Preparation of [^{13}C]Allyl Chloride and the Bis(allyl)-rhodium Chloride Dimer.[6] Lithium chloride (3.00 g, 70 mmol) was added to a solution of [1-^{13}C]allyl tosylate (2.79 g, 13 mmol) in absolute methanol (10 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature with vigorous stirring. After 2 h, TLC analysis showed all the tosylate had been consumed. The mixture was connected to a Schlenk flask through a U-tube, degassed by several freeze–pump–thaw cycles, and then distilled at room temperature into the Schlenk flask, which was cooled to −196 °C. After ca. 2 h, the distillation was complete. The flask was warmed to room temperature, and cyclohexane (100 μL) was added as an internal GC standard; GC analysis showed that the allyl chloride had been formed quantitatively.

Freshly sublimed $[(OC)_2RhCl]_2$ was added to the above-described solution of allyl chloride, and a 5 N solution of KOH in water was added until the solution reached ca. pH 6 (too much base causes the solution to turn from bright yellow to red). The solution was briefly held at reduced pressure to remove excess allyl chloride, and then water (10 mL) was added. The resulting yellow precipitate was filtered out, and the mother liquors were concentrated at reduced pressure to yield more material. The combined yield of $[(allyl)_2RhCl]_2$ was 400 mg (74%). An aliquot was recrystallized from CH_2Cl_2/methanol for X-ray analysis. Analytical data for the complex are as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (dd, $^3J_{C-H}$ = 8.2, J_{H-H} = 7.2 Hz, 0.5 H), 5.13 (dd, $^1J_{C-H}$ = 157.8, J_{H-H} = 7.2 Hz, 0.5 H), 5.8 (m, 1 H), 4.10 (dd, J_{H-H} = 12.1, $^3J_{C-H}$ = 4.4 Hz, 0.5 Hz), 4.10 (dd, $^1J_{C-H}$ = 161.7, J_{H-H} = 12.3 Hz, 0.5 H), 2.54 (dd, $^3J_{C-H}$ = 7.6, J_{H-H} = 6.2 Hz, 0.5 H), 2.54 (dd, $^1J_{C-H}$ = 156.0, J_{H-H} = 6.0 Hz, 0.5 H), 1.86 (dd, $^1J_{C-H}$ = 161.7, J_{H-H} = 11.6 Hz, 0.5 H), 1.86 (dd, $^3J_{C-H}$ = 4.4, J_{H-H} = 11.6 Hz, 0.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.5 (d, J_{Rh-C} = 11.9 Hz), 76.5 (d, J_{Rh-C} = 5.8 Hz); IR (KBr) δ 3044, 2983, 1454, 1391, 1245, 1017, 1000, 962, 913, 901, 564, 547 cm^{-1}; HRMS calcd for $^{12}C_8{}^{13}C_4Rh_2Cl_2H_{20}$ *m/e* 443.9186, found *m/e* 443.9179; LRMS *m/e* 444 (2, >97% ^{13}C), 222 (24), 187 (15), 186 (99), 184 (42), 145 (100), 144 (38), 143 (71), 103 (36), 84 (55), 69 (85), 68 (61).

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Supplementary Material Available: A figure showing a unit cell and tables of crystallographic details, anisotropic thermal parameters, and H atom coordinates and thermal parameters (3 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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Transformation of Alkynylphosphine Oxides and Alkynylphosphonium Cations to 2-Alkylidene-1,2-dihydro-3-phosphete Ligands by Pt–H Addition and Rearrangement Reactions†

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Summary: The reactions of [*trans*-Pt(H)(PEt_3)$_2$(THF)]$^+$ with several di- or trialkynylphosphine oxides or phosphonium cations are reported. Regioselective addition of the Pt–H bond to one of the alkynyl substituents of the substrate O=P(C≡CMe)$_3$ or [$Me_2P(C{\equiv}CCMe_3)_2$]$^+$ occurs to give Pt,P-μ-alkenylidene complexes. A similar addition to the substrates O=P(C≡CCMe$_3$)$_2$R, where R is Ph or Me, or to [MeP(C≡CCMe$_3$)$_3$]$^+$ occurs with a subsequent insertion of a second alkynyl substituent to form 2-alkylidene-1,2-dihydrophosphete ligands. A reaction using [(Me)(Ph)P(C≡CCMe$_3$)$_2$]$^+$ as substrate affords both Pt,P-μ-alkenylidene and heterocyclic products.

