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Contribution from the Institute of Chemistry, Faculty of Sciences, University of Belgrade, 11001 Belgrade, Yugoslavia,
Departments of Chemistry, University of Nevada, Reno, Nevada 89557, and University of Warwick,
Coventry CV47AL, England, and Laboratoire de Chimie des Métaux de Transition et Catalyse
Associé au CNRS (UA424) Institut le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France

Intramolecular [4 + 2] Diels-Alder Cycloaddition Reactions of Phospholes with Vinylphosphines Promoted by Nickel

Lj. Solujić,[1a] Emil B. Milosavljević,[1a] John H. Nelson,*,[1b] Nathaniel W. Alcock,[1c] and Jean Fischer[1d]

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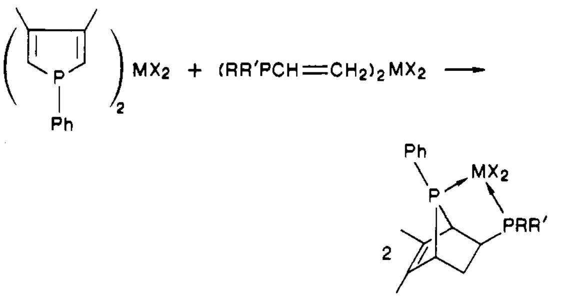
The reaction of divinylphenylphosphine with 1-phenyl-3,4-dimethylphosphole in the presence of anhydrous nickel(II) bromide leads to the formation of a single diastereomer of bromo[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)-phosphine]nickel(II) bromide, $[LNiBr]^+Br^-$, as the result of two sequential stereoselective intramolecular [4 + 2] Diels-Alder cycloadditions. This reaction provides a facile route to a new type of conformationally rigid tridentate phosphine. This new complex has been characterized by elemental analysis, physical properties, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, electronic and infrared spectroscopy, and cyclic voltammetry. The ligand has been isolated after liberation from nickel by cyanide displacement in a two-phase solvent system (CH_2Cl_2/H_2O) and converted to its trisulfide. It has also been transferred to palladium, platinum, and ruthenium to form the pentacoordinate $LPdCl_2$, the four-coordinate square-planar $[LPtCl]^+Cl^-$, and *mer*-L $Ru(PPh_3)Cl_2$ and *trans*-L_2RuCl_2, respectively. The last complex contains two dangling-arm phosphines. These complexes have been characterized by the above techniques, including X-ray crystallography for *mer*-$LRu(PPh_3)Cl_2$. This molecule crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions $a = 11.916$ (3) Å, $b = 22.074$ (7) Å, $c = 18.309$ (4) Å, $\beta = 104.43$ (2)°, and $V = 4664$ (2) Å^3, with $Z = 4$. Refinement converged to $R = 0.038$ for 5033 independent observed ($I/\sigma(I) \geq 3.0$) reflections. The two Ru-P(bridging) distances are slightly different (2.350 (1), 2.320 (1) Å) and are longer than Ru-P(exocyclic) (2.308 (1) Å). The C-P-C angles for the bridging phosphorus atoms are small (79.5 (2), 79.1 (2)°). Bromobis[2-(vinylphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]nickel(II) bromide was a minor product of the reaction of divinylphenylphosphine, 1-phenyl-3,4-dimethylphosphole, and nickel(II) bromide. The reaction of vinyldiphenylphosphine, 1-phenyl-3,4-dimethylphosphole, and nickel(II) bromide resulted in the formation of mono- and bis(2-(diphenylphosphino)-7-phenylphosphanorbornene) nickel(II) complexes. These complexes were also characterized by the above-mentioned techniques, including X-ray crystallography for dibromo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]-nickel(II). This molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions $a = 12.177$ (3) Å, $b = 12.448$ (3) Å, $c = 8.664$ (2) Å, $\alpha = 100.83$ (2)°, $\beta = 99.11$ (2)°, $\gamma = 81.11$ (2)°, and $V = 1263.0$ Å^3, with $Z = 2$. Refinement converged to $R = 0.038$ for 2692 independent observed ($I/\sigma(I) > 3$) reflections. The donor abilities of the two phosphorus donors are different: Ni-P distances are 2.135 (1) and 2.169 (1) Å, the C-P-C angle for the bridging phosphorus is 81.4 (2)°, and the Ni-Br (2.3433 (8), 2.3230 (8) Å) distances are significantly different. The chelate ring is conformationally rigid, and the molecule contains four asymmetric centers.

Introduction

We have recently shown[2,3] that reaction of a vinylphosphine complex of palladium or platinum with a phosphole complex of palladium or platinum results in the facile formation of a new class of chelating diphosphine: 2-phosphino-7-phosphabicyclo[2.2.1]-hept-5-ene (reaction 1). This intramolecular [4 + 2] Diels-Alder cycloaddition reaction does not occur in the absence of the metal ion. Reaction 1 requires the prior preparation, isolation, and purification of both the phosphole and vinylphosphine complexes. Since phosphine and phosphole complexes of nickel are substitutionally labile[4] in solution, we reasoned that nickel might promote similar reactions, but with the advantage of not having to first isolate the phosphole and vinylphosphine complexes in addition to the considerable reduction in cost of nickel relative to that of palladium and platinum. Moreover, since nickel(II) has a much greater propensity for coordination numbers of 5 and 6 than do either palladium(II) or platinum(II), we hoped that reactions of vinylphosphines with phospholes in the presence of nickel(II) would lead to new types of ligands.



