as the $(OC)_xM(H)(\eta^5\text{-}c\text{-}C_5H_5)^-$ structures by their failure to undergo further ion/molecule reactions with H_2S, $(CH_3)_3SiH$, and SO_2.

The reactions of $(OC)_3Mn^-$ and $(OC)_2Fe^{\bullet-}$ with acetylene occurred exclusively by ligand substitution terminating in the generation of the ions $M(C_2H_2)_x^-$, where M = Mn, x = 3, and M = Fe, x = 2. These terminal product ions and the intermediate $(OC)Mn(C_2H_2)_2^-$ did not react with D_2, suggesting that they are saturated acetylene complexes rather than metallacycles observed in the cyclooligomerization of acetylene by transition-metal catalysts.

The results observed in the reactions of the fragment negative ions $(OC)_3Mn^-$ and $(OC)_2Fe^{\bullet-}$ with 1,3-butadiene are rationalized by the same mechanism developed for the reaction of the neutral complex $Cr(CO)_3$ with 1,3-pentadiene.

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Synthesis, Characterization, and Reaction Chemistry of Chiral Half-Sandwich Ruthenium Phosphaallyl Complexes

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The complexes $[(\eta^5\text{-}C_5H_5)Ru(R_3P)_2(NCCH_3)]^+PF_6^-$, where R_3P is vinyldiphenylphosphine (DPVP) and divinylphenylphosphine (DVPP), reversibly dissociate CH_3CN to form η^3-phosphaallyl complexes. These complexes have been characterized by elemental analyses, infrared spectroscopy, thermal analysis, cyclic voltammetry, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^1H/^{13}C$ HETCOR, 2D-HOJ, NOESY, and COSY nuclear magnetic resonance spectroscopy. Solution equilibrium thermodynamics show that the η^1–η^3 conversion is endothermic and is entropy driven. $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}Ph_2PCH{=}CH_2)(\eta^3\text{-}Ph_2PCH{=}CH_2)]PF_6$ (**3**) has been characterized by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ with a = 9.754 (3) Å, b = 22.528 (6) Å, c = 19.840 (5) Å, β = 100.46 (2)°, and Z = 4. The structure was refined by least-squares methods with R_F = 0.035 for 3925 independent observed ($I \geq 3\sigma(I)$) reflections. The Ru–P bond distance for the η^3-$Ph_2PCH{=}CH_2$ ligand (2.276 (1) Å) is significantly shorter than that for the η^1-$Ph_2PCH{=}CH_2$ ligand (2.315 (1) Å). The Ru–C distance to the α-carbon of the η^3-bound phosphine (2.176 (3) Å) is significantly shorter than that to the β-carbon (2.244 (4) Å), and these distances are respectively shorter and longer than the average Ru–C distance to the η^5-C_5H_5 ring (2.215 (4) Å). The C_α–C_β distance (1.399 (5) Å) is considerably longer and the $PC_\alpha C_\beta$ bond angle (119.0 (3)°) considerably smaller for the η^3-phosphine than for the η^1-phosphine (1.306 (5) Å, 127.5 (3)°). Compound **3** reacts with good donor ligands L (L = N_3^-, CH_3CN, $H_2NCH_2CH{=}CH_2$, $(CH_3)_2CHCN$, PhCN, PhNC, and CO) to displace the coordinated vinyl moiety, forming $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH{=}CH_2)_2N_3]$ or $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH{=}CH_2)_2L]PF_6$. $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH{=}CH_2)_2CO]PF_6$ (**11**) has been characterized by X-ray crystallography. It crystallizes in the triclinic $P\bar{1}$ space group with a = 19.065 (4) Å, b = 10.825 (2) Å, c = 9.433 (2) Å, α = 100.08 (2)°, β = 103.37 (2)°, γ = 84.27 (2)°, and Z = 2. The structure was refined by least-squares methods with R_F = 0.054 for 5045 independent observed ($I \geq 3\sigma(I)$) reflections. The two Ru–P bond distances are equal (2.320 (1), 2.324 (1) Å) and longer than those in compound **3**. The $PC_\alpha C_\beta$ bond angles are equal (125.4 (4), 125.5 (5)°), as are the C_α–C_β distances (1.313 (7), 1.316 (8) Å). Reaction of compound **3** with RLi (R = CH_3, CH_3, PhC≡C, $CH_3C{\equiv}C$) induces a novel migration of vinyl from phosphorus to ruthenium, probably by way of λ^5-phosphoranide intermediates.

Introduction

The allyl ligand is prominent[2] in organometallic chemistry. Equilibria between η^1- and η^3-allyls have received considerable attention[3] and are likely to be responsible for the wide range of reactivities exhibited by metal–allyl complexes. Phosphaallyl complexes have only recently been reported[4-9] and were previously expected to be unstable. The syn–anti isomerization[6,10] of phosphaallyl complexes is believed to proceed via η^1–η^3 interconversion of the phosphaallyl in accord with the common mechanism

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for syn–anti isomerization of allyls. Allyl complexes, particularly cationic complexes, are highly electrophilic and undergo nucleophilic addition with a variety of nucleophiles.[11-19] Additions occur at either the central[18] or terminal carbons.[19]

Herein we report the first examples of reversible interconversion of a two-electron-donor vinylphosphine and a four-electron-donor neutral phosphaallyl equivalent, the reactivity of the phosphaallyl moiety toward nucleophiles, and the structure of the phosphaallyl complex in solution and in the solid state.

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. Phenyldivinylphosphine (DVPP) and diphenylvinylphosphine (DPVP) were obtained from Organometallics, Inc. All reactions involving phosphines were conducted under a nitrogen atmosphere. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 1800 FT-infrared spectrometer as KBr pellets. Cyclic voltammograms were recorded as previously described.[20] The $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer or at 121.56 MHz on a General Electric GN-300 spectrometer in the FT mode. The ^1H, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 300, 300, and 75 MHz, respectively, on a General Electric GN-300 spectrometer. Heteronuclear chemical shift correlated (HETCOR), homonuclear chemical shift correlated (COSY), 2D-HOJ, and 2D-NOE NMR spectra were obtained as previously described.[21] Proton and carbon chemical shifts are relative to internal Me_4Si, and phosphorus chemical shifts are relative to internal PF_6^- (δ = −144.95 ppm) or external H_3PO_4 (δ = 0) with a positive value being downfield of the respective reference. Thermal gravimetric analyses (TGA) were obtained on a Du Pont 9900 thermal analysis apparatus under flowing nitrogen at a scan rate of 5 °C/min. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$,[22] $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_6)]Cl$,[23] $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$,[24] $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(CO)]PF_6$,[24] $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2\{P(OCH_3)_3\}]PF_6$,[24] and PhNC[25] were prepared by literature procedures.

B. Syntheses. (Acetonitrile)cyclopentadienylbis(vinyldiphenylphosphine)ruthenium(II) Hexafluorophosphate (1). To a solution of 0.500 g (1.15 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ in 20 mL of acetonitrile was added 0.60 mL (2.51 mmol) of vinyldiphenylphosphine under nitrogen. The resulting solution was stirred magnetically overnight at ambient temperature, and then the solvent was removed on a rotary evaporator at 40 °C to produce an orange oil. The oil was triturated with diethyl ether, and the resulting yellow crystals were isolated by filtration, washed with diethyl ether, and recrystallized from $CH_2Cl_2/(C_2H_5)_2O$ to give 0.876 g (99.9%) of yellow crystals, mp 170–171 °C. Anal. Calcd for $C_{35}H_{34}F_6NP_3Ru$: C, 54.15; H, 4.38; N, 1.80. Found: C, 53.90, 53.80; H, 4.40, 4.30; N, 1.90, 1.90. IR (KBr): ν_{CN} 2300 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 39.72 (s, 2 P, Ph_2PVy), −144.95 (septet, $^1J(PF)$ = 716 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 2.36 (t, $^5J(PH)$ = 1.50 Hz, 3 H, CH_3CN), 4.62 (s, 5 H, C_5H_5), 5.07 (ddd, $^3J(PH)$ = 17.73, $^3J(ac)$ = 17.73, $^2J(bc)$ = 1.80 Hz, 2 H, H_c), 5.72 (ddd, $^2J(PH)$ = 24.04, $^3J(ac)$ = 17.73, $^3J(ab)$ = 12.32 Hz, 2 H, H_a), 5.79 (ddd, $^3J(PH)$ = 36.97, $^3J(ab)$ = 12.32, $^2J(bc)$ = 1.80 Hz, 2 H, H_b), 6.9–7.6 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 4.33 (s, CH_3CN), 82.59 (t, $^2J(PC)$ = 1.66 Hz, C_5H_5), 127.88 (s, CH_3CN), 128.36 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.75 Hz, C_m), 128.61 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.98 Hz, C_m), 128.99 (s, C_β), 130.07 (s, C_p), 130.81 (s, C_p), 132.05 (five lines, $^1J(PC)$ = 40.23, $^3J(PC)$ = −1.54, $^2J(PP)$ = 36.82 Hz, C_α), 133.22 (T, $|^2J(PC) + {}^4J(PC)|$ = 10.13 Hz, C_o), 132.92 (five lines, $^1J(PC)$ = 44.76, $^3J(PC)$ = 4.5, $^2J(PP)$ = 36.82 Hz, C_i), 133.92 (T, $|^2J(PC) + {}^4J(PC)|$ = 11.19 Hz, C_o), 135.52 (five lines, $^1J(PC)$ = 44.76, $^3J(PC)$ = 4.5, $^2J(PP)$ = 36.82 Hz, C_i).

(Acetonitrile)cyclopentadienylbis(divinylphenylphosphine)ruthenium(II) Hexafluorophosphate (2). As for complex **1**, from 0.500 g (1.15 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ and 0.60 mL (2.51 mmol) of divinylphenylphosphine were obtained 0.777 g (99.9%) of yellow crystals, mp 144–145 °C. Anal. Calcd for $C_{27}H_{30}F_6NP_3Ru$: C, 47.96; H, 4.44; N, 2.07. Found: C, 48.10, 47.90; H, 4.30, 4.30; N, 1.80, 1.90. IR (KBr): ν_{CN} = 2280 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 32.43 (s, 2 P, $PhPVy_2$), −144.95 (septet, $^1J(PF)$ = 716 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 2.31 (t, $^5J(PH)$ = 1.50 Hz, 3 H, CH_3CN), 4.65 (s, 5 H, C_5H_5), 5.23 (ddd, $^3J(PH)$ = 18.93, $^3J(ac)$ = 18.03, $^2J(bc)$ = 1.20 Hz, 2 H, H_c), 5.63 (ddd, $^3J(PH)$ = 18.93, $^3J(a'c')$ = 18.16, $^2J(b'c')$ = 1.32 Hz, 2 H, $H_{c'}$), 5.87 (ddd, $^3J(PH)$ = 36.66, $^3J(ab)$ = 12.02, $^2J(bc)$ = 1.20 Hz, 2 H, H_b), 6.05 (m, $^2J(PH)$ = 24.82, $^3J(a'c')$ = 18.16, $^3J(a'b')$ = 11.90 Hz, 2 H, $H_{a'}$), 6.06 (m, $^3J(PH)$ = 28.96, $^3J(a'c')$ = 18.16, $^2J(b'c')$ = 1.32 Hz, 2 H, $H_{b'}$), 6.23 (ddd, $^2J(PH)$ = 24.04, $^3J(ac)$ = 18.03, $^3J(ab)$ = 12.02 Hz, 2 H, H_a), 7.3–7.5 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 4.22 (s, CH_3CN), 81.68 (t, $^2J(PC)$ = 1.89 Hz, C_5H_5), 127.53 (s, CH_3CN), 128.58 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.82 Hz, C_m), 129.03 (s, C_p), 130.51 (s, C_β), 130.74 (s, C_β), 132.35 (five lines, $^1J(PC)$ = 39.66, $^2J(PP)$ = 39.14, $^3J(PC)$ = 3.87 Hz, C_α), 132.53 (T, $|^2J(PC) + {}^4J(PC)|$ = 10.81 Hz, C_o), 132.67 (five lines, $^2J(PP)$ = 39.14, $^1J(PC)$ = 29.30, $^3J(PC)$ = 3.68 Hz, C_i), 133.12 (five lines, $^1J(PC)$ = 41.52, $^2J(PP)$ = 39.14, $^2J(PC)$ = 1.78 Hz, C_α).