Very little information is known about the synthesis and chemistry of molecules containing a 1,2-dihydrophosphete ring system.[1] In recent years, synthetic routes to these rare heterocycles have been reported utilizing the reaction chemistry of transition-metal, organometallic compounds. Mathey and co-workers have reported examples of the formation of complexes containing 1,2-dihydrophosphete ligands from (1) the thermal ring opening of the corresponding phosphirene complexes,[2] (2) reaction of a 7-phosphanorbornadiene complex with a Cr–alkylidene complex,[3] (3) [2 + 2] cycloaddition of phosphaalkene complexes with ynamines and ethoxyacetylene,[4] and, (4) the spontaneous cyclization of η^1-1-phosphadiene complexes.[5] In selected cases, oxidation of 1,2-dihydrophosphete complexes gave the free heterocycle as the corresponding *P*-oxide. Dötz and co-workers have reported the formation of a 1,2-dihydrophosphete ligand by reaction of an alkylidene complex with a phosphaalkyne.[6] Very recently, Doxsee and Tumas independently reported the formation of 1,2-dihydrophosphetes by a transmetalation reaction between a titanacyclobutene complex and various alkyl- or aryldichlorophosphines.[7]

We also reported recently that the Pt–H bond of cationic platinum hydride complexes adds regioselectively to the alkynyl substituent of the phosphine oxide, O=PPh_2(C≡CPh), to give a Pt,P-μ-alkenylidene complex. A similar addition presumably occurs with the trialkynyl-

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phosphine oxide, O=P(C≡CCMe$_3$)$_3$; however, subsequent insertion of a *second* alkynyl substituent into the Pt–C(alkenylidene) bond leads upon rearrangement to the formation of a 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligand.[8] This synthetic method has been successfully extended to the formation of analogous unsaturated, four-membered heterocycles of Si, S, and As.[9] We now report the results of extending this Pt–H addition reaction to include, as substrates, four additional di- or trialkynylphosphine oxides and three di- or trialkynylphosphonium salts. This study was undertaken to determine the general scope of the formation of 1,2-dihydrophosphetes by this method and to prepare such heterocyclic compounds containing phosphonium centers within the heterocyclic ring. These latter compounds might serve as precursors to more reactive ylide derivatives. Also, this synthetic method is the only known route to 1,2-dihydrophosphete heterocycles that contain *exo*-alkylidene substitution on the four-membered ring.

Experimental Section

Materials and Methods. The details of solvent purification and instrumental specifications were reported previously.[8] All manipulations were performed under an atmosphere of dry, prepurified nitrogen and at room temperature unless otherwise indicated. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The known phosphine oxides O=P(C≡CCH$_3$)$_3$, **1a**, and O=P(C≡CCMe$_3$)$_2$(Ph) [mp 84–87 °C; lit. oil], **1b**, were prepared by published procedures.[10] The cationic platinum hydride salts **2a** and **2b** were prepared from the neutral chloride derivatives by reaction with the appropriate silver salt as described previously.[8]

Preparation of O=P(C≡CCMe$_3$)$_2$(Me) (1c). This phosphine oxide was prepared according to standard procedures.[10,11] To a solution of 7.38 mmol of Li(C≡CCMe$_3$) in diethyl ether at −78 °C was added dropwise a solution of 7.38 mmol of dichloromethylphosphine in diethyl ether. The reaction solution was warmed to room temperature and was kept at that temperature for 2 h, at which time the pH of the solution was found to basic. The solvent was removed at reduced pressure to give a yellow oil that was subsequently dissolved in benzene. Lithium chloride was removed by filtration of this solution through a thin layer of alumina. The benzene was removed at reduced pressure. The obtained colorless oil was treated with a slight excess of H_2O_2 in acetone to give a yellow oil upon evaporation of the solvent. The oil residue was washed with 2 × 20 mL of pentane at −78 °C to give **1c** in 39% yield as a colorless solid: mp 57–58 °C. ^{1}H NMR (CDCl$_3$) δ 1.27 (s, 18, CMe$_3$), 1.80 (d, 3, Me, $^2J_{PH}$ = 16.1 Hz). IR (KBr, cm^{-1}) ν (C≡C) 2201, 2170; ν (P—O) 1201.