(1)

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were purified by standard procedures if necessary. Vinyldiphenylphosphine and divinylphenylphosphine were obtained from Organometallics, Inc. Anhydrous nickel bromide was obtained from Aldrich Chemical Co. 1-Phenyl-3,4-dimethylphosphole (DMPP) was prepared by the previously described method.[5] All reactions involving the phosphines were conducted under an N_2 atmosphere. All solvents were dried by standard procedures. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Conductance measurements were carried out at 25 °C on 1.00×10^{-3} M nitromethane solutions by using a Yellow Springs Instruments conductivity cell, Model No. 3403, and measured with an Industrial Instruments conductivity bridge, Model RC16B 2, which was adapted for use with a Tektronix Type 310 oscilloscope. Conductance ranges were taken from published values.[6] All cyclic voltammograms were recorded at 25 ± 0.1 °C in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) by using an EG&G PAR electrochemical system consisting of a Model RE0073 recorder, a Model 173 potentiostat, and a Model 175 universal programmer. A three-electrode system with instrumental *iR* compensation was used throughout. The working and auxiliary electrodes were a platinum disk and wire, respectively. The reference electrode was Ag/AgCl (CH_2Cl_2; saturated LiCl). The test solution was separated from the reference electrode by a salt bridge containing a Vycor plug and was filled with the solvent/supporting electrolyte system. Temperature regulation was achieved with a Brinkman Lauda K-2/R temperature controller with the electrochemical cell immersed in the constant-temperature bath. As recommended by IUP-

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(1) (a) University of Belgrade. (b) University of Nevada. (c) University of Warwick. (d) Université Louis Pasteur.

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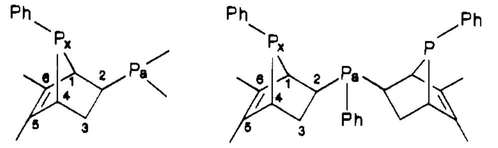
Table I. ^{31}P NMR Data for the Obtain Compounds[a]

compd	$\delta(^{31}P)$		$^2J_{P_aP_x}$, Hz	$\Delta(P_x)$[b]	$\Delta(P_a)$[b]	other
	$\delta(P_x)$	$\delta(P_a)$				
1	130.5 (2 P, d)	54.7 (1 P, t)	68.4	41.7	51.8	
2	138.4 (2 P, t)	22.5 (2 P, t)	51.3	...	...	
3	88.8 (2 P, d)	2.9 (1 P, t)	56.1	...	...	
4	88.5 (2 P, s)	51.8 (1 P, s)	0	...	...	
5	132.4 (2 P, dd)	65.6 (1 P, dt)	41.5	43.6	62.7	24.4 (1 P, dt, P_b)[c]
6	145.1 (2 P)[d]	29.6 (2 P)	270.9	56.3	26.7	89.5 (2 P, s, P_b)[e]
7	112.9 (2 P, d)	62.5 (1 P, t)	19.5	24.1	59.6	
8	105.8 (2 P, d)	53.8 (1 P, t)	17.1[f]	17.0	50.9	
9	134.4 (1 P, d)	45.9 (1 P, d)	73.2	...	...	
10	136.3 (2 P, t)	16.5 (2 P, t)	50.0	...	...	

[a] taken on $CDCl_3$ solutions. All shifts are in ppm, positive and downfield of 85% H_3PO_4. Line shapes are given in parentheses: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublets of triplets. [b] $\Delta(P) = \delta(\text{complex}) - \delta(\text{ligand})$. [c] PPh_3: $J_{P_aP_b} = 273.8$ Hz, $J_{P_bP_x} = 24.4$ Hz. [d] AA′XX′ spin system: $J_{P_xP_x'} = 31.5$ Hz, $J_{P_aP_a'} = -26$ Hz; coupling constants could be reversed. [e] Uncoordinated 7-phosphanorbornene moiety. [f] $J_{PtP_a} = 2653$ Hz, $J_{PtP_x} = 2224$ Hz.

Table II. $^{13}C\{^1H\}$ NMR Data for the Obtained Diphosphine and Triphosphine Compounds[a]



compd	C_1	C_2	C_3	C_4	$C_{5,6}$	5,6-CH_3
1	49.23[b] (14.6, 14.6)[c]	35.54 (19.5, 42.7)	30.42 (7.2, 6.3)	54.45 (32.4, 17.1)	137.53, 137.53	13.62, 14.94
2	49.29 (12.1, 12.1)	28.70 m	31.60 m	56.50 m	138.42, 138.42	14.04, 14.88
3	51.28 (9.8, 4.9)	41.22 (21.4, 26.4)	32.51 (26.4, 26.4)	53.60 (9.8, 9.8)	139.00, 139.40	13.45, 14.12
4	51.35 (49.1, 4.9)	45.02 (19.5, 42.6)	28.33 (18.3, 0)	53.27 (52.1, 0)	138.28, 138.28	14.17 (4.0), 14.62 (4.1)
5	48.93 (12.7, 12.7)	41.53 (34.0, 16.6)	30.15 (0, 0)	60.86 (33.2, 16.6)	136.20, 136.20	14.10, 14.64
6	51.18 (9.9, 4.4)	41.16 (20.0, 20.8)	32.85 (28.6, 0)	56.00 m	138.80, 139.00	13.40, 13.93, 14.01
	49.21 (9.8, 0)	37.55 (20.8, 0)	32.61 (22.4, 0)	55.20 (10.9, 2.9)	139.33	14.12, 14.38, 14.74
	48.90 (21.2, 0)	33.50 m	32.20 (27.2, 0)	53.51 (8.4, 8.4)		
7	46.93 m	32.0 m	29.50 m	54.80 m	136.90, 136.90	13.90, 15.00
8	49.05 (16.6, 16.6)	34.67 (15.4, 31.5)	32.15 (6.8, 6.8)	55.60 m	137.10, 137.10	13.71, 14.83
9	47.45 (27.6, 0)	32.70 m	31.81 m	53.85 m	136.70, 136.70	13.77, 14.86
10	50.87 m	35.30 m	28.62 m	54.60 m	138.28, 138.28	13.80, 15.18

[a] The phenyl carbon resonances were not assigned. They appear in the δ 127–135 ppm region as overlapping multiplets. [b] In ppm. [c] Values in parentheses are J_{P_a-C} and J_{P_x-C} values in Hz.

