Palladium-Catalyzed Phosphaketene Decarbonylation: Diphosphaureylene Intermediates in Diphosphene Formation

Marie-Anne David, Denyce K. Wicht, and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Glenn P. A. Yap, Louise M. Liable-Sands, and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received August 27, 1997

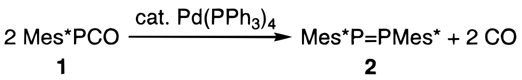
*Summary: Pd(PPh$_3$)$_4$-catalyzed decarbonylation of the phosphaketene Mes*PCO (**1**, Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$) gives the diphosphene Mes*P═PMes* (**2**). Related reactions of **1** with zerovalent Pd and Pt phosphine complexes afford diphosphaureylene complexes ML$_2$[Mes*PC(O)-PMes*] (L$_2$ = chelating diphosphine), whose structure and properties depend markedly on the metal and ancillary ligands; Pd(dppf)[Mes*PC(O)PMes*] (**12**, dppf = 1,1′-bis(diphenylphosphino)ferrocene) also catalyzes the title reaction.*

Decarbonylation of the phosphaketene[1] Mes*PCO (**1**, Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$) by metal complexes usually results in stoichiometric P═C bond cleavage and yields products derived from the phosphinidene Mes*P.[2] We report here a new reaction of **1**: Pd-catalyzed decarbonylation to give the diphosphene Mes*P═PMes* (**2**), the formal result of phosphinidene coupling.[3] Related stoichiometric Pd and Pt chemistry yields diphosphaureylene [Mes*PC(O)PMes*] complexes, which appear to be involved in P−P bond formation.

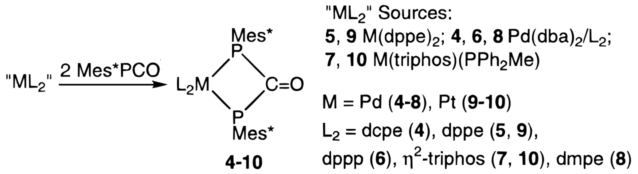
Pd(PPh$_3$)$_4$ catalyzes decarbonylation of **1** to yield **2** (∼5 turnovers/h, THF, room temperature). The reaction is quantitative by ^{31}P NMR, and diphosphene **2** was isolated after recrystallization as orange crystals in 70% yield (Scheme 1).[4] Although the Pd catalyst could be recovered, monitoring of the reaction by IR and ^{31}P NMR shows that Pd(PPh$_3$)$_3$(CO) (**3**)[5] is formed and decomposes on workup. Independently prepared **3** also catalyzes the formation of **2**, at a similar rate.[6]

Related Pt and Pd chemistry with chelating diphosphine ligands provides insight into the mechanism of the catalytic reaction. A variety of zerovalent metal precursors react with 2 equiv of **1** to give the diphosphaureylene complexes ML$_2$[Mes*PC(O)PMes*] (M = Pd, L$_2$ = dcpe (**4**), dppe (**5**), dppp (**6**), η^2-triphos (**7**), dmpe (**8**); M = Pt, L$_2$ = dppe (**9**), η^2-triphos (**10**)) (Scheme 2).[7]

Scheme 1



Scheme 2



Complexes **8**−**10**, like the previously reported Pt(dmpe)[Mes*PC(O)PMes*] (**11**),[2d] are orange to red, but Pd compounds **4**−**7** are green. ^{31}P NMR data also shows large differences between **4**−**7** and **8**−**11** (AA′XX′ spin systems, Table 1). The chemical shift (ppm) of the diphosphaureylene P nuclei ranges from 14.0 to 51.8 for **8**−**11** but from 134.7 to 176.8 for **4**−**7**. Moreover, the green complexes show a larger cis J_{PP} coupling within the diphosphaureylene ligand (353−433 Hz) and a smaller trans J_{PP} coupling (89−126 Hz) than the red analogs, for which J_{cis} ranges from 191 to 158 Hz and J_{trans} from 217 to 196 Hz. In both sets of complexes, these chemical shifts and cis J_{PP} coupling constants

---

[1] Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785−786.