Preparation of [CH$_3$P(C≡CCMe$_3$)$_3$][BF$_4$] (5a). To a solution of 1.95 mmol of P(C≡CCMe$_3$)$_3$[11a] in CH$_2$Cl$_2$ at −78 °C was added 0.277 g (1.87 mmol) of [Me$_3$O][BF$_4$]. The mixture was warmed to room temperature and was stirred for 16 h. The solvent was then removed at reduced pressure to give a white solid that was recrystallized from ether/pentane solution at −20 °C to give 0.272 g (38%) of **5a** as colorless needles: mp 115–117 °C. ^{1}H NMR (CDCl$_3$) δ 1.36 (s, 27, CMe$_3$), 2.56 (d, 3, CH$_3$, $^2J_{PH}$ = 16 Hz). Anal. Calcd for C$_{19}$H$_{30}$BF$_4$P: C, 60.65; H, 8.04. Found: C, 60.95; H, 8.08.

Preparation of [(CH$_3$)$_2$P(C≡CCMe$_3$)$_2$][BF$_4$] (5b). The same method used for the preparation of **5a** was followed for the preparation of **5b**. Compound **5b** was isolated as white crystals in 51% yield: mp 131–132 °C. ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 18, CMe$_3$), 2.33 (d, 6, CH$_3$, $^2J_{PH}$ = 16 Hz). Anal. Calcd for C$_{14}$H$_{24}$BF$_4$P: C, 54.22; H, 7.80. Found: C, 54.08; H, 8.01.

Preparation of [(C$_6$H$_5$)(CH$_3$)P(C≡CCMe$_3$)$_2$][BF$_4$] (5c). The same method used for the preparation of **5a** was followed for the preparation of **5c**. Compound **5c** was isolated as white crystals in 32% yield: mp 144–145 °C. ^{1}H NMR (CDCl$_3$) δ 1.48 (s, 18, CMe$_3$), 2.54 (d, 3, CH$_3$, $^2J_{PH}$ = 16 Hz), 7.5–8.0 (m, 5, Ph). ^{31}P{H} NMR (CDCl$_3$) δ −20.9 (s, P). Anal. Calcd for C$_{19}$H$_{26}$BF$_4$P: C, 61.31; H, 7.04. Found: C, 61.30; H, 7.16.

Preparation of {*cis*-Pt[OP(C≡CMe)$_2$-(*E*)-C=C(Me)(H)](PEt$_3$)$_2$}[SbF$_6$] (3a). To a solution of 0.102 g (0.62 mmol) of **1a** in CH$_2$Cl$_2$ at −78 °C was added 0.62 mmol of **2a** as a solution in CH$_2$Cl$_2$. The reaction solution was stirred for 22 h at −20 °C, and then the solvent was removed at reduced pressure. The residue was washed with 2 × 5 mL of THF and then was dried at reduced pressure to give 0.21 g (40%) of **3a** as a white solid: mp 210–211 °C dec. ^{1}H NMR (CD$_2$Cl$_2$) δ 1.04–1.35 (m, 18, PCH$_2$*CH$_3$*), 1.67–2.05 (m, 15, P*CH$_2$*CH$_3$, C=C*CH$_3$*), 2.10 (d, 6, C≡CMe, $^3J_{PH}$ = 4.6 Hz), 6.71 (d of m, 1, C=CH, $^3J_{HH}$ = 7.7 Hz, $^3J_{P(O)H}$ = 66 Hz, $^4J_{PH}$ = 7.7 Hz, $^3J_{PtH}$ = 62 Hz). ^{31}P{H} NMR (CD$_2$Cl$_2$) δ 8.1 (d of d, PEt$_3$, $^2J_{PP}$ = 16 Hz, $^3J_{P(O)P}$ = 8 Hz, $^1J_{PtP}$ = 4089 Hz), 15.7 (d of d, PEt$_3$, $^2J_{PP}$ = 16 Hz, $^3J_{P(O)P}$ = 27 Hz, $^1J_{PtP}$ = 2296 Hz), 24.6 (d of d, P=O, $^2J_{PtP}$ = 286 Hz, $^3J_{P(O)P}$ = 8 and 24 Hz). IR (KBr, cm^{-1}) ν (C≡C) 2220; ν (P=O) 1150. Anal. Calcd for C$_{21}$H$_{40}$F$_6$OP$_3$PtSb: C, 30.31; H, 4.82. Found: C, 30.30; H, 4.73.