AC[7] for electrochemistry in nonaqueous solvents, the ferrocenium ion (Fc^+)/ferrocene (Fc) couple was used as the reference, and all potentials reported herein are given vs this couple. TBAP (Fluka, purum) was recrystallized from ethanol/water and dried under vacuum at 100 °C overnight. Far-infrared spectra were recorded on a Perkin-Elmer 1800 FT infrared spectrophotometer as polyethylene pellets. Electronic spectra were obtained on 6×10^{-5}–2×10^{-4} M solutions of the complexes in dichloromethane in 1.00-cm quartz cuvettes with use of a Cary 14 spectrophotometer. 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 300 MHz on one or more of the following: Varian VXR-300, General Electric QE-300 and GN-300, and Bruker AC-300 spectrometers. The $^{13}C\{^1H\}$ NMR spectra were recorded at 75 MHz on one of the above-mentioned spectrometers. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4, with a positive value being downfield of the respective reference.

(B) Synthesis. Bromo[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine]nickel(II) Bromide–Dichloromethane (1). A mixture of 1.68 g (7.7 mmol) of anhydrous nickel(II) bromide, 2.90 g (15.4 mmol) of DMPP, 1.25 g (7.7 mmol) of divinylphenylphosphine, and 200 mL of acetonitrile was refluxed under nitrogen for 12 h. The solution obtained was evaporated to dryness on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (20 mL) and the solution filtered. Anhydrous diethyl ether (5 mL) was added to the filtrate, and the solution was left at room temperature for 24 h. The resultant dark red crystalline product, **1** (2.5 g, 43%), was isolated by filtration, washed with absolute ethanol, recrystallized from CH_2Cl_2/Et_2O, and vacuum-dried overnight; mp 244–246 °C. IR: ν_{NiBr} 279.5 cm^{-1}. $\Lambda_m(CH_3NO_2) = 69.30\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 1.42 (s, CH_3, 6 H), 1.57 (s, CH_3, 6 H), 1.95 (m, H_4, 2 H), 2.53 (s, H_1, 2 H), 3.35 (m, H_3, 2 H), 3.47 (s, H_5, 2 H), 3.60 (m, H_2, 2 H), 7.2–7.7 (m, Ar H, 15H). The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data are given in Tables I and II, respectively. Anal. Calcd for $C_{34}H_{37}Br_2NiP_3 \cdot CH_2Cl_2$: C, 49.92; H, 4.67. Found: C, 50.00; H, 4.71. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

Bromobis[2-(vinylphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]nickel(II) Bromide (2). The filtrate obtained after the separation of complex **1** was left in a refrigerator for several hours, and by this time there crystallized out a mixture of the products **1** and **2** (0.5 g), which was isolated by filtration. The filtrate obtained was evaporated to dryness, and the residue was dissolved in acetone (~30 mL). The solution was filtered, and after addition of about 20 mL of anhydrous diethyl ether orange crystals (0.4 g, 6%) of **2** formed. These were recrystallized from acetone/ether and vacuum-dried overnight; mp 198–200 °C. IR: ν_{NiBr} 282 cm^{-1}; ν_{NiP} 366, 378 cm^{-1}. $\Lambda_m(CH_3NO_2) = 92.70\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 1.38 (s, CH_3, 3 H), 1.43 (s, CH_3, 3 H), 1.74 (m, H_4, 1 H), 2.70 (m, H_2, H_3, 2 H), 3.17 (s, H_1, 1 H), 3.55 (s, H_5, 1 H), 5.04 (ddd, $^3J_{PH} = 25.6$ Hz, $^3J_{HH} = 18.5$ Hz, $^3J_{HH} = 11.2$ Hz, H_c, 1 H), 5.72 (ddd, $^3J_{PH} = 8$ Hz, $^3J_{HH} = 11.2$ Hz, $^3J_{HH} = 18.5$ Hz, H_b, 1 H), 5.92 (ddd, $^3J_{PH} = 12.8$ Hz, $^3J_{HH} = 18.5$ Hz, $^3J_{HH} = 18.5$ Hz, H_a, 1 H), 7.2–8.0 (m, Ar H, 10 H). Anal. Calcd for $C_{44}H_{48}Br_2NiP_4$: C, 57.49; H, 5.26. Found: C, 57.09; H, 5.07.

Phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine (3). To a solution of 1 g (1.2 mmol) of recrystallized complex **1** in 200 mL of CH_2Cl_2 was added 50 mL of a saturated aqueous sodium cyanide solution under nitrogen. The mixture was stirred vigorously at room temperature for 45 min to produce a colorless CH_2Cl_2 phase and a yellow-orange aqueous phase. The CH_2Cl_2 layer was separated, filtered through Celite and anhydrous magnesium sulfate, and concentrated to a volume of 20 mL. Addition of ethanol (~10 mL) afforded 0.5 g (80%) of **3** in the form of colorless crystals. The substance was recrystallized from CH_2Cl_2/EtOH and vacuum-dried; mp 158–164 °C. ^1H NMR ($CDCl_3$): δ 1.49 (s, CH_3, 6 H), 1.66 (s, CH_3, 6 H), 2.10 (m, H_4, 2 H), 2.35 (m, H_2, H_3, 4 H), 2.7 (s, H_1, 2 H), 3.05 (s, H_5, 2 H),

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(7) Gritzner, G.; Kuta, J. *Recommendations on Reporting Electrode Potentials in Nonaqueous Solvents*; IUPAC; p 1528.

7–8 (m, Ar H, 15 H). Anal. Calcd for $C_{34}H_{37}P_3$: C, 75.82; H, 6.92. Found: C, 75.84; H, 7.24.

Phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine *P,P′,P″*-Trisulfide–Dichloromethane (4). To a solution containing 0.84 g (1 mmol) of compound **1** in 200 mL of CH_2Cl_2 was added 50 mL of a saturated aqueous sodium cyanide solution under nitrogen. The mixture was agitated with a nitrogen stream for 45 min (until the CH_2Cl_2 layer was colorless). The CH_2Cl_2 layer was separated and filtered through Celite and anhydrous magnesium sulfate under nitrogen. To the filtrate were added 0.10 g of S_8 and 2 drops of 1-methylimidazole, and the mixture was stirred under nitrogen at room temperature for 12 h. The solution obtained was reduced to 10 mL on a rotary evaporator, 5 mL of hexane was added, and the mixture was left standing at ambient temperature overnight. The resultant colorless crystals were isolated by filtration, recrystallized from CH_2Cl_2/hexane, and vacuum-dried: yield 0.63 g (79%); mp 214–216 °C. IR: $\nu_{P=S}$ 610 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.28 (s, CH_3, 6 H), 1.54 (s, CH_3, 6 H), 2.50 (m, $^3J_{PH}$ = 29.82 Hz, $^3J_{PH}$ = 10.92 Hz, H_4, 2 H), 3.07 (s, H_1, 2 H), 3.43 (m, $^3J_{PH}$ = 16.05 Hz, H_2, H_3, 4 H), 3.61 (s, H_5, 2 H), 7.1–7.8 (m, Ar H, 15 H). Anal. Calcd for $C_{34}H_{37}P_3S_3{\cdot}CH_2Cl_2$: C, 58.41; H, 5.46. Found: C, 58.64; H, 5.55. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

***mer*-Dichloro(triphenylphosphine)[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine]ruthenium(II) (5).** The same procedure as described for the liberation of the triphosphine ligand from the nickel complex **1** was followed. The obtained CH_2Cl_2 solution of the triphosphine ligand was added to 0.96 g (1 mmol) of dichlorotris(triphenylphosphine)ruthenium(II). The mixture was refluxed under nitrogen for 4 h. The solution obtained was evaporated on a rotary evaporator to a volume of 15 mL and after addition of about 5 mL of hexane allowed to stand in a refrigerator for 1 h. The solution was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in diethyl ether (~20 mL), filtered, and left at room temperature for 24 h; by this time, 0.6 g (62%) of **5** crystallized out in the form of pale brown crystals. The substance was vacuum-dried overnight; mp 210–212 °C. IR: ν_{RuCl} 325 cm^{-1}. $\Lambda_m(CH_3NO_2)$ = 14.80 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.10 (s, CH_3, 6 H), 1.4 (m, H_4, 2 H), 1.75 (s, CH_3, 6 H), 3.00 (s, H_1, 2 H), 3.10 (m, H_3, 2 H), 3.45 (s, H_5, 2 H), 3.84 (m, H_2, 2 H), 6.8–7.3 (m, Ar H, 30 H). Anal. Calcd for $C_{52}H_{52}Cl_2P_4Ru$: C, 64.20; H, 5.39; Cl, 7.29. Found: C, 64.27; H, 5.41; Cl, 7.19.

***trans*-Dichlorobis[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo-[2.2.1]hept-5-en-2-yl)phosphine]ruthenium(II) (6).** The CH_2Cl_2 solution of the triphosphine ligand, obtained by cyanide displacement from 0.84 g (1 mmol) of complex **1**, was added to 0.45 g (0.47 mmol) of dichlorotris(triphenylphosphine)ruthenium(II). The mixture was refluxed under nitrogen for 4 h. The obtained solution was evaporated to a volume of 10 mL on a rotary evaporator, diethyl ether (~5 mL) was added, and the mixture was left in a refrigerator overnight. The separated pale yellow crystals of **6** (0.3 g, 50%) were isolated by filtration, recrystallized from CH_2Cl_2/Et_2O, and vacuum-dried overnight; mp 237–239 °C. IR: ν_{RuCl} 322 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (s, CH_3, 6 H), 1.37 (s, CH_3, 3 H), 1.42 (s, CH_3, 3 H), 1.48 (s, CH_3, 3 H), 1.50 (s, CH_3, 3 H), 1.52 (s, CH_3, 6 H), 1.75–4.0 (m, ring H's, 20 H), 6.5–8.0 (m, Ar H, 30 H). Anal. Calcd for $C_{68}H_{74}Cl_2P_6Ru$: C, 65.38; H, 5.97; Cl, 5.68. Found: C, 65.20; H, 6.22; Cl, 5.36.

Dichloro[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-en-2-yl)phosphine]palladium(II) (7). The CH_2Cl_2 solution of the triphosphine ligand, obtained by cyanide displacement from 0.84 g (1 mmol) of complex **1**, was added to 0.38 g (1 mmol) of dichlorobis(benzonitrile)palladium(II), and the mixture was stirred under nitrogen at room temperature for 5 h. The solution obtained was evaporated on a rotary evaporator to a volume of 10 mL and after addition of anhydrous diethyl ether (~5 mL) left at room temperature for 24 h. The separated pale yellow crystals were isolated by filtration and washed with diethyl ether. The substance was recrystallized from CH_2Cl_2/Et_2O and vacuum-dried; yield 0.50 g (71%); dec pt >248 °C. $\Lambda_m(CH_3NO_2)$ = 18.73 Ω^{-1} cm^2 mol^{-1}. IR: ν_{PdCl} 309, 288 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50 (s, CH_3, 6 H), 1.65 (s, CH_3, 6 H), 2.25 (m, H_4, 2 H), 2.70 (s, H_1, 2 H), 2.90 (m, H_3, 2 H), 3.20 (s, H_5, 2 H), 4.00 (m, H_2, 2 H), 7.2–7.9 (m, Ar H, 15 H). Anal. Calcd for $C_{34}H_{37}Cl_2P_3Pd$: C, 57.04; H, 5.21. Found: C, 56.90; H, 4.97.

Chloro[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine]platinum(II) Chloride–3.5-Dichloromethane (8). The same procedure as described for the preparation of **7** was followed. From 0.47 g (1 mmol) of dichlorobis(benzonitrile)platinum(II) was obtained 0.4 g (50%) of pale yellow crystals; dec pt >320 °C. IR: ν_{PtCl} 286.5 cm^{-1}. $\Lambda_m(CH_3NO_2)$ = 68.36 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.54 (s, CH_3, 6 H), 1.65 (s, CH_3, 6 H), 2.38 (m, H_4, 2 H), 2.69 (s, H_1, 2 H), 3.0 (m, H_3, 2 H), 3.34 (s, H_5, 2 H), 4.35 (m, H_2, 2 H), 7.3–7.8 (m, Ar H, 15 H). Anal. Calcd for $C_{34}H_{37}Cl_2P_3Pt{\cdot}3.5CH_2Cl_2$: C, 40.88; H, 4.02. Found: C, 40.90; H, 3.60. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

