) and Benzaldehyde in the Absence of Catalyst. A solution of PHMe(Is) (50 mg, 0.2 mmol) in toluene (0.5 mL) was transferred into an NMR tube, which was fitted with a septum. Benzaldehyde (21 mg, 20 μL, 0.2 mmol) was added via microliter syringe, and the mixture was monitored over time, by ^{31}P NMR spectroscopy. No reaction was observed after 3 days.

Catalytic Reaction of *tert*-Butyl Acrylate with Benzaldehyde and PHMe(Is). Synthesis of Three-Component Product 10c. To Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (8.2 mg, 0.012 mmol, 5 mol %) in toluene-d_8 (0.2 mL) was added PHMe(Is) (60 mg, 0.24 mmol) in toluene-d_8 (0.3 mL). Benzaldehyde (25.5 mg, 24.4 μL, 0.24 mmol) was added via microliter syringe. The reaction mixture was transferred to an NMR tube and monitored by ^{31}P NMR spectroscopy. The only species observed in the mixture after 1 week were Pt((*R*,*R*)-Me-Duphos)(H)(PMeIs) and unreacted PHMe(Is). *tert*-Butyl acrylate (35 μL, 0.24 mmol) was added via microliter syringe. After 3 h PMe(Is)($CH_2CH_2CO_2$*t*-Bu) (**3c**, δ −47.2), along with four other diastereomeric phosphines **10c** (δ −50.9, −51.4, −52.0, −52.9), was observed in the reaction mixture (the **3c**/**10c** ratio was 1:1.1). The Pt species observed during and after catalysis was Pt-((*R*,*R*)-Me-Duphos)(*t*-Bu acrylate).[1] The ratio between the phosphines was essentially the same after 1 day. The catalyst was removed from the reaction mixture on a silica column (10 cm height, 1 cm diameter), using a 9:1 petroleum ether/THF mixture as eluent. The catalyst did not elute. A colorless oil was obtained. HRMS: *m*/*z* calcd for **10c**, $C_{30}H_{46}O_3P^+$ (MH^+) 485.3185, found 485.3184. ^{31}P{^{1}H} NMR (toluene-d_8): δ −50.9, −51.4, −52.0, −52.9 (ratio 3.4:5.4:3.2:1). **Pt((*R*,*R*)-Me-Duphos)(H)(PMeIs)**. ^{31}P-{^{1}H} NMR (toluene-d_8, 21 °C): δ 77.7 (dd, *J* = 129, 9, J_{Pt-P} = 1657), 70.4 (J_{Pt-P} = 1910), −55.3 (d, *J* = 129, 9, J_{Pt-P} = 970).

Catalytic Reaction of *tert*-Butyl Acrylate with 5 equiv of Benzaldehyde and PHMe(Is). To Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) (8.2 mg, 0.012 mmol, 5 mol %) in toluene (0.2 mL) was added PHMe(Is) (60 mg, 0.24 mmol) in toluene (0.3 mL). The mixture was transferred to an NMR tube, which was fitted with a septum. Benzaldehyde (127 mg, 122 μL, 4.8 mmol), followed by *tert*-butyl acrylate (35 μL, 0.24 mmol), was added via microliter syringe, under N_2. After 10 min, PMeIs($CH_2CH_2CO_2$*t*-Bu) (**3c**, δ −46.5) and the four diastereomers of the hydroxyphosphine product **10c** (δ −50.2, −50.8, −51.3, −52.3, in an approximate ratio 4:4:4:1) were observed, along with unreacted PHMe(Is). The approximate ratio **3c**/**10c** was 1:3.0. The only Pt species observed during catalysis was Pt((*R*,*R*)-Me-Duphos)(*tert*-butyl acrylate).[1] The reaction was complete after 24 h.