Preparation of {*trans*-Pt[C=C(CMe$_3$)P(O)(Ph)C=C(CMe$_3$)(H)](PEt$_3$)$_2$(H$_2$O)][BF$_4$] (4a). To a solution of 0.134 g (0.47 mmol) of **1b** in 4 mL of THF was added 0.46 mmol of **2b** as a solution in THF. The reaction solution was stirred for 1.5 h during which time a white solid precipitated from solution. The solid was isolated and was washed with 10 mL of ether to give upon drying 0.10 g (26%) of **4a** as a white solid: mp 240–242 °C dec. ^{1}H NMR (CDCl$_3$) δ 1.00 (s, 9, CMe$_3$), 1.10–1.32 (m, 18, PCH$_2$*CH$_3$*), 1.24 (s, 9, CMe$_3$), 1.78–2.05 (m, 12, P*CH$_2$*CH$_3$), 5.05 (s, 2, H$_2$O), 6.15 (d, 1, C=CH, $^3J_{P(O)H}$ = 39.2 Hz, $^4J_{PtH}$ = 2.2 Hz), 7.35–7.83 (m, 5, Ph). ^{31}P{H} NMR (CD$_3$OD) δ 14.14, 16.02 (ABq, PEt$_3$, $^2J_{PP}$ = 360 Hz, $^1J_{PtP(A)} \approx {}^1J_{PtP(B)}$ = 2678 Hz), 34.20 (s, P(O), $^3J_{PtP}$ = 652 Hz). Anal. Calcd for C$_{30}$H$_{56}$BF$_4$O$_2$P$_3$Pt: C, 43.75; H, 6.85; P, 11.28. Found: C, 43.84; H, 6.63; P, 11.33.

Preparation of {*trans*-Pt[C=C(CMe$_3$)P(O)(CH$_3$)C=C(CMe$_3$)(H)](PEt$_3$)$_2$(H$_2$O)][BF$_4$] (4b). To a solution of 0.089 g (0.40 mmol) of **1c** in THF was added 0.40 mmol of **2b** in a solution of THF. After 30 min of reaction, a moderate excess of water was added to the reaction solution and then the solvent was removed at reduced pressure. The reaction residue was washed with 3 × 5 mL of pentane and then with 3 × 5 mL of ether. Crystallization of this residue from CH$_2$Cl$_2$/pentane solution at −20 °C afforded 0.052 g (17%) of **4b** as a white solid: mp 194–215 °C dec. ^{1}H NMR (CDCl$_3$) δ 1.05–1.30 (m, 18, PCH$_2$*CH$_3$*), 1.26 (s, 9, CMe$_3$), 1.35 (s, 9, CMe$_3$), 1.66 (d, 3, PCH$_3$, $^2J_{PH}$ = 11.7 Hz), 1.70–1.96 (m, 12, P*CH$_2$*CH$_3$), 5.40 (br s, 2, H$_2$O), 6.06 (d, 1, C=CH, $^3J_{PH}$ = 44.6 Hz). ^{31}P{H} NMR (CDCl$_3$) δ 12.1, 12.9 (ABq, PEt$_3$, $^2J_{PP}$ = 375 Hz, $^1J_{PtP(A)} \approx {}^1J_{PtP(B)}$ = 2723 Hz), 34.2 (s, P(O), $^3J_{PtP}$ = 624 Hz). IR (KBr, cm^{-1}) ν (PO) 1135. Anal. Calcd for C$_{25}$H$_{54}$BF$_4$O$_2$P$_3$Pt: C, 39.43; H, 7.15; P, 12.20. Found: C, 39.02; H, 7.16; P, 12.10.