[2] (a) Champion, D. H.; Cowley, A. H. *Polyhedron* **1985**, *4*, 1791−1792. (b) Cowley, A. H.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734−6735. (c) David, M.-A.; Paisner, S. N.; Glueck, D. S. *Organometallics* **1995**, *14*, 17−19. (d) David, M.-A.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4040−4042.

[3] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587−4589.

[4] **Pd-catalyzed formation of 2.** Addition of Pd(PPh$_3$)$_4$ (6 mg, 0.005 mmol) to an orange solution of Mes*PCO (33 mg, 0.11 mmol) in 1 mL of THF immediately gave a dark brown solution; the ^{31}P NMR spectrum of the mixture after 2 h showed that **2** was formed quantitatively (11 turnovers). The solvent was removed, and the residue was extracted with 5 mL of petroleum ether. Cooling the resulting orange solution to −25 °C gave 21 mg of **2** (70%).

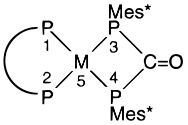
[5] (a) Kudo, K.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1971**, *33*, 393−398. (b) Morandini, F.; Consiglio, G.; Wenzinger, F. *Helv. Chim. Acta* **1979**, *62*, 59−61.

[6] Since the title reaction is not synthetically useful, we did not carry out detailed rate studies or attempt to maximize turnover number. However, after catalysis by Pd(PPh$_3$)$_4$ was complete, if more **1** was added to the reaction mixture, it was also converted to **2** at a similar rate.

[7] Abbreviations used: dba = dibenzylideneacetone, triphos = MeC(CH$_2$PPh$_2$)$_3$, dppp = Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$, dcpe = Cy$_2$PCH$_2$CH$_2$PCy$_2$ (Cy = cyclo-C$_6$H$_{11}$), dppf = Ph$_2$PC$_5$H$_4$FeC$_5$H$_4$PPh$_2$. Synthetic details and characterization data for the new complexes are included in the Supporting Information; an example follows. **Synthesis of 5.** To a solution of Pd(dppe)$_2$ (151 mg, 0.168 mmol) in THF (1 mL) was added Mes*PCO (102 mg, 0.335 mmol) dissolved in THF (1 mL). The mixture became deep green immediately and was stirred at room temperature in the dark for 1 h. The solvent was removed in vacuo. The green residue was washed with petroleum ether (40 mL), filtered, dissolved in a minimum of THF, layered with petroleum ether, and cooled to −25 °C to give **5** as a green powder (129 mg, 71% yield). Green needles can be obtained by recrystallization from THF/petroleum ether or by slow evaporation of a THF solution. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.48−7.42 (m, 8H), 7.34−7.30 (m, 8H), 7.16−7.11 (m, 8H), 2.19−2.13 (m, 4H), 1.47 (36H), 1.34 (18H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 226.5 (t, $^1J_{P-C}$ = 64 Hz, quat, CO), 157.2 (br, quat Ar), 149.8 (quat Ar), 134.8−134.0 (m, quat Ar), 133.8−133.6 (m, Ar), 132.9−132.4 (m, quat Ar), 130.7 (Ar), 128.9−128.8 (m, Ar), 122.9 (br, Ar), 39.4 (quat), 35.4 (quat), 34.1 (*ortho* Me), 31.6 (*para* Me), 26.3−25.8 (m, CH$_2$). IR(KBr): 3053, 2953, 2903, 1590, 1521, 1478, 1434, 1391, 1358, 1309, 1278, 1211, 1100, 1025, 1000, 921, 876, 821, 743, 695, 651, 586, 524, 482 cm^{-1}. Anal. Calcd. for C$_{63}$H$_{82}$OP$_4$Pd: C, 69.69; H, 7.63. Found: C, 69.31; H, 7.64.