Cyclopentadienyl(η^1-vinyldiphenylphosphine)(η^3-vinyldiphenylphosphine)ruthenium(II) Hexafluorophosphate (3). Fluffy yellow microcrystals of complex **1** (1.00 g, 1.28 mmol) were heated in a vacuum oven (0.5 mmHg) at 70–75 °C for 7 days and then recrystallized from $CHCl_3$/petroleum ether (70–110 °C). The product was isolated by filtration, washed with petroleum ether, and dried in vacuo to obtain 0.94 g (99.8%) of yellow crystals, mp 210 °C dec. Anal. Calcd for $C_{33}H_{31}F_6P_3Ru$: C, 53.90; H, 4.22; N, 0. Found: C, 53.60, 53.60; H, 4.10, 4.00; N, 0, 0. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 24.16 (d, $^2J(PP)$ = 43.94 Hz, 1 P, η^3-Ph_2PVy) 42.33 (d, $^2J(PP)$ = 43.94 Hz, 1 P, η^1-Ph_2PVy), −144.95 (septet, $^1J(PF)$ = 716 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 2.41 (m, $^3J(PH)$ = 21.94, $^3J(PH)$ = 10.52, $^3J(a'c')$ = 6.1, $^2J(b'c')$ = 2.96 Hz, 1 H, $H_{c'}$), 4.06 (m, $^3J(PH)$ = 22.24, $^3J(PH)$ = 4.51, $^3J(a'b')$ = 8.65, $^2J(b'c')$ = 2.96 Hz, 1 H, $H_{b'}$), 4.08 (m, $^2J(PH)$ = 15.03, $^3J(PH)$ = 10.52, $^3J(a'b')$ = 8.65, $^3J(a'c')$ = 6.1 Hz, 1 H, $H_{a'}$), 4.54 (ddd, $^2J(PH)$ = 25.24, $^3J(ac)$ = 18.33, $^3J(ab)$ = 12.32 Hz, 1 H, H_a), 4.92 (s, 5 H, C_5H_5), 5.12 (ddd, $^3J(PH)$ = 18.33, $^3J(ac)$ = 18.33, $^2J(bc)$ = 0.9 Hz, 1 H, H_c), 5.61 (ddd, $^3J(PH)$ = 37.57, $^3J(ab)$ = 12.32, $^2J(bc)$ = 0.9 Hz, 1 H, H_b), 6.9–7.81 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 34.09 (dd, $^1J(PC)$ = 32.19, $^2J(PC)$ = 1.70 Hz, $C_{\alpha'}$), 43.57 (d, $^2J(PC)$ = 5.29 Hz, $C_{\beta'}$), 85.23 (t, $^2J(PC)$ = 1.35 Hz, C_5H_5), 125.05 (dd, $^1J(PC)$ = 52.86, $^3J(PC)$ = 5.63 Hz, C_i), 128.59 (d, $^3J(PC)$ = 10.28 Hz, C_m), 128.80 (d, $^3J(PC)$ = 10.50 Hz, C_m), 129.44 (d, $^3J(PC)$ = 12.39 Hz, C_m), 129.59 (d, $^3J(PC)$ = 12.47 Hz, C_m), 129.65 (d, $^1J(PC)$ = 44.44 Hz, C_α), 130.62 (d, $^4J(PC)$ = 2.34 Hz, C_p), 130.74 (d, $^2J(PC)$ = 3.70 Hz, C_β), 131.58 (d, $^4J(PC)$ = 2.26 Hz, C_p), 131.66 (dd, $^1J(PC)$ = 52.90, $^3J(PC)$ =

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3.78 Hz, C_i), 131.83 (d, ^4J(PC) = 3.10 Hz, C_p), 132.39 (d, ^4J(PC) = 3.02 Hz, C_p), 132.66 (d, ^2J(PC) = 10.43 Hz, C_o), 132.77 (d, ^2J(PC) = 11.64 Hz, C_o), 132.97 (d, ^2J(PC) = 12.70 Hz, C_o), 134.44 (dd, ^1J(PC) = 48.52, ^3J(PC) = 2.72 Hz, C_i), 135.04 (d, ^2J(PC) = 11.56 Hz, C_o).

Cyclopentadienyl(η^1-divinylphenylphosphine)(η^3-divinylphenylphosphine)ruthenium(II) Hexafluorophosphate (4). As for complex **3**, vacuum drying a sample of complex **2** for 3 days at 70–75 °C (0.5 mmHg) gave a 50% mixture of complex **2** and the title compound. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 17.68 (d, ^2J(PP) = 43.94 Hz, 1 P, η^3-$PhPVy_2$), 35.54 (d, ^2J(PP) = 43.94 Hz, 1 P, $PhPVy_2$), −144.95 (septet, ^1J(PF) = 716 Hz, 1 P, PF_6^-).

(η^5-C_5H_5)Ru(DVPP)$_2$Cl (5). To a solution of complex **2** (0.50 g) in 10 mL of dichloromethane was added 3 mL of an aqueous solution of $[(CH_3)_4N]Cl$ (0.24 g). Then ethanol (95%) was added until a single phase formed. After the mixture was stirred for 3 h at room temperature, the solvents were removed on a rotary evaporator. Two products, $[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2(CH_3CN)]Cl$ and $(\eta^5\text{-}C_5H_5)Ru(DVPP)_2Cl$, were obtained at this stage. They were extracted into $CHCl_3$, the $CHCl_3$ was removed on a rotary evaporator, and the residue was refluxed in 1,2-dichloroethane for an additional 6 h to give the title product. It was isolated as a yellow powder by removing the solvent on a rotary evaporator; yield 85%. $^{31}P\{^1H\}$ NMR ($CDCl_3$); δ): 30.94 (s). ^1H NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 4.29 (s, 5 H, C_5H_5), 5.25 (ddd, ^3J(PH) = 18.03, ^3J(ac) = 18.03, ^2J(bc) = 1.50 Hz, 2 H, H_c), 5.57 (ddd, ^3J(PH) = 18.03, ^3J(a′c′) = 18.03, ^2J(b′c′) = 1.80 Hz, 2 H, $H_{c'}$), 5.70 (ddd, ^3J(PH) = 21.94, ^3J(ab) = 12.02, ^2J(bc) = 1.50 Hz, H_b), 5.87 (ddd, ^3J(PH) = 26.75, ^2J(a′b′) = 12.02, ^2J(b′c′) = 1.80 Hz, $H_{b'}$), 6.1–6.5 (overlapped 16-line m, 2 H, H_a, $H_{a'}$) 7.2–7.6 (m, 10 H, Ph).

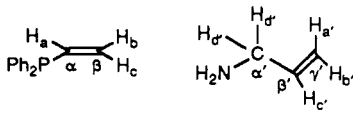
[(η^5-C_5H_5)Ru(η^3-DPVP)(CO)]PF_6 (6). This compound was obtained as a minor product in the preparation of complex **14** (see preparation for complex **14**). $^{31}P\{^1H\}$ NMR (CD_3NO_2; δ (multiplicity, *J* value, assignment)): 75.42 (s, 1 P, DPVP) −144.95 (septet, ^1J(PF) = 706.71 Hz, 1 P, PF_6^-). ^1H NMR (CD_3NO_2; δ (multiplicity, *J* value, assignment)): 2.90 (ddd, ^3J(PH) = 24.92, ^3J(ac) = 11.72, ^2J(bc) = 3.0, 1 H, H_c), 3.74 (ddd, ^3J(PH) = 21.34, ^3J(ab) = 10.22, ^2J(bc) = 3.0 Hz, 1 H, H_b), 4.94 (s, 5 H, C_5H_5), 6.15 (ddd, ^2J(PH) = 2.4, ^3J(ac) = 11.72, ^3J(ab) = 10.22 Hz, 1 H, H_a), 7.4–7.9 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR (CD_3NO_2; δ (multiplicity, *J* value, assignment)): 38.24 (d, 10.3 Hz, CH_2), 44.5 (unresolved, CH), 87.61 (s, C_5H_5), 129.0–137.0 (unresolved, Ph).

[(η^5-C_5H_5)Ru(DVPP)$_2${$(CH_3)_2$CHCN}]PF_6 (7). To a yellow solution of 0.20 g of complex **3** in 4 mL of CH_2Cl_2 in a 10-mL NMR tube was added 0.3 mL of isobutyronitrile under N_2. After 10 min all of the starting compound was converted to the title complex, which was evidenced by a singlet $^{31}P\{^1H\}$ resonance for the reaction mixture. Diethyl ether was then added to the solution. A yellow crystalline solid formed, which was isolated by filtration, washed with dry ether several times, and dried in air. An analytical example was obtained as a yellow crystalline solid in 95% isolated yield by recrystallization from CH_2Cl_2/ether; mp 204–205 °C. Anal. Calcd for $C_{37}H_{38}F_6NP_3Ru$: C, 55.25; H, 4.72. Found: C, 54.87; H, 4.86. IR (KBr): ν_{CN} = 2265 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 40.0 (s, 2 P, DPVP), −144.95 (septet, ^1J(PF) = 713 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 1.17 (d, ^3J(HH) = 6.91 Hz, 6 H, $(CH_3)_2$CHCN), 3.22 (m, ^4J(PH) = 1.05, ^3J(HH) = 6.91 Hz, 1 H, $(CH_3)_2CH$CN), 4.64 (s, 5 H, C_5H_5), 5.08 (ddd, ^3J(PH) = 18.19, ^3J(ac) = 7.96, ^2J(bc) = 1.50 Hz, 2 H, H_c), 5.67 (ddd, ^2J(PH) = 15.17, ^3J(ab) = 12.17, ^3J(ac) = 7.96 Hz, 2 H, H_a), 5.82 (ddd, ^3J(PH) = 35.01, ^3J(ab) = 12.17, ^2J(bc) = 1.50 Hz, 2 H, H_b), 6.9–7.6 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 19.65 (s, $(CH_3)_2$CHCN), 21.87 (s, CHCN), 82.90 (t, ^2J(PC) = 1.62 Hz, C_5H_5), 127.0 (s, CHCN), 128.37 (T, $|^3J$(PC) + ^5J(PC)$|$ = 9.75 Hz, C_m), 128.65 (T, $|^3J$(PC) + ^5J(PC)$|$ = 10.05 Hz, C_m), 128.96 (s, C_β), 130.14 (s, C_p), 130.91 (s, C_p), 131.90 (m, C_α), 132.23 (T, $|^2J$(PC) + ^4J(PC)$|$ = 10.35 Hz, C_o), 132.93 (five lines, ^2J(PP) = 27.49, ^2J(PC) = 46.75, ^3J(PC) = 6.24 Hz, C_i), 134.06 (T, $|^2J$(PC) + ^4J(PC)$|$ = 11.19 Hz, C_o), 135.90 (five lines, ^2J(PP) = 27.49, ^2J(PC) = 64.91, ^3J(PC) = −17.52 Hz, C_i).

[(η^5-C_5H_5)Ru(DVPP)$_2$(PhCN)]PF_6 (8). To a solution of complex **3** (0.25 g) in 10 mL of CH_2Cl_2 was added 0.2 mL of benzonitrile. The solution was stirred for 5 min at room temperature. The solvent was then removed on a rotary evaporator to give a yellow oil. Then ether was added to the yellow oil to induce crystallization. The crystalline solid which formed was washed with diethyl ether several times and recrystallized from CH_2Cl_2/ether. The yellow crystalline solid which formed was collected by filtration and dried in vacuo, affording 0.25 g (87.7%) of the title product, mp 196 °C dec. Anal. Calcd for $C_{40}H_{36}F_6NP_3Ru$: C, 57.30; H, 4.29. Found: C, 57.06; H, 4.42. IR (KBr): ν_{CN} = 2250 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 39.43 (s, 2 P, DPVP), −144.95 (septet, ^1J(PF) = 713 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 4.73 (s, 5 H, C_5H_5), 5.10 (ddd, ^3J(PH) = 18.33, ^3J(ac) = 16.98, ^2J(bc) = 1.80 Hz, 2 H, H_c), 5.74 (ddd, ^2J(PH) = 25.54, ^3J(ac) = 16.98, ^3J(ab) = 12.32 Hz, 2 H, H_a), 5.86 (ddd, ^3J(PH) = 34.71, ^3J(ab) = 12.32, ^2J(bc) = 1.80 Hz, 2 H, H_b), 6.9–7.7 (m, 25 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 83.32 (s, C_5H_5), 111.34 (s, $C_{i'}$), 119.0 (s, CN), 128.49 (T, $|^3J$(PC) + ^5J(PC)$|$ = 9.22 Hz, C_m), 128.75 (T, $|^3J$(PC) + ^5J(PC)$|$ = 9.74 Hz, C_m), 129.41 (s, C_β), 129.48 (s, $C_{m'}$), 130.27 (s, C_p), 131.07 (s, C_p), 131.91 (m, C_α), 132.25 (T, $|^2J$(PC) + ^4J(PC)$|$ = 10.43 Hz, C_o), 132.52 (s, $C_{o'}$), 133.60 (s, $C_{p'}$), 134.09 (T, $|^2J$(PC) + ^4J(PC)$|$ = 11.11 Hz, C_o), 135.50 (m, C_i). The primed carbons are the PhCN carbons.

