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Ruthenium(II)-Promoted Site-Selective Intramolecular Diels-Alder Reactions

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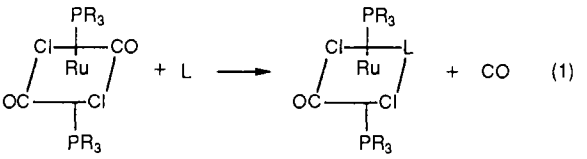
The complex *trans,trans,trans*-dichlorodicarbonylbis(1-phenyl-3,4-dimethylphosphole)ruthenium(II) (**1**) undergoes intramolecular Diels-Alder [4 + 2] cycloadditions with vinyldiphenylphosphine, divinylphenylphosphine, vinyldiethylphosphine, phenyl vinyl sulfoxide, and *N,N*-dimethylacrylamide in dichloromethane at room temperature stereoselectivity in high yield to produce single diastereomers of *mer-trans*-dichlorocarbonyl-(1-phenyl-3,4-dimethylphosphole[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**2**), *mer-trans*-dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**3**), *mer-trans*-dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(diethylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**4**), *mer-trans*-dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(phenylsulfinyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene]ruthenium(II) (**5**), and *mer-trans*-dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(dimethylamino)carbonyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**6**), respectively. In like manner, reactions of *trans,-trans,trans*-dichlorodicarbonylbis(vinyldiphenylphosphine)ruthenium(II) (**7**) with 1-phenyl-3,4-dimethylphosphole produces *mer-trans*-dichlorocarbonyl(vinyldiphenylphosphine)[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene]ruthenium(II) (**8**). All these compounds contain conformationally rigid, chiral bidentate ligands. They have been characterized by elemental analysis, physical properites, cyclic voltammetry, infrared spectroscopy, and ^1H $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^1H/^{13}C$ HETCOR, and $^1H/^1H$ COSY nuclear magnetic resonance spectroscopy. The structures of **6** and **8** were confirmed by X-ray crystallography at −100 °C. Both crystallize in the monoclinic space group $P2_1/n$ in unit cells of the following dimensions: **6**, a = 21.555 (6) Å, b = 10.794 (3) Å, c = 26.743 (8) Å, β = 91.91 (2)°, ρ(calcd) = 1.443 g cm^{-3}, Z = 8; **8**, a = 10.173 (3) Å, b = 20.908 (6) Å, c = 17.136 (4) Å, β = 98.31 (2)°, ρ(calcd) = 1.485 g cm^{-3}, Z = 4. Refinements converged to R = 0.045 and R = 0.030 with 4192 and 3949 independent reflections, respectively. Some of these new complexes were tested as catalysts for the homogeneous hydrogenation of 1-hexene and found to be relatively poor catalysts.

Introduction

We[2-6] and Mathey[7] have found that coordination of a phosphole to a transition metal polarizes the phosphole C=C double bonds and substantially increases its enophilicity in [4 + 2] cycloaddition reactions. The diastereoselectivity of these reactions is metal dependent, as is the nature of the Diels-Alder partner. To date, except for our brief report[4] on the ruthenium-promoted reactions, we have only been able to promote intramolecular [4 + 2] Diels-Alder cycloadditions between coordinated phospholes and coordinated vinylphosphines.[2,3,5,6] Because chelating ligands containing both hard and soft donor atoms (P,O; P,N; etc.) often readily dissociate one end of the chelate, providing access[8,9] for an incoming substrate, they are attractive ligands for the preparation of homogeneous catalysts. We[10-12] and Mawby and coworkers[13] have independently shown that ligand substitution reactions of *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ complexes occur regiospecifically to produce *mer-trans*-$(R_3P)_2LRu(CO)Cl_2$ according to reaction 1. In these reactions the incoming ligand occupies the site vacated



(1)

by the departing carbon monoxide. Since ruthenium(II) is a good Lewis acid for a wide variety of Lewis bases,[14] we hypothesized that *trans,trans,trans*-dichlorodicarbonylbis(1-phenyl-3,4-dimethylphosphole)ruthenium(II) might react with compounds containing the E—CH=CH_2 moiety (where E is a donor atom such as O, N, S, or P) to provide a new class of conformationally rigid, asymmetric, hemilabile[15] ligands that could be catalytically useful. Accordingly, we have probed the scope and limitations of such ruthenium(II)-promoted intramolecular [4 + 2] Diels-Alder cycloadditions. Some of the products formed were tested for their ability to catalyze the homogeneous hydrogenation of 1-hexene.

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. DMPP (1-phenyl-3,4-dimethylphosphole)[16] and *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$[4,17] were synthesized by published methods. Phenyldivinylphosphine, diphenylvinylphosphine, diallylphenylphosphine, and diethylvinylphosphine were obtained from Organometallics, Inc., *N,N*-dimethylacrylamide was purchased from Alfa, and the other dienophiles were obtained from Aldrich. All reactions involving the phosphines were conducted under an N_2 atmosphere. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Infrared spectra were recorded on a Perkin-Elmer 599 infrared spectrometer as CsI pellets or as Nujol mulls on KBr plates. The $^{31}P\{^1H\}$ and some $^{13}C\{^1H\}$ NMR spectra were recorded at 40.26 and 25.00 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. The ^1H and $^1H\{^{31}P\}$ NMR spectra were recorded at 500 or 300 MHz on one or more of the following

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spectrometers: Varian VXR-300, Varian VXR-500, General Electric QE-300 or GN-300, and IBM NR-300 AF. $^{13}C\{^1H\}$ NMR spectra were recorded at 75 or 125 MHz on one or more of the above-mentioned spectrometers. Heteronuclear chemical shift correlated (HETCOR) and homonuclear chemical shift correlated (COSY) spectra were obtained as previously described.[18] Proton and carbon chemical shifts are relative to internal Me_4Si, and phosphorus chemical shifts are relative to external 85% H_3PO_4, with a positive value being downfield of the respective reference. Cyclic voltammetry[19] and homogeneous hydrogenation experiments[20] were performed as previously described.

B. Synthesis. *trans,trans,trans*-Dichlorodicarbonylbis(1-phenyl-3,4-dimethylphosphole)ruthenium(II) (1):[17] orange crystals, mp 164 °C; IR (Nujol) ν_{RuCO} 2004, ν_{RuCl} 327 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 27.42; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.5 (t, "J_{PC}" = 11.72 Hz, CH_3), 125.0 (t, "J_{PC}" = 49.82 Hz, C_β), 128.6 (t, "J_{PC}" = 10.2 Hz, C_m), 130.2 (s, C_p), 131.0 (t, "J_{PC}" = 10.3 Hz, C_o), 131.4 (t, "J_{PC}" = 46.8 Hz, C_i), 150.9 (t, "J_{PC}" = 11.7 Hz, C_α), 193.1 (t, $^2J_{PC}$ = 13.2 Hz, CO). ("J_{PC}" = $|^nJ_{PC} + {}^{n+2}J_{PC}|$; C_i, C_o, C_m, and C_p are the phenyl ipso, ortho, meta, and para carbons, respectively); ^1H NMR ($CDCl_3$) δ 2.10 (s, CH_3, 12 H), 6.89 (filled-in doublet, "J_{PH}" = 32.2 Hz, ring H, 4 H), 7.3–7.9 (m, Ph, 10 H) ("J_{PH}" = $|^nJ_{PH} + {}^{n+2}J_{PH}|$). Anal. Calcd for $C_{26}H_{26}Cl_2O_2P_2Ru$: C, 51.69; H, 4.30. Found: C, 51.53; H, 4.18.

***trans,trans,trans*-Dichlorodicarbonylbis(vinyldiphenylphosphine)ruthenium(II) (7)**: yellow crystals, dec pt 178 °C; IR (Nujol) ν_{RuCO} 2002, ν_{RuCl} 335 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16.64; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 128.3 (t, "J_{PC}" = 9.8 Hz, C_m), 130.3 (s, C_β), 130.6 (s, C_p), 130.9 (t, "J_{PC}" = 48.8 Hz, C_α), 131.5 (t, "J_{PC}" = 45.0 Hz, C_i), 133.7 (t, "J_{PC}" = 10.8 Hz, C_o), 194.9 (t, $^2J_{PC}$ = 12.25 Hz, CO); ^1H NMR ($CDCl_3$) δ 5.22 (m, H_c, 2 H), 6.02 (m, H_b, 2 H), 7.15 (m, H_a, 2 H; second-order $[ABCX]_2$ spin system, J_{ab} = 12.0 Hz, J_{ac} = 18.3 Hz, J_{bc} = 1.2 Hz), 7.3–8.0 (m, Ph, 20 H). Anal. Calcd for $C_{30}H_{26}Cl_2O_2P_2Ru$: C, 55.24; H, 3.99. Found: C, 55.36; H, 4.03.