S0276-7333(97)00761-9 CCC: $14.00

Table 1. ^{31}P **NMR Data for Pd and Pt Diphosphaureylene Complexes**[a]



M = Pd (**4-8**), Pt (**9-11**)
L_2 = dcpe (**4**), dppe (**5**, **9**), dppp (**6**),
η^2-triphos (**7**, **10**), dmpe (**8**, **11**)

complex	$\delta(P_1)$	$\delta(P_3)$	$^2J_{12}$	$^2J_{13}$	$^2J_{14}$	$^2J_{34}$
4[b]	61.8	134.7	75	−22.5	123.6	363
5[c]	41.5	142.8	80	−33	126	353
6[b]	3.5	172.3	131	−40	89	428
7[b,d]	5.2	176.8	126	−38	90	433
8[b]	26.5	51.8	50	−18	211	170
9[e,f]	50.5	48.5	17	−2.7	202	175
10[d,f,g]	2.1	50.9	39	−5.5	196.3	190.8
11[b,f,h]	32.0	14.0	10	−5.5	216.5	158

[a] Chemical shifts in ppm (85% H_3PO_4 external reference); coupling constants in Hertz. [b] In CD_2Cl_2. [c] In CD_2Cl_2/C_6D_6. [d] Uncoordinated triphos arm resonance: for **7**, δ −25; for **10**; δ −26.5. [e] In THF-d_8. [f] Pt−P couplings: for **9**, $J_{15} = 2477$, $J_{35} = 1145$; for **10**, $J_{15} = 2459$, $J_{35} = 1085$; for **11**, $J_{15} = 2435$, $J_{35} = 1103$. [g] In C_6D_6. [h] David, M.-A.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4040−4042.

increase with the cone angle and the bite angle of the ancillary diphosphine ligand.

These spectroscopic observations suggest a structural difference between the two sets of complexes, which was confirmed by X-ray crystallography.[8] The PtPC(O)P ring in Pt complex **9** (Figure 1) is essentially planar (fold angle between PMP and PCP planes = 5.4°), but in Pd analog **6** (Figure 2) this ring is puckered with fold angles of 29.3° and 31.0° in the two independent molecules. This puckering (Figure 3) suggests a contribution from a π-allyl resonance structure as in analogous oxatrimethylenemethane complexes.[9]

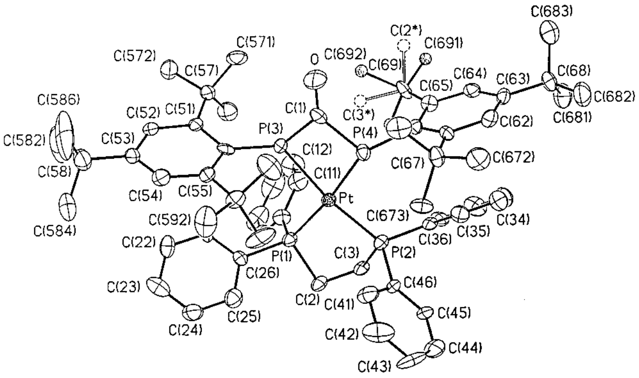


Figure 1. ORTEP diagram of **9**. A *tert*-butyl group (C2*,-C3*) is rotationally disordered in two positions with a 50/50 distribution. The disordered carbon atoms were refined isotropically. Selected bond lengths (Å): Pt−P(1) 2.276(3); Pt−P(2) 2.288(3); Pt−P(3) 2.377(4); Pt−P(4) 2.347(3); P(3)−C(1) 1.805(12); P(4)−C(1) 1.794(12); O−C(1) 1.248(10). Selected bond angles (deg): P(1)−Pt−P(2) 85.02(11); P(1)−Pt−P(4) 172.24(10); P(2)−Pt−P(4) 102.52(12); P(1)−Pt−P(3) 100.79(12); P(2)−Pt−P(3) 171.24(11); P(4)−Pt−P(3) 71.95(10); C(1)−P(3)−Pt 92.8(4); C(1)−P(4)−Pt 94.1(4); O−C(1)−P(4) 128.9(11); O−C(1)−P(3) 130.2(11); P(4)−C(1)−P(3) 100.9(5).