The catalyst was removed from the reaction mixture on a silica column (5 cm height, 0.6 cm diameter), using a 9:1 petroleum ether/THF mixture as eluent. Some catalyst also eluted. A pale yellow oil (114 mg) was obtained. This mixture contained **10c** (mostly) plus **3c** and PhCHO, which were identified by multinuclear NMR spectroscopy. Phosphines **10c** were not obtained in pure form, but they were identified spectroscopically.

^{31}P{^{1}H} NMR (C_6D_6): δ −47.1 (**3c**), −51.0 (**a**), −51.6 (**b**), −52.1 (**c**), −53.0 (**d**). The ratio **3c**:**10c** = 1:3.3. The ratio **a**:**b**:**c**:**d** = 3.2:3.2:3.5:1. In an attempt to measure the enantiomeric excess of the diastereomers of **10c**, the mixture was added to (*S*)-[Pd-($NMe_2CH(Me)C_6H_4$)Cl]$_2$ (^{31}P NMR (C_6D_6): δ 12.0, 9.8, 9.5, 9.3, 8.2, 7.2, 7.1, 3.3). Separately, a sample of independently synthesized **3c** was also added to the Pd reporter complex (^{31}P NMR (C_6D_6): δ 12.0, 9.8 corresponding to the two diastereomeric Pd complexes). The signals at δ 9.5/9.3 and 7.2/7.1 due to Pd complexes of **10c**

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

were in ~1:1 ratio, but these spectra did not provide enough information to assess the ee of **10c**.

The following NMR data are reported for a mixture of four diastereomers of **10c**, **a**:**b**:**c**:**d** = 3.2:3.2:3.5:1, unless otherwise indicated. Selected ^{1}H NMR (C_6D_6) signals: δ 4.98 (t, J = 6, **d**), 4.90 (dd, J = 6, 3), 4.86 (t, J = 6), 4.79 (dd, J = 6, 3). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.62 (*C*O$_2$*t*-Bu), 174.59 (*C*O$_2$*t*-Bu), 174.12 (m, *C*O$_2$*t*-Bu), 156.2−156.0 (m, quat), 150.9−150.8 (m, quat), 143.6 (quat, Ph, **d**), 143.2 (quat, Ph, **c**), 142.8 (quat, Ph), 142.6 (quat, Ph), 131.7−131.4 (m, quat), 130.0 (Ph), 129.5 (Ph, **d**), 129.3 (Ph), 129.2 (Ph, **c**), 128.8−128.6 (m, Ph), 128.1−127.9 (m, Ph), 127.5 (Ph), 127.4 (Ph), 127.3 (Ph), 127.2 (Ph), 122.8−122.6 (m, Is), 81.31 (O*C*Me$_3$, **d**), 81.30 (O*C*Me$_3$, **c**), 81.1 (O*C*Me$_3$), 81.0 (O*C*Me$_3$), 76.9 (d, J = 14, CH, **c**), 76.4 (d, J = 12, CH), 76.1 (d, J = 12, CH, **d**), 75.9 (d, J = 11, CH), 54.3 (d, J = 28, *C*H-OH), 53.7 (d, J = 27, *C*H-OH, **c**), 53.6 (d, J = 24, *C*H-OH), 53.1 (d, J = 25, *C*H-OH, **d**), 35.15−34.99 (m, CH, *i*-Pr), 32.1−31.8 (m, CH, *i*-Pr), 30.6 (d, J = 16, CH$_2$), 30.2 (d, J = 16, CH$_2$, **d**), 28.7 (d, J = 15, CH$_2$), 28.4 (C(*C*H$_3$)$_3$), 28.34 (C(*C*H$_3$)$_3$, **d**), 28.31 (C(*C*H$_3$)$_3$), 28.2 (C(*C*H$_3$)$_3$), 28.1 (d, J = 16, CH$_2$), 25.7−25.1 (m, Me, Is), 24.5−24.3 (m, Me, Is), 14.7 (d, J = 33), 13.3 (d, J = 17, 2 P-Me), 12.4 (d, J = 18, P-Me, **d**), 12.1 (d, J = 18, P-Me).

