PH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 552 (M, 5), 412 (M – 5CO, 100).

21: yield 1.2 g (48%); colorless oil; ^{31}P NMR (C_6D_6) δ 23.4 (*AB*, $^1J_{AB}$ = 61.0, P(O)(OEt)$_2$), –20.9 (*AB*, PH); ^1H NMR (C_6D_6) δ 0.98 (t, ^3J(H–H) = 7.1, CH_2CH_3), 1.00 (t, ^1J(H–H) = 7.1, CH_2CH_3), 1.25 (s, C–CH_3), 3.51 (s, OCH_2CH_2O), 3.88 (m, OCH_2CH_3), 4.16 (dt, ^1J(H–P) = 318.6, ^3J(H–H) = 5.9, PH); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 504 (M, 10), 364 (M – 5CO, 100). Anal. Calcd for $C_{17}H_{26}O_{10}P_2Cr$: C, 40.49; H, 5.20. Found: C, 40.19; H, 5.45.

Synthesis of the 1-Phosphacycloalkene Complexes 17a and 22. Water (0.15 mL) was added with continuous magnetic stirring to a suspension of silica gel (1.5 g, silica gel 60, Merck, 70–230 mesh) in dichloromethane. After a few minutes, the acetal **15a** (2 mmol) and oxalic acid (60 mg) were added and stirring was continued at room temperature for 20 h. Sodium carbonate was added to neutralize the mixture. The solid phase was separated by filtration. Drying with $MgSO_4$ and evaporation of the solvent gave crude **16a**. DABCO (2 mmol) was added to a THF solution of **16a**. The reaction was complete in a few minutes. Complex **17a** was purified by chromatography with pentane.

The same procedure was used for the synthesis of **22** from **21**. The cyclization reaction in the presence of DABCO was complete after 1.5 h at 40 °C.

17a: yield 0.33 g (57%); pale yellow solid; mp < 50 °C; ^{31}P NMR (C_6D_6) δ 224.3; ^1H NMR (C_6D_6) δ 1.85 (d, ^3J(H–P) = 26.7, CH_3); ^{13}C NMR (C_6D_6) δ 18.54 (d, ^2J(C–P) = 12.1, CH_3), 26.45 (s, CH_2), 33.76 (d, J(C–P) = 6.0 Hz, CH_2), 44.29 (s, CH_2), 194.29 (d, ^1J(C–P) = 42.8, P=C), 215.48 (d, ^2J(C–P) = 18.1, cis CO), 221.54 (trans CO); IR (decalin) ν(CO) 2070 (m), 1960 (vs) cm^{-1}; mass spectrum m/z 292 (M, 26), 152 (M – 5CO, 100). Anal. Calcd for $C_{10}H_9PO_5Cr$: C, 41.11; H, 3.11. Found: C, 41.20; H, 3.19.

22: yield 0.29 g (47%); pale yellow oil; ^{31}P NMR (pentane) δ 214.1; ^1H NMR (C_6D_6) δ 1.55 (d, ^3J(H–P) = 28.8, CH_3); ^{13}C NMR (C_6D_6) δ 23.0 (d, J(C–P) = 8.1), 24.48 (d, J(C–P) = 8.6), 25.40 (d, J(C–P) = 14.6), 30.62 (s), 38.99 (d, J(C–P) = 12.1), 187.26 (d, ^1J(C–P) = 35.2, P=C), 215.98 (d, ^2J(C–P) = 18.2, cis CO), 221.96 (trans CO); IR (decalin) ν(CO) 2070 (m), 1950 (vs) cm^{-1}; mass spectrum m/z 306 (M, 26), 166 (M – 5CO, 100). Anal. Calcd for $C_{11}H_{11}O_5PCr$: C, 43.15; H, 3.62. Found: C, 41.28; H, 3.60.

Synthesis and Methanol-Trapping Reaction of the Phosphacyclopentene Complex 17b. Water (0.15 mL) was added to a stirred suspension of silica gel (1.5 g) in dichloromethane. Trichloroacetic acid (0.33 g, 2 mmol) and the acetal **15b** (2 mmol) were added, and the mixture was stirred at room temperature for 2 h. Neutralization with sodium carbonate, filtration of the solid phase, and drying with $MgSO_4$ gave crude **16b**. DABCO (2 mmol) was added to a THF/methanol (1/1) solution of **16b**. The reaction was complete in about 10 min. The two isomers of compound **18** were obtained separately after chromatography with hexane/ether (99/1) as eluent. Total yield: 0.43 g (56%). Isomer ratio: 85/15.