***mer-trans*-Dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (2).** To 1.05 g (1.74 mmol) of **1** in 25 mL of CH_2Cl_2 under N_2 was added 0.67 mL (2.5 mmol) of vinyldiphenylphosphine via syringe. The resulting solution was stirred magnetically for 24 h at ambient temperature and filtered, and the solution volume was reduced to approximately 10 mL on a rotary evaporator. Ethanol (95%) was added to induce crystallization, and the yellow plates that resulted were isolated by filtration, washed with 95% ethanol and anhydrous diethyl ether, and vacuum-dried overnight: yield 1.34 g (97.6%), mp 216–220 °C; IR (Nujol) ν_{RuCO} 1995, ν_{RuCl} 328 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.42 (dd, $J_{P_bP_c}$ = 30.85 Hz, $J_{P_aP_b}$ = 32.21 Hz, P_b), 22.45 (dd, $J_{P_aP_b}$ = 32.21 Hz, $J_{P_aP_c}$ = 257.19 Hz, P_a), 142.43 (dd, $J_{P_aP_c}$ = 257.19 Hz, $J_{P_bP_c}$ = 30.85 Hz, P_c); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.78 (s, 5,6-CH_3), 14.98 (s, 5,6-CH_3), 17.45 (d, J_{PC} = 10.42 Hz, phosphole CH_3), 17.47 (d, J_{PC} = 10.53 Hz, phosphole CH_3), 30.32 (dd, J_{PC} = 15.24, 5.85 Hz, C_3), 35.97 (dd, J_{PC} = 42.27, 23.05 Hz, C_2), 46.35 (d, J_{PC} = 26.76 Hz, C_4), 53.89 (dd, J_{PC} = 31.28, 11.51 Hz, C_1), 127.38 (d, J_{PC} = 8.79 Hz, C_m), 127.66 (d, J_{PC} = 9.53 Hz, C_m), 127.75 (d, J_{PC} = 9.32 Hz, C_m), 127.87 (d, J_{PC} = 8.88 Hz, C_m), 128.90, 129.22, 129.81, 129.98 (all s, C_p), 130.0 (d, J_{PC} = 62.9 Hz, C_i), 131.35 (d, J_{PC} = 9.08 Hz, C_o), 131.51 (d, J_{PC} = 8.58 Hz, C_o), 131.9 (d, J_{PC} = 37.5 Hz, C_i), 132.17 (d, J_{PC} = 35.83 Hz, C_i), 133.13 (d, J_{PC} = 8.73 Hz, C_o), 134.01 (d, J_{PC} = 43.0 Hz, C_α), 134.1 (d, J_{PC} = 43.0 Hz, C_α), 135.18 (d, J_{PC} = 10.0 Hz, C_o), 137.66 (s, $C_{5,6}$), 149.48 (d, J_{PC} = 8.71 Hz, C_β), 149.84 (d, J_{PC} = 8.18 Hz, C_β), 197.61 (dt, J_{PC} = 104.14, 12.58 Hz, CO); ^1H NMR ($CDCl_3$) δ 1.54 (m, J_{PH} = 20.2 Hz, H_4, 1 H), 1.59 (s, CH_3, 3 H), 1.66 (s, CH_3, 3 H), 1.95 (s, CH_3, 3 H), 1.97 (s, CH_3, 3 H), 2.79 (dd, J_{PH} = 22.1 Hz, J_{34} = 12.0 Hz, H_3, 1 H), 3.04 (dt, J_{PH} = 44.0 Hz, J_{23} = 8.1 Hz, J_{24} = 8.1 Hz, 1 H), 3.28 (s, H_1, 1 H), 3.75 (s, H_5, 1 H), 6.99 (d, J_{PH} = 29.0 Hz, phosphole ring H, 2 H), 7.18–7.83 (m, Ph, 20 H). Anal. Calcd for $C_{39}H_{39}Cl_2OP_3Ru$: C, 59.42; H, 4.95. Found: C, 59.31; H, 4.69.

***mer-trans*-Dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (3).** As for **2**, from 1.05 g (1.74 mmol) of **1** and 2.0 mmol of divinylphenylphosphine were obtained 1.25 g (97.3%) of yellow plates: mp 206 °C; IR (Nujol) ν_{RuCO} 1993, ν_{RuCl} 320 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 13.69 (t, J_{ac} = J_{bc} = 33.78 Hz, P_b), 25.05 (dd, J_{ab} = 256.03 Hz, J_{bc} = 33.78 Hz, P_a), 142.43 (dd, J_{ab} = 256.03 Hz, J_{ac} = 33.78 Hz, P_c); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.83 (s, 5,6-CH_3), 14.91 (s, 5,6-CH_3), 17.07 (d, J_{PC} = 10.84 Hz, phosphole CH_3), 17.52 (d, J_{PC} = 10.80 Hz, phosphole CH_3), 29.55 (dd, J_{PC} = 15.0, 6.22 Hz, C_3), 35.32 (dd, J_{PC} = 40.83, 25.97 Hz, C_2), 46.37 (d, J_{PC} = 27.71 Hz, C_4), 52.67 (dd, J_{PC} = 31.75, 11.56 Hz, C_1), 127.16 (d, J_{PC} = 24.07 Hz, C_α), 127.59 (d, J_{PC} = 27.69 Hz, C_α), 127.63 (d, J_{PC} = 10.52 Hz, C_β), 127.99 (d, J_{PC} = 9.56 Hz, C_m), 129.15 (s, C_p), 129.87 (s, C_p), 130.45 (s, C_p), 131.33 (d, J_{PC} = 45.40 Hz, C_α), 131.56 (d, J_{PC} = 10.07 Hz, C_o), 133.28 (d, J_{PC} = 39.4 Hz, C_i), 135.36 (d, J_{PC} = 10.26 Hz, C_o), 137.43 (s, $C_{5,6}$), 149.24 (d, J_{PC} = 7.99 Hz, C_β), 150.23 (d, J_{PC} = 8.0 Hz, C_β), 197.66 (dt, J_{PC} = 103.96, 11.0 Hz, CO); ^1H NMR ($CDCl_3$) δ 1.41 (m, J_{PH} = 26.3 Hz, J_{PH} = 20.6 Hz, J_{34} = 13.1 Hz, J_{24} = 10.1 Hz, H_4, 1 H), 1.55 (s, 5,6-CH_3, 3 H), 1.59 (s, 5,6-CH_3, 3 H), 1.72 (s, phosphole CH_3, 3 H), 1.83 (s, phosphole CH_3, 3 H), 2.63 (dd, J_{PH} = 20.6 Hz, J_{34} = 13.1 Hz, H_3, 1 H), 2.7 (dt, J_{PH} = 43.1 Hz, J_{24} = 9.4 Hz, J_{PH} = 9.4 Hz, H_2, 1 H), 3.21 (s, H_5, 1 H), 3.52 (s, H_1, 1 H), 5.45 (ddd, J_{PH} = 15.26 Hz, J_{ac} = 18.53 Hz, J_{bc} = 1.15 Hz, H_c, 1 H), 6.03 (ddd, J_{PH} = 30.59 Hz, J_{ab} = 12.42 Hz, J_{bc} = 1.15 Hz, H_b, 1 H), 6.59 (ddd, J_{PH} = 24.67 Hz, J_{ab} = 12.42 Hz, J_{ac} = 18.53 Hz, H_a, 1 H), 6.76 (d, J_{PH} = 32.17 Hz, phosphole ring H, 1 H), 6.95 (d, J_{PH} = 31.49 Hz, phosphole ring H, 1 H), 7.3–8.0 (m, Ph, 15 H). Anal. Calcd for $C_{35}H_{37}Cl_2P_3Ru$: C, 56.94; H, 5.01. Found: C, 56.78; H, 4.87.

***mer-trans*-Dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(diethylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (4).** As for **2**, from 0.267 g (0.442 mmol) of **1** and 0.5 mmol of diethylvinylphosphine were obtained 0.29 g (94.8%) of yellow rods: mp 203 °C; IR (Nujol) ν_{RuCO} 1993, ν_{RuCl} 320 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 24.25 (dd, $J_{P_aP_b}$ = 34.19 Hz, $J_{P_aP_c}$ = 41.03 Hz, P_b), 25.65 (dd, $J_{P_aP_b}$ = 34.19 Hz, $J_{P_bP_c}$ = 263.28 Hz, P_a), 144.21 (dd, $J_{P_aP_c}$ = 41.03 Hz, $J_{P_bP_c}$ = 263.28 Hz, P_c); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 8.16 (d, J_{PC} = 8.20 Hz, CH_2CH_3), 8.27 (d, J_{PC} = 5.2 Hz, CH_2CH_3), 12.24 (d, J_{PC} = 18.7 Hz, CH_2), 12.55 (d, J_{PC} = 21.0 Hz, CH_2), 13.82 (s, phosphole CH_3), 14.86 (s, phosphole CH_3), 28.65 (d, J_{PC} = 25.5 Hz, C_3), 30.84 (dd, J_{PC} = 44.74, 23.35 Hz, C_2), 47.00 (d, J_{PC} = 25.54 Hz, C_4), 52.72 (dd, J_{PC} = 35.3, 12.5 Hz, C_1), 127.85 (d, J_{PC} = 8.9 Hz, C_m), 128.06 (d, J_{PC} = 8.5 Hz, C_m), 128.12 (d, J_{PC} = 90.1 Hz, C_α), 129.1 (s, C_p), 129.33 (d, J_{PC} = 92.4 Hz, C_α), 129.73 (s, C_p), 131.51 (d, J_{PC} = 9.9 Hz, C_o), 131.64 (d, J_{PC} = 9.2 Hz, C_o), 131.9 (d, J_{PC} = 37.8 Hz, C_i), 137.3 (d, J_{PC} = 32.5 Hz, C_i), 137.66 (s, $C_{5,6}$), 148.95 (d, J_{PC} = 7.18 Hz, C_β), 149.40 (d, J_{PC} = 8.16 Hz, C_β), 197.6 (dt, J_{PC} = 90.32, 11.4 Hz, CO); ^1H NMR ($CDCl_3$) δ 1.00 (dt, J_{PH} = 14.73 Hz, J_{HH} = 7.51 Hz, CH_2CH_3, 3 H), 1.08 (dt, J_{PH} = 12.32 Hz, J_{HH} = 7.51 Hz, CH_2CH_3, 3 H), 1.56 (s, 5,6-CH_3, 6 H), 2.04 (s, phosphole CH_3, 3 H), 2.05 (m, H_4, 1 H), 2.06 (s, phosphole CH_3, 3 H), 2.41 (m, CH_2, 4 H), 2.83 (dd, J_{PH} = 16.53 Hz, J_{34} = 12.62 Hz, H_3, 1 H), 3.17 (s, H_1, 1 H), 3.19 (d, J_{PH} = 31.9 Hz, H_2, 1 H), 3.20 (s, H_5, 1 H), 6.90 (d, J_{PH} = 31.3 Hz, phosphole ring H, 2 H), 7.2–7.75 (m, Ph, 10 H). Anal. Calcd for $C_{31}H_{39}Cl_2OP_3Ru$: C, 53.79; H, 5.63. Found: C, 53.62; H, 5.47.