Pt((*R*,*R*)-Me-Duphos)(Me)(PPh$_2$) (11). PHPh$_2$ (18.7 mg, 0.1 mmol) was added with a microsyringe to a stirring solution of Pt((*R*,*R*)-Me-Duphos)(Me)(Cl) (55.2 mg, 0.1 mmol) in THF (10 mL). NaOSiMe$_3$ (11.3 mg, 0.1 mmol) in THF (5 mL) was added to the reaction mixture, which immediately turned yellow. The slurry was filtered through Celite, and the filtrate was concentrated under vacuum. Petroleum ether was added to the yellow residue, yielding a yellow precipitate, which was washed with petroleum ether. Drying the precipitate under vacuum yielded 65 mg (93%) of yellow powder.

Anal. Calcd for $C_{31}H_{41}P_3Pt$: C, 53.06; H, 5.89. Found: C, 52.65; H, 6.19. ^{31}P{^{1}H} NMR (C_6D_6): δ 66.9 (dd, J = 142, 9, J_{Pt-P} = 1929), 63.1 (dd, J = 18, 9, J_{Pt-P} = 1749), −28.9 (dd, J = 142, 18, J_{Pt-P} = 1077). ^{1}H NMR (C_6D_6): δ 8.00 (broad, 4H, Ar), 7.36−7.18 (m, 6H, Ar), 7.07−6.99 (m, 4H, Ar), 3.26−3.19 (m, 1H, CH), 2.73−2.54 (m, 1H, CH), 2.53−2.46 (m, 1H, CH), 2.40−2.25 (m, 2H, CH$_2$), 2.05−1.95 (m, 1H, CH), 1.88−1.76 (m, 2H, CH$_2$), 1.75−1.65 (m, 2H, CH$_2$), 1.59 (dd, J = 18, 7, 3H, CH$_3$), 1.53−1.27 (m, 2H, CH$_2$), 1.20 (dd, J = 18, 7, 3H, CH$_3$), 1.06 (ddd, J = 14, 14, 4, J_{Pt-H} = 66, 3H, Pt-CH$_3$), 0.63 (dd, J = 15, 8, 3H, CH$_3$), 0.61 (dd, J = 15, 8, 3H, CH$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.6−146.7 (m, quat), 145.6 (dd, J = 36, 34, quat), 138.8−137.8 (m, quat), 136.1 (broad, Ar), 133.6 (dd, J = 57, 14), 130.8 (d, J = 40), 127.7 (d, J = 5, Ar), 125.7 (broad, Ar), 42.2 (d, J = 27), 41.4 (d, J = 26), 37.8 (broad), 37.6, 37.3−37.1 (m), 35.7 (d, J = 24), 34.9−34.5 (m), 17.9 (m, Me), 17.3 (d, J = 10, Me), 14.6 (Me), 14.1 (Me), 3.5 (dd, J = 89, 6, Pt-Me).

Reaction of Pt Hydrocarbyl Phosphido Complexes 11−15 with Activated Alkenes (Table S1, Supporting Information). These experiments were all performed in NMR tubes, by a general procedure, and the results are summarized in Table S1 and Scheme 6 and discussed in the text. Since many experiments differed only in scale or stoichiometry, only representative ones are included here; see the Supporting Information for details.

Reaction of *t*-Bu acrylate with Pt(dppe)(Me)(PPh$_2$) (14) at Low Temperature (entry 1, Table S1). A solution of Pt(dppe)(Me)(PPh$_2$) (**14**, 40 mg, 0.05 mmol) in toluene-d_8 (0.5 mL) was transferred into an NMR tube, which was fitted with a septum. The NMR tube was cooled to −50 °C, and *tert*-butyl acrylate (7 μL, 6.4 mg, 0.05 mmol) was added with a microliter syringe. The tube was immediately inserted in the NMR spectrometer, which was previously cooled to −50 °C, and the reaction was monitored by ^{31}P and ^{1}H NMR spectroscopy, from −75 °C to room temperature.