Dibromo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]nickel(II) (9). A mixture of 1.68 g (7.7 mmol) of anhydrous nickel(II) bromide, 1.45 g (7.7 mmol) of DMPP, 1.63 g (7.7 mmol) of vinyldiphenylphosphine, and 200 mL of acetonitrile was stirred under nitrogen for 6 h. The separated red crystalline product, **9** (2.1 g, 44%), was isolated by filtration, washed with absolute ethanol, recrystallized from CH_2Cl_2/Et_2O, and vacuum-dried; mp 232–234 °C. IR: ν_{NiBr} 281.5, 288 cm^{-1}; ν_{NiP} 374, 389 cm^{-1}. $\Lambda_m(CH_3NO_2)$ = 12.01 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.35 (s, CH_3, 3 H), 1.63 (s, CH_3, 3 H), 1.95 (m, H_4, 1 H), 2.55 (m, H_3, 1 H), 2.70 (s, H_1, 1 H), 3.20 (m, H_2, 1 H), 3.53 (s, H_5, 1 H), 7.2–8.3 (m, Ar H, 15 H). Anal. Calcd for $C_{26}H_{26}Br_2NiP_2$: C, 50.45; H, 4.23. Found: C, 50.27; H, 4.22.

Bromobis[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]nickel(II) Bromide–1.5-Dichloromethane (10). To a suspension of 1.68 g (7.7 mmol) of anhydrous nickel(II) bromide in 200 mL of acetonitrile were added 2.90 g (15.4 mmol) of DMPP and 3.26 g (15.4 mmol) of vinyldiphenylphosphine. The mixture was refluxed under nitrogen for 4 h. The solution obtained was reduced in volume to 30 mL and filtered. After the solution stood at room temperature for 24 h, the brown crystals that formed were isolated by filtration, recrystallized from CH_2Cl_2/Et_2O, and vacuum-dried to yield 1.6 g (20%) of **10**, mp 224–226 °C. IR: ν_{NiBr} 280 cm^{-1}; ν_{NiP} 363, 381 cm^{-1}. $\Lambda_m(CH_3NO_2)$ = 93.90 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (s, CH_3, 6 H), 1.34 (s, CH_3, 6 H), 1.65 (m, H_4, 2 H), 2.9 (m, H_3, 2 H), 3.05 (s, H_1, 2 H), 3.30 (s, H_5, 2 H), 3.49 (m, H_2, 2 H), 6.7–7.8 (m, Ar H, 30 H). Anal. Calcd for $C_{52}H_{52}Br_2NiP_4{\cdot}1.5CH_2Cl_2$: C, 56.03; H, 4.83. Found: C, 55.86; H, 4.84. The presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy.

(C) X-ray Data Collection and Processing. Crystals of dibromo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene]nickel(II) (**9**) were obtained by slow evaporation of a CH_2Cl_2/MeOH solution at room temperature. A red 0.31 × 0.24 × 0.18 mm parallelepiped was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation. A systematic search in reciprocal space showed that crystals of **9** belong to the triclinic system. The unit cell dimensions and their standard deviations were obtained and refined at room temperature with Cu Kα radiation (λ = 1.5405 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{26}H_{26}Br_2NiP_2$, mol wt 618.97, a = 12.177 (3) Å, b = 12.448 (3) Å, c = 8.664 (2) Å, α = 100.83 (2)°, β = 99.11 (2)°, γ = 81.11 (2)°, V = 1263.0 Å^3, Z = 2, μ = 61.556 cm^{-1}, $F(000)$ = 620, space group $P\bar{1}$ assumed on the basis of a N_Z statistical test.

The vertical and horizontal spertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step scan used was $\Delta\theta = 1.0 + 0.143 \tan\theta$ with a step width of 0.05° and scan speed of 0.024° s^{-1}. A total of 3283 $\pm h, k, l$ reflections were recorded ($4° < \theta < 57°$). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SPD/PDP package[8] was used with the exception of a local data-reduction program.

Three standard reflections measured every 1 h during the entire data-collection period showed no significant trend. The raw step-scan data were converted to intensities by using the Lehmann–Larson method[9] and then corrected for Lorentz, polarization, and absorption factors, the last computed by the empirical method of Walker and Stuart[10] since face indexation was not possible (transmission factors between 0.72 and 1.24). A unique data set of 2692 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revelaed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) with isotropic temperature factors such that $B(H) = 1 + B_{eq}(C)$ Å^2 but were not refined. The full least-squares refinement converged to $R(F)$ = 0.038 and $R_w(F)$ = 0.058 ($\sigma(F^2) = (\sigma^2_{counts} + (pI)^2)$. The unit-weight observation was 1.48 for p = 0.08. A final difference map revelaed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients

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Table III. Atom Coordinates (×10^4) for $C_{52}H_{52}Cl_2P_4Ru$ (**5**)