***mer-trans*-Dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-(phenylsulfinyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (5).** As for **2**, from 1.00 g (1.66 mmol) of **1** and 0.257 g (1.69 mmol) of phenyl vinyl sulfoxide were obtained 1.09 g (92.2%) of pale yellow needles: mp 225 °C; IR (Nujol) ν_{RuCO} 1989, ν_{RuCl} 328, ν_{SO} 1092 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 23.40 (d, $J_{P_aP_b}$ = 310.1 Hz, P_a), 140.92 (d, $J_{P_aP_b}$ = 310.1 Hz, P_b); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.87 (s, 5,6-CH_3), 15.06 (s, 5,6-CH_3), 17.14 (d, J_{PC} = 11.6 Hz, phosphole CH_3), 17.50 (d, J_{PC} = 11.71 Hz, phosphole CH_3), 29.31 (d, J_{PC} = 13.33 Hz, C_3), 46.10 (dd, J_{PC} = 25.1, 3.1 Hz, C_1), 51.29 (d, J_{PC} = 31.36 Hz, C_4), 69.93 (d, J_{PC} = 33.45 Hz, C_2), 124.40 (d, J_{PC} = 44.89, C_α), 125.12 (d, J_{PC} = 6.0 Hz, C_i), 125.64 (d, J_{PC} = 45.15 Hz, C_α), 127.66 (s, C_m), 127.74 (d, J_{PC} = 11.73 Hz, C_m), 128.26 (d, J_{PC} = 42.86 Hz, C_i), 128.74 (s, C_o), 129.56 (d, J_{PC} = 2.4 Hz, C_p), 130.74 (s, C_p), 132.43 (s, $C_{5,6}$), 132.47 (s, $C_{5,6}$), 151.53 (d, J_{PC} = 7.36 Hz, C_β), 152.11 (d, J_{PC} = 8.53 Hz, C_β), 192.89 (t, J_{PC} = 12.41, CO); ^1H NMR ($CDCl_3$) δ 1.39 (m, J_{PH} = 22.5 Hz, J_{34} = 13.13 Hz, J_{24} = 9.1 Hz, H_4, 1 H), 1.55 (s, 5,6-CH_3, 3 H), 1.67 (s, 5,6-CH_3, 3 H), 1.77 (s, phosphole CH_3, 3 H), 1.93 (s, phosphole CH_3, 3 H), 3.13 (dd, J_{23} = 3.8 Hz, J_{34} = 13.13 Hz, H_3, 1 H), 3.48 (s, H_5, 1 H), 3.54 (ddt, J_{PH} = 27.59 Hz, J_{12} = J_{23} = 3.8 Hz, J_{24} = 9.1 Hz, H_2, 1 H), 3.74 (dd, J_{PH} = J_{12} = 3.8 Hz, H_1, 1 H), 6.48 (d, J_{PH} = 29.8 Hz, phosphole ring H, 2 H), 7.2–8.5 (m, Ph, 15 H). Anal. Calcd for $C_{33}H_{34}Cl_2OP_2RuS$: C, 55.64; H, 4.77. Found: C, 55.71; H, 4.90.

***mer-trans*-Dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-((dimethylamino)carbonyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (6).** As for **2**, from 1.395 g (2.31 mmol) of **1** and 0.22 mL of *N,N*-dimethylacrylamide were obtained 1.49 g (95.9%) of yellow rods: dec pt 216–223 °C; IR (Nujol) ν_{RuCO} 1952, ν_{RuCl} 329, ν_{CO}(aminocarbonyl) 1590 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 31.0 (d, $J_{P_aP_b}$ = 322.27 Hz, P_a), 125.22 (d, $J_{P_aP_b}$ = 322.27 Hz, P_b); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.17 (s, 5,6-CH_3), 14.51 (s, 5,6-CH_3), 17.55 (d, J_{PC} = 11.03 Hz, phosphole CH_3), 17.75 (d, J_{PC} = 11.03 Hz, phosphole CH_3), 30.62 (d, J_{PC} = 19.95 Hz, C_3), 37.44 (s, NCH_3), 38.61 (s, NCH_3), 40.77 (d, J_{PC} = 18.13 Hz, C_4), 46.05 (dd, J_{PC} = 24.26, 3.55 Hz, C_1), 51.60 (d, J_{PC} = 27.28 Hz, C_2), 125.13 (d, J_{PC} = 35.0 Hz, C_i), 125.33 (d, J_{PC} = 43.83,

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Table I. Crystal and Refinement Data for Compounds **6** and **8**

	6	**8**
formula	$C_{30}H_{35}Cl_2NO_2P_2Ru$	$C_{41}H_{39}Cl_2OP_3Ru$
fw	675.54	812.68
a, Å	21.555 (6)	10.173 (3)
b, Å	10.794 (3)	20.908 (6)
c, Å	26.743 (8)	17.316 (4)
β, deg	91.91 (2)	98.31 (2)
space group	$P2_1/n$	$P2_1/n$
Z	8	4
ρ(calcd), g cm^{-3}	1.443	1.480
μ, cm^{-1}	70.056	7.309
abs factor range	0.79–1.53	0.92–1.05
temp, °C	−100	−100
final $R(F)$	0.045	0.030
final $R_w(F)$	0.068	0.043

C_α), 126.51 (d, J_{PC} = 43.15 Hz, C_α), 127.92 (d, J_{PC} = 8.69 Hz, C_m), 128.04 (d, J_{PC} = 8.99 Hz, C_m), 129.10 (s, C_p), 129.62 (s, C_p), 131.12 (d, J_{PC} = 37.79 Hz, C_i), 131.49 (d, J_{PC} = 8.54 Hz, C_o), 132.50 (d, J_{PC} = 8.91 Hz, C_o), 134.57 (d, J_{PC} = 2.04 Hz, $C_{5,6}$), 134.62 (d, J_{PC} = 1.89 Hz, $C_{5,6}$), 149.82 (d, J_{PC} = 8.99 Hz, C_β), 150.96 (d, J_{PC} = 10.66 Hz, C_β), 180.64 (s, aminocarbonyl CO), 201.57 (dd, J_{PC} = 14.13, 12.85 Hz, CO); ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 5,6-CH_3, 3 H), 1.60 (s, 5,6-CH_3, 3 H), 1.77 (m, J_{PH} = 30 Hz, J_{34} = 12.2 Hz, J_{24} = 7.5 Hz, H_4, 1 H), 2.02 (s, phosphole CH_3, 3 H), 2.04 (s, phosphole CH_3, 3 H), 2.42 (s, NCH_3, 3 H), 3.08 (s, NCH_3, 3 H), 3.09 (s, H_5, 1 H), 3.15 (m, H_3, 1 H), 3.34 (m, J_{PH} = 12 Hz, H_2, 1 H), 3.48 (m, H_1, 1 H), 6.90 (d, J_{PH} = 31.2 Hz, phosphole ring H, 2 H), 7.25–7.85 (m, Ph, 10 H). Anal. Calcd for $C_{30}H_{35}Cl_2NO_2P_2Ru$: C, 53.36; H, 5.18; N, 2.07. Found: C, 53.10; H, 4.97; N, 1.98.