18 (minor isomer): colorless solid; mp < 50 °C, ^{31}P NMR (ether) δ 190.1; ^1H NMR (C_6D_6) δ 2.79 (m, CH (Ph)), 2.77 (d, ^3J(H–P) = 12.4, OCH_3); ^{13}C NMR (C_6D_6) δ 24.55 (s, CH_2), 33.67 (s, CH_2), 37.55 (d, J(C–P) = 21.6, CH_2), 54.18 (s), 57.84 (d, J(C–P) = 17.61), 216.9 (d, ^2J(C–P) = 14.6, cis CO); IR (decalin) ν(CO) 2070 (m), 1960 (s), 1940 (vs) cm^{-1}; mass spectrum m/z 386 (M, 12), 246 (M – 5CO, 100).

18 (major isomer): colorless oil; ^{31}P NMR (hexane/ether) δ 207.2; ^1H NMR (C_6D_6) δ 3.01 (d, ^3J(H–P) = 11.8, OCH_3), 3.1 (m, CH (Ph)); ^{13}C NMR (C_6D_6) δ 25.47 (s, CH_2), 32.81 (d, J(C–P) = 6.5, CH_2), 35.76 (d, J(C–P) = 19.6, CH_2), 52.34 (d, J(C–P) = 6.5), 54.64 (d, J(C–P) = 12.1), 216.31 (d, ^2J(C–P) = 15.1, cis CO), 221.2 (d, ^2J(C–P) = 6.0, trans CO); IR (decalin) ν(CO) 2065 (m), 1955 (s), 1940 (vs) cm^{-1}. Anal. Calcd for $C_{16}H_{15}O_6PCr$: C, 49.75; H, 3.91. Found: C, 49.75; H, 3.91.

Dimerization of the 1-Phosphacyclopentene Complex 17a to Compound 19. When kept in concentrated solution, complex **17a** dimerizes slowly to complex **19**. **19** was separated from the remaining **17a** by column chromatography with hexane/ether (90/10) as eluent.

19: colorless solid; mp 179 °C dec; ^{31}P NMR (CH_2Cl_2) δ 78.75 (*AB*, $^1J_{AB}$ = 224.6), 63.92 (*AB*); ^1H NMR ($CDCl_3$) δ 1.39 (dd, ^3J(H–P) = 17.2, ^3J(H–H) = 6.8, CHCH_3), 2.08 (d, ^3J(H–P) = 10.3, =C–CH_3), 6.25 (d, ^3J(H–P) = 27.6, =CH); ^{13}C NMR ($CDCl_3$) δ 16.79 (d, J(C–P) = 15.5), 17.54 (d, J(C–P) = 9.1), 26.14 (s), 30.31 (dd, J(C–P) = 22.4, 8.8), 32.65 (dd, J(C–P) = 18.3, 6.1), 33.30 (s), 37.27 (d, J(C–P) = 6.5), 38.88 (d, J(C–P) = 9.6), 135.75 (d, J(C–P) = 15.1, C=C), 140.61 (dd, J(C–P) = 12.2, 3.1, C=C); IR (CH_2Cl_2) ν(CO) 2070 (m), 2060 (m), 1950 (vs), 1940 (sh) cm^{-1}; mass spectrum m/z 584 (M, 15), 444 (M – 5CO, 47), 304 (M – 10CO, 45), 253 ((CO)$_5$Cr(PC$_5$H$_{10}$), 100). Anal. Calcd for $C_{20}H_{18}O_{10}P_2Cr$: C, 41.11; H, 3.11. Found: C, 40.86; H, 3.25.

Notes

Solid-State Structure of the Bis(allyl)rhodium Chloride Dimer

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Summary: ^{13}C NMR analysis of the solid, labeled bis(allyl)rhodium chloride dimer suggested a structure simpler than that reported previously as determined by X-ray crystallographic analysis. Reexamination of the solid-state structure of this compound showed it to be consistent with the simpler, NMR-determined structure.