atom	*x*	*y*	*z*
Ru	392.6 (3)	99.6 (2)	182.3 (2)
Cl1	−177.4 (10)	2949.2 (5)	2172.5 (6)
Cl2	690.0 (10)	372.2 (6)	1496.9 (6)
P1	−47.8 (10)	1060.5 (5)	2955.4 (6)
P2	2209.2 (9)	456.8 (5)	171.8 (6)
P3	1501.5 (9)	2496.9 (5)	546.3 (6)
P4	−1572.6 (10)	3070.9 (6)	163.5 (6)
C1	−1087 (4)	8140 (2)	6456 (3)
C2	−1972 (4)	8420 (3)	5933 (4)
C3	−2701 (5)	8818 (3)	6167 (4)
C4	−2549 (6)	8939 (3)	6917 (5)
C5	−1688 (6)	8669 (3)	7445 (4)
C6	−958 (4)	8266 (2)	7214 (3)
C7	−21 (4)	7700 (2)	5223 (2)
C8	86 (4)	8375 (2)	5145 (2)
C9	−495 (5)	8685 (3)	4429 (3)
C10	822 (4)	8602 (2)	5746 (2)
C11	1205 (5)	9238 (2)	5894 (3)
C12	1264 (4)	8103 (2)	6325 (2)
C13	2008 (4)	7629 (2)	6015 (2)
C14	1207 (4)	7440 (2)	5236 (2)
C15	3230 (3)	7419 (2)	7499 (2)
C16	2889 (4)	7764 (2)	8032 (2)
C17	3680 (4)	8115 (2)	8543 (2)
C18	4824 (4)	8129 (2)	8528 (3)
C19	5169 (4)	7794 (2)	8007 (3)
C20	4384 (4)	7438 (2)	7496 (3)
C21	3102 (3)	6341 (2)	6644 (2)
C22	3080 (3)	5975 (2)	7376 (2)
C23	3686 (4)	5377 (2)	7351 (3)
C24	4889 (4)	5278 (2)	7836 (3)
C25	3091 (4)	5029 (2)	6803 (3)
C26	3401 (5)	4427 (2)	6532 (4)
C27	2022 (4)	5367 (2)	6356 (3)
C28	2530 (4)	5907 (2)	5993 (2)
C29	1252 (4)	5217 (2)	7777 (2)
C30	1002 (4)	4618 (2)	7590 (3)
C31	717 (5)	4226 (3)	8110 (3)
C32	698 (4)	4427 (3)	8809 (3)
C33	936 (5)	5016 (3)	8998 (3)
C34	1220 (4)	5412 (2)	8468 (3)
C35	−2136 (4)	5600 (2)	6347 (2)
C36	−1421 (4)	5155 (2)	6204 (3)
C37	−1863 (6)	4598 (3)	5925 (3)
C38	−3026 (7)	4479 (3)	5812 (3)
C39	−3727 (5)	4917 (3)	5954 (3)
C40	−3309 (5)	5478 (3)	6222 (3)
C41	−2738 (4)	6813 (2)	6111 (3)
C42	−2762 (5)	6844 (3)	5354 (3)
C43	−3608 (6)	7169 (3)	4865 (4)
C44	−4428 (5)	7473 (4)	5111 (4)
C45	−4400 (5)	7457 (4)	5851 (4)
C46	−3558 (5)	7132 (3)	6362 (3)
C47	−1902 (4)	6334 (2)	7644 (2)
C48	−1952 (4)	5796 (2)	8010 (3)
C49	−2121 (5)	5790 (3)	8731 (3)
C50	−2250 (5)	6308 (3)	9093 (3)
C51	−2167 (5)	6853 (3)	8745 (3)
C52	−1981 (4)	6867 (2)	8030 (3)

Table IV. Selected Bond Distances (Å) for Complex **5**

Ru–P1	2.320 (1)	C8–C10	1.322 (6)
Ru–P2	2.308 (1)	C23–C25	1.321 (6)
Ru–P3	2.350 (1)	C10–C12	1.529 (6)
Ru–P4	2.429 (1)	C22–C23	1.510 (6)
Ru–Cl1	2.470 (1)	C17–C13	1.566 (6)
Ru–Cl2	2.420 (1)	C21–C22	1.571 (6)
P1–C7	1.866 (4)	C13–C14	1.562 (5)
P3–C27	1.863 (5)	C21–C28	1.549 (6)
P2–C21	1.849 (4)	C7–C14	1.566 (6)
P2–C13	1.859 (4)	C27–C28	1.559 (7)
P2–C15	1.855 (4)	C8–C9	1.487 (6)
P3–C29	1.823 (5)	C10–C11	1.481 (6)
P1–C7	1.866 (4)	C25–C26	1.496 (7)
C7–C8	1.508 (6)	C23–C24	1.502 (6)
C25–C27	1.527 (6)		

Table V. Selected Angles (deg) for Complex **5**

Cl1–Ru–Cl2	168.7	Ru–P4–C41	115.4 (2)
Cl2–Ru–P1	97.5	Ru–P4–C47	114.8 (1)
Cl2–Ru–P2	91.0	Ru–P4–C35	121.0 (2)
Cl1–Ru–P3	87.5	C7–P1–C12	79.1 (2)
Cl1–Ru–P1	89.4	C22–P3–C27	79.5 (2)
Cl1–Ru–P2	99.1	P1–C7–C14	101.2 (2)
Cl2–Ru–P3	89.5	C7–C8–C9	120.4 (4)
Cl2–Ru–P4	89.1	C9–C8–C10	128.7 (4)
Cl1–Ru–P4	97.3	C8–C10–C12	110.3 (4)
P1–Ru–P3	157.5	P1–C12–C10	102.5 (3)
P3–Ru–P4	104.3	C10–C12–C13	112.7 (3)
P1–Ru–P4	97.3	C8–C7–C14	105.3 (4)
P1–Ru–P2	78.7	P1–C7–C8	102.5 (3)
P2–Ru–P3	79.8	C7–C8–C10	110.5 (4)
P2–Ru–P4	175.9	C8–C10–C11	128.4 (4)
Ru–P1–C7	115.4 (1)	C11–C10–C12	121.3 (4)
Ru–P1–C12	112.9 (1)	P1–C12–C13	96.7 (3)
Ru–P1–C1	126.4 (2)	C12–C13–C14	103.7 (3)
Ru–P2–C15	126.7 (2)	P2–C13–C12	102.9 (3)
Ru–P2–C21	106.7 (1)	P2–C13–C14	112.7 (3)
Ru–P2–C13	107.4 (1)	P2–C21–C28	113.9 (3)
Ru–P3–C27	117.2 (1)	P2–C15–C16	123.8 (3)
Ru–P3–C29	125.1 (2)	P2–C21–C22	102.1 (3)
Ru–P3–C22	109.7 (1)		

come from ref 11 and 12, respectively.

Pale brown blocklike crystals of *mer*-dichloro(triphenylphosphine)[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine]ruthenium(II) (**5**) were obtained by slow evaporation of an ether solution at room temperature. Intensity data were taken with a Syntex $P2_1$ four-circle diffractometer. The unit cell dimensions and their standard deviations were obtained at room temperature with Mo Kα radiation (λ = 0.71069 Å) by using 15 reflections ($25 < 2\theta < 27°$). Final results: $C_{52}H_{52}Cl_2P_4Ru$, mol wt 972.89, a = 11.916 (3) Å, b = 22.074 (7) Å, c = 18.309 (4) Å, β = 104.43 (2)°, V = 4664 (2) Å^3, Z = 4, μ = 6.14 cm^{-1}, $F(000)$ = 2008. Systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) indicated space group $P2_1/n$.