***mer-trans*-Dichlorocarbonyl(vinyldiphenylphosphine)[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (8).** As for **2**, from 1.247 g (1.91 mmol) of **7** and 0.36 g (1.91 mmol) of 1-phenyl-3,4-dimethylphosphole were obtained 1.48 g (95.4%) of yellow plates: mp 206 °C; IR (Nujol) ν_{RuCO} 1991, ν_{RuCl} 318 cm^{-1}; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 18.78 (dd, J_{ac} = 31.4 Hz, J_{ab} = 280.2 Hz, P_a), 40.03 (dd, J_{ab} = 280.2 Hz, J_{bc} = 31.4 Hz, P_b), 127.45 (t, J_{ac} = J_{bc} = 31.4 Hz, P_c); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 13.93 (s, 5,6-CH_3), 14.89 (s, 5,6-CH_3), 29.97 (dd, J_{PC} = 15.77, 5.60 Hz, C_3), 33.03 (dd, J_{PC} = 37.38, 24.78 Hz, C_2), 46.83 (d, J_{PC} = 21.79 Hz, C_4), 54.63 (dd, J_{PC} = 32.31, 14.0 Hz, C_1), 127.04 (d, J_{PC} = 8.04 Hz, C_m), 127.52 (d, J_{PC} = 9.59 Hz, C_m), 127.57 (d, J_{PC} = 9.36 Hz, C_m), 128.24 (d, J_{PC} = 7.77 Hz, C_m), 128.25 (d, J_{PC} = 8.01 Hz, C_m), 129.00 (s, C_p), 129.21 (s, C_p), 129.68 (s, C_p), 129.87 (s, C_p), 130.59 (s, C_p), 130.79 (s, C_p), 131.16 (d, J_{PC} = 40.8 Hz, C_α), 131.25 (d, J_{PC} = 8.98 Hz, C_o), 132.95 (d, J_{PC} = 8.10 Hz, C_o), 133.22 (d, J_{PC} = 9.47 Hz, C_o), 133.76 (d, J_{PC} = 9.43 Hz, C_o), 134.50 (d, J_{PC} = 9.71 Hz, C_o), 137.14 (s, $C_{5,6}$), 201.00 (dt, J_{PC} = 101.95, 12.02 Hz, CO); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 5,6-CH_3, 3 H), 1.62 (s, 5,6-CH_3, 3 H), 1.76 (m, J_{PH} = 39.4 Hz, J_{PH} = 9.4 Hz, J_{24} = 7.5 Hz, J_{34} = 13.1 Hz, H_4, 1 H), 3.03 (dd, J_{PH} = 22.5 Hz, J_{34} = 13.1 Hz, H_3, 1 H), 3.22 (s, H_1, 1 H), 3.41 (dt, J_{PH} = 41.25 Hz, J_{PH} = J_{24} = 7.5 Hz, H_2, 1 H), 3.55 (s, H_5, 1 H), 4.84 (ddd, J_{PH} = 18.0 Hz, J_{ac} = 18.0 Hz, J_{bc} = 1.43 Hz, H_c, 1 H), 5.64 (ddd, J_{PH} = 34.13 Hz, J_{ab} = 11.9 Hz, J_{bc} = 1.43 Hz, H_b, 1 H) 6.67 (ddd, J_{PH} = 18.2 Hz, J_{ac} = 18.0 Hz, J_{ab} = 11.9 Hz, H_a, 1 H), 6.9–8.0 (m, Ph, 25 H). Anal. Calcd for $C_{41}H_{39}Cl_2OP_3Ru$: C, 60.62; H, 4.80. Found: C, 60.54; H, 4.61.

C. X-ray Data Collection and Processing. Pale yellow rods of **6** and plates of **8** were isolated from $CHCl_3/CH_3OH$ solutions at room temperature. Crystal data and details of data collection are given in Table I. Systematic searches in reciprocal space with a Philips PW 1100/16 automatic diffractometer showed that crystals of both **6** and **8** belong to the monoclinic system. Quantitative data were obtained at −100 °C, achieved by using a locally built gas flow device. The resulting data sets were transferred to a VAX (**6**) or a PDP 11/60 (**8**) computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX (**6**) or SDP/PDP package (**8**)[21] was used with the exception of a local data reduction program.

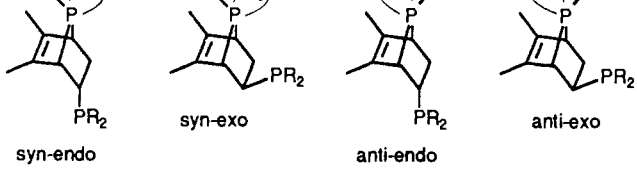
Three standard reflections measured every 1 h during the entire data collection periods showed no significant trends.

The raw step-scan data were converted to intensities by using the Lehman–Larsen method[22] and were then corrected for Lorentz and polarization factors.

The structures were solved by using the heavy-atom method. For **6** the asymmetric part of the unit cell contains two crystallographically nonequivalent molecules. 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 the structure factor calculation by their computed coordinates (C–H = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3[B_{eqv}(C)]$ Å^2 (**6**) or $B(H) = 1 + B_{eqv}(C)$ Å^2 (**8**) but were not refined. At this stage absorption corrections were applied by using the method of Walker and Stuart,[23] since face indexation was not possible under the cold gas stream. Full least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$ with $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$ converged to the values given in Table I. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 24. Final atom coordinates for **6** and **8** are given in Tables II and III and selected bond lengths and angles in Tables IV and V, respectively.

Results

Reactions of *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ with a neutral donor ligand (L, reaction 1) lead regiospecifically to *mer-trans*-$(R_3P)_2L(CO)Cl_2$. When R_3P is a 3,4-dimethylphosphole and L is a vinylphosphine, vinyl sulfoxide, or vinyl amide, the initial ligand substitution products contain the phosphole and the vinyl donor in mutually cis positions. Coordination of both the phosphole and the vinyl donor enhances their reactivities,[2-6] and facile intramolecular [4 + 2] Diels–Alder cycloadditions ensue at ambient temperature in high yield as illustrated in Scheme I. That these cycloadditions occur intramolecularly within the ruthenium coordination sphere is established by the stereochemistry of the resulting 2-substituted 7-phosphanorbornene. Prior coordination of the phosphole and dienophile fixes the stereochemistry of three of the stereocenters in the resultant syn-exo diastereomer. Were these reactions to occur intermolecularly, outside the coordination sphere, four diastereomers (viz. syn-exo, syn-endo, anti-exo, and anti-endo) could result, with the endo diastereomers being highly



favored.[7] In each case the ligand substitution and ensuing Diels–Alder cycloaddition are site-selective and stereoselective, forming racemic mixtures of only one stereoisomer, as shown by multinuclear NMR spectroscopy.[3-6] Though the chemistry of mixed-donor-atom bidentate ligands is well established,[25] compounds **5** and **6** are the first examples of the formation of such ligands by intramolecular Diels–Alder cycloadditions. Furthermore, the 7-phosphanorbornene ligands contain a conformationally rigid chiral backbone, unlike previously reported functional phosphines. A similar reaction between complex **1** and diallylphenylphosphine produced *mer-trans*-dichlorocarbonylbis(1-phenyl-3,4-dimethylphosphole)(diallylphenylphosphine)ruthenium(II) via reaction 1 ($\delta(^{31}P)$ 26.51 (d), −6.44 (t); J_{PP} = 38.6 Hz), which did not undergo a Diels–Alder cycloaddition probably because diallylphenylphosphine is too poor a dienophile.[3] Similar reactions of complex **1** with the following ligands produced inseparable mixtures of products but not Diels–Alder reactions: 2-vinylpyridine, phenyl vinyl sulfide, methyl vinyl ketone, *trans*-4-phenyl-3-buten-2-one, phenyl vinyl sulfone, 1-vinylimidazole, 3-(diethylamino)-1-propyne, vinylpyrrolidinone, 3-aminocrotonitrile, and acrylonitrile. An exhaustive effort was

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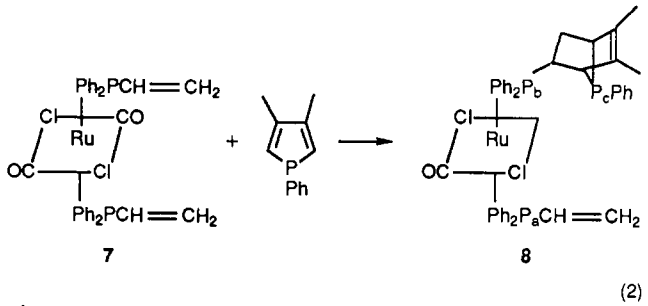
Table II. Atom Coordinates for $C_{30}H_{35}Cl_2NO_2P_2Ru$ (**6**)