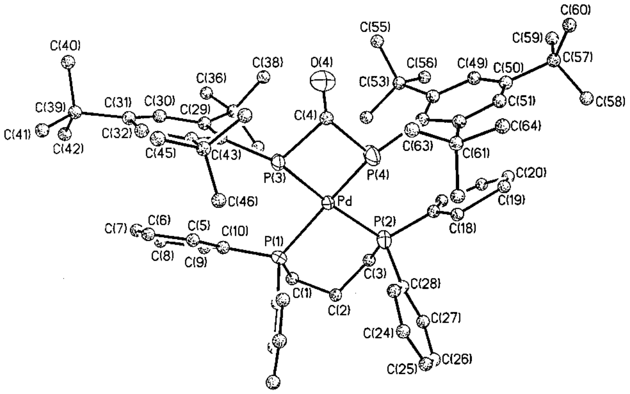


Figure 2. ORTEP diagram of **6**, showing one of the two independent molecules in the asymmetric unit. Data for one of these molecules, selected bond lengths (Å): Pd−P(1) 2.382(5); Pd−P(2) 2.348(5); Pd−P(3) 2.398(5); Pd−P(4) 2.356(6); P(3)−C(4) 1.95(2); P(4)−C(4) 1.79(2); O(4)−C(4) 1.11(2). Selected bond angles (deg): P(1)−Pd−P(2) 90.3(2); P(1)−Pd−P(4) 160.2(2); P(2)−Pd−P(4) 97.2(2); P(1)−Pd−P(3) 97.7(2); P(2)−Pd−P(3) 166.8(2); P(4)−Pd−P(3) 72.0(2); C(4)−P(3)−Pd 89.0(6); C(4)−P(4)−Pd 94.5(7); O(4)−C(4)−P(4) 136(2); O(4)−C(4)−P(3) 127(2); P(4)−C(4)−P(3) 96.5(11).

Diphenylphosphino-ligated palladium complexes **5**−**7** decompose in THF solution to afford diphosphene **2** (at room temperature for **6** and **7** and 65 °C for **5**). This suggests a possible mechanism for the catalysis (Scheme 3), in which diphosphene **2** is formed from related diphosphaureylene intermediates by CO extrusion from the diphosphaureylene ring[10] and P=P bond formation, in a formal reductive elimination from Pd(II).[11] Consistent with this description of the reactivity, the more electron-rich Pt and dialkylphosphino-ligated Pd complexes **4** and **8**−**11** do not form **2**. The increase in reactivity with diphosphine bite angle from **5** to **6** and **7** may be rationalized by a destabilization of the

---

(8) Crystal data for **6**: $C_{64}H_{84}OP_4Pd$, fw = 1099.59, monoclinic, $P2_1$, $a = 10.539(2)$ Å, $b = 20.538(3)$ Å, $c = 27.777(5)$ Å, $\beta = 91.607(4)°$, $V = 6010(2)$ Å^{3,} $Z = 4$, $T = 218(2)$ K, $D_{calc} = 1.215$ g/cm^3, $R(F) = 12.98\%$, $R(wF^2) = 26.66\%$ for 10 148 independent observed reflections ($3° \le 2\theta \le 58°$). Despite several recrystallizations, the best crystals that could be obtained were extremely weak diffractors and the reflections were diffuse. Because systematic absences in the data contained weak violations (ca. 1.5σ) to the 2_1 screw axis and showed the absence of a glide plane, the space group options $P2$, $P2/m$, Pm, $P2_1$, and $P2_1/m$ were allowed. From these options, those without mirror plane symmetry were preferred and those with mirror plane symmetry were initially rejected, because the potential mirror-plane is misaligned with the crystallographic *ac* plane. Of the remaining options, solution and refinement was successful in $P2_1$ only. There are two crystallographically independent but chemically equivalent molecules in the asymmetric unit. The refined value of the Flack parameter suggested the possibility of a racemic twin, and a 60/40 model minimized *R*. Disorder was observed in the methyl carbons of the Mes* *tert*-butyl groups, but attempts to model it were incomplete; they were fixed as rigid tetrahedra and refined isotropically. The carbonyl carbon atom in each of the two molecules, C(4) and C(4′), was also refined isotropically. Crystal data for **9**: $C_{63}H_{82}OP_4Pt$, fw = 1174.26, monoclinic, $P2_1/c$, $a = 10.736(3)$ Å, $b = 19.13(2)$ Å, $c = 29.16(2)$ Å, $\beta = 99.44(3)°$, $V = 5908(8)$ Å^3, $Z = 4$, $T = 298(2)$ K, $D_{calc} = 1.320$ g/cm^3, $R(F) = 4.07\%$, $R(wF^2) = 4.50\%$ for 3605 independent observed reflections ($4° \le 2\theta \le 42°$). The carbon atoms of one of the *tert*-butyl groups on the supermesityl ligand were equally disordered over two positions, so its carbon atoms were refined isotropically. The structure of **5** was also determined, but only serves to establish the connectivity: $C_{63}H_{82}OP_4Pd$, triclinic, $P\bar{1}$, $a = 10.394(4)$ Å, $b = 13.493(6)$ Å, $c = 25.17(2)$ Å, $\alpha = 75.75(5)°$, $\beta = 88.41(5)°$, $\gamma = 78.80(3)°$, $V = 3355(4)$ Å^3, $Z = 2$, $T = 293(2)$K, $D_{calc} = 1.074$ g/cm^3, $R(F) = 14.42\%$, $R(wF^2) = 34.70\%$.