The Pt−dialkyl product Pt(dppe)(Me)(CH(CO$_2$*t*-Bu)CH$_2$PPh$_2$) (**A-14**, Table 2) was observed immediately after addition of the acrylate at −50 °C, but disappeared on warming above 0 °C. The phosphines PPh$_2$CH$_2$CH$_2$CO$_2$*t*-Bu (**3a**)[10] and PPh$_2$(CH$_2$CH(CH$_2$CH$_2$CO$_2$*t*-Bu)(CO$_2$*t*-Bu)) (**7a1**)[15] were observed immediately after addition of the acrylate at −50 °C in an approximate ratio **3a**:**7a1** = 4:3. The ratio varied little on warming the reaction mixture to room temperature (over ~4 h), but the mixture was mostly **7a1** after 1 day. One diastereomer of **B-14** (δ −20.0, −50 °C) could also be observed immediately after the addition of the acrylate. Once the temperature reached −20 °C, the second diastereomer of **B-14** was also observed (Table 3). The ratio between the two diastereomers was almost unchanged over 1 day (~1:1.5). The amount of starting compound **14** decreased over time, but it was still observed, after 1 day, as was an unidentified peak at −11.7 ppm. Note that unreacted *tert*-butyl acrylate was always observed in the ^{1}H NMR spectrum.

Excess *tert*-butyl acrylate (0.5 equiv) was added, and the reaction mixture was monitored over time, at room temperature. The Pt−PPh$_2$ ^{31}P NMR signal disappeared after 1 day, but it could be observed again in the mixture after 4 days. Phosphines **3a** and **7a1** were still observed; the latter became the major PPh$_2$ species after 4 days, while the amount of **B-14** decreased. The Pt complex **C** (Table 4) was the major Pt(dppe) component in the mixture after 1 h and remained the major component over time. Peaks due to alkene **16** were also observed in the ^{1}H NMR spectrum after 4 days.

More acrylate (0.5 equiv) was added. Once again, **14** disappeared, to reappear after 2 weeks, while **B-14** remained unchanged. The major components of the mixture were **C** and phosphine **7a1**. After 8 days new peaks in the PPh$_2$ region, which showed no Pt−P coupling, could be observed. Their intensity increased slightly over time, and presumably they belong to tertiary phosphines that contain more *tert*-butyl acrylate molecules (δ −18.7, −19.9, −22.2; **7an**, n > 1). Also, after 2 weeks, the *tert*-butyl acrylate almost disappeared, but a large amount of its dimer (**16**) was observed by ^{1}H NMR spectroscopy.

Reaction of Pt(dppe)(Me)(PPh$_2$) (14) with 10 equiv of *tert*-Butyl Acrylate with or without 1 equiv of H$_2$O (entry 3, Table S1). A suspension of Pt(dppe)(Me)(PPh$_2$) (**14**, 79 mg, 0.1 mmol) in toluene (0.5 mL) was transferred into an NMR tube fitted with a septum. H$_2$O (2 mg, 2 μL, 0.1 mmol) was added with a microliter syringe, followed by *tert*-butyl acrylate (128 mg, 144 μL, 1 mmol). The mixture was monitored by ^{31}P NMR spectroscopy. After 15 min, no unreacted Pt(dppe)(Me)(PPh$_2$) was observed. The main components of the mixture were phosphines **7a1** and **3a** and an unidentified Pt compound (δ 39.7 (J_{Pt-P} = 1844), 37.1 (J_{Pt-P} = 3454)). Compound **B-14** (1:1 mixture of diastereomers) and a small amount of **C** were also observed. After 3 days the major PPh$_2$-containing species was phosphine **7a1**, along with small amounts of **3a**. More **C** was observed, while the amount of **B-14** decreased. The unidentified Pt compound was still observed, along with another unidentified Pt species (δ 32.0). Some other small peaks (maybe analogues of Pt−dialkyls **B-14** containing more acrylates) were also observed: δ 48.1, 48.0, 47.7, 45.6, −18.5, −19.7. After 6 days, the amount of the δ 31.8 species (J_{Pt-P} = 3736, likely Pt(dppe)$_2$)[36] increased. After several weeks, a small amount of crystals had formed in the NMR tube; they were identified crystallographically as cation **17a** (Supporting Information).