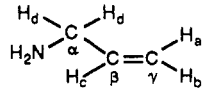
[(η^5-C_5H_5)Ru(DPVP)$_2$(PhNC)]PF_6 (9). This product was prepared in the same manner as for complex **8**. Recrystallization from CH_2Cl_2/ether in the freezer gave a shiny yellow crystalline solid in 90% yield; mp 200–202 °C. Anal. Calcd for $C_{40}H_{36}F_6NP_3Ru$: C, 57.30; H, 4.29. Found: C, 57.05; H, 4.40. IR (KBr): ν_{NC} = 2130 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 40.55 (s, 2 P, DPVP), −144.95 (septet, ^1J(PF) = 712.7 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 4.99 (s, 5 H, C_5H_5), 5.61 (ddd, ^3J(PH) = 18.46, ^3J(ac) = 17.99, ^2J(bc) = 1.99 Hz, 2 H, H_c), 5.75 (ddd, ^2J(PH) = 26.56, ^3J(ac) = 17.99, ^3J(ab) = 12.22 Hz, 2 H, H_a), 5.85 (ddd, ^3J(PH) = 37.22, ^3J(ab) = 12.22, ^3J(bc) = 1.99 Hz, 2 H, H_b), 6.8–7.6 (m, 25 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 87.55 (s, C_5H_5), 125.65 (s, $C_{i'}$ and $C_{o'}$), 128.53 (T, $|^3J$(PC) + ^5J(PC)$|$ = 10.96 Hz, C_m), 128.88 (T, $|^3J$(PC) + ^5J(PC)$|$ = 10.20 Hz, C_m), 129.41 (s, $C_{m'}$ and $C_{p'}$), 129.70 (s, C_β), 130.51 (s, C_p), 131.46 (s, C_p), 131.97 (m, C_α), 132.29 (five lines, ^2J(PP) = 29.92, ^1J(PC) = 33.97, ^3J(PC) = 4.12 Hz, C_i), 135.21 (six lines, ^2J(PP) = 29.92, ^1J(PC) = 59.81, ^3J(PC) = 7.32 Hz, C_i), 161.17 (t, ^2J(PC) = 21.01 Hz, −NC). The primed carbons are the PhNC carbons.

[(η^5-C_5H_5)Ru(DPVP)$_2$(H_2NCH_2CH=CH_2)]PF_6 (10). To a solution of complex **3** (100 mg, 0.136 mmol) in 4 mL of CH_2Cl_2 in a 10-mL NMR tube was added 1 mol equiv of allylamine (0.01 mL). The reaction was monitored by phosphorus NMR spectroscopy. After 15 h at ambient temperature, 99% of the starting complex **3** was converted to the title compound, which has a singlet phosphorus resonance. Removal of the solvent on a rotary evaporator and recrystallization from CH_2Cl_2/ether at low temperature afforded a yellow crystalline solid in nearly quantitative yield; mp 220 °C dec. Anal. Calcd for $C_{36}H_{38}F_6NP_3Ru$: C, 54.55; H, 4.83. Found: C, 54.17; H, 5.04.



$^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 42.03 (s, 2 P, DPVP), −144.95 (septet, ^1J(PF) = 712.89 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 1.51 (s, 2 H, NH_2), 3.39 (q, ^3J(d′c′) = ^4J(d′a′) = ^4J(d′b′) = 6.31 Hz, 2 H, $H_{d'}$), 4.71 (s, 5 H, C_5H_5), 4.91 (ddt, ^3J(a′c′) = 17.13, ^3J(a′d′) = 6.31, ^2J(a′b′) = 1.05 Hz, 1 H, $H_{a'}$), 4.98 (ddd, ^3J(PH) = 17.43, ^3J(ac) = 15.32, ^2J(bc) = 1.80 Hz, 2 H, H_c), 5.07 (ddt, ^3J(b′c′) = 10.22, ^4J(b′d′) = 6.31, ^2J(a′b′) = 1.05 Hz, 1 H, $H_{b'}$), 5.65–6.05 (m, 2 H, H_a and H_b), 5.94 (ddt, ^3J(b′c′) = 10.22, ^3J(a′c′) = 17.13, ^3J(c′d′) = 6.31 Hz, 1 H, $H_{c'}$), 7.0–7.6 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, *J* value, assignment)): 56.49 (s, $C_{\alpha'}$), 80.86 (s, C_5H_5), 117.90 (s, $C_{\gamma'}$), 128.81 (T, $|^3J$(PC) + ^5J(PC)$|$ = 3.8 Hz, C_m), 128.83 (t, $|^3J$(PC) + ^5J(PC)$|$ = 3.8 Hz, C_m), 129.74 (s, C_β), 130.40 (s, C_p), 130.74 (s, C_p), 131.99 (five lines, ^2J(PP) = 23.33, ^1J(PC) = 54.97, ^3J(PC) = 8.45 Hz, C_α), 132.61 (T, $|^2J$(PC) + ^4J(PC)$|$ = 10.64 Hz, C_o), 133.26 (m, C_i), 133.41 (T, $|^2J$(PC) + ^4J(PC)$|$ = 10.79 Hz, C_o),

135.01 (m, C_i), 136.66 (s, C_β). The primed carbons are the allylamine carbons.

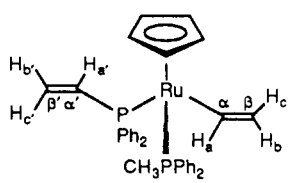


NMR data for $H_2NCH_2CH{=}CH_2$: ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 1.00 (s, 2 H, NH_2), 3.75 (dt, ^3J(cd) = 5.41, ^4J(ad) = ^4J(bd) = 1.5 Hz, 2 H, H_d), 4.91 (ddd, ^3J(bc) = 10.52, ^4J(bd) = ^4J(ab) = 1.5 Hz, 1 H, H_b), 5.02 (dq, ^3J(ac) = 17.13, ^2J(ab) = ^2J(ad) = 1.5 Hz, 1 H, H_a), 5.84 (ddt, ^3J(ac) = 17.13, ^3J(bc) = 10.52, ^3J(cd) = 5.41 Hz, 1 H, H_c). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 44.47 (s, C_α), 113.17 (s, C_γ), 139.58 (s, C_β).

[(η^5-C_5H_5)Ru(DPVP)$_2$(CO)]PF$_6$ (11). After CO (1 atm) was bubbled through a refluxing solution of complex **3** (0.50 g) in 1,2-dichloroethane (20 mL) for about 4 h, the solution lightened in color. Removal of the solvent on a rotary evaporator afforded a pale yellow crystalline solid. It was recrystallized from acetone/chloroform to give an off-white crystalline solid in 95% isolated yield. This product was also prepared by the following two methods. (a) After CO (1 atm) was bubbled through a refluxing solution of complex **1** (0.5 g) in 1,2-dichloroethane for about 8 h, the solvent was removed and the product was recrystallized from acetone/chloroform several times to remove the pale yellow color. The isolated yield was 90%. (b) To a solution of [(η^5-C_5H_5)Ru(CO)(CH_3CN)$_2$]PF_6 (0.50 g, 1.2 mmol) in CH_3NO_2 (20 mL) was added 2 mol equiv of DPVP (0.60 mL) under N_2. The solution was refluxed for 4 h, and then the solvent was removed on a rotary evaporator. The product was purified by recrystallization from acetone/chloroform. The isolated yield was 85%; mp 182–183 °C. IR (KBr): ν_{CO} = 1982 cm^{-1}. Anal. Calcd for $C_{34}H_{31}F_6P_3Ru{\cdot}0.5CH_3NO_2$: C, 52.18; H, 4.12. Found: C, 52.09; H, 4.07. $^{31}P\{^1H\}$ NMR (CD_3NO_2; δ (multiplicity, J value, assignment)): 36.22 (s, 2 P, DPVP), −144.95 (septet, ^1J(PF) = 713 Hz, 1 P, PF_6^-). ^1H NMR (CD_3NO_2; δ (multiplicity, J value, assignment)): 5.17 (m, ^3J(BX) = 19.10, ^3J(PH) = 18.03, ^3J(AX) = −0.48 Hz, 2 H, H_X), 5.48 (s, 5 H, C_5H_5), 5.92 (m, ^3J(PH) = 28.25, ^3J(BX) = 19.10, ^3J(AB) = 12.02 Hz, 2 H, H_B), 5.96 (m, ^2J(PA) = 35.16, ^3J(AB) = 12.02, ^3J(AX) = −0.48 Hz, 2 H, H_A), 7.0–7.7 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_3NO_2; δ (multiplicity, J value, assignment)): 91.41 (t, ^3J(PC) = 1.32 Hz, C_5H_5), 130.12 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.66 Hz, C_m), 130.39 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.88 Hz, C_m), 131.77 (s, C_p), 132.38 (s, C_p), 133.16 (s, C_β), 133.57 (T, $|^2J(PC) + {}^4J(PC)|$ = 10.43 Hz, C_o), 135.42 (T, $|^2J(PC) + {}^4J(PC)|$ = 11.49 Hz, C_o), 132.53 (unresolved, m, C_α), 134.87 (unresolved m, C_i), 202.68 (t, ^2J(PC) = 17.34 Hz, CO).

(η^5-C_5H_5)Ru(DPVP)$_2$(N_3) (12). To a solution of complex **3** (0.20 g) in CH_2Cl_2 (20 mL) was added an aqueous solution of sodium azide (NaN_3; 0.1 g in 3 mL of water). Then ethanol was added to form a single phase. After the mixture was stirred at room temperature for 4 h, 10 mL of water was added to produce two phases. The organic layer was collected, washed with water several times, and dried over magnesium sulfate. The solvent was removed, and the product was recrystallized from $CHCl_3$/petroleum ether. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.74.

[(η^5-C_5H_5)Ru(DPVP)(DPMP)(CH=CH$_2$)] (13). To a solution of complex **3** (100 mg) in dry THF (50 mL) at −78 °C was added 1.2 mL of CH_3Li (1.4 M) under N_2. The solution was stirred for 1 h and then warmed to room temperature. At this time 5 mL of water was added to hydrolyze the excess CH_3Li. After removal of solvents on a rotary evaporator, ether (3 × 10 mL) was added to extract the product. The combined ether solutions were filtered over magnesium sulfate and evaporated to dryness to afford the yellow solid in 69% yield. Anal. Calcd for $C_{34}H_{34}P_2Ru{\cdot}0.5Et_2O$: C, 67.28; H, 6.11. Found: C, 66.98; H, 6.19.