Preparation of {*cis*-Pt[(*E*)-CP(CH$_3$)$_2$(C≡CCMe$_3$)=C(CMe$_3$)(H)](PEt$_3$)$_2$(py)][BF$_4$]$_2$ (6a). To a solution of 0.31 mmol of **2a** in CH$_2$Cl$_2$ at −78 °C was added 0.31 mmol of **5b**. The reaction solution was warmed to room temperature and was stirred for 14 h. Pyridine (0.20 mL) was then added to the reaction solution. After an additional reaction time of 3 h, the solvent was removed at reduced pressure. The reaction residue was crystallized from CH$_2$Cl$_2$/pentane solution at −20 °C to give 0.078 g (28%) of **6a** as white crystals: mp 109–112 °C dec. ^{1}H NMR (CD$_2$Cl$_2$) δ 1.05–1.35 (m, 18, PCH$_2$*CH$_3$*), 1.18 (s, 9, CMe$_3$), 1.25 (s, 9, CMe$_3$), 1.38–1.70 (m, 6, P*CH$_2$*CH$_3$), 1.53 (d, 3, PCH$_3$, $^2J_{PH}$ = 15 Hz), 1.85–2.25 (m, 6, P*CH$_2$*CH$_3$), 2.47 (d, 3, PCH$_3$, $^2J_{PH}$ = 15 Hz), 7.43 (d of d, C=CH, $^3J_{PH}$ = 69 Hz, $^4J_{PH}$ = 11 Hz), 7.70–9.10 (m, 5, py). ^{31}P{H} NMR (CD$_2$Cl$_2$) δ −10.5 (d, PEt$_3$, $^3J_{PP}$ = 35 Hz, $^2J_{PP}$ < 8 Hz, $^1J_{PtP}$ = 2784 Hz), −6.8 (d, PEt$_3$, $^3J_{PP}$ = 22 Hz, $^2J_{PP}$ < 8 Hz, $^1J_{PtP}$ = 3389 Hz), 1.7 (d of d, PMe$_2$, $^3J_{PP}$ = 22 and 35 Hz, $^2J_{PtP}$ = 2081 Hz). Anal. Calcd for C$_{31}$H$_{60}$B$_2$F$_8$NP$_3$Pt: C, 40.99; H, 6.66. Found: C, 40.76; H, 6.76.

Preparation of {*trans*-Pt[C=C(CMe$_3$)P(CH$_3$)(C≡CCMe$_3$)C=C(CMe$_3$)(H)](PEt$_3$)$_2$(py)][SbF$_6$][BF$_4$] (7a). To a

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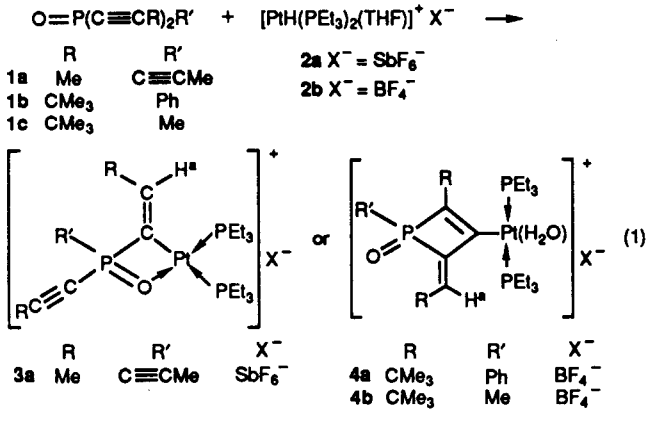
solution of 0.146 mmol of **2a** in CH_2Cl_2 at −78 °C was added 0.054 g (0.144 mmol) of **5a**. The reaction solution was warmed to room temperature and was stirred for 14 h. Pyridine (0.20 mL) was then added to the reaction solution. After an additional reaction time of 3 h, the solvent was removed at reduced pressure. The reaction residue was crystallized from CH_2Cl_2/pentane solution at −20 °C to give 0.030 g (19%) of **7a** as a white solid: mp 216–218 °C dec. ^{1}H NMR ($CDCl_3$) δ 1.10–1.20 (m, 18, PCH_2CH_3), 1.25 (s, 9, CMe_3), 1.30 (s, 9, CMe_3), 1.50 (s, 9, CMe_3), 1.50–1.70 (m, 12, PCH_2CH_3), 2.19 (d, 3, PCH_3, $^2J_{PH}$ = 10 Hz), 6.80 (d, 1, C=CH, $^3J_{PH}$ = 40 Hz, $^4J_{PtH}$ = 7 Hz), 7.70–8.80 (m, 5, py). ^{31}P{H} NMR ($CDCl_3$) δ 2.85 (s, PEt_3, $^1J_{PtP}$ = 2457 Hz), 12.5 (s, PMe, $^3J_{PtP}$ = 571 Hz). Anal. Calcd for $C_{36}H_{66}BF_{10}NP_3SbPt$: C, 38.48; H, 5.92. Found: C, 38.14; H, 5.98.