A data set of 5033 reflections having $I > 3\sigma(I)$, which was used for determining and refining the structure, was corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method (range of transmission factors 0.88–0.93). Three standard reflections were monitored every 200 reflections and showed a slight decrease (3% total); the data were scaled to correct for this. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were inserted at calculated positions (C–H = 0.95 Å) with fixed isotropic temperature factors and were not refined, except for the methyl groups, which were treated as rigid bodies. Final refinement was by least-squares methods in cascaded large blocks. A weighting scheme of the form $1/(\sigma^2(F) + gF^2)$ with g = 0.0004 was used and shown to be satisfactory by weight analysis. Final R = 0.038 and R_w = 0.038. Computing was with the SHELXTL system[13] on a Data General DG30 computer. Scattering factors and anomalous dispersion factors were taken from ref 11.

Final atom coordinates for **5** and **9** are given in Tables III and VI, respectively.

Results

(A) Reaction of DMPP with Divinylphenylphosphine and Nickel(II) Bromide. These reagents react in acetonitrile to produce two compounds, **1** and **2**, according to reaction 2.

Both **1** and **2** exhibit low-field resonances in their $^{31}P\{^1H\}$ NMR spectra (Table I) that are typical of phosphorus contained in a 7-phosphabicyclo[2.2.1]hept-5-ene.[2,3,14–18] Thus, it may be

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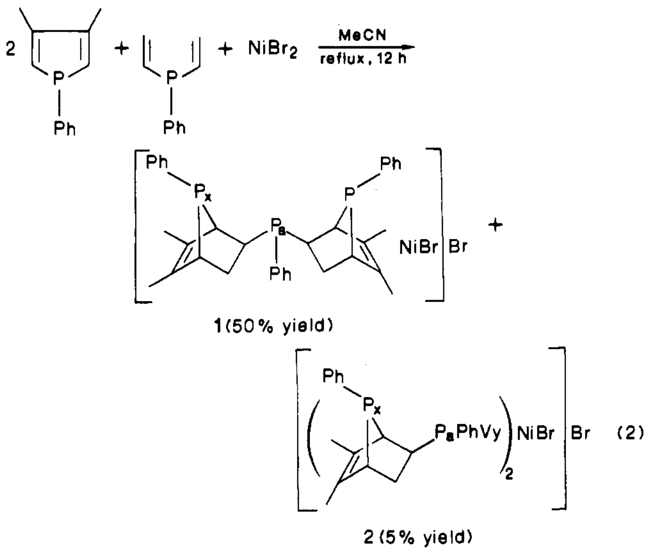
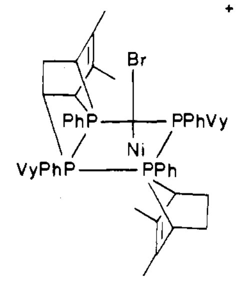


1(50% yield)

2(5% yield)

concluded that both products are Ni(II) phosphine complexes derived from [4 + 2] Diels–Alder cycloadditions of a phosphole with a vinylphosphine.[2,3,18]

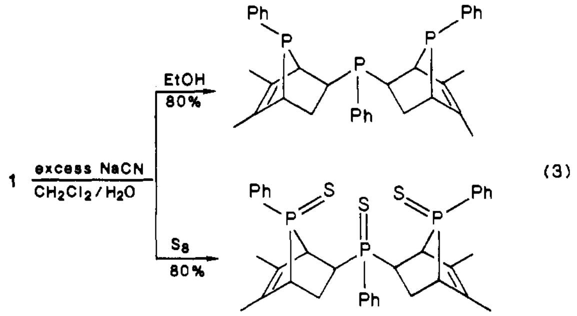
One of them, **2**, gives a first-order A_2X_2 $^{31}P\{^1H\}$ NMR spectrum, indicating that the Ni(II) coordination sphere contains two trans-oriented unsymmetrical bidentate phosphines. Since this complex behaves as a 1:1 electrolyte in nitromethane, it is concluded that a pentacoordinate cation is present in solution. By a comparison of the electronic spectrum of this compound (400 nm (sh), ϵ = 3062 mol^{-1} cm^{-1}; 342 nm, ϵ = 9494 mol^{-1} cm^{-1}) with the spectra of some low-spin complexes with the $[NiP_4Br]^+$ chromophore,[19-21] it may be assumed that **2** has square-pyramidal geometry:



An inspection of the electronic and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, the last being an AX_2 type, shows that the major product of reaction 2, **1**, is the diamagnetic four-coordinate Ni(II) complex of a new class of triphosphine: phenylbis(7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine, which is coordinated through two 7-phospha phosphorus atoms and a phosphino phosphorus atom as a tridentate ligand. The complex is a 1:1 electrolyte in nitromethane and exhibits one symmetric electronic absorption band in the visible region of the spectrum (434 nm, ϵ = 4350 mol^{-1} cm^{-1}), consistent with a four-coordinate planar structure. Complexes **1** and **2** were also obtained as the only products, but in much lower yield, by reactions in which the molar ratios of the reactants were 1:1:1 and 2:2:1, respectively.

The triphosphine ligand may be liberated from nickel by using sodium cyanide in a two-phase (CH_2Cl_2/H_2O) system under nitrogen (reaction 3), and in contrast to the case for 2-phosphino-7-phosphabicyclo[2.2.1]hept-5-enes[2,3] the compound can be isolated in pure form as a colorless solid. Its trisulfide is readily formed by reaction with sulfur.