$^{31}P\{^1H\}$ NMR (C_6D_6; δ (multiplicity, J value, assignment)): 55.89 (d, 40.51 Hz, 1 P, DPMP), 42.34 (d, 40.51 Hz, 1 P, DPVP). ^1H NMR (C_6D_6; δ (multiplicity, J value, assignment)): 1.40 (d, ^2J(PH) = 8.41 Hz, 3 H, CH_3), 4.54 (s, 5 H, C_5H_5), 4.99 (ddd, ^3J(PH) = 16.52, ^3J(a'c') = 18.18, ^2J(b'c') = 1.80 Hz, 1 H, $H_{c'}$), 5.41 (ddd, ^3J(PH) = 20.74, ^3J(a'b') = 12.32, ^2J(b'c') = 1.80 Hz, 1 H, $H_{b'}$), 5.99 (ddd, ^2J(PH) = 26.15, ^3J(a'c') = 18.18, ^3J(a'b') = 12.32 Hz, 1 H, $H_{a'}$), 6.06 (ddd, ^4J(PH) = 18.33, ^3J(ac) = 18.23, ^2J(bc) = 1.50 Hz, 1 H, H_c), 6.73 (dddd, ^4J(PH) = 19.33, ^4J(PH) = 8.87, ^3J(ab) = 11.12, ^2J(bc) = 1.50 Hz, 1 H, H_b), 6.90–7.60 (m, 20 H, Ph), 7.87 (dddd, ^3J(PH) = 19.53, ^3J(PH) = 17.60, ^3J(ac) = 18.23, ^3J(ab) = 11.12 Hz, 1 H, H_a). $^{13}C\{^1H\}$ NMR (C_6D_6; δ (multiplicity, J value, assignment)): 15.34 (d, ^1J(PC) = 29.17 Hz, CH_3), 85.87 (t, ^2J(PC) = 1.66 Hz, C_5H_5), 122.83 (t, ^3J(PC) = 3.60 Hz, C_β), 125.27 (d, ^2J(PC) = 1.51 Hz, $C_{\beta'}$), 128.97 (s, C_p), 129.05 (s, C_p), 131.26 (d, ^3J(PC) = 9.52 Hz, C_m), 133.47 (d, ^3J(PC) = 9.75 Hz, C_m), 133.57 (d, ^2J(PC) = 11.11 Hz, C_o), 134.62 (d, ^2J(PC) = 11.11 Hz, C_o), 136.60 (d, ^1J(PC) = 36.58 Hz, $C_{\alpha'}$), 138.73 (d, ^1J(PC) = 42.17 Hz, C_i), 139.95 (dd, ^1J(PC) = 39.30, ^3J(PC) = 2.49 Hz, C_i), 140.95 (d, ^1J(PC) = 38.62 Hz, C_i), 145.31 (dd, ^1J(PC) = 37.71, ^3J(PC) = 1.89 Hz, C_i), 157.63, (t, ^2J(PC) = 17.87 Hz, C_α).

Reaction of Complex 3 with Propynyllithium. This reaction was carried out in the same manner as the reaction above. The reaction gave a mixture of two products, A and B, in a 1:3 ratio ($^{31}P\{^1H\}$ NMR (ether): A, δ 50.85 (AB), 48.78 (AB), ^2J(AB) = 41.79 Hz; B, δ 50.50 (AB), 36.33 (AB), ^2J(AB) = 45.26 Hz). Fractional crystallization in ether converted these two complexes to another product ($^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.14 (AB), 51.06 (AB), ^2J(AB) = 40.21 Hz).

Reaction of Complex 3 with (Phenylethynyl)lithium. This reaction was carried out in the same manner as for the reaction of **3** with CH_3Li. PhC≡CLi was generated in situ from PhC≡CH and n-C_4H_9Li. Three products (A, B, C in a 3:2:0.5 ratio) were observed in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in THF: A, δ 51.99 (d), 48.63 (d), ^2J(PP) = 43.19 Hz; B, δ 46.72 (d), 27.01 (d), ^2J(PP) = 41.79 Hz; C, δ 50.26 (d), 36.22 (d), ^2J(PP) = 48.42 Hz. These substances were not isolated or further characterized.

Reaction of Complex 3 with n-Butyllithium. This reaction was also carried out in the same manner as the reaction above. However, the phosphorus NMR spectrum of the reaction mixture in THF showed a single product with a singlet $^{31}P\{^1H\}$ resonance (δ 47.89 ppm). This product could not be isolated without decomposition.

[(η^5-C_5H_5)Ru(CO)(DPVP)(CH_3CN)]PF$_6$ (14). Under a purge of N_2, 0.38 mL of DPVP was added to a solution containing 1.0 g of [(η^5-C_5H_5)Ru(CO)(CH_3CN)$_2$]PF_6 in 25 mL of CH_3NO_2. The flask was stoppered with a septum under N_2, and the solution was stirred at ambient temperature overnight. Evaporation of solvent and crystallization of the residue from CH_2Cl_2/ether afforded two crops of nice yellow crystalline solids in 90% combined yield. The first crop of crystals (0.021 g) is a minor product, which has the formula [(η^5-C_5H_5)Ru(CO)(η^3-DPVP)]PF_6. The major product (1.267 g) is the title compound. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 41.45 (s, 1 P, DPVP), −144.95 (septet, ^1J = (PF) = 714.74 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 2.10 (d, ^5J(PH) = 1.20 Hz, 3 H, $NCCH_3$), 5.16 (s, 5 H, C_5H_5), 5.45 (ddd, ^3J(PH) = 21.34, ^3J(ac) = 18.03, ^2J(bc) = 0.60 Hz, 1 H, H_b), 6.19 (ddd, ^3J(PH) = 41.47, ^3J(ab) = 12.00, ^2J(bc) = 0.60 Hz, 1 H, H_b), 6.80 (ddd, ^3J(PH) = 22.84, ^3J(ac) = 18.03, ^3J(ab) = 12.00 Hz, 1 H, H_a), 7.2–7.8 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 3.59 (d, ^4J(PC) = 5.82 Hz, CH_3), 128.95 (s, NC), 129.15 (d, ^3J(PC) = 11.19 Hz, 2 C_m), 130.84 (d, ^1J(PC) = 57.29 Hz, C_α), 131.16 (s, C_p), 131.92 (s, C_p), 132.25 (d, ^2J(PC) = 7.26 Hz, 2 C_o), 132.77 (d, ^1J(PC) = 49.05 Hz, 2 C_i), 132.95 (s, C_β), 199.86 (d, ^2J(PC) = 18.74 Hz, CO).

[(η^5-C_5H_5)Ru{P(OCH$_3$)$_3$}(CH_3CN)$_2$]PF$_6$ (15). This compound was prepared according to the literature method;[24] mp 107–108 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 153.05 (s, 1 P, $P(OCH_3)_3$), −144.95 (septet, ^1J(PF) = 713.0 Hz, PF_6^-). ^1H NMR (acetone-d_6; δ (multiplicity, J value, assignment)): 2.53 (d, ^5J(PH) = 1.4 Hz, 6 H, $NCCH_3$), 3.65 (d, ^3J(PH) = 11.9 Hz, 9 H, $P(OCH_3)_3$), 4.82 (d, ^2J(PH) = 0.9 Hz, 5 H, C_5H_5).

[(η^5-C_5H_5)Ru{P(OCH$_3$)$_3$}(DPVP)(CH_3CN)]PF$_6$ (16). To a yellow solution of the complex prepared above (0.12 g) in 20 mL of CH_2Cl_2 was added 1.2 mL of DPVP by syringe under N_2. The flask was stoppered with a septum, and the solution was stirred

Table I. X-ray Experimental Parameters for Complexes 3 and 11

	3	11
formula	$C_{33}H_{31}F_6P_3Ru \cdot 2C_6H_5Cl$	$C_{34}H_{31}F_6OP_3Ru \cdot CHCl_3$
fw	960.72	882.99
a, Å	9.754 (3)	19.065 (4)
b, Å	22.528 (6)	10.825 (2)
c, Å	19.840 (5)	9.433 (2)
α, deg		100.08 (2)
β, deg	100.46 (2)	103.37 (2)
γ, deg		84.27 (2)
space group	$P2_1/c$	$P\bar{1}$
Z	4	2
d(calcd), g cm^{-3}	1.488	1.576
μ, cm^{-1}	57.814	8.140
abs factor range	0.83–1.22	0.96–1.02
temp, °C	−100	20
final $R(F)$[a]	0.035	0.054
final $R_w(F)$	0.059	0.075

[a] Minimizing $\sum w(|F_o| - |F_c|)^2$ with $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$.

magnetically for 12 h. The solvent was then removed on a rotary evaporator, and the residue was washed with ether several times. Recrystallization from CH_2Cl_2/ether gave the title product in 90% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 149.69 (d, $^2J(PP)$ = 68.36 Hz, 1 P, $P(OCH_3)_3$), 43.84 (d, $^2J(PP)$ = 68.36 Hz, 1 P, DPVP), −144.95 (septet, $^1J(PF)$ = 713.0 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 2.31 (s, 3 H, $NCCH_3$), 3.47 (d, $^3J(PH)$ = 11.42 Hz, 9 H, $P(OCH_3)_3$), 4.79 (s, 5 H, C_5H_5), 5.11 (t, $^3J(PH) = {}^3J(ac)$ = 17.73 Hz, 1 H, H_c), 6.02 (dd, $^3J(PH)$ = 36.06, $^3J(ab)$ = 12.32 Hz, 1 H, H_b), 6.67 (ddd, $^2J(PH)$ = 24.64, $^3J(ac)$ = 17.73, $^3J(ab)$ = 12.32 Hz, 1 H, H_a), 7.4–7.8 (m, 10 H, Ph).

$[(\eta^5\text{-}C_5H_5)Ru\{P(OCH_3)_3\}(DVPP)(NCCH_3)]PF_6$ (17). This compound was prepared in the same manner as that of the analogous compound above. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ (multiplicity, J value, assignment)): 150.71 (d, $^2J(PP)$ = 66.48 Hz, 1 P, $P(OCH_3)_3$), 36.06 (d, $^2J(PP)$ = 66.48 Hz, 1 P, DVPP), −144.95 (septet, $^1J(PF)$ = 713.0 Hz, 1 P, PF_6^-).

C. X-ray Data Collection and Processing. Crystals of complex 3 suitable for X-ray crystallography were grown from chlorobenzene/ether at low temperature. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of complex 3 belong to the monoclinic system.

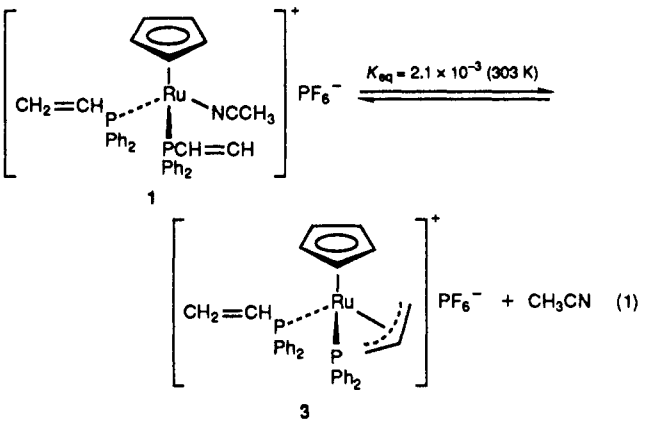
Suitable single crystals of complex 11 were obtained by slow evaporation of an acetone/$CHCl_3$ solution at room temperature. A systematic search in reciprocal space using a crystal cut out from a cluster of crystals and an Enraf-Nonius CAD4-F automatic diffractometer showed that crystals of 11 belong to the triclinic system.

Quantitative data for complex 3 were obtained at −100 °C, achieved using a locally built gas-flow device. For complex 11, data were obtained at room temperature. All experimental parameters used for complexes 3 and 11 are given in Table I. The resulting data sets for these two complexes were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[26] was used with the exception of a local data reduction program.

The structures were solved using the heavy-atom method. After refinement of the heavy atoms, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for the hydrogen atoms; they were introduced in structure factor calculatons by their computed coordinates (C–H = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2 but were not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart,[27] especially for complex 3, since face indexation was not possible under the cold gas stream. Absorption corrections for 11 were calculated from the ψ scans of four reflections. Full least-squares refinements were done; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 28.

Results and Discussion

A. Syntheses and Characterization. The compound $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+PF_6^-$[24] reacts cleanly with vinyldiphenylphosphine and divinylphenylphosphine to produce the $[(\eta^5\text{-}C_5H_5)Ru(R_3P)_2(CH_3CN)]^+PF_6^-$ complexes in high yield. Both compounds are stable yellow crystalline solids that exhibit single ν_{CN} frequencies in the expected region of their infrared spectra and single ^{31}P resonances for the coordinated phosphines in their ^{31}P NMR spectra. Over a period of days in $CDCl_3$ solution, compound 1 slowly dissociates CH_3CN, producing an equilibrium mixture of 1 and the phosphaallyl complex 3 (reaction 1). This equilibrium is evidenced by the singlet ^{31}P resonance for 1 diminishing in intensity as a doublet of doublets for 3 slowly appears.