atom	x	y	z	B,[a] Å²	atom	x	y	z	B,[a] Å²
Ru1	0.14830 (4)	0.11401 (8)	0.15785 (3)	2.93 (2)	Ru2	0.12813 (4)	0.29883 (8)	0.68929 (3)	2.99 (2)
Cl1	0.0411 (1)	0.0475 (3)	0.1589 (1)	4.29 (7)	Cl3	0.2346 (1)	0.3197 (3)	0.6667 (1)	4.23 (7)
Cl2	0.2574 (1)	0.1618 (3)	0.1557 (1)	3.94 (6)	Cl4	0.0229 (1)	0.2515 (3)	0.7092 (1)	3.94 (6)
P1	0.1499 (1)	0.1091 (3)	0.2448 (1)	2.93 (6)	P3	0.1493 (1)	0.2907 (3)	0.7750 (1)	3.06 (6)
C1	0.2203 (5)	0.0634 (9)	0.2814 (4)	2.6 (2)	C31	0.246 (5)	0.144 (1)	0.8040 (4)	3.3 (2)
C2	0.1936 (5)	0.0263 (9)	0.3315 (4)	3.3 (3)	C32	0.1557 (6)	0.150 (1)	0.8551 (4)	4.3 (3)
C3	0.1407 (5)	−0.029 (1)	0.3255 (4)	3.3 (3)	C33	0.2116 (5)	0.203 (1)	0.8522 (4)	4.3 (3)
C4	0.1212 (5)	−0.0418 (9)	0.2702 (4)	2.7 (2)	C34	0.2247 (5)	0.238 (1)	0.7995 (4)	3.8 (3)
C5	0.1025 (5)	−0.099 (1)	0.3632 (4)	4.6 (3)	C35	0.1274 (7)	0.083 (1)	0.8977 (5)	6.2 (4)
C6	0.2326 (6)	0.043 (1)	0.3782 (4)	4.7 (3)	C36	0.2610 (7)	0.214 (2)	0.8929 (5)	7.1 (4)
C7	0.2357 (5)	−0.056 (1)	0.2542 (4)	3.7 (3)	C37	0.2302 (5)	0.118 (1)	0.7690 (4)	3.8 (3)
C8	0.1719 (5)	−0.128 (1)	0.2471 (4)	3.2 (2)	C38	0.1668 (6)	0.053 (1)	0.7724 (4)	4.4 (3)
C9	0.1566 (5)	−0.158 (1)	0.1934 (4)	3.1 (2)	C39	0.1355 (5)	0.0236 (9)	0.7217 (4)	3.2 (2)
O1	0.1690 (3)	−0.0830 (6)	0.1584 (2)	3.3 (2)	O3	0.1381 (3)	0.0993 (6)	0.6863 (3)	3.5 (2)
N1	0.1293 (4)	−0.2644 (8)	0.1809 (3)	3.3 (2)	N2	0.1064 (4)	−0.0826 (7)	0.7161 (3)	3.4 (2)
C10	0.1098 (5)	−0.288 (1)	0.1292 (4)	4.5 (3)	C40	0.1015 (6)	−0.176 (1)	0.7555 (5)	5.0 (3)
C11	0.1098 (5)	−0.356 (1)	0.2186 (4)	3.8 (3)	C41	0.0724 (6)	−0.109 (1)	0.6695 (5)	5.5 (3)
C12	0.1151 (5)	0.2412 (9)	0.2760 (4)	2.8 (2)	C42	0.1227 (5)	0.413 (1)	0.8137 (4)	3.3 (3)
C13	0.0596 (5)	0.287 (1)	0.2566 (4)	3.9 (3)	C43	0.0608 (6)	0.421 (1)	0.8254 (5)	5.8 (3)
C14	0.0344 (5)	0.394 (1)	0.2760 (4)	4.4 (3)	C44	0.0378 (6)	0.522 (1)	0.8521 (5)	5.7 (3)
C15	0.0664 (6)	0.458 (1)	0.3131 (4)	4.3 (3)	C45	0.0779 (6)	0.613 (1)	0.8682 (4)	5.0 (3)
C16	0.1230 (5)	0.415 (1)	0.3319 (4)	4.0 (3)	C46	0.1387 (6)	0.608 (1)	0.8572 (4)	4.8 (3)
C17	0.1470 (5)	0.305 (1)	0.3132 (4)	4.1 (3)	C47	0.1618 (5)	0.508 (1)	0.8306 (4)	4.2 (3)
P2	0.1440 (1)	0.1086 (3)	0.0698 (1)	3.28 (7)	P4	0.1000 (1)	0.3068 (3)	0.6031 (1)	3.34 (7)
C18	0.0716 (5)	0.143 (1)	0.0395 (4)	4.1 (3)	C48	0.0241 (5)	0.371 (1)	0.5908 (4)	4.0 (3)
C19	0.0727 (6)	0.246 (1)	0.0130 (5)	5.0 (3)	C49	0.0279 (6)	0.481 (1)	0.5693 (4)	4.3 (3)
C20	0.1348 (6)	0.303 (1)	0.0129 (4)	4.4 (3)	C50	0.0924 (6)	0.514 (1)	0.5563 (4)	4.3 (3)
C21	0.1786 (5)	0.238 (1)	0.0386 (4)	4.3 (3)	C51	0.1358 (5)	0.429 (1)	0.5685 (4)	3.7 (3)
C22	0.0185 (7)	0.302 (1)	−0.0149 (6)	8.4 (4)	C52	−0.0246 (7)	0.575 (1)	0.5618 (5)	6.7 (4)
C23	0.1473 (7)	0.422 (1)	−0.0147 (6)	8.0 (4)	C53	0.1076 (7)	0.636 (1)	0.5292 (5)	6.7 (4)
C24	0.1753 (6)	−0.031 (1)	0.0409 (4)	4.3 (3)	C54	0.1080 (5)	0.173 (1)	0.5644 (4)	3.7 (3)
C25	0.1405 (7)	−0.101 (1)	0.0064 (5)	5.3 (3)	C55	0.0694 (7)	0.142 (1)	0.5260 (5)	7.2 (4)
C26	0.1685 (8)	−0.212 (1)	−0.0128 (5)	7.6 (4)	C56	0.0782 (9)	0.041 (1)	0.4956 (6)	9.6 (5)
C27	0.2287 (8)	−0.240 (1)	0.0022 (6)	8.1 (4)	C57	0.1265 (8)	−0.031 (1)	0.5034 (5)	7.6 (5)
C28	0.2614 (7)	−0.169 (1)	0.0346 (5)	7.1 (4)	C58	0.1703 (8)	−0.008 (1)	0.5423 (5)	7.2 (4)
C29	0.2365 (6)	−0.065 (1)	0.0539 (5)	4.9 (3)	C59	0.1609 (6)	0.098 (1)	0.5741 (5)	5.4 (3)
C30	0.1291 (5)	0.273 (1)	0.1539 (4)	3.8 (3)	C60	0.1180 (5)	0.462 (1)	0.6903 (4)	3.0 (2)
O2	0.1171 (4)	0.3792 (8)	0.1495 (3)	4.9 (2)	O4	0.1122 (4)	0.5695 (7)	0.6888 (3)	4.4 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

made to promote each of these reactions. Reactions were attempted in CH_2Cl_2, $CHCl_3$, and C_2H_5OH at room temperature under N_2, in a sealed glass tube at 80 °C, and in a high-pressure flask at 100 °C. In all cases no Diels–Alder reaction occurred.

Complex **7** reacted cleanly in high yield (reaction 2) with 1-phenyl-3,4-dimethylphosphole to also undergo a Diels–Alder reaction producing compound **8**. Reaction of the *trans*-bis-



(2)

(phosphole) complex with a vinylphosphine gives rise to the 7-phospha phosphorus trans to phosphole, whereas a reaction of the trans-*bis*(vinylphosphine) complex with a phosphole places the 7-phospha phosphorus trans to CO. Thus, these reactions allow for site-selective formation of 2-phosphino-7-phosphanorbornene ligands within the coordination sphere of ruthenium(II). In contrast to the *mer-trans*-$(R_3P)_3Ru(CO)Cl_2$ complexes, which relatively rapidly thermally isomerize[10,12,13,17] to the *mer-cis*-$(R_3P)_3Ru(CO)Cl_2$ complexes, these complexes are geometrically stable and isomerize exceedingly slowly. This is consistent with the isomerization mechanism[10] for the former complexes, which involves dissociation of the phosphorus donor trans to carbon monoxide. The chelate ring of the 2-phosphino-7-phosphanorbornene ligands does not undergo facile dissociation of one donor, giving rise to a considerably higher activation energy for geometric isomerization.

Discussion

Phosphorus NMR and Infrared Spectroscopy. All of the Diels–Alder products display single ν_{RuCl} and ν_{CO} stretching frequencies (see Experimental Section) as expected for a *trans*-$RuCl_2(CO)$ moiety.[26] The aminocarbonyl CO stretching frequency for **6** (1590 cm^{-1}) indicates oxygen coordination,[27] and the SO stretching frequency (1092 cm^{-1}) for **5** indicates sulfur coordination.[27] Each of these products displays single resonances for each phosphorus nucleus in their $^{31}P\{^1H\}$ NMR spectra, confirming[28] that each complex was formed as a racemic mixture of only one diastereomer. The resonance corresponding to the bridgehead phosphorus is downfield[3,4,29] (125.22–144.31 ppm), while the resonance corresponding to the 2-phosphino phosphorus occurs in the region typical of a phosphine coordinated to ruthenium(II) in a five-membered chelate ring[30] (13.69–40.03 ppm). The chemical shift of the phosphole phosphorus changes only slightly from 27.42 ppm for **1** to the range 22.25–34.19 ppm for compounds **2**–**6**. The magnitudes of $^2J_{PP}$ (31–33 Hz for cis coupling and 256–280.2 Hz for trans coupling) are typical of six-coordinate ruthenium(II) complexes.[10,31] The phosphorus

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Table III. Atom Coordinates for $C_{41}H_{39}Cl_2OP_3Ru$ (**8**)