In a companion experiment on the same scale, but without deliberately added water, after 20 min, the starting phosphido complex was consumed, and the major Pt complex present was **B-14**, plus a little **C**, and small amounts of the phosphines **3a** and **7a1**, as in a related smaller-scale experiment (entry 2, Table S1).

Synthesis of PPh$_2$(CH$_2$CH(CN)(CH$_2$CH$_2$CN) (7a1′) by Pt-

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Catalyzed Reaction of $H_2C{=}C(CN)(CH_2CH_2CN)$ (2-methyleneglutaronitrile) with $PHPh_2$.[15] To Pt((*R,R*)-Me-Duphos)(*trans*-stilbene) (8.2 mg, 0.012 mmol, 5 mol %) in toluene (0.2 mL) was added $PHPh_2$ (44.7 mg, 0.24 mmol) in toluene (0.3 mL). The mixture was transferred into an NMR tube, which was fitted with a septum. 2-Methyleneglutaronitrile (25.5 mg, 26.1 μL, 0.24 mmol) was added via a microliter syringe. The reaction went to completion in ~1 day, according to ^{31}P NMR spectroscopy. The catalyst was removed 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 total of 70 mg (99% yield) of a colorless oil was obtained.

Adducts of the oxidized phosphine with both a proton and a sodium ion were observed by mass spectroscopy.[1] HRMS: *m/z* calcd for $C_{18}H_{18}N_2OP^+$ (MOH^+) 309.1157, found 309.1147. HRMS: *m/z* calcd for $C_{18}H_{17}N_2NaOP^+$ ($MONa^+$) 331.0976, found 331.0983. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −20.4. ^{1}H NMR (C_6D_6): δ 7.30−7.20 (m, 4H, Ph), 7.10−7.03 (m, 6H, Ph), 2.12−2.03 (m, 1H, CH), 1.90 (dd, J = 14, 8, 1H), 1.68 (dd, J = 17, 7, 1H), 1.56−1.48 (m, 1H), 1.43−1.32 (m, 1H), 1.22−1.14 (m, 1H), 1.13−1.05 (m, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.6 (d, J = 13, quat), 137.5 (d, J = 13, quat), 133.6 (d, J = 20, Ph), 133.3 (d, J = 19, Ph), 129.9 (Ph), 129.8 (Ph), 129.41 (d, J = 7, Ph), 129.36 (d, J = 6, Ph), 120.2 (d, J = 6, CN), 118.2 (CN), 31.5 (d, J = 17, CH_2), 29.3 (d, J = 10, CH_2), 28.8 (d, J = 21, CH), 14.8 (CH_2). Addition of a slight excess of (*S*)-[$Pd(NMe_2CH(Me)C_6H_4)Cl]_2$ showed that the phosphine was formed in 16% ee ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.3, 33.9, ratio 1:1.4, 16% ee).