The equilibrium constant was evaluated as a function of temperature by $^{31}P\{^1H\}$ NMR spectroscopy in order to understand the driving force for the formation of the phosphaallyl complex. It was found that $\Delta H°_{eq} = 41.8 \pm 2$ kJ/mol and $\Delta S°_{eq} = 146 \pm 4$ eu, establishing that the formation of the phosphaallyl complex is entropy-driven. Since this is the first example of an equilibrium between an η^1-vinylphosphine and an η^3-phosphaallyl, we sought to isolate and fully characterize the η^3-phosphaallyl complex. As described in the Experimental Section, heating the η^1 complex in vacuo for several days at 70–75 °C (0.5 mmHg) quantitatively liberates acetonitrile and produces the η^3-phosphaallyl complex 3. That equilibrium 1 is reversible was established by adding 1 mol equiv of CH_3CN to a $CDCl_3$ solution of complex 3. Upon addition of acetonitrile the doublet of doublets in the $^{31}P\{^1H\}$ NMR spectrum of complex 3 was immediately replaced by a singlet at the chemical shift found for pure complex 1 in $CDCl_3$. Thermal gravimetric analysis of 1 at a heating rate of 5 °C/min under flowing nitrogen showed that loss of CH_3CN in the solid state is slow and gradual. Quantitative loss occurs at 220 °C under these conditions, 50 °C above the compound's melting point.

Complexes of the type $(\eta^5\text{-}C_5H_5)M(CO)(\eta^3\text{-}C_3H_5)$[29-32] (M

(26) Frenz, B. A. The Enraf-Nonius *CAD4-ADP*. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(27) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(28) (a) Cromer, D. T.; Walker, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2b. (b) *Ibid.*, Table 2.31.

(29) Hsu, L. Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W. L. *Organometallics* **1989**, *8*, 241.

(30) Faller, J. W.; Johnson, B. V.; Dryja, T. P. *J. Organomet. Chem.* **1974**, *65*, 395. Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. King, R. B.; Ishaq, M. *Inorg. Chim. Acta* **1970**, *4*, 258.

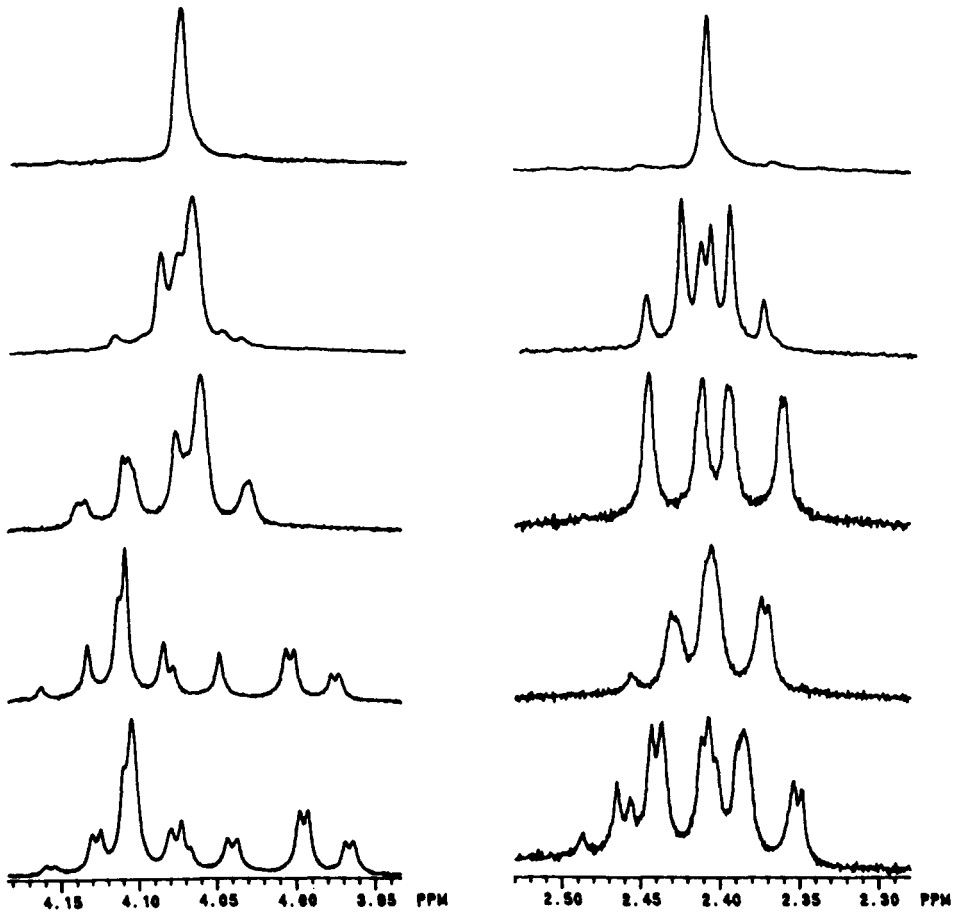
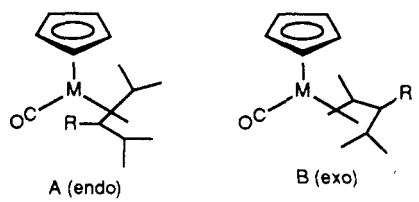


Figure 2. ^1H NMR spectra (300 MHz) in the phosphaallyl proton region for compound **3** (from bottom to top): normal spectrum; $^1H\{^{31}P\}$ decoupling of the vinylphosphine phosphorus (P_b); $^1H\{^{31}P\}$ decoupling of the phosphaallyl phosphorus (P_a); $^1H\{^{31}P\}$ broad-band phosphorus decoupling (analysis of the ABX spin system so obtained gave the proton chemical shifts and proton–proton coupling constants); $^1H\{^{31}P$ BB, ^1H selective}. The singlet observed at δ 2.41 under these conditions demonstrates that only one isomer is present in solution.

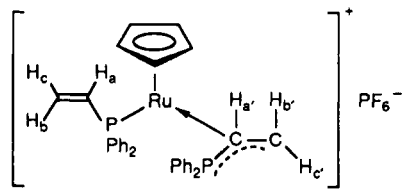
= Fe, Ru) undergo conformational equilibria between two isomeric species which differ in the orientation of the allyl moiety, as illustrated by A and B. When R = CH_3, the



exo isomer B is destabilized relative to the endo isomer A by virtue of interligand steric effects. The conformational interconversions of some similar allyl isomers have been studied by dynamic NMR techniques.[31,32] It thus is of interest to determine the structure of compound **3** in solution in order to assess whether the phosphaallyl moiety behaves in an analogous fashion. This was accomplished by a complete assignment of the ^1H NMR spectrum of compound **3**, which was made as follows. A COSY spectrum (Figure 1, supplementary material) showed that in addition to the C_5H_5 singlet resonance there are three separate tightly coupled sets of protons: the phenyl protons, the vinyl protons, and the three upfield phosphaallyl protons. The last group appear as three second-order multiplets at δ 2.41 (one proton), 4.06 (one proton), and 4.08 (one proton). An APT ^{13}C NMR spectrum established that the carbon resonance at δ 34.09 was due to the CH group and that at δ 43.57 was due to the CH_2 group of the phosphaallyl moiety. A $^1H/^{13}C$ HETCOR spectrum showed that the carbon resonance at δ 34.09 correlates with the proton resonance at δ 4.06 and the carbon resonance at δ 43.57 is correlated with the proton resonances at δ 2.41 and 4.08. Hence, one of the two CH_2 protons resonates at 2.41 ppm. The ^1H NMR spectra with selective and broad-band ^{31}P decoupling (Figure 2) established that $H_{c'}$ is the proton whose chemical shift occurs at δ 2.41. This is a typical chemical shift for $H_{c'}$ in metal allyl complexes.[30,32] The chemical shift of $H_{c'}$ in the exo isomer generally occurs upfield of that in the endo isomer.[32] However, since only one isomer was formed, it is not possible to compare the spectra of the exo and endo isomers. For a free phosphaalkene such as Cl—P̈=CH_2, ^2J(PH) is large for the anti hydrogen.[33] A similar observation holds true for related phosphorus-containing π complexes even when the phosphorus lone pair is σ-bonded to another metal center.[6] Inspection of ^2J(PH) data for iron phosphaallyl complexes[6] indicates that ^2J(PH) is large (27–30 Hz) for exo phosphaallyl complexes and small (0–2 Hz) for the endo isomers. For complex **3** ^2J(PH) = 15.03 Hz. The ^2J(PH) value for another similar phosphaallyl complex, [(η^5-C_5H_5)Ru(CO)(η^3-DPVP)]PF_6 (**6**), is 2.4 Hz (vide infra). Thus, we

(31) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211.
(32) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101.
(33) Pellerin, B.; Denis, J. M.; Perrocheau, J.; Carrie, R. *Tetrahedron Lett.* **1986**, *27*, 5723.

conclude that **3** is an exo isomer and **6** is an endo isomer.



3 (exo)

In the exo isomer **3**, protons $H_{a'}$ and $H_{b'}$ are proximate to the C_5H_5 ring protons, whereas proton $H_{c'}$ is distal from the C_5H_5 ring protons. As demonstrated by a 2D-NOE experiment (Figure 3, supplementary material), one or both of the protons $H_{a'}$ and $H_{b'}$ show a significant NOE with the C_5H_5 ring protons. The J(HH) and J(PH) couplings were further confirmed by a 2D-HOJ experiment (Figure 4, supplementary material).

Both the ruthenium atom and the phosphaallyl C_α carbon of **3** are stereogenic atoms.[34] Hence, four diastereomers are possible for compound **3**. The two vinylphosphines in **1** should have equal probability of becoming the phosphaallyl moiety. Interligand steric interactions between the phosphine substituents and the C_5H_5 ring lead to enantioface selection in the coordination of the prochiral vinyl groups. As a result, a racemic mixture of only two of the four possible diastereomers is formed, both of which possess the exo conformation. The molecule is not dynamic in solution (−60 °C to room temperature in $CDCl_3$ and room temperature to 80 °C in CD_3NO_2).

In order to confirm the molecular structure assigned by NMR spectroscopic techniques, the X-ray crystal structure of **3** (Figure 5) was obtained. Atom coordinates are given in Table II and selected bond distances and angles in Table III. As can be seen from Figure 5, the phosphaallyl moiety has an exo orientation. The complex has a pseudooctahedral geometry and is an 18-electron complex containing an η^1-$Ph_2PCH{=}CH_2$ (two-electron donor) and an η^3-$Ph_2PCH{=}CH_2$ group (four-electron donor). The Ru–C15 bond distance (2.176 (3) Å) is shorter than both the Ru–C16 (2.244 (4) Å) and Ru–P2 (2.276 (1) Å) bond distances, similar to what is observed for (allyl)(η^5-C_5H_5)Ru(CO) complexes[29] and Mo[9] and Co[8] phosphaallyl complexes. The Ru–P2 distance is shorter than the Ru–P1 (2.315 (1) Å) bond distance, and the C15–C16 bond distance (1.399 (5) Å) is longer than the C1–C2 (1.306 (5) Å) bond distance. The C15–C16 distance is comparable to similar distances in Pd[35] (1.356 (13) Å), Mo[9] (1.397 (5) Å), and Co[8] (1.421 (7) Å) phosphaallyl complexes. The P2–C15–C16 bond angle (119.1 (3)°) is almost the same as the P1–C1–C2 (119.6 (4)°) angle in an Fe[36] phosphaallyl complex and considerably smaller than the P1–C1–C2 (127.5 (3)°) bond angle or the comparable P–C–C bond angles (124.5 (8) and 125.8 (7)°) in the Pd[35] phosphaallyl complex. The C17, P2, C15, C16, H14, H15, and H16 atoms are approximately coplanar (the deviations from their mean plane are respectively 0.073 (4), −0.07 (1), −0.030 (4), 0.012 (4), −0.036 (4), 0.034 (4), and 0.018 (4) Å) as in most allyl and phosphaallyl complexes. The dihedral angle between this plane and the C_5H_5 plane is 17.1 (3)°, which compares to 16.5° in *exo*-(η^5-C_5H_5)Ru(2-methylallyl)(CO) and 68.5° in the endo isomer.[29] Complex **3** is the first example of a monometallic complex containing a neutral four-electron-donor phosphaallyl ligand. All previously reported phosphaallyl complexes contain anionic five-electron donors coordinated to two or three metal centers[8-10,36] or neutral four-electron donors coordinated to two metals.[35]