atom	*x*	*y*	*z*	*B*,[a] Å²
Ru	0.12158 (3)	0.09380 (2)	0.72653 (2)	1.663 (7)
Cl1	0.3154 (1)	0.04217 (6)	0.79774 (7)	2.51 (2)
Cl2	−0.0743 (1)	0.15067 (5)	0.66933 (6)	2.28 (2)
P1	0.0525 (1)	0.12054 (6)	0.84995 (6)	2.08 (2)
P2	0.2166 (1)	0.19637 (5)	0.74470 (6)	1.87 (2)
P3	0.0179 (1)	−0.00876 (6)	0.71341 (6)	1.93 (2)
C	0.1822 (4)	0.0829 (2)	0.6297 (3)	2.12 (9)
O	0.2199 (3)	0.0772 (2)	0.5711 (2)	3.25 (7)
C1	0.0426 (4)	0.2084 (2)	0.8547 (3)	2.37 (9)
C2	0.0299 (4)	0.2207 (2)	0.9396 (3)	2.7 (1)
C3	0.1033 (5)	0.1797 (3)	0.9855 (3)	3.1 (1)
C4	0.1783 (4)	0.1355 (2)	0.9370 (3)	2.6 (1)
C5	−0.0532 (6)	0.2751 (3)	0.9618 (3)	4.1 (1)
C6	0.1352 (6)	0.1783 (3)	1.0719 (3)	4.4 (1)
C7	0.1893 (4)	0.2234 (2)	0.8425 (2)	2.07 (9)
C8	0.2766 (4)	0.1795 (2)	0.9017 (3)	2.5 (1)
C9	−0.0946 (4)	0.0881 (2)	0.8843 (3)	2.15 (9)
C10	−0.2122 (5)	0.0893 (2)	0.8337 (3)	2.9 (1)
C11	−0.3284 (5)	0.0655 (3)	0.8564 (3)	3.7 (1)
C12	−0.3265 (5)	0.0400 (3)	0.9295 (3)	3.5 (1)
C13	−0.2082 (5)	0.0386 (3)	0.9801 (3)	3.5 (1)
C14	−0.0940 (5)	0.0629 (3)	0.9586 (3)	3.1 (1)
C15	0.1492 (4)	0.2593 (2)	0.6762 (3)	2.11 (9)
C16	0.1734 (5)	0.2548 (2)	0.5992 (3)	2.8 (1)
C17	0.1237 (6)	0.3001 (3)	0.5452 (3)	3.7 (1)
C18	0.0521 (5)	0.3510 (3)	0.5664 (3)	3.8 (1)
C19	0.0296 (6)	0.3565 (3)	0.6419 (3)	3.9 (1)
C20	0.0781 (5)	0.3103 (2)	0.6969 (3)	3.1 (1)
C21	0.3941 (4)	0.2080 (2)	0.7459 (3)	2.11 (9)
C22	0.4648 (4)	0.1685 (2)	0.7013 (3)	2.5 (1)
C23	0.5973 (4)	0.1807 (2)	0.6979 (3)	2.8 (1)
C24	0.6597 (4)	0.2312 (2)	0.7386 (3)	2.8 (1)
C25	0.5937 (5)	0.2691 (2)	0.7833 (3)	3.1 (1)
C26	0.4599 (5)	0.2586 (2)	0.7866 (3)	2.9 (1)
C27	−0.1595 (4)	−0.0106 (2)	0.6786 (3)	2.30 (9)
C28	−0.2497 (5)	−0.0396 (3)	0.7191 (3)	3.4 (1)
C29	−0.3850 (5)	−0.0358 (3)	0.6929 (3)	4.5 (1)
C30	−0.4305 (5)	−0.0038 (3)	0.6242 (3)	3.9 (1)
C31	−0.3406 (5)	0.0226 (2)	0.5816 (3)	3.2 (1)
C32	−0.2063 (4)	0.0197 (2)	0.6089 (3)	2.40 (9)
C33	0.0857 (4)	−0.0631 (2)	0.6452 (2)	1.95 (9)
C34	0.0059 (5)	−0.0971 (2)	0.5895 (3)	2.5 (1)
C35	0.0614 (5)	−0.1362 (2)	0.5368 (3)	2.8 (1)
C36	0.1972 (5)	−0.1419 (2)	0.5418 (3)	2.9 (1)
C37	0.2775 (5)	−0.1088 (2)	0.5998 (3)	2.8 (1)
C38	0.2229 (4)	−0.0694 (2)	0.6504 (3)	2.4 (1)
C39	0.0355 (4)	−0.0523 (2)	0.8036 (3)	2.6 (1)
C40	0.1111 (6)	−0.1027 (2)	0.8218 (3)	3.5 (1)

[a] Anistropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Selected Bond Distances (Å) for Compounds **6** and **8**

6		**8**	
Ru1–Cl1	2.421 (3)	Ru–Cl1	2.423 (1)
Ru1–Cl2	2.410 (3)	Ru–Cl2	2.407 (1)
Ru1–P1	2.324 (3)	Ru–P1	2.410 (1)
Ru1–O1	2.173 (6)	Ru–P2	2.355 (1)
Ru1–P2	2.355 (3)	Ru–P3	2.386 (1)
Ru1–C30	1.77 (1)	Ru–C	1.882 (4)
P1–C1	1.85 (1)	P1–C1	1.842 (4)
P1–C4	1.878 (9)	P1–C4	1.858 (4)
P1–C12	1.827 (9)	P1–C9	1.820 (4)
C1–C2	1.53 (1)	C1–C2	1.516 (6)
C1–C7	1.52 (1)	C1–C7	1.570 (5)
C2–C3	1.29 (1)	C2–C3	1.325 (7)
C3–C4	1.53 (1)	C3–C4	1.525 (6)
C4–C8	1.58 (1)	C4–C8	1.548 (6)
C7–C8	1.59 (1)	C7–C8	1.556 (6)
C8–C9	1.50 (1)	C7–P2	1.845 (4)
C30–O2	1.18 (1)	C–O	1.141 (5)
C9–O1	1.27 (1)		
C9–N1	1.33 (1)		

NMR and infrared spectral data establish the coordination geometries shown in Scheme I.

Table V. Selected Bond Angles (deg) for Compounds **6** and **8**

6		**8**	
Cl1–Ru1–Cl2	175.1 (1)	Cl1–Ru–Cl2	173.6 (4)
Cl1–Ru1–P1	87.93 (9)	Cl1–Ru–P1	88.41 (4)
Cl1–Ru1–O1	84.6 (2)	Cl1–Ru–P2	92.84 (4)
Cl1–Ru1–P2	89.64 (9)	Cl1–Ru–C	93.0 (1)
Cl1–Ru1–C30	93.9 (3)	Cl1–Ru–P3	87.94 (4)
Cl2–Ru1–P1	92.67 (9)	Cl2–Ru–P1	85.43 (3)
Cl2–Ru1–O1	90.5 (2)	Cl2–Ru–P2	84.52 (4)
Cl2–Ru1–P2	89.3 (1)	Cl2–Ru–C	92.9 (1)
Cl2–Ru1–C30	91.0 (3)	Cl2–Ru–P3	94.39 (3)
P1–Ru1–O1	88.5 (2)	P1–Ru–P2	80.62 (4)
P1–Ru1–P2	176.9 (1)	P1–Ru–C	173.3 (1)
P1–Ru1–C30	94.4 (3)	P1–Ru–P3	96.40 (4)
O1–Ru1–P2	89.1 (2)	P2–Ru–C	92.7 (1)
O1–Ru1–C30	176.6 (4)	P2–Ru–P3	176.89 (4)
P2–Ru1–C30	87.9 (4)	C–Ru–P3	90.2 (1)
C1–P1–C4	81.4 (4)	C1–P1–C4	80.3 (2)
C18–P2–C21	89.9 (5)		

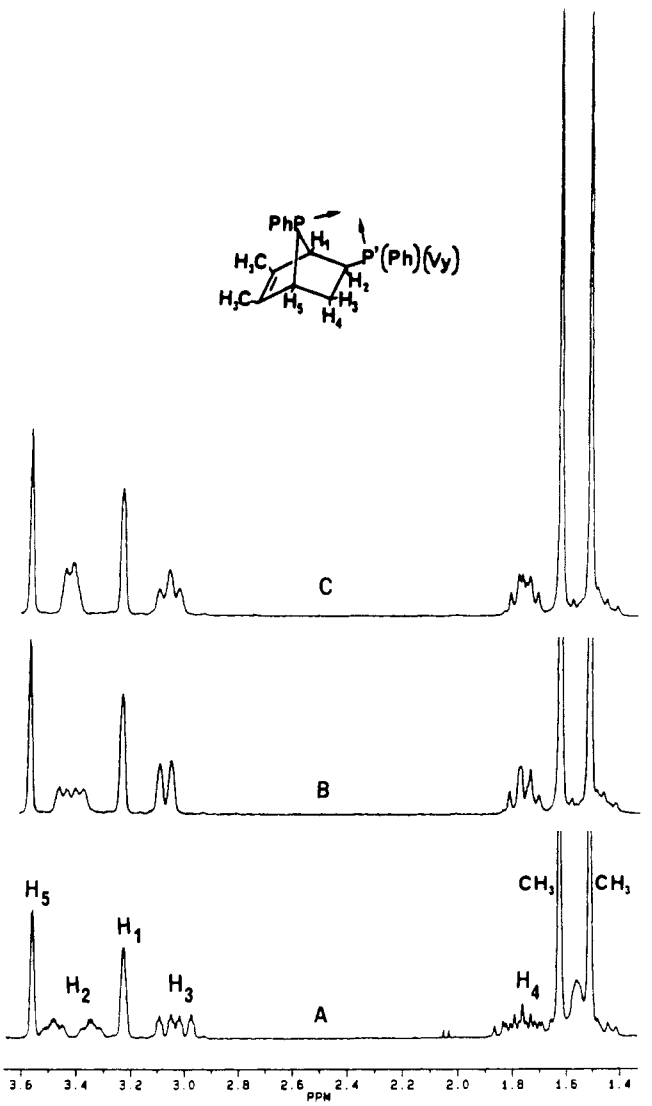
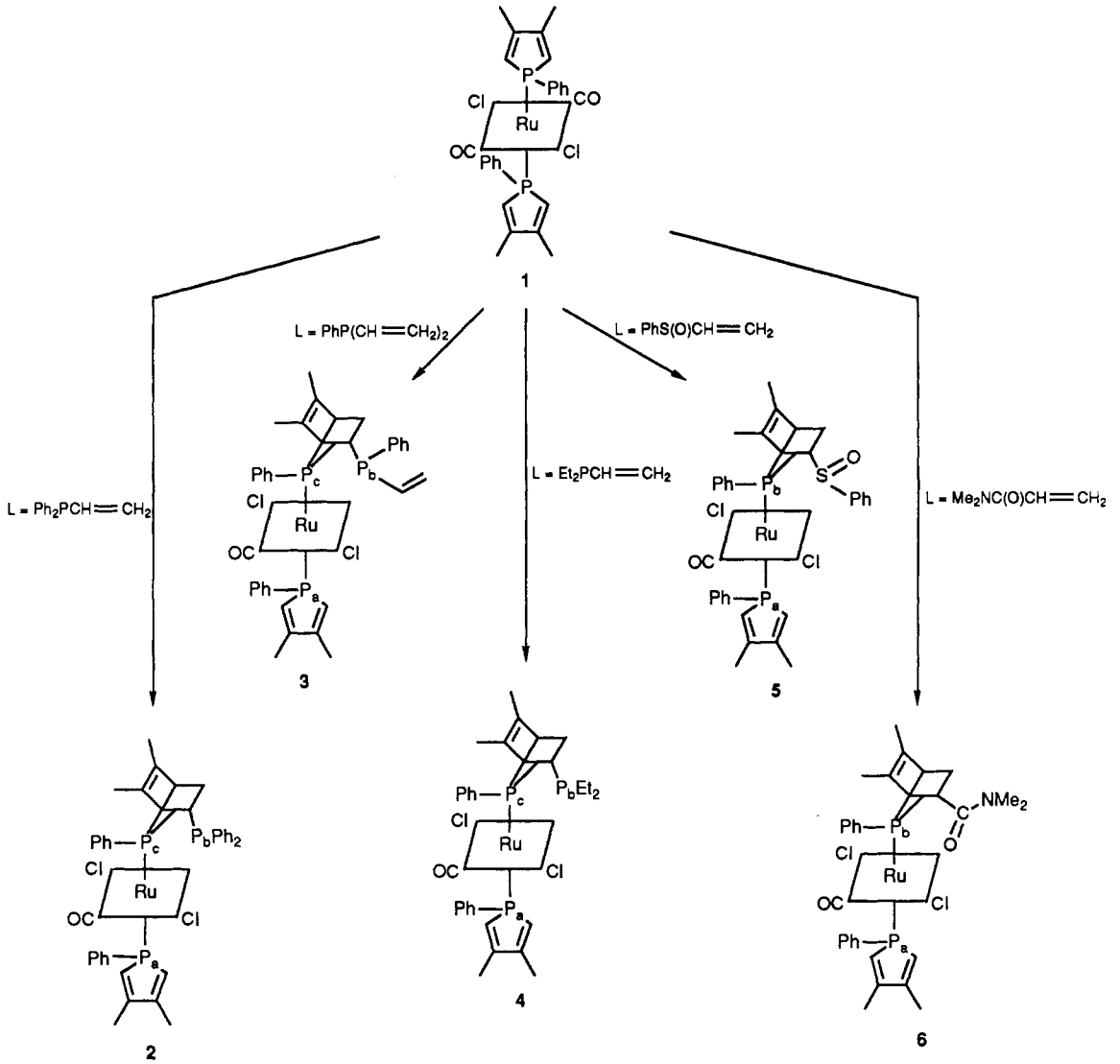