In conjunction with studies of oxide-bound organorhodium complexes, we prepared the ^{13}C-labeled (allyl)rhodium chloride dimer, **1**, and examined its ^{13}C NMR spectrum in the solid state. Complex **1** was prepared from [(OC)$_2$RhCl]$_2$ and [1-^{13}C]allyl chloride. The ^{13}C NMR spectrum of **1** was obtained by using a JEOL GX 270 instrument operating at 67.9 MHz.[2] It consisted simply of two resonances of equal intensity at δ 77.2 and 45.2 and was similar to that for the material recorded in solution [δ 76.5 (J_{Rh-C} = 6.8 Hz) and 44.5 (J_{Rh-C} = 11.9 Hz)]. That only two signals were observed suggested a simple substitution geometry about the Rh, inconsistent with the reported structure[1] proposing some double-bond localization for the allyl ligands and noting unequal rhodium–

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(2) Conditions for this experiment were as follows: cross-polarization mixing time 1.5 ms; field strength for Hartman–Hahn match 50 kHz; ν_{rot} 5400 Hz; 100 transients.

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Table I. Structure Determination Summary

Crystal Data	
empirical formula	$C_{12}H_{20}Cl_2Rh_2$
color, habit	yellow, rectangular chunk
cryst size	0.20 × 0.22 × 0.44
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	a = 7.148 (2) Å
	b = 7.740 (2) Å
	c = 13.129 (2) Å
	β = 94.38 (2)°
V	724.3 (2) Å^3
Z	2
fw	441.0
D(calcd)	2.02 g/cm^3
abs coeff	25.5 cm^{-1}
F(000)	432
final R indices	R = 2.1%, R_w = 2.4%
goodness-of-fit	1.55

Bond Lengths (Å)

Rh–Cl	2.505 (1)	Rh–C(1)	2.244 (5)
Rh–C(2)	2.141 (5)	Rh–C(3)	2.124 (5)
Rh–C(4)	2.117 (4)	Rh–C(5)	2.144 (5)
Rh–C(6)	2.224 (5)	Rh–Cl(A)	2.513 (1)
C(1)–C(2)	1.388 (7)	C(2)–C(3)	1.419 (7)
C(4)–C(5)	1.413 (7)	C(5)–C(6)	1.396 (7)

Bond Angles (deg)

Cl–Rh–C(1)	92.7 (1)	Cl–Rh–C(2)	124.2 (1)
C(1)–Rh–C(2)	36.8 (2)	Cl–Rh–C(3)	159.4 (1)
C(1)–Rh–C(3)	67.0 (2)	C(2)–Rh–C(3)	38.9 (2)
Cl–Rh–C(4)	92.5 (1)	C(1)–Rh–C(4)	111.6 (2)
C(2)–Rh–C(4)	89.8 (2)	C(3)–Rh–C(4)	98.1 (2)
Cl–Rh–C(5)	109.0 (1)	C(1)–Rh–C(5)	141.5 (2)
C(2)–Rh–C(5)	106.9 (2)	C(3)–Rh–C(5)	90.1 (2)
C(4)–Rh–C(5)	38.7 (2)	Cl–Rh–C(6)	87.8 (1)
C(1)–Rh–C(6)	178.7 (2)	C(2)–Rh–C(6)	142.2 (2)
C(3)–Rh–C(6)	112.5 (2)	C(4)–Rh–C(6)	67.1 (2)
C(5)–Rh–C(6)	37.2 (2)	Cl–Rh–Cl(A)	85.4 (1)
C(1)–Rh–Cl(A)	87.7 (1)	C(2)–Rh–Cl(A)	107.3 (1)
C(3)–Rh–Cl(A)	90.1 (1)	C(4)–Rh–Cl(A)	160.7 (1)
C(5)–Rh–Cl(A)	124.5 (1)	C(6)–Rh–Cl(A)	93.6 (1)
Rh–Cl–Rh(A)	94.6 (1)	Rh–C(1)–C(2)	67.6 (3)
Rh–C(2)–C(1)	75.6 (3)	Rh–C(2)–C(3)	69.9 (3)
C(1)–C(2)–C(3)	118.6 (4)	Rh–C(3)–C(2)	71.2 (3)
Rh–C(4)–C(5)	71.7 (3)	Rh–C(5)–C(4)	69.6 (3)
Rh–C(5)–C(6)	74.5 (3)	C(4)–C(5)–C(6)	117.5 (5)
Rh–C(6)–C(5)	68.3 (3)		

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
Rh	949 (1)	1760 (1)	834 (1)	31 (1)
Cl	1605 (2)	−1382 (1)	573 (1)	38 (1)
C(1)	−1206 (6)	1202 (7)	1946 (3)	47 (2)
C(2)	−327 (7)	2782 (7)	2129 (3)	49 (2)
C(3)	−395 (7)	4022 (6)	1331 (4)	51 (2)
C(4)	3633 (6)	2191 (7)	1588 (4)	50 (2)
C(5)	3476 (6)	3202 (7)	690 (4)	51 (2)
C(6)	3127 (7)	2341 (7)	−239 (4)	50 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

chlorine bonds. Therefore, we reexamined 1 by X-ray crystallography. In contrast to the previous report,[1] we find, consonant with ^{13}C NMR results, that a more typical structure exists.