Because the DVPP ligand is structurally similar to DPVP, we thought that complex **4** could be obtained from complex **2**. However, heating **2** in vacuo for long time periods only caused partial conversion to **4**. Attempted separation of **4** from **2** was not successful by either column chromatography on silica gel or fractional crystallization from a variety of solvent mixtures. An alternative route to **4** could be conversion of **2** to a chloride complex (re-

Table II. Atom Coordinates for 3[a]

atom	*x*	*y*	*z*	*B*, Å²
Ru	0.11813 (3)	0.19367 (1)	0.09265 (1)	2.349 (7)
P1	0.3234 (1)	0.15523 (4)	0.06781 (5)	2.28 (2)
C1	0.4848 (4)	0.1663 (2)	0.1279 (2)	2.68 (9)
C2	0.5706 (4)	0.1257 (2)	0.1574 (2)	3.7 (1)
C3	0.3159 (4)	0.0754 (2)	0.0566 (2)	2.65 (8)
C4	0.3015 (5)	0.0387 (2)	0.1122 (2)	4.0 (1)
C5	0.2914 (5)	−0.0223 (2)	0.1030 (3)	5.1 (1)
C6	0.2932 (5)	−0.0467 (2)	0.0409 (3)	5.4 (1)
C7	0.3062 (5)	−0.0125 (2)	−0.0141 (3)	5.0 (1)
C8	0.3176 (4)	0.0484 (2)	−0.0064 (2)	3.6 (1)
C9	0.3702 (4)	0.1824 (2)	−0.0116 (2)	2.55 (8)
C10	0.2704 (4)	0.2051 (2)	−0.0639 (2)	3.12 (9)
C11	0.3056 (5)	0.2259 (2)	−0.1239 (2)	3.9 (1)
C12	0.4423 (5)	0.2244 (2)	−0.1322 (2)	4.1 (1)
C13	0.5438 (5)	0.2025 (2)	−0.0809 (2)	4.0 (1)
C14	0.5068 (4)	0.1809 (2)	−0.0212 (2)	3.26 (9)
P2	0.1982 (1)	0.28874 (4)	0.09777 (5)	2.46 (2)
C15	0.1579 (4)	0.2595 (2)	0.1741 (2)	3.06 (9)
C16	0.2248 (5)	0.2076 (2)	0.2016 (2)	3.20 (9)
C17	0.0844 (4)	0.3500 (2)	0.0684 (2)	2.79 (8)
C18	−0.0028 (5)	0.3467 (2)	0.0046 (2)	4.0 (1)
C19	−0.0923 (5)	0.3928 (2)	−0.0179 (3)	4.5 (1)
C20	−0.0956 (4)	0.4428 (2)	0.0218 (2)	4.0 (1)
C21	−0.0105 (5)	0.4460 (2)	0.0846 (2)	4.3 (1)
C22	0.0807 (5)	0.4001 (2)	0.1083 (2)	3.7 (1)
C23	0.3757 (4)	0.3151 (2)	0.1061 (2)	2.94 (9)
C24	0.4341 (4)	0.3225 (2)	0.0469 (2)	3.39 (9)
C25	0.5703 (4)	0.3407 (2)	0.0528 (3)	4.3 (1)
C26	0.6489 (5)	0.3522 (2)	0.1149 (3)	5.0 (1)
C27	0.5929 (5)	0.3458 (2)	0.1730 (3)	5.7 (1)
C28	0.4536 (5)	0.3276 (2)	0.1694 (2)	3.8 (1)
C29	−0.0075 (4)	0.1111 (2)	0.0836 (2)	3.6 (1)
C30	−0.0030 (4)	0.1322 (2)	0.0173 (2)	3.31 (9)
C31	−0.0693 (4)	0.1880 (2)	0.0097 (2)	3.8 (1)
C32	−0.1120 (4)	0.2018 (2)	0.0718 (3)	3.9 (1)
C33	−0.0735 (4)	0.1545 (2)	0.1174 (2)	3.8 (1)
P3	0.1649 (1)	0.73366 (5)	0.19409 (5)	3.36 (2)
F1	0.1966 (3)	0.8001 (1)	0.1742 (2)	5.75 (7)
F2	0.3235 (3)	0.7267 (1)	0.2282 (1)	5.25 (7)
F3	0.2029 (3)	0.7119 (1)	0.1233 (1)	5.65 (7)
F4	0.1383 (3)	0.6664 (1)	0.2137 (2)	6.04 (7)
F5	0.1314 (3)	0.7555 (2)	0.2646 (2)	7.63 (8)
F6	0.0098 (3)	0.7396 (2)	0.1572 (2)	9.5 (1)
Cl1	0.3537 (2)	0.44948 (9)	0.31077 (8)	8.56 (5)
C34	0.1788 (6)	0.4617 (3)	0.2899 (2)	5.9 (1)
C35	0.1316 (6)	0.5167 (2)	0.2674 (3)	5.9 (1)
C36	−0.0181 (8)	0.5275 (3)	0.2490 (3)	8.0 (2)
C37	−0.1071 (7)	0.4859 (4)	0.2514 (3)	10.0 (2)
C38	−0.0472 (7)	0.4249 (3)	0.2768 (3)	8.1 (2)
C39	0.0874 (6)	0.4143 (3)	0.2953 (3)	6.8 (1)
Cl2	0.2200 (2)	0.40935 (8)	0.9114 (1)	10.13 (5)
C40	0.3745 (5)	0.4323 (2)	0.8906 (3)	5.9 (1)
C41	0.4526 (7)	0.3948 (3)	0.8560 (3)	7.2 (2)
C42	0.5741 (6)	0.4162 (3)	0.8423 (3)	6.4 (1)
C43	0.6236 (6)	0.4722 (3)	0.8612 (3)	6.5 (1)
C44	0.5568 (9)	0.5082 (3)	0.8942 (3)	9.6 (2)
C45	0.4180 (6)	0.4860 (3)	0.9090 (3)	6.2 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

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action 2) followed by reaction with $AgBF_4$ (reaction 3).

$$[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2(CH_3CN)]PF_6 + Me_4NCl \rightarrow [(\eta^5\text{-}C_5H_5)Ru(DVPP)_2Cl] + Me_4NPF_6 \quad (2)$$

$$[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2Cl] + AgBF_4 \rightarrow [(\eta^5\text{-}C_5H_5)Ru(DVPP)(\eta^3\text{-}DVPP)]BF_4 + AgCl \quad (3)$$

At room temperature, reaction 2 gave a mixture of $[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2(CH_3CN)]Cl$ and $[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2Cl]$. The former complex was completely converted to the latter at 80 °C in refluxing 1,2-dichloroethane. Reaction 3 produced an inseparable mixture of the desired phosphaallyl complex and two other as yet unidentified products.

Thermal gravimetric analysis of **2** at a heating rate of 5 °C/min under flowing nitrogen showed that, as for **1**, loss of acetonitrile is gradual and is complete by 259 °C under these conditions. This is about 40 °C higher than the formation temperature of **3** under the same conditions. Further, there is no evidence for an equilibrium such as (1) between **2** and **4** in solution. The relative ease of formation of **3** compared to that of **4** may well be due to the size of the substituents on phosphorus, akin to the Thorpe–Ingold effect.[37]

The $[(\eta^5\text{-}C_5H_5)Ru(CO)(\eta^3\text{-}DPVP)]PF_6$ (**6**) complex was obtained as a minor product from the reaction of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(CO)]PF_6$ with 1 mol equiv of DPVP. Its $^{31}P\{^1H\}$ NMR spectrum in CD_3NO_2 exhibits a singlet at δ 75.42, more than 50 ppm downfield of the η^3-DPVP resonance for **3**. The ^1H NMR spectrum (Figure 6, supplementary material) supports the η^3-bonding mode, as two of the resonances for the vinyl protons occur far upfield (δ 2.90 and 3.74). However, in contrast to what was observed for **3**, the third vinyl proton resonance for **6** is found in the normal vinyl region (δ 6.15). Selective phosphorus decoupling (Figure 6) together with APT and $^1H/^{13}C$ HETCOR spectra allowed assignment of the chemical shifts. Proton H_a has the smallest coupling to phosphorus ($^2J(PH)$ = 2.4 Hz). Comparison of the chemical shifts and $J(PH)$ coupling constants of **3** and **6** suggested that **6** is an endo isomer. The relative downfield chemical shift for H_a is consistent with the data reported for most endo $CpRu^{II}$ and $CpRu^{IV}$ allyl complexes[38] and some endo phosphaallyl complexes.[6] Complex **6** is not dynamic in solution (room temperature to 80 °C in CD_3NO_2).

B. Reactivity of Phosphaallyl Complex 3. In view of the unusual nature of the η^3-phosphaallyl complex, a preliminary study of the reactivity of **3** was undertaken. It is well-known that allyl complexes are susceptible to nucleophilic attack.[2,11-19,39] In principle, the chiral phosphaallyl complex **3** could react with nucleophiles at any of four sites:[39-41] the metal center, phosphorus,[8-10] or the α-[41] or β-carbons[39] of the phosphaallyl ligand. The metal center is potentially the most electrophilic site, as it bears a positive charge.

Complex **3** reacts with nucleophiles that are good two-electron-donor ligands (CH_3CN, $(CH_3)_2CHCN$, PhCN, PhNC, CO, and N_3^-) under mild conditions, at the metal center, displacing the coordinated vinyl moiety (reaction 4).

$$[(\eta^5\text{-}C_5H_5)Ru(DVPP)(\eta^3\text{-}DVPP)]PF_6 + L \rightarrow [(\eta^5\text{-}C_5H_5)Ru(DVPP)_2L]PF_6 \text{ or } [(\eta^5\text{-}C_5H_5)Ru(DVPP)_2N_3] \quad (4)$$

This is evidenced by rapid disappearance of the two doublet resonances and appearance of a singlet resonance in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures. In each case these reactions are quantitative. The $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra of the products are unexceptional and are consistent with their formulations.

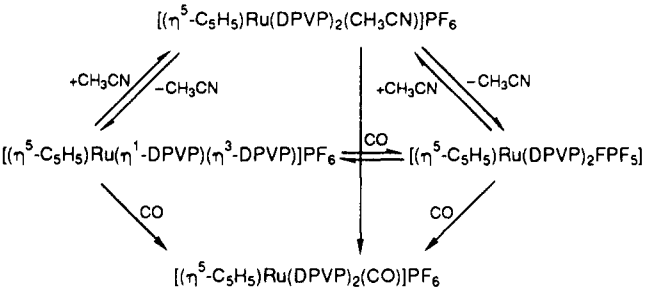
However, the vinyl proton resonances of $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CO)]PF_6$ displayed a second-order ABXZ (A, B,

Table III. Selected Bond Distances (Å) and Angles (deg) for Complex 3[a]

Ru–P1	2.315 (1)	P1–C1	1.810 (3)
Ru–P2	2.276 (1)	P1–C3	1.811 (4)
Ru–C15	2.176 (3)	P1–C9	1.824 (4)
Ru–C16	2.244 (4)	C1–C2	1.306 (5)
Ru–C29	2.217 (4)	P2–C15	1.761 (4)
Ru–C30	2.215 (4)	P2–C17	1.800 (4)
Ru–C31	2.230 (4)	P2–C23	1.810 (4)
Ru–C32	2.215 (4)	C15–C16	1.399 (5)
Ru–C33	2.201 (4)		
P1–Ru–P2	93.34 (3)	C16–Ru–C32	116.4 (2)
P1–Ru–C15	111.6 (1)	C16–Ru–C33	96.0 (1)
P1–Ru–C16	89.4 (1)	C29–Ru–C30	37.0 (1)
P1–Ru–C29	99.0 (1)	C29–Ru–C31	61.6 (1)
P1–Ru–C30	89.9 (1)	C29–Ru–C32	61.8 (1)
P1–Ru–C31	116.5 (1)	C29–Ru–C33	37.1 (1)
P1–Ru–C32	151.3 (1)	C30–Ru–C31	36.9 (1)
P1–Ru–C33	134.4 (1)	C30–Ru–C32	61.8 (1)
P2–Ru–C15	46.5 (1)	C30–Ru–C33	62.0 (1)
P2–Ru–C16	74.3 (1)	C31–Ru–C32	36.8 (2)
P2–Ru–C29	166.8 (1)	C31–Ru–C33	61.7 (2)
P2–Ru–C30	139.0 (1)	C32–Ru–C33	37.1 (2)
P2–Ru–C31	108.4 (1)	C1–Ru–C3	103.2 (2)
P2–Ru–C32	105.0 (1)	C1–P1–C9	101.4 (2)
P2–Ru–C33	131.7 (1)	C3–P1–C9	103.8 (2)
C15–Ru–C16	36.9 (1)	P1–C1–C2	127.5 (3)
C15–Ru–C29	130.8 (1)	C15–P2–C17	110.1 (2)
C15–Ru–C30	158.2 (1)	C15–P2–C23	113.8 (2)
C15–Ru–C31	126.8 (2)	C17–P2–C23	107.5 (2)
C15–Ru–C32	96.9 (1)	P2–C15–C16	119.1 (3)
C15–Ru–C3	98.7 (1)	C30–C29–C33	107.8 (4)
C16–Ru–C29	110.4 (1)	C29–C30–C31	108.0 (3)
C16–Ru–C30	146.6 (1)	C30–C31–C32	107.9 (3)
C16–Ru–C31	153.3 (2)	C31–C32–C33	108.0 (4)
P1–C3–C4	119.6 (3)	C29–C33–C32	108.2 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme I