Reaction of Pt(dppe)(Me)(OH) (22) with $PPh_2CH_2CH_2CN$ (3a′). A solution of $PPh_2CH_2CH_2CN$ (7 mg, 0.03 mmol) in toluene (0.2 mL) was added to a suspension of Pt(dppe)(Me)(OH) (**22**, 19 mg, 0.03 mmol) in toluene (0.3 mL). The mixture was transferred into an NMR tube and monitored by ^{31}P NMR spectroscopy. After 1.5 h, no unreacted Pt(dppe)(Me)(OH) was observed, but $PPh_2CH_2CH_2CN$ was a major component of the mixture, along with Pt(dppe)(Me)($CH(CN)CH_2PPh_2$) (**A-14′**). Small amounts of Pt(dppe)(Me)(PPh_2) (**14**) and the cation $[(Pt(dppe)(Me))_2(\mu\text{-}PPh_2)]^+$ (**17a**) and very small amounts of the two diastereomers of Pt(dppe)(Me)($(CH(CN)CH_2)_2PPh_2$) (**B-14′**) and $PPh_2CH_2CH(CN)CH_2CH_2CN$ (**7a1**) were also observed. Over time, yellow crystals (perhaps Pt(dppe)(Me)(PPh_2), which is not very soluble in toluene) were observed on the walls of the NMR tube. An unidentified, symmetrical Pt species (δ 31.9, J_{Pt-P} = 3735), probably $Pt(dppe)_2$, was observed,[36] and the amount of **14** increased, at the expense of **A-14′**. After 2 weeks, the solution was separated from the crystals and the solvent was removed under vacuum. Toluene-d_8 (0.5 mL) was added to the mixture, which was transferred to an NMR tube. According to $^{31}P\{^1H\}$ NMR spectroscopy, the mixture consisted of Pt(dppe)(Me)(PPh_2), $Pt(dppe)_2$, and unreacted $PPh_2CH_2CH_2CN$.

Reaction of Pt((*R,R*)-Me-Duphos)(Ph)(OH) (23) with $PPh_2CH_2CH_2CN$ (3a′). A solution of $PPh_2CH_2CH_2CN$ (9 mg, 0.04 mmol) in toluene (0.2 mL) was added to a solution of Pt((*R,R*)-Me-Duphos)(Ph)(OH) (**23**, 21 mg, 0.04 mmol) in toluene (0.3 mL). The mixture was transferred into an NMR tube and monitored by ^{31}P NMR spectroscopy. After 1 h (~50% conversion), Pt((*R,R*)-Me-Duphos)(Ph)($CH(CN)CH_2PPh_2$) (**A**, 2 diastereomers, ~1:1) and a small amount of Pt((*R,R*)-Me-Duphos)(Ph)(PPh_2) were observed. Reaction proceeded slowly over 2 weeks, when a small amount of Pt((*R,R*)-Me-Duphos)(Ph)(OH) was still observed.

Pt((*R,R*)-Me-Duphos)(Ph)($CH(CN)CH_2PPh_2$). $^{31}P\{^1H\}$ NMR (toluene): diastereomer **a**: δ 65.2 (d, J = 3, J_{Pt-P} = 1676), 61.7 (dd, J = 19, 3, J_{Pt-P} = 2171), −12.9 (d, J = 19, J_{Pt-P} = 194); diastereomer **b**: δ 62.3 (J_{Pt-P} = 1669), 59.4 (dd, J = 7, 3, J_{Pt-P} = 2173), −14.8 (d, J = 7, J_{Pt-P} = 115).

Pt((*R,R*)-Me-Duphos)(Ph)(PPh_2). $^{31}P\{^1H\}$ NMR (toluene): δ 61.9 (dd, J = 128, 11, J_{Pt-P} = 1886), 59.2 (dd, J = 16, 11, J_{Pt-P} = 1602), −35.4 (dd, J = 128, 16, J_{Pt-P} = 1027).