Preparation of {*cis*-Pt[(*E*)-CP(CH$_3$)(C$_6$H$_5$)(C≡CCMe$_3$)=C(CMe$_3$)(H)](PEt$_3$)$_2$(py)}[SbF$_6$]$_2$ (6b) and {*trans*-Pt[C=C(CMe$_3$)P(CH$_3$)(C$_6$H$_5$)C=C(CMe$_3$)(H)](PEt$_3$)$_2$(py)}[SbF$_6$]$_2$ (7b). The procedure reported above for the preparation of **6a** and **7a** was followed in this preparation with 0.93 mmol of **2a** and 0.93 mmol of **5c**. Compounds **6b** and **7b** were isolated, respectively, by fractional crystallization from CH_2Cl_2/ether and CH_2Cl_2/ether/pentane solutions at −20 °C only with great difficulty to give pure products as white solids. Complex **6b** (0.035 g, 3%): mp 204–206 °C dec. ^{1}H NMR (acetone-d_6) δ 1.13–1.27 (m, 9, PCH_2CH_3), 1.36–1.52 (m, 9, PCH_2CH_3), 1.56 (s, 9, CMe_3), 1.59 (s, 9, CMe_3), 1.59–1.79 (m, 6, PCH_2CH_3), 2.31–2.59 (m, 6, PCH_2CH_3), 2.55 (d, 3, PCH_3, $^2J_{PH}$ = 14 Hz), 7.00–8.90 (m, 11, C_6H_5 + py + C=CH). ^{31}P{H} NMR (acetone-d_6) δ −8.85 (d, PEt_3, $^2J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 3300 Hz), 6.24 (d of d, PEt_3, $^2J_{PP}$ = 20 Hz, $^3J_{PP}$ = 20 Hz, $^1J_{PtP}$ = 2068 Hz), 11.15 (d, PMe, $^3J_{PP}$ = 20 Hz, $^2J_{PtP}$ = 181 Hz). Anal. Calcd for $C_{36}H_{62}F_{12}NP_3PtSb_2$: C, 34.09; H, 4.93. Found: C, 34.29; H, 5.04. Complex **7b** (0.215 g, 18%): mp 212–214 °C dec. ^{1}H NMR (CD_2Cl_2) δ 1.07 (s, 9, CMe_3), 1.15–1.35 (m, 18, PCH_2CH_3), 1.37 (s, 9, CMe_3), 1.7–2.10 (m, 12, PCH_2CH_3), 2.19 (d, 3, PCH_3, $^2J_{PH}$ = 12 Hz), 6.87 (d, 1 C=CH, $^3J_{PH}$ = 51 Hz, $^4J_{PtH}$ = 7 Hz), 7.65–8.80 (m, 10, C_6H_5 + py); ^{31}P{H} NMR (CD_2Cl_2) δ 7.2 (s, PEt_3, $^1J_{PtP}$ = 2474 Hz), 49.8 (s, PMe, $^3J_{PtP}$ = 100 Hz). Anal. Calcd for $C_{36}H_{62}F_{12}NP_3PtSb_2$: C, 34.09; H, 4.93. Found: C, 34.69; H, 5.13.

Results and Discussion

Reaction of the di- or trialkynylphosphine oxides, **1a–1c**, with one of the platinum hydride salts, **2a** or **2b**, gives either a Pt,P–μ-alkenylidene product, **3a**, or a 2-alkylidene-1,2-dihydrophosphete *P*-oxide product, **4a** or **4b**, as shown in eq 1. We have also obtained very reliable spectroscopic evidence that O=P(C≡CPh)$_2$Me reacts with **2a** to give a Pt,P–μ-alkenylidene product **3b** (where R = Ph, R′ = Me, and X^- = SbF_6^-).

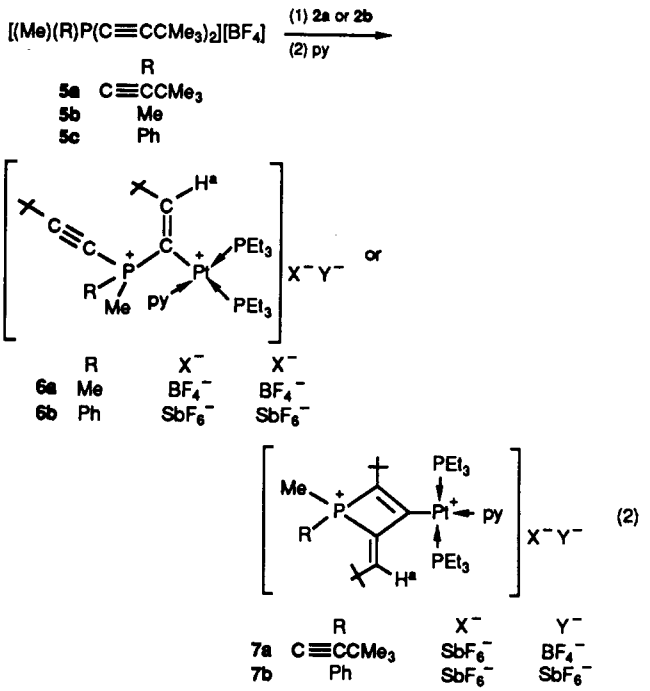


(1)