Figure 1. 300-MHz $^1H\{^{31}P\}$ NMR spectra of **8** in $CDCl_3$ at 300 K: (A) normal ^1H spectrum in the aliphatic region; (B) spectrum with the 2-phosphino phosphorus, P_c, decoupled; (C) spectrum with the 7-phospha phosphorus, P_b, decoupled.

Proton and Carbon NMR Spectroscopy. Assignment of the proton and carbon NMR spectra required a combination of ^1H, $^1H\{^{31}P\}$, $^1H/^1H$ COSY, 2-DJ, and $^1H/^{13}C$ HETCOR experiments, as previously detailed[3] for the 2-phosphino-7-phosphanorbornene

(31) Pankowski, M.; Chadkiewicz, W.; Simonin, M. *Inorg. Chem.* **1985**, *24*, 533.

Scheme I



complexes of palladium(II) and platinum(II). These assignments were accomplished in the following manner. The $^1H\{^{31}P\}$ NMR spectra (Figure 1) allow assignment of the chemical shifts of the ring protons 1–5. From previous studies,[3] large values of $^3J_{PH}$ to the 7-phospha phosphorus are expected for protons 2 and 4. Proton 3 is expected to have nearly equal magnitude $^3J_{PH}$ couplings to both the 2-phosphino and 7-phospha phosphorus atoms, and protons 1 and 5 are expected to have very small PH couplings. Decoupling the vinyldiphenylphosphine phosphorus has no effect on the ring proton resonances but clearly decouples the vinyl protons (Figure 2) as expected.[18] These results also confirm the ^{31}P chemical shift assignments.

Figures 3 and 4 are examples of HETCOR spectra for **3**. The phosphole methyl carbons show a reasonable magnitude of $^3J_{PC}$ (~10 Hz), while the 5,6-methyl carbons are generally not coupled to phosphorus. The C/H correlations of these resonances then enabled assignment of the respective proton resonances. Carbon 3 is the only ring CH_2 carbon and should show C/H correlation with protons 3 and 4 as well as have large $^2J_{PC}$ coupling to P_c and smaller $^2J_{PC}$ coupling to P_b. Carbon 4 should only show $^1J_{PC}$ coupling to P_c, should have no coupling to P_b, and should be correlated with proton 5. Carbon 2 should show large $^1J_{PC}$ coupling to P_b and large $^2J_{PC}$ coupling to P_c and be correlated with proton 2. Finally, carbon 1 should show large $^1J_{PC}$ coupling to P_c and moderate $^2J_{PC}$ coupling to P_b and be correlated with proton 1.

Assignments of the phenyl, vinyl, and phosphole ring carbon resonances were accomplished similarly as exemplified by Figure 4. The vinyl β- and α-carbon resonances were identified by their

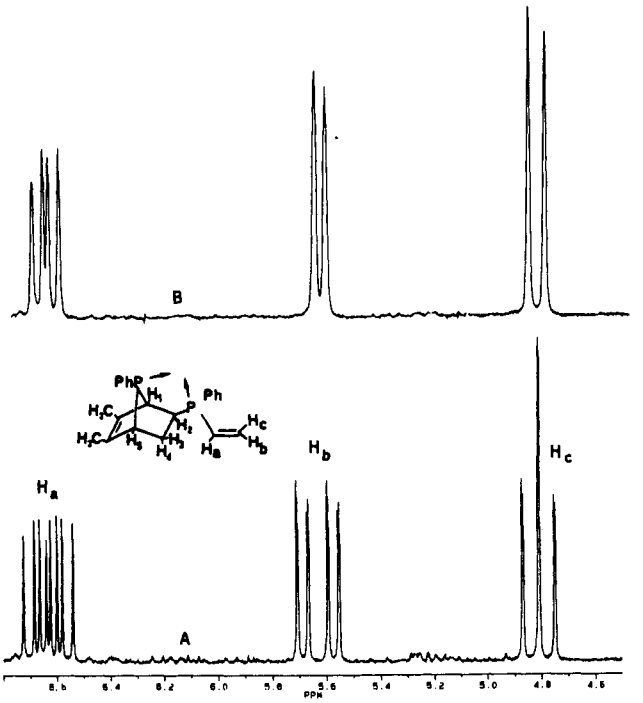


Figure 2. 300-MHz $^1H\{^{31}P\}$ NMR spectra of **8** in $CDCl_3$ at 300 K: (A) normal ^1H spectrum in the vinyl region; (B) spectrum with the vinyldiphenylphosphine phosphorus, P_a, decoupled.

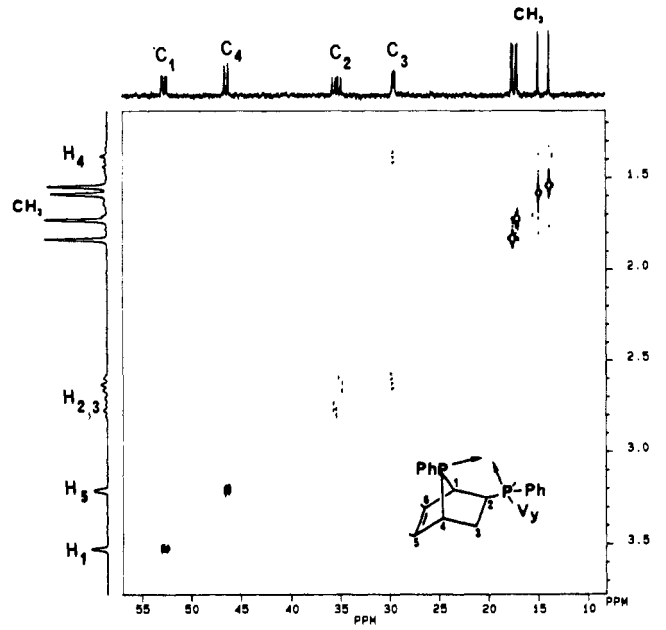


Figure 3. Heteronuclear 2-D $^1H/^{13}C$ chemical shift correlation for **3** in $CDCl_3$ at 75 MHz (^{13}C) and 300 K. This expansion shows the ring carbons (C_1–C_4) and the methyl carbons. Carbon 1-D and proton 1-D spectra are shown on the top and left sides, respectively. P–C couplings are responsible for splittings in the carbon domain, while P–H and H–H couplings are responsible for splittings in the proton domain.