Reaction of Pt(dppe)(Me)(OH) (22) with $PPh_2CH_2CH(CN)CH_2CH_2CN$ (7a1′). A solution of $PPh_2CH_2CH(CN)CH_2CH_2CN$ (17 mg, 0.06 mmol) in toluene (0.2 mL) was added to a suspension of Pt(dppe)(Me)(OH) (36 mg, 0.06 mmol) in toluene (0.3 mL). The mixture was transferred into an NMR tube and monitored by ^{31}P NMR spectroscopy. After 30 min, no unreacted Pt(dppe)(Me)(OH) was observed, but **7a1′** was a major component of the mixture, along with Pt(dppe)(Me)(PPh_2) (**14**). A little of the cation $[(Pt(dppe)(Me))_2(\mu\text{-}PPh_2)]^+$ (**17a**) and a very small amount of $PPh_2CH_2CH_2CN$ (**3a′**) were also observed. Over time, a symmetrical Pt complex (δ 31.9, J_{Pt-P} = 3735, likely $Pt(dppe)_2$)[36] formed, and the amount of $PPh_2CH_2CH_2CN$ (**3a′**) also increased. After two weeks, the solvent was removed under vacuum. Toluene-d_8 (0.5 mL) was added to the mixture, which was transferred to an NMR tube. According to $^{31}P\{^1H\}$ NMR spectroscopy, the mixture consisted of Pt(dppe)(Me)(PPh_2), $Pt(dppe)_2$, $PPh_2CH_2CH_2CN$, and unreacted $PPh_2CH_2CH(CN)CH_2CH_2CN$. ^{1}H NMR spectroscopy did not show the presence of any vinyl species.

Pt(dppe)(Cl)($CH(Me)CO_2t$-Bu) (20). To a stirring solution of Pt(dppe)(Me)(Cl) (**19**, 451 mg, 0.7 mmol) in CH_2Cl_2 (20 mL) was added N_2CHCO_2t-Bu (215 μL, 1.6 mmol) via a microliter syringe. The mixture was stirred for 16 h. The colorless solution was concentrated under vacuum, and petroleum ether was added to the residue, yielding a white precipitate. The white product was washed with petroleum ether (3 × 10 mL) and dried under vacuum, yielding 450 mg (85%) of white powder. Recrystallization from CH_2Cl_2 and petroleum ether gave crystals of a CH_2Cl_2 solvate suitable for X-ray crystallography.

Anal. Calcd for $C_{33}H_{37}ClO_2P_2Pt{\cdot}CH_2Cl_2$: C, 48.44; H, 4.66. Found: C, 48.84; H, 5.04. The presence of CH_2Cl_2 was detected by ^{1}H NMR (CD_2Cl_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 43.1 (d, J = 3, J_{Pt-P} = 4196), 42.8 (d, J = 3, J_{Pt-P} = 1898). ^{1}H NMR (CD_2Cl_2): δ 8.16−8.12 (m, 2H), 7.92−7.87 (m, 2H), 7.86−7.82 (m, 2H), 7.62−7.58 (m, 1H), 7.54−7.40 (m, 13H), 2.62−2.29 (m, 4H), 1.79−1.71 (m, 1H), 1.50 (9H), 0.62 (t, J = 8, J_{Pt-H} = 34, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.0 (d, J = 4, C=O), 135.4 (d, J = 12, Ar), 134.0 (d, J = 11, Ar), 133.6 (d, J = 11, Ar), 132.7 (d, J = 11, Ar), 132.3 (d, J = 2, Ar), 131.8 (d, J = 47, quat), 131.5 (d, J = 3, Ar), 131.3 (d, J = 2, Ar), 131.2 (d, J = 3, Ar), 130.5 (d, J = 44, quat), 129.18 (Ar), 129.17 (Ar), 129.10 (Ar), 129.08 (Ar), 129.06 (Ar), 128.97 (Ar), 128.86 (Ar), 128.78 (Ar), 128.7 (d, J = 57, quat), 127.0 (d, J = 60, quat), 77.4 (*C*Me$_3$), 31.9 (dd, J = 43, 17), 29.1 (C*Me*$_3$), 28.9 (dd, J = 87, 4), 26.1 (dd, J = 35, 8), 15.1 (d, J = 5, CH_3).