The NMR data of **3a**, which are particularly diagnostic of the Pt,P–μ-alkenylidene structure, are the following: (1) there is a large $^3J_{PtH}$ coupln g of 62 Hz between the Pt nucleus and the alkenylidene proton, H^a; and (2) in the ^{31}P NMR spectrum, the PEt_3 phosphorus nuclei of the *cis*-PtL_2 fragment exhibit the expected weak coupling to each other, $^2J_{PP}$ = 16 Hz, and very nonequivalent coupling to the Pt nucleus, $^1J_{PtP}$ = 2296 and 4089 Hz. The corresponding NMR data of **4a** or **4b**, which are particularly diagnostic of the 2-alkylidene-1,2-dihydrophosphete *P*-oxide ligand system, are the following: (1) there is very weak $^4J_{PtH}$ coupling (2.2 Hz or less) between the Pt nucleus and the alkylidene proton, H^a; and (2) in the ^{31}P NMR spectrum, the PEt_3 phosphorus nuclei of the *trans*-PtL_2 fragment exhibit the expected strong coupling to each other, $^2J_{PP}$ of 360 or 375 Hz, respectively, and essentially equivalent coupling to the Pt nucleus, $^1J_{PtP} \approx$ 2678 or 2723 Hz, respectively. As observed previously, and of special importance, the ^{31}P resonance for the *trans*-PtL_2 fragment appears as an AB quartet pattern. The two PEt_3 ligands are slightly nonequivalent because of the dissymmetry of the phosphine oxide center.[8]

The aquo ligands observed in **4a** or **4b** are obtained from exogenous sources or from the intentional addition of water to the reaction solution prior to purification. Proton resonances for these aquo ligands are observed at δ 5.05 or 5.40, respectively.[8]

Reaction of the di- or trialkynylphosphonium salts, **5a–5c**, with **2a** or **2b** followed by quenching the reaction through the addition of pyridine gives either the Pt,P–μ-alkenylidene products **6a** and **6b** or the alkylated 2-alkylidene-1,2-dihydrophosphete products, **7a** and **7b**, as shown in eq 2. The yields of isolated products from these

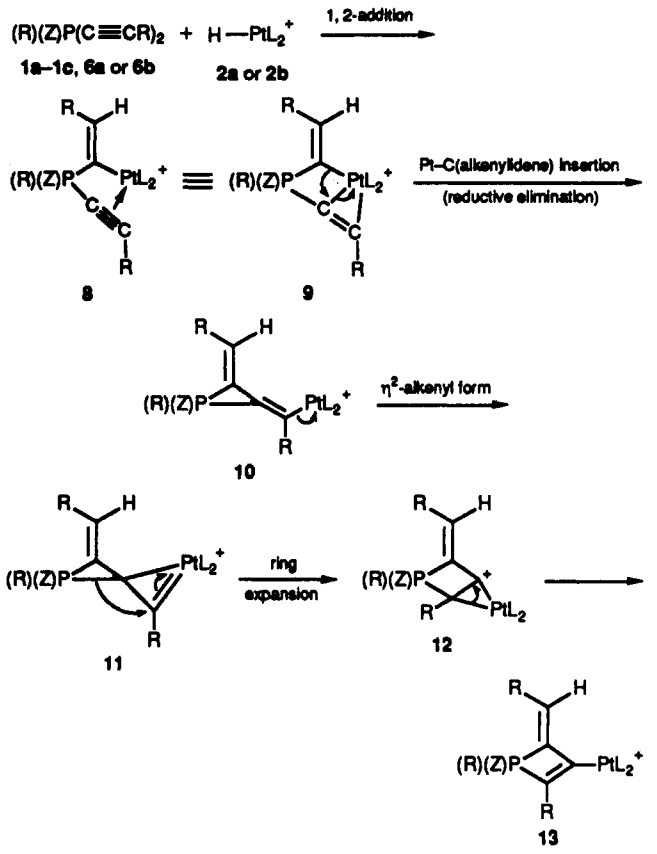


(2)

reactions are low probably because reaction must occur between two cationic species and because reaction of **5a** or **5c** with **2b** gives three possible combinations of anionic counterions. All yields are calculated from the amount of product isolated as crystalline material.