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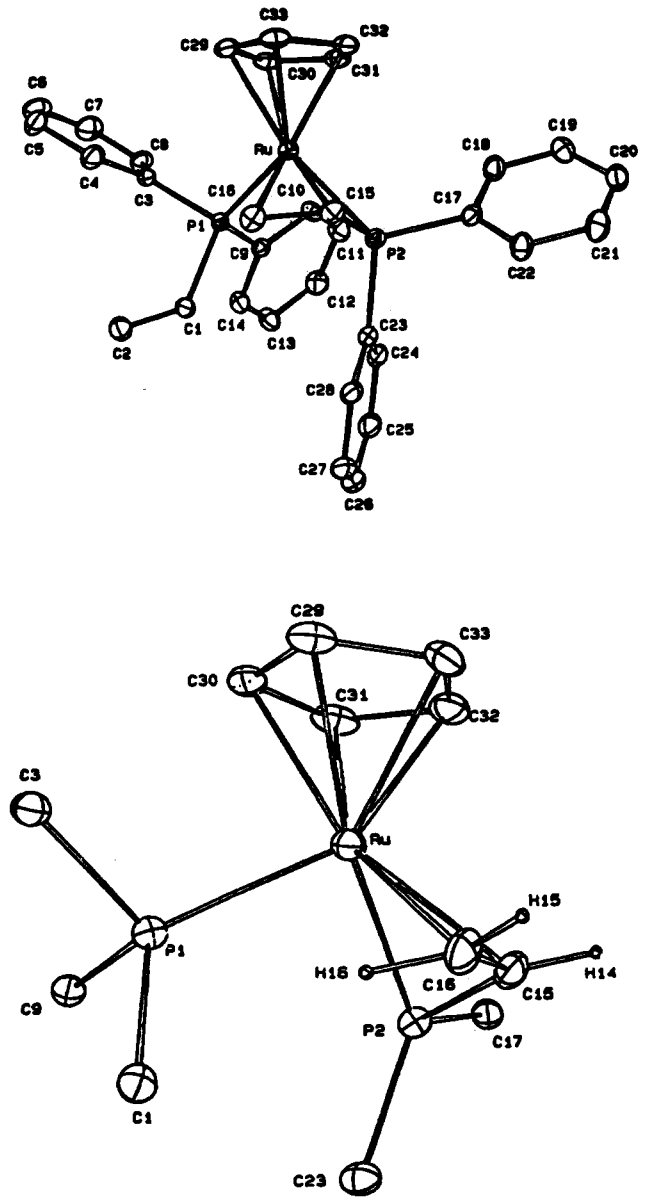

Figure 5. (top) Ortep drawing of the cation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DPVP)(\eta^3\text{-}DPVP)]PF_6$ showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted. (bottom) Abbreviated Ortep drawing showing attached hydrogens on the phosphoallyl moiety. Phenyl and β-vinyl carbon atoms are omitted for clarity.

X = ^{1}H, Z = ^{31}P) pattern. Complete assignment of the ^{1}H NMR spectrum of this complex required phosphorus decoupling. This complex was also prepared by two other routes (reactions 5 and 6).

$$[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_2(CO)]PF_6 + 2DPVP \xrightarrow[-CH_3CN]{+CH_3NO_2} [(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CO)]PF_6 \quad (5)$$

$$[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CH_3CN)]PF_6 + CO \xrightarrow[-CH_3CN]{+ClCH_2CH_2Cl} [(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CO)]PF_6 \quad (6)$$

Phosphorus-31 NMR spectroscopic monitoring of reaction 6 showed that instead of a mixture of starting material and CO substitution product being formed, a mixture of four compounds, starting material ($\delta(^{31}P)$ 39.72), phosphaallyl complex **3** ($\delta(^{31}P)$ 42.33 (d), 24.16 (d), $^2J(PP)$ = 43.94 Hz), CO substitution product **11** ($\delta(^{31}P)$ 36.22), and

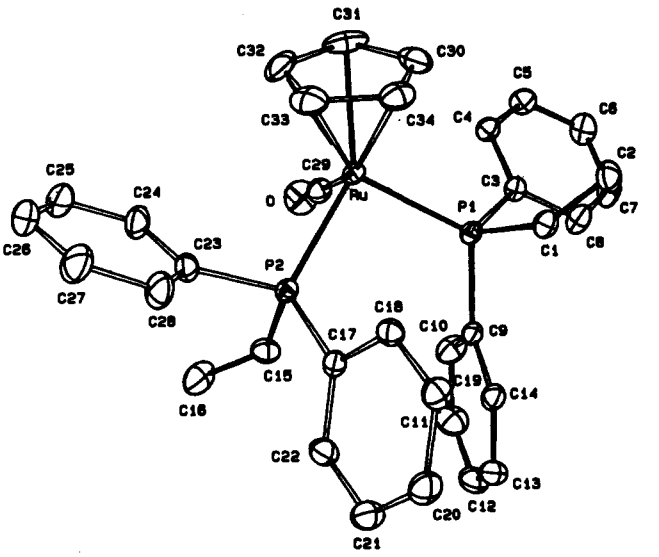

Figure 7. Ortep drawing of the cation of $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2CO]PF_6$ showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

$[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2FPF_5]$ ($\delta(^{31}P)$ 30.39 (s), −142.24 (m, $^1J(PF)$ = 631 Hz)), were initially formed according to Scheme I.

Thus, substitution of CH_3CN by CO probably occurs by a dissociative process. $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CO)]PF_6$ is the sole product after long reaction times. Mathey and co-workers[6] studied the reactions of their anionic phosphaallyl iron–tungsten complex with CO at 5 atm and with phosphines. They concluded that in their system CO and PR_3 attacked tungsten, not iron, concomitant with conversion of a bridging CO to a terminal CO on iron. By comparison of the reactivities of the neutral and anionic phosphaallyl ligands, it seems that the neutral phosphaallyl ligand is more substitutionally labile.

For the $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2L]PF_6$ complexes, as the steric bulk of L increases and its donor ability decreases, L would be expected to dissociate to a greater extent and the equilibrium constants for equilibria analogous to (1) should increase. We find the following at 303 K: L = CH_3CN, $K_{eq} = 2.1 \times 10^{-3}$; L = $(CH_3)_2CHCN$, $K_{eq} = 2.5 \times 10^{-3}$; L = PhCN, $K_{eq} = 1.8 \times 10^{-3}$. This is not consistent with the relative donor numbers of these nitriles (14.1, 15.4, and 11.9, respectively).[42] None of the other complexes dissociate L to a measurable extent.

The crystal structure of $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CO)]PF_6$ (**11**; Figure 7) consists of isolated cations and anions with no short contacts. Atom coordinates are listed in Table IV, and Table V lists selected bond distances and angles. The cation has distorted-octahedral geometry, has no symmetry, and contains a linear carbonyl ligand (Ru–C29 = 1.867 (5) Å; Ru–C29–O = 177.9°; C29–O = 1.124 (6) Å), and two phosphines that are equidistant from ruthenium (Ru–P1 = 2.320 (1) Å; Ru–P2 = 2.324 (1) Å). Ru–P distances are longer than those in **3**. The P–C_α–C_β angles are equal (125.5 (4), 125.5 (5)°), as are the C_α–C_β distances (1.313 (7), 1.316 (8) Å).

Coordinated vinylphosphines are susceptible to Michael additions,[43-46] and since the vinyl group of $[(\eta^5\text{-}C_5H_5)Ru$-

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Table IV. Atom Coordinates for 11[a]

atom	x	y	z	B, Å²
Ru	0.25509 (2)	0.74993 (4)	0.18898 (5)	2.657 (8)
P1	0.13912 (8)	0.8192 (1)	0.0813 (2)	2.75 (3)
C1	0.1206 (3)	0.9809 (5)	0.1641 (7)	3.4 (1)
C2	0.0767 (4)	1.0166 (6)	0.2545 (8)	4.5 (2)
C3	0.0669 (3)	0.7345 (5)	0.1117 (7)	3.2 (1)
C4	0.0800 (3)	0.6389 (5)	0.1951 (7)	3.5 (1)
C5	0.0232 (4)	0.5830 (6)	0.2203 (8)	4.5 (2)
C6	−0.0469 (4)	0.6207 (6)	0.1650 (9)	5.1 (2)
C7	−0.0601 (4)	0.7120 (7)	0.074 (1)	6.0 (2)
C8	−0.0041 (4)	0.7708 (6)	0.0503 (8)	4.7 (2)
C9	0.1134 (3)	0.8207 (5)	−0.1165 (6)	3.1 (1)
C10	0.0926 (4)	0.7105 (7)	−0.2112 (8)	5.0 (2)
C11	0.0727 (5)	0.7102 (8)	−0.3613 (8)	5.8 (2)
C12	0.0719 (4)	0.8144 (8)	−0.4190 (8)	5.5 (2)
C13	0.0942 (4)	0.9227 (7)	−0.3302 (7)	4.7 (2)
C14	0.1153 (3)	0.9273 (6)	−0.1779 (7)	3.6 (1)
P2	0.30997 (8)	0.7907 (1)	0.0075 (2)	2.83 (3)
C15	0.2890 (4)	0.6833 (6)	−0.1643 (7)	4.0 (1)
C16	0.3366 (5)	0.6193 (7)	−0.2342 (9)	6.0 (2)
C17	0.2941 (3)	0.9452 (5)	−0.0469 (6)	2.9 (1)
C18	0.2806 (3)	1.0501 (5)	0.0561 (6)	3.3 (1)
C19	0.2655 (3)	1.1683 (6)	0.0158 (7)	3.8 (1)
C20	0.2626 (4)	1.1822 (6)	−0.1288 (8)	4.6 (2)
C21	0.2758 (4)	1.0805 (6)	−0.2324 (7)	4.5 (2)
C22	0.2919 (3)	0.9628 (6)	−0.1898 (7)	3.9 (1)
C23	0.4082 (3)	0.7723 (6)	0.0679 (7)	3.6 (1)
C24	0.4390 (4)	0.6559 (7)	0.1043 (8)	4.9 (2)
C25	0.5120 (4)	0.6407 (8)	0.1563 (9)	6.2 (2)
C26	0.5561 (4)	0.739 (1)	0.180 (1)	7.0 (2)
C27	0.5260 (4)	0.8532 (9)	0.147 (1)	6.6 (2)
C28	0.4521 (4)	0.8695 (7)	0.0889 (9)	5.4 (2)
O	0.2307 (3)	0.4889 (4)	0.0279 (6)	6.2 (1)
C29	0.2397 (3)	0.5878 (5)	0.0859 (7)	3.6 (1)
C30	0.2346 (4)	0.8094 (8)	0.4128 (7)	5.4 (2)
C31	0.2758 (5)	0.6960 (7)	0.4123 (8)	6.0 (2)
C32	0.3422 (4)	0.7173 (8)	0.3859 (8)	6.0 (2)
C33	0.3410 (4)	0.8439 (8)	0.3705 (8)	5.4 (2)
C34	0.2741 (4)	0.9007 (6)	0.3884 (7)	4.8 (2)
P3	0.2048 (2)	0.3310 (2)	0.4441 (3)	6.15 (6)
F1	0.2685 (4)	0.3402 (7)	0.5775 (8)	12.6 (2)
F2	0.1665 (4)	0.2553 (8)	0.5204 (8)	13.7 (2)
F3	0.2396 (5)	0.2033 (6)	0.3832 (9)	13.2 (3)
F4	0.1427 (5)	0.3120 (8)	0.308 (1)	18.2 (3)
F5	0.2491 (5)	0.3960 (6)	0.3614 (9)	15.7 (3)
F6	0.1766 (5)	0.4628 (7)	0.491 (1)	14.8 (3)
C35	0.4178 (8)	0.277 (1)	0.352 (2)	12.2 (5)
Cl1	0.4510 (4)	0.1439 (5)	0.4224 (8)	20.2 (3)
Cl2	0.4439 (4)	0.2839 (9)	0.1924 (7)	27.6 (3)
Cl3	0.4500 (4)	0.4040 (5)	0.4695 (7)	18.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 11[a]