(9) Kemmitt, R. D. W.; Moore, M. R. *Transition Met. Chem.* **1993**, *18*, 348−352. Since the Pd−C distance in **6** (3.068(10) and 3.100(10) Å) is nonbonding (and similar to that in **9** (3.055(6) Å)), the contribution from such an allyl structure is likely to be minor.

(10) For related reactions, see: (a) Becher, H. J.; Langer, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 842−843. (b) Appel, R.; Paulen, W. *Chem. Ber.* **1983**, *116*, 2371−2373. (c) Appel, R.; Paulen, W. *Chem. Ber.* **1983**, *116*, 109−113. (d) King, R. B.; Wu, F.-J.; Holt, E. M. *J. Organomet. Chem.* **1990**, *383*, 295−305.

(11) Reductive elimination of diphenylphosphido groups from Pd(II) to afford Ph_2PPPh_2 has been proposed. Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748−753.

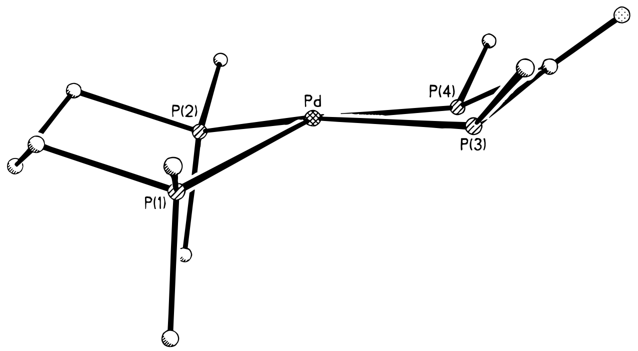
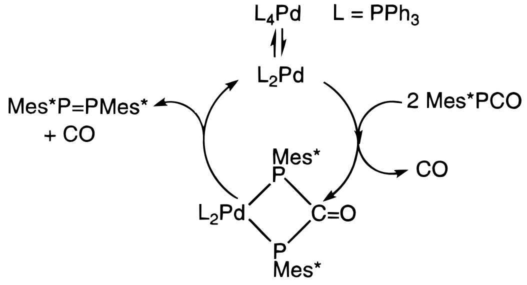
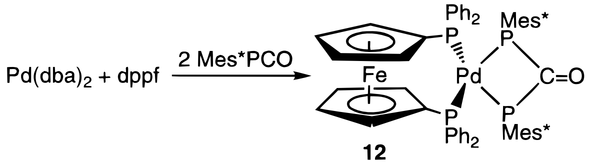


Figure 3. ORTEP diagram of **6**, showing one of the two independent molecules. Phenyl and Mes* groups have been removed for clarity, to emphasize the pucker of the PdPCP ring.

Scheme 3



Scheme 4



12

distorted square planar ground state by increasing steric interactions between the PPh_2 and PMes* groups.