The ^{1}H and ^{31}P NMR data of **6a** and **6b** support the structure shown in eq 2, even though the resonances of the alkenylidene proton, H^a, appear in the aromatic region of the spectrum. For complex **6a**, the resonance of H^a shows $^3J_{PH}$ and $^4J_{PH}$ coupling of 69 and 11 Hz, respectively. The values of the corresponding coupling constants to H^a in **3a** are 66 and 7.7 Hz. These values are consistent with a cis orientation of H^a relative to the Pt moiety and a trans relative orientation of H^a and the phosphonium center. The ^{31}P NMR data of **6a** and **6b** clearly indicate a cis geometry at the platinum center. The PEt_3 resonances are nonequivalent in both complexes and exhibit small $^2J_{PP}$ coupling constants of less than 8 Hz and of 20 Hz and very

Scheme I



nonequivalent $^1J_{PtP}$ coupling constants to the Pt nucleus of 2784, 3389 and 2068, 3300 Hz, respectively. The observation of separate resonances for the two phosphonium methyl substituents in the ^1H NMR spectrum of **6a** indicates a restricted rotational structure for this molecule.

For compounds **7a** and **7b**, the proton resonances for the alkylidene protons, H^a, exhibit the expected small coupling to the Pt nucleus ($^4J_{PtH}$ = 7 Hz) in addition to $^3J_{PH}$ coupling of 40 and 51 Hz, respectively, between H^a and the phosphorus nucleus of the phosphonium moiety. The phosphorus resonances of the PEt_3 groups in these compounds appear quite unexpectedly as singlets. Apparently, the dissymmetry at the phosphonium center does not perturb the symmetrical environment near the platinum center, although rapid inversion at the phosphonium center would also explain this observation. In **7a** and **7b**, the values of the Pt–PEt_3 $^1J_{PtP}$ coupling constants are 2457 and 2474 Hz, respectively, as expected for a *trans*-PtL_2 geometry.[8]

Although mechanistic studies of the reactions shown in eq 1 or eq 2 have not been performed, we propose a revised mechanism for the formation of these products as shown in Scheme I based on our continuing study of analogous reactions with dialkynylsilanes.[8,9a] Regioselective addition of the Pt–H bond of **2a** or **2b** to an alkynyl substituent of a phosphorus substrate would give a Pt,P-μ-alkenylidene product, such as **8**. With the phosphine oxide substrates **1a** or O=P(C≡CPh)$_2$Me, the $^+$P–O$^-$ functional group probably coordinates to the cationic Pt center as has been confirmed for the Pt,P-μ-alkenylidene product resulting from the reaction of **2a** with O=P(C≡CPh)Ph_2.[8] With the phosphonium substrates **5b** or **5c**, the added pyridine stabilizes this product through its coordination to the Pt(II) atom. Presumably, this addition proceeds through a *cis*-$PtL_2(H)(\eta^2$-alkyne) intermediate, and the *cis*-PtL_2 structure is retained in these products. Complex **8** can be represented by the oxidative-addition structure, **9**. Direct insertion of a second alkynyl group into the Pt–C(alkenylidene) bond with the regioselectivity indicated would give the bis(alkylidene)phosphirane structure **10**. The cationic, 14-electron Pt(II) center within **10** could be stabilized through formation of an η^2-alkenyl complex, **11**.[12,13] Ring expansion would give **12** as a metal-stablized carbocation, and rearrangement of **12** to **13** would form the observed 2-alkylidene-1,2-dihydrophosphete heterocycle as found in products **4a**, **4b**, **7a**, and **7b**.

Conversion of the Pt,P-μ-alkenylidene intermediate to the corresponding heterocycle apparently occurs only when R is *tert*-butyl and, presumably, only when sufficient backside steric repulsive interactions are present within the phosphorus substrate. Clearly, more mechanistic information is needed to support the complex mechanism proposed in Scheme I.[14] On the basis of the synthetic results reported above, we intend to study the possible thermal conversion of **3a** to the corresponding heterocycle and the mechanistic features of the reaction of **5c** with **2a** (which gives both Pt,P-μ-alkenylidene and heterocyclic products as the pyridine adducts).

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(13) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435.
(14) A referee has suggested that another mechanism, which we proposed earlier,[8] involving cleavage of a P–C(alkynyl) bond and transfer of an alkynyl substituent to the Pt(II) atom might be a mechanistic route preferred by phosphine oxide and phosphonium reagents based on the observed reactivity of phosphirane oxides.[15]
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