Ru–P1	2.320 (2)	C1–C2	1.314 (9)
Ru–P2	2.324 (2)	P2–C15	1.809 (7)
Ru–C29	1.867 (6)	P2–C17	1.812 (6)
Ru–C30	2.209 (7)	C15–C16	1.32 (1)
Ru–C31	2.221 (7)	O–C29	1.124 (8)
Ru–C32	2.241 (7)	C30–C31	1.39 (1)
Ru–C33	2.253 (7)	C30–C34	1.38 (1)
Ru–C34	2.250 (7)	C31–C32	1.39 (1)
P1–C1	1.823 (6)	C32–C33	1.40 (1)
P1–C3	1.829 (6)	C33–C34	1.39 (1)
P1–C9	1.819 (6)	P2–C23	1.828 (6)
P1–Ru–P2	96.28 (5)	C30–Ru–C34	36.1 (3)
P1–Ru–C29	90.9 (2)	C31–Ru–C32	36.4 (3)
P1–Ru–C30	91.6 (2)	C31–Ru–C33	60.7 (3)
P1–Ru–C31	119.0 (3)	C31–Ru–C34	60.8 (3)
P1–Ru–C32	152.0 (2)	C32–Ru–C33	36.3 (3)
P1–Ru–C33	131.8 (3)	C32–Ru–C34	60.5 (3)
P1–Ru–C34	98.0 (2)	C33–Ru–C34	36.0 (3)
P2–Ru–C29	89.3 (2)	C1–P1–C3	103.8 (3)
P2–Ru–C30	147.4 (2)	C1–P1–C9	104.6 (3)
P2–Ru–C31	144.2 (3)	C3–P1–C9	102.0 (3)
P2–Ru–C32	107.9 (3)	P1–C1–C2	125.3 (5)
P2–Ru–C33	92.0 (2)	C15–P2–C17	104.4 (3)
P2–Ru–C34	111.3 (2)	C15–P2–C23	104.7 (3)
C29–Ru–C30	122.3 (3)	C17–P2–C23	103.9 (3)
C29–Ru–C31	95.7 (3)	P2–C15–C16	125.5 (6)
C29–Ru–C32	103.0 (3)	C31–C30–C34	109.5 (7)
C29–Ru–C33	136.7 (3)	C30–C31–C32	107.1 (7)
C29–Ru–C34	156.3 (3)	C31–C32–C33	108.0 (7)
C30–Ru–C31	36.5 (3)	C32–C33–C34	108.0 (7)
C30–Ru–C32	60.4 (3)	C30–C34–C33	107.4 (7)
C30–Ru–C33	60.1 (3)	O–C29–Ru	177.9 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$(\eta^1$-DPVP)$(\eta^3$-DPVP)]PF^6 is coordinated to a relatively electron-rich ruthenium(III) center, we reacted this complex with allylamine. Instead of a Michael addition, a stoichiometric amount of allylamine simply coordinated to ruthenium, displacing the coordinated vinyl group. However, when a solution of **3** in CH_2Cl_2 was reacted with a large excess of allylamine, a mixture of two products was formed in a 1:4 ratio. The major product is the ligand substitution product ($\delta(^{31}P)$ 42.37), and the minor product ($\delta(^{31}P)$ 66.60 (d), 32.57 (d), $^2J(PP)$ = 3.91 Hz) is probably the Michael addition product. The latter was not isolated or further characterized.

Both *n*-butyl- and *tert*-butyllithium react with free DPVP to form the α-lithiated products $Ph_2PC(Li)HCH_2R$.[41] Complex **3** reacts with CH_3Li in dry THF at −78 °C to produce **13**. The $^{31}P\{^1H\}$ NMR spectrum of **13** is devoid of a resonance for PF_6^- at δ −144.95 and displays two doublets (δ 55.89, 42.34, $^2J(PP)$ = 40.51 Hz). The ^1H NMR spectrum of **13** shows the presence of two different vinyl groups (Figure 8) in a 1:1 ratio. One set of vinyl resonances occurs in the region expected for a coordinated $Ph_2PCH{=}CH_2$ ligand, while the other is found in the region typical[46] of an $MCH{=}CH_2$ group. In addition, the $MCH{=}CH_2$ protons exhibit spin–spin coupling to two ^{31}P nuclei instead of only one, typical of a vinyl group bound to an $(R_3P)_2M$ moiety.[46-48] In its $^{13}C\{^1H\}$ NMR spectrum, the C_α resonance of this vinyl group appeared as a triplet (δ 157.63, $^2J(PC)$ = 17.87 Hz) and a doublet methyl carbon resonance was observed at δ 15.34 ($^1J(PC)$ = 29.17 Hz). A doublet methyl resonance (δ 1.40, $^2J(PH)$ = 8.41 Hz) was also observed in the ^1H NMR spectrum. These ^1H and ^{13}C chemical shifts and PH and PC coupling constants are typical of Ph_2PCH_3 coordinated to a metal.[49,50]

Thus, $[(\eta^5\text{-}C_5H_5)Ru(DPVP)(Ph_2PCH_3)(CH{=}CH_2)]$ (**13**) is probably formed by initial attack of CH_3^- on the phosphorus atom of η^3-DPVP, forming a λ^5-phosphoranide[51] intermediate, followed by migration of

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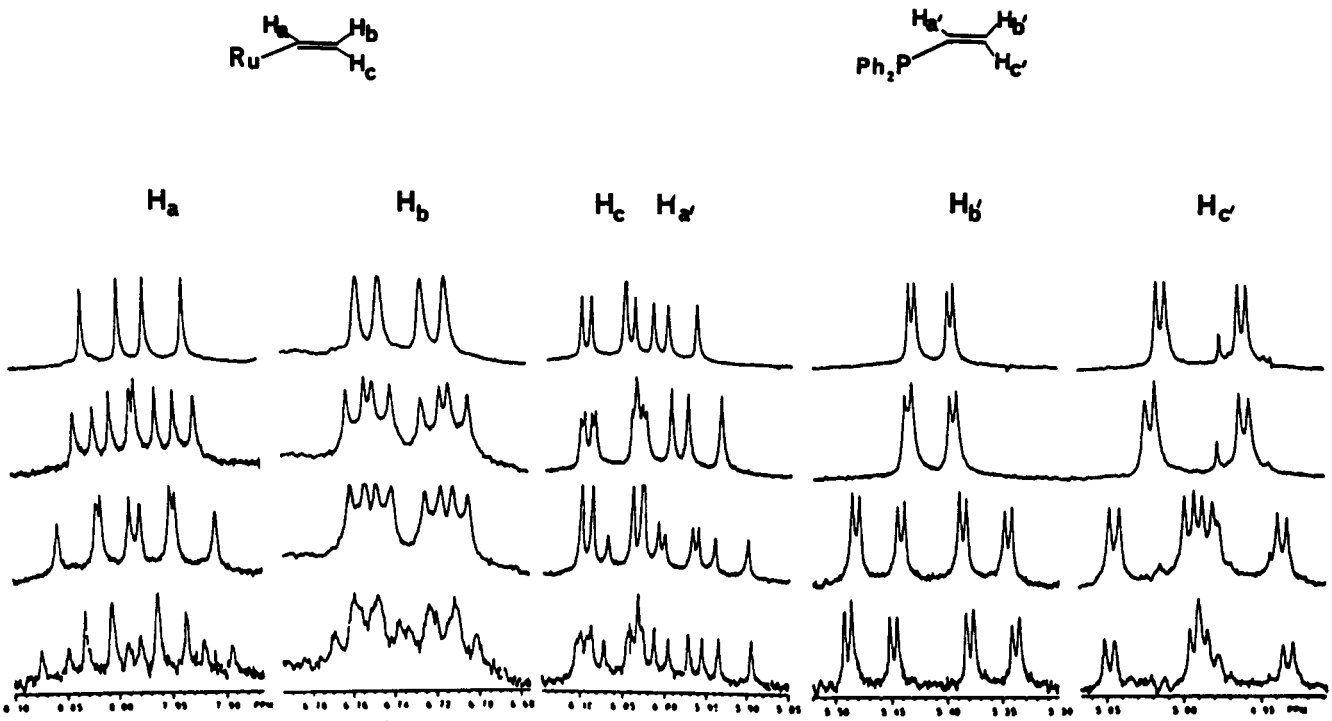

Figure 8. Expansion of the 300-MHz $^1H\{^{31}P\}$ NMR spectra of **13** in C_6D_6 at 25 °C (from bottom to top): normal spectrum; irradiation of phosphorus at 55.89 ppm; irradiation of phosphorus at 42.34 ppm; $^1H\{^{31}P$ BB$\}$.

the vinyl group from phosphorus to ruthenium. Since attack of the hard nucleophile CH_3^- occurred exclusively on the phosphaallyl phosphorus, we thought that other hard nucleophiles would react in a similar fashion. While $H_3CC{\equiv}C^-$ gave a similar compound, $[(\eta^5\text{-}C_5H_5)Ru(DPVP)(Ph_2PC{\equiv}CCH_3)(CH{=}CH_2)]$, as the major product ($\delta(^{31}P)$ 50.50, 36.33 (AB), $^2J(PP)$ = 45.26 Hz), $PhC{\equiv}C^-$ gave a mixture of two similar products in roughly equal amounts (A, $\delta(^{31}P)$ 51.99 (d), 48.63 (d), $^2J(PP)$ = 43.19 Hz; B, $\delta(^{31}P)$ 46.72 (d), 27.01 (d), $^2J(PP)$ = 41.79 Hz) and a minor unidentified product (C, $\delta(^{31}P)$ 50.26 (d), 36.22 (d), $^2J(PP)$ = 48.42 Hz). However, reaction of **3** with *n*-BuLi resulted in attack at the ruthenium center to produce $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2Bu]$ ($\delta(^{31}P)$ 47.89). The failure of *n*-BuLi to attack at phosphorus may imply that *n*-butyl migrates from phosphorus to ruthenium more readily than does vinyl or that it attacked the metal center directly. It should be pointed out that except for the product of reaction of CH_3Li with **3**, the reaction products from $CH_3C{\equiv}CLi$, $PhC{\equiv}CLi$, and *n*-BuLi are not very stable. They decompose to unidentified materials on standing in solution.

The redox properties of compounds **1–3** were investigated by cyclic voltammetry. It was found that compounds **1** and **2** underwent quasireversible one-electron oxidations at 0.76 and 0.70 V, respectively, and no observable reductions and compound **3** underwent a quasireversible one-electron reduction of −2.01 V and no observable oxidation (all potentials are relative to Fc/Fc^+).[52] Thus, formation of the phosphaallyl destabilizes Ru(III) and stabilizes Ru(I), as might be expected.[20,53]

The compounds $[(\eta^5\text{-}C_5H_5)Ru(DPVP)(CO)(CH_3CN)]PF_6$ and $[(\eta^5\text{-}C_5H_5)Ru(R_3P)\{P(OCH_3)_3\}(CH_3CN)]PF_6$ (R_3P = DPVP and DVPP) are all stable in solution and showed no evidence of dissociation of CH_3CN either in solution or upon heating in a vacuum oven.

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Supplementary Material Available: For the structure studies of **3** and **11**, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*), the COSY spectrum of **3** (Figure 1), an expansion of the 2D-NOE spectrum of **3** (Figure 3), the 2D-HOJ spectrum of **3** (Figure 4), the ^1H and $^1H\{^{31}P\}$ NMR spectra of **6** (Figure 6), and unit-cell packing diagrams for **3** and **11** (25 pages); listings of observed and calculated structure factors (×10) for **3** and **11** (39 pages). Ordering information is given on any current masthead page.

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