We have not yet carried out kinetic studies or obtained direct evidence for intramolecular P−P bond formation, but this mechanistic hypothesis suggested related studies of the dppf ligand, whose large bite angle is known to promote reductive elimination in Pd(0)-catalyzed coupling reactions.[12] Bright green Pd(dppf)-[Mes*PC(O)PMes*] (**12**), rapidly formed on addition of 2 equiv of **1** to a mixture of $Pd(dba)_2$ and dppf (Scheme 4),[13] displays an apparent A_2X_2 ^{31}P NMR spectrum (C_6D_6: δ 212.7; 15.6 (J_{AX} = 15 Hz)), in contrast to the AA′XX′ spectra seen for the rest of this series. This observation is consistent with the pseudotetrahedral C_{2v} structure illustrated in Scheme 4, as in Mathey's analogous metalladiphospholene complexes.[14] In solution, complex **12** decomposes to **2** and unidentified Pd complexes in hours at room temperature but it is stable when generated in the presence of excess phosphaketene **1**; under these conditions, **1** is catalytically converted to **2** and, once **1** is consumed, **12** decomposes. Complex **12** also decomposed slowly in solution at −60 °C but could be isolated as a pure green solid by recrystallization in the presence of excess **1** and stored in the solid state at room temperature for days. Isolated **12** catalyzes formation of **2** from **1**, but not as quickly as $Pd(PPh_3)_4$ (~1 turnover/h).[6]

In conclusion, we have observed the novel Pd-catalyzed decarbonylative coupling of phosphaketene **1**. Related chemistry with chelating diphosphines suggests that the catalysis proceeds via diphosphaureylene intermediates, whose structure and reactivity depend both on the metal and on the ancillary ligands. Further mechanistic studies on these and related compounds with M−P bonds will be required to provide support for this hypothesis and to compare metal-mediated reactions which lead to formation of bonds to phosphorus[15] to the well-studied processes that make bonds to carbon.[16]

Acknowledgment. We thank Dartmouth College and the Petroleum Research Fund, administered by the American Chemical Society, for partial support and Johnson-Matthey/Alfa/Aesar for loans of Pd and Pt salts.

Supporting Information Available: Text giving experimental details and characterization data for complexes **4** and **6**−**10** and tables of the crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H-atom coordinates for **6** and **9** (29 pages). Ordering information is given on any current masthead page.

OM970761J

---

(12) (a) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158−163. (b) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249−259.

(13) **Pd(dppf)[Mes*PC(O)PMes*] (12)**. Mes*PCO (48 mg, 0.16 mmol) was added to a red-purple solution of $Pd(dba)_2$ (30 mg, 0.052 mmol) and dppf (36 mg, 0.065 mmol) in CH_2Cl_2 (5 mL). After the solution turned green (a few minutes), the solvent was removed under vacuum and the resulting green residue was washed with petroleum ether (in which it is sparingly soluble), then dissolved in acetonitrile. Addition of petroleum ether gave an immiscible mixture; green flakes of the product, which formed at the interface at −20 °C, were collected, washed with petroleum ether, and dried in vacuo to give 20 mg (31% yield) of **12**. An analytical sample (green crystals of a methylene chloride solvate, as confirmed by ^1H NMR) was obtained by further recrystallization from CH_2Cl_2/petroleum ether in the presence of Mes*PCO. ^1H NMR (C_6D_6): δ 7.76 (br, 7H), 7.42 (4H), 7.0−6.86 (m, 13H), 4.15 (4H), 3.76 (4H), 1.69 (36H), 1.35 (18H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 212.7 (t, J = 15 Hz), 15.6 (t, J = 15 Hz). IR(KBr): 2959, 1595, 1478, 1436, 1390, 1361, 1094, 740, 693, 489 cm^{-1}. Anal. Calcd for $C_{71}H_{86}FeOP_4Pd{\cdot}CH_2Cl_2$: C, 65.18; H, 6.70. Found: C, 64.94; H, 6.48. FAB-MS (3-NBA): m/z 1305, 1241 $(MH)^+$, 937 $(M - Mes*PCO)^+$, 660 (M − Mes*PCOPMes*). HRMS calcd for $C_{71}H_{87}FeOP_4Pd$ $(MH)^+$ 1241.4092, found 1241.4075.

(14) Sillett, G.; Ricard, L.; Patois, C.; Mathey, F. *J. Am. Chem. Soc.* **1992**, *114*, 9453−9457. It is also possible that the spectrum is a special case of the AA′XX′ system where some of the couplings are equivalent (see Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1997**, *16*, 1253−1259) or that P−P bond formation has occurred and **12** is a pseudotetrahedral Pd(0) complex of a three-membered ring ligand.

(15) For related studies, see: Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040.

(16) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933−4941. (b) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857−1867. (c) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115−6128.