Generation of Pt(dppe)(Me)($CH(Me)CO_2t$-Bu) (21). Method I. A solution of $MeCH(ZnBr)(CO_2t\text{-}Bu){\cdot}THF$ (195.5 mg, 0.56 mmol) in THF (10 mL) was added to a stirring slurry of Pt(dppe)(Me)(Cl) (**19**, 214.6 mg, 0.33 mmol) in THF (10 mL). The reaction mixture immediately turned clear. ^{31}P NMR spectroscopy showed that the only Pt species present in the mixture was **21**. The solution was concentrated under vacuum, and the residue was dissolved in toluene. The slurry was filtered through Celite, and the filtrate was concentrated under vacuum. Petroleum ether was added to the white residue, yielding a white precipitate. Drying the precipitate under vacuum yielded 220 mg of white powder. Analyzing the product by ^{31}P NMR (C_6D_6 or THF-d_8) showed the presence of **21**, Pt(dppe)Me_2 (major impurity), and unreacted Pt(dppe)(Me)(Cl).

Method II. To a stirring slurry of Pt(dppe)(Cl)($CH(Me)CO_2t$-Bu) (**20**, 100 mg, 0.13 mmol) in toluene (20 mL) was added $ZnMe_2$ (71.6 μL of a 2 M solution in toluene, 0.14 mmol) via a microliter syringe, and a white precipitate formed immediately. The slurry was filtered through Celite, and the filtrate was concentrated under vacuum. Petroleum ether was added to the white residue, yielding a white precipitate. Drying the precipitate under vacuum yielded 50 mg of white powder. Analyzing the product by ^{31}P NMR (THF-d_8) showed the presence of **21** along with Pt(dppe)Me_2 and unreacted **20** as impurities. Crystals suitable for X-ray crystallography were obtained when the THF-d_8 solution was kept at −25

°C for 7 days. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 48.7 (d, $J = 5$, $J_{Pt-P} = 1802$), 47.6 (d, $J = 5$, $J_{Pt-P} = 2118$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 48.9 (d, $J = 5$, $J_{Pt-P} = 1794$), 47.3 (d, $J = 5$, $J_{Pt-P} = 2094$). ^1H NMR (C_6D_6): δ 8.08−8.01 (m, 2H, Ar), 7.68−7.56 (m, 4H, Ar), 7.37−7.29 (m, 2H, Ar), 7.26−7.20 (m, 2H, Ar), 7.19−7.13 (m, 2H, Ar), 7.06−6.95 (m, 8H, Ar), 3.84−3.75 (m, $J_{Pt-H} = 118$, 1H, Pt-CH), 2.09−1.74 (m, 4H), 1.66 (9H, *t*-Bu), 1.48 (t, $J = 7$, $J_{Pt-H} = 58$, 3H, Me), 1.31 (t, $J = 7$, $J_{Pt-H} = 68$, 3H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 180.4 (m, $J_{Pt-C} = 45$, C═O), 135.7 (d, $J = 12$, $J_{Pt-C} = 18$, Ar), 134.1 (d, $J = 11$, Ar), 133.9 (d, $J = 12$, Ar), 132.7 (d, $J = 11$, Ar), 131.3 (d, $J = 2$, Ar), 130.9 (d, $J = 2$, Ar), 130.8 (d, $J = 2$, Ar), 130.3 (d, $J = 2$, Ar), 129.2 (d, $J = 10$, Ar), 129.1 (d, $J = 10$, Ar), 128.91 (d, $J = 10$, Ar), 128.86 (d, $J = 10$, Ar); the remaining four expected Ar peaks could not be assigned confidently; 76.3 (CMe_3), 30.4−29.8 (m, CH_2), 29.8 ($C(CH_3)_3$), 24.0 (dd, $J = 83$, 4, $J_{Pt-C} = 547$, Pt-CH), 17.1 (d, $J = 6$, $J_{Pt-C} = 30$, CH_3), 3.6 (dd, $J = 92$, 7, Pt-Me).

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Supporting Information Available: Details of the X-ray crystallographic studies, including CIF documents, and additional experimental and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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