Crystallographic data for 1 are summarized in Tables I and II. The structure was solved by conventional heavy-atom techniques. Hydrogens were located on a difference Fourier map. During the final stages of refinement, all non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogens were fixed at the observed positions. The analytical scattering factors for the neutral atoms were used,[3] and all non-hydrogen

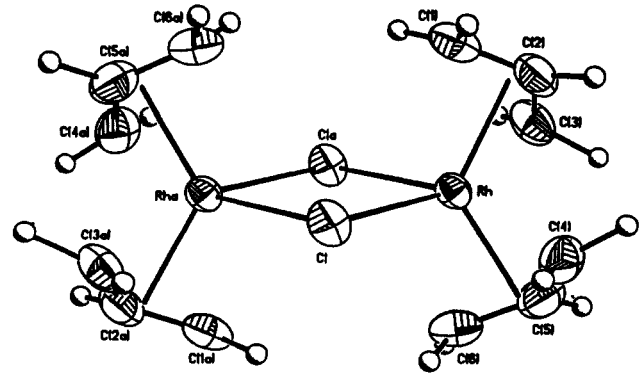

Figure 1. X-ray crystallographic structure of 1.

scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[4] A labeled drawing of the final crystallographic model is shown in Figure 1. (The unit cell packing diagram and tables of hydrogen atomic coordinates and anisotropic thermal parameters are supplied as supplementary material.) The molecule is located at an inversion center in the crystal and thus has exact C_i symmetry. The Rh–Rh distance is 3.689 (1) Å. The two crystallographically nonequivalent Rh–Cl bonds have lengths of 2.505 (1) and 2.513 (1) Å, a difference of only 0.008 Å vs 0.042 Å as reported.[1] Furthermore, the C–C bonds of the allyl system are nearly identical, demonstrating that no double-bond localization[1] exists.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Ether was distilled from Na/benzophenone ketyl. Toluenesulfonyl chloride was recrystallized prior to use. $[Rh(CO)_2Cl]_2$ was prepared by a literature method.[5] Chromatography was performed with Merck grade 60 silica gel. NMR spectra were recorded on a General Electric QE300 spectrometer; gas chromatography was performed on a Hewlett-Packard 5890 instrument with a Supelco SPB-1 30-m capillary column.

[1-^{13}C]Allyl Tosylate. Vinylmagnesium bromide (50 mL, 1 M in THF, 50 mmol) was added to ^{13}C-labeled paraformaldehyde (1.00 g, 30 mmol, Cambridge Isotope Laboratories), and the mixture was stirred 3 days at room temperature until a clear solution was obtained. The reaction mixture was poured into a separatory funnel containing 100 mL of ether and 25 mL of water. Following hydrolysis, enough 6 N H_2SO_4 was added to dissolve the precipitated salts. The organic layer was then separated, and the aqueous layer was extracted twice more with ether (100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and cannulated slowly into a round-bottom flask containing toluenesulfonyl chloride (5.72 g, 30 mmol), NaH (60% suspension in oil, 2.40 g, 60 mmol), and ether (50 mL) at room temperature. The reaction was stirred for 1 h until TLC analysis showed no toluenesulfonyl chloride remained. Filtration and removal of solvent in vacuo, followed by chromatography (90:10 hexane/EtOAc), gave 4.22 g (66%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 5.79 (m, 1 H), 5.34–5.18 (m, 2 H), 4.50 (ddd, J_{C-H} = 149.6 Hz, J_{H-H} = 6.1, 1.1 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 92.04; IR (neat) 3092, 3068, 2927, 1599, 1364, 1190, 1177, 1098, 964, 938, 910, 836, 816, 776 cm^{-1} HRMS calcd for $^{12}C_9{}^{13}CH_{12}O_3S$ m/e 213.0541, found m/e 213.0546; LRMS (EI) m/e 213 (12; >97% ^{13}C), 157 (20), 156 (79), 155 (83), 139 (13), 108 (14), 107 (17), 93 (14), 92 (92), 91 (100).

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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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Registry No. 1, 132774-72-2; [1-^{13}C]allyl tosylate, 132774-71-1.

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-

† Submitted for the Stille Memorial issue.

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