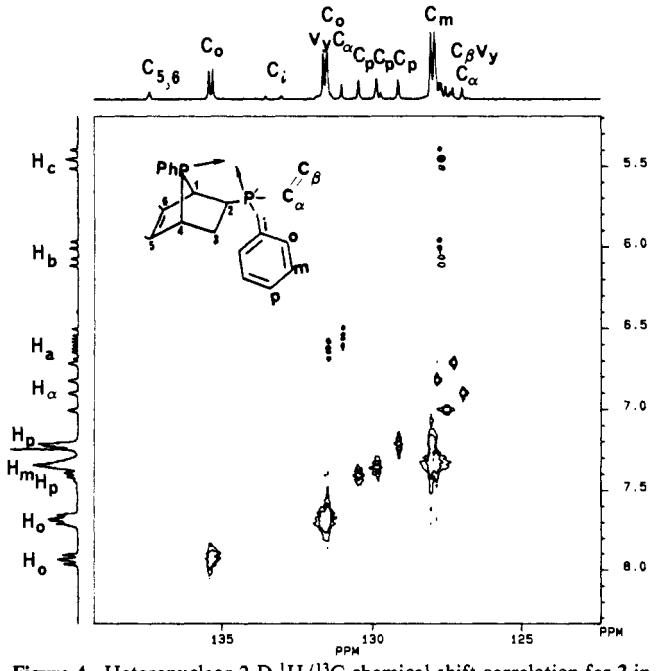


Figure 4. Heteronuclear 2-D $^1H/^{13}C$ chemical shift correlation for **3** in $CDCl_3$ at 75 MHz (^{13}C) and 300 K. This expansion shows the phenyl, vinyl, and phosphole ring carbons.

correlations with protons H_c and H_b and with H_a, respectively. The diastereotopic phosphole C_α carbon resonances were identified by their correlations with the diastereotopic phosphole H_α resonances. The remaining resonances were then assigned on the basis of similarities in their chemical shifts and coupling constants with those of analogous compounds.[3] These assignments were then affirmed by $^1H/^1H$ COSY and 2-DJ experiments. The spectral data (see the Experimental Section) are fully consistent with the assigned structures and corroborate the conclusion from the $^{31}P\{^1H\}$ NMR data that racemic mixtures of single diastereomers were formed in each reaction.

Crystal Structure Analyses. In order to gain conclusive support for the structures of these compounds and to characterize the new ligand systems, X-ray crystal structures of compounds **6** and **8**

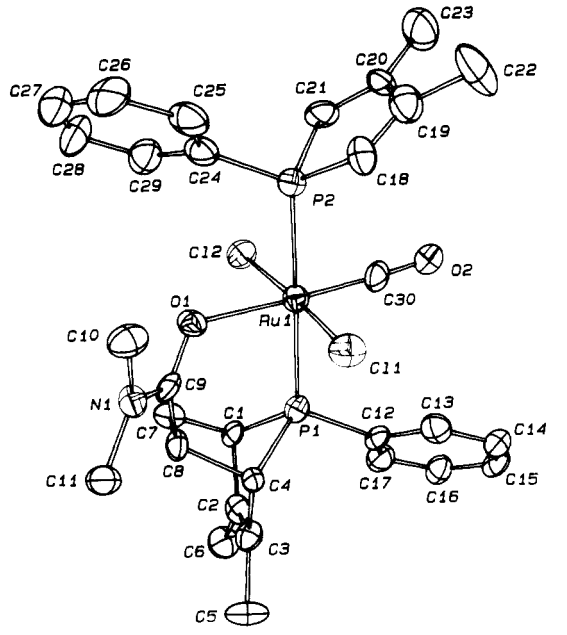


Figure 5. Ortep plot of one of the two independent molecules of *mer-trans*-dichlorocarbonyl(1-phenyl-3,4-dimethylphosphole)[2-((dimethylamino)carbonyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**6**) showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

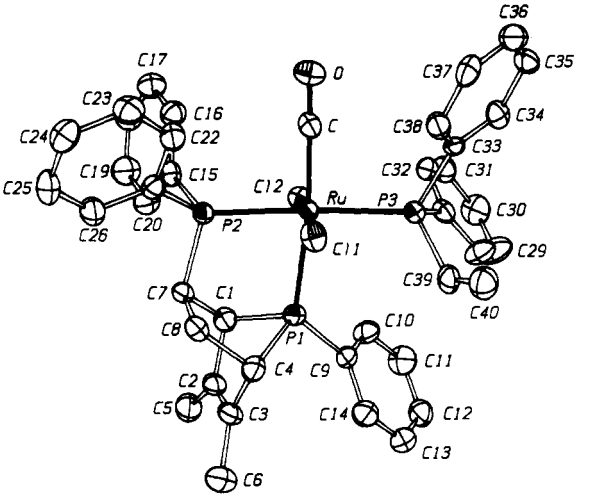


Figure 6. Ortep plot of *mer-trans*-dichlorocarbonyl(vinyldiphenylphosphine)[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) (**8**) showing the atom-labeling scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

were obtained. The structures of these molecules are shown in Figures 5 and 6, respectively. Selected bond distances and angles are listed in Tables IV and V. Both complexes exist as discrete molecules with no abnormal intermolecular contacts. The asymmetric part of the unit cell of **6** contains two crystallographically nonequivalent molecules. Data for both molecules are given in the supplementary material, but only one of them will be discussed as they are not significantly different. Neither complex **6** nor **8** contains any element of symmetry, and both complexes are chiral. The geometry of the Ru(II) coordination spheres is distorted octahedral. Complex **6** is less distorted than complex **8** as a result of the larger bite of the six-membered chelate ring in complex **6**. As indicated by the IR data, the aminocarbonyl moiety is coordinated to ruthenium through oxygen. The Ru–P2 distance (2.355 (3) Å) is, as expected, longer than the Ru–P1 distance (2.324 (3) Å). For complex **8**, the three ruthenium–phosphorus bond distances are significantly different (Ru–P1 = 2.410 (1) Å; Ru–P(2) = 2.355 (1) Å; Ru–P(3) = 2.386 (1) Å), with the shortest distance being trans to a phosphorus donor and the longest trans to CO. The relative trans influences[32] are also evidenced

Table VI. Redox Characteristics of the Complexes[a]

compd	Ru(II)/Ru(III) $E_{1/2}$ (ΔE_p)	compd	Ru(II)/Ru(III) $E_{1/2}$ (ΔE_p)
2	0.62 (65)	**5**	1.15[b]
3	0.59 (70)	**6**	0.62 (77)
4	0.56 (60)	**7**	0.62 (60)

[a] In CH_2Cl_2 containing 0.1 M TBAP at 25 °C; v = 200 mV s^{-1}; in volts vs Fc^+/Fc (ΔE_p in millivolts). [b] E_{p_a} only.

Table VII. Isomerization and Hydrogenation of 1-Hexene by Ruthenium(II) Complexes

complex	turnover no.[a] formation of hexane	loss of 1-hexene	formation of 2-hexene
3	6.6	9.6	2.7
5	13.6	45.3	31.2
6	57.5	NA[b]	NA
8	8.4	13.2	4.2
mer-trans-$(Ph_2MeP)_3Ru(CO)Cl_2$[c]	44	NA	NA
mer-trans-$(PhMe_2P)_3Ru(CO)Cl_2$[c]	34	NA	NA
mer-trans-$(Me_3P)_3Ru(CO)Cl_2$[c]	24	NA	NA

[a] In moles of substrate per mole of ruthenium per hour. [b] NA = not available. [c] Data from ref 20.

in the Ru–C distances (**6**, 1.77 (1) Å; **8**, 1.882 (4) Å) and in the CO distances (**6**, 1.27 (1) Å; **8**, 1.141 (5) Å). These distances imply stronger Ru–CO bonding in **6** than in **8** and are consistent with the relative magnitudes of ν_{CO} (**6**, 1952 cm^{-1}; **8**, 1991 cm^{-1}) for these two compounds. In both complexes the chelate rings are rigid and contain bridgehead phosphorus atoms with small CPC angles (**6**, 81.4 (4)°; **8**, 80.3 (2)°). These small angles are typical of compounds of this type[3] and are in part responsible for the extreme downfield shifts of the associated ^{31}P resonances for the 7-phospha phosphorus nuclei. The remaining distances and angles are unexceptional.

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

Electrochemistry. The cyclic voltammograms of the complexes were recorded in dichloromethane with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Pertinent data are summarized in Table VI. Except for **5** all the complexes were reversibly oxidized to Ru(III) species. No oxidation to Ru(IV) nor reduction to Ru(I) was seen in the potential range accessible with the electrode/electrolyte/solvent system employed.[19] Also, except for **5**, the oxidation potential is virtually independent of the type of the diphosphine ligand. It depends almost exclusively upon the chromophore. For a series[19] of *mer-trans*-$(R_3P)_3Ru(CO)Cl_2$ complexes the Ru(II)/Ru(III) oxidation potentials lie in the range 0.51–0.61 V, suggesting that the 2-phosphino-7-phosphanorbornene ligands do not impart any unusual stability to Ru(III).

Catalysis. Four of these Diels–Alder products were tested for their ability to catalyze the homogeneous hydrogenation of 1-hexene under conditions identical with those of our previous studies on $(R_3P)_2Ru(CO)_2Cl_2$ and $(R_3P)_3Ru(CO)Cl_2$ complexes.[20] The results are given in Table VII. As can be seen from the data in Table VII, none of these complexes are very good catalysts. However, the mixed-donor hemilabile ligand containing catalysts are the most efficient, and the aminocarbonyl complex is a more efficient catalyst than similar complexes with monodentate phosphines.[20] The two mixed-donor ligand complexes were also tested for their ability to hydrogenate nitrobenzene, cyclohexanone, benzonitrile, and 2-butanone under similar conditions. Complex **5** hydrogenated cyclohexanone with a turnover number of 3.4 mol of cyclohexanol per mole of **5** per hour. No hydrogenation of any of the other substances was observed.

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Supplementary Material Available: For the two structure studies, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (U's) and an Ortep plot of the other independent molecule of **6** (19 pages); listings of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.