The triphosphine may be transferred to other metals following its displacement from nickel. Thus, reaction of a CH_2Cl_2 solution of the liberated triphosphine, L, with $(Ph_3P)_3RuCl_2$, in a 1:1 molar



ratio, produces only one isomer (**5**), which corresponds to the $LRu(PPh_3)Cl_2$ stoichiometry and exhibits only one ruthenium–chlorine stretching frequency at 325 cm^{-1}. This indicates that the obtained isomer has chlorides in mutually trans positions as well as that triphenylphosphine is trans to the central phosphorus of a meridionally coordinated triphosphine ligand, L. This is consistent with the $^{31}P\{^1H\}$ NMR spectrum of **5** (Figure 1). This spectrum, as expected, contains three different resonances (2:1:1 integrated intensity ratio) corresponding to three different types of phosphorus atoms. The 7-phospha phosphorus resonance appears as a low-field doublet of doublets due to coupling with the phosphino and PPh_3 phosphorus nuclei, with values for $^2J_{PP}$ that are typical for cis coupling constants.[22] The phosphino phosphorus resonance appears as a doublet of triplets with a large $^2J_{PP}$ coupling (~280 Hz) to the triphenylphosphine phosphorus and a smaller coupling to the 7-phospha phosphorus atoms (~42 Hz). The same is true for the triphenylphosphine phosphorus resonance except that the $^2J_{PP}$ value arising from coupling to the 7-phospha phosphorus atoms is smaller (~25 Hz).

The reaction of L with $(Ph_3P)_3RuCl_2$ in a 2:1 molar ratio produced L_2RuCl_2 (**6**). From the facts that **6** is a nonelectrolyte in nitromethane and exhibits only one ruthenium–chlorine stretching frequency in the expected region (ν_{RuCl} = 322 cm^{-1}), it may be concluded that at least one triphosphine, L, is not coordinated as a tridentate ligand. From its $^{31}P\{^1H\}$ NMR spectrum (Figure 2) the conclusion can be drawn that in this compound both triphosphines are coordinated to Ru(II) as bidentate ligands with the central phosphino phosphorus atoms in mutually cis positions and with two 7-phospha phosphorus atoms as "dangling arms". The resonance for the uncoordinated 7-phospha phosphorus nuclei appears as a singlet with a chemical shift that is very close to that of the free ligand (89.5 vs 88.8 ppm, respectively). A ^{31}P chemical shift correlated (COSY) spectrum shows that these phosphorus nuclei are not coupled with the coordinated phosphorus nuclei. The four phosphorus nuclei within the coordination sphere give rise to a second-order $[AX]_2$ spin system, establishing the cis orientation of the two unsymmetrical bidentate ligands. A trans orientation would give rise to a first order A_2X_2 spin system.

The reactions of CH_2Cl_2 solutions of the liberated ligand L with $(PhCN)_2MCl_2$ (M = Pd and Pt) produce $LPdCl_2$ and $[LPtCl]^+Cl^-$, respectively. In both of these complexes the ligand is tridentate. The molar conductances of these two complexes support the structures as written: pentacoordinate nonelectrolyte (M = Pd) and four-coordinate square-planar 1:1 electrolyte (M = Pt). The ^1H and $^{13}C\{^1H\}$ NMR spectra of the palladium complex are broad, suggesting that in $CDCl_3$ solution an equilibrium between $LPdCl_2$ and $[LPdCl]^+Cl^-$ exists.

(B) Reaction of DMPP with Vinyldiphenylphosphine and Nickel(II) Bromide. These compounds react in acetonitrile to produce two products, **9** and **10**, according to reactions 4a and 4b, both involving intramolecular [4 + 2] Diels–Alder cycloadditions. The ratio of the yields of these two products depends upon the reaction stoichiometry and temperature. When the reactants were mixed in a 1:1:1 stoichiometric ratio in acetonitrile at room temperature, complex **9** was formed as the major product. In contrast, complex **10** was the only isolated product when the

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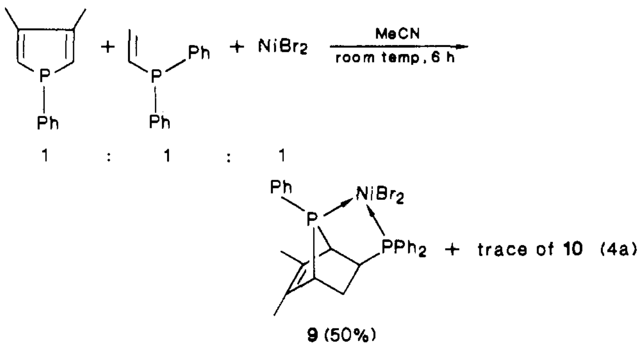

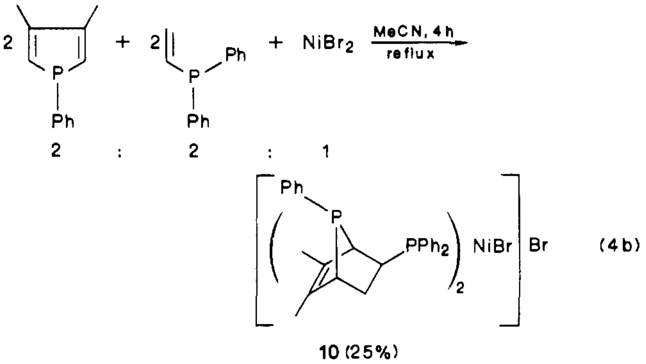

reaction was carried out in refluxing acetonitrile with a 2:2:1 molar ratio of the reactants. Complex **9** is a nonelectrolyte in nitromethane and exhibits one symmetrical band in the visible region of its electronic absorption spectrum (478 nm, ϵ = 1500 mol^{-1} cm^{-1}), which is consistent with a square-planar four-coordinate structure.

Taking into account the facts that **10** is a 1:1 electrolyte in nitromethane as well as that its $^{31}P\{^1H\}$ NMR spectrum is similar to that of complex **2** (A_2X_2 spin system), we assume that **10** also has a square-pyramidal geometry. Its electronic absorption spectrum (387 nm, ϵ = 8180 mol^{-1} cm^{-4}) is consistent with this assumption.

Discussion

A central feature of these intramolecular [4 + 2] Diels–Alder cycloaddition reactions is their high diastereoselectivity. As can be inferred from their $^{31}P\{^1H\}$ NMR spectra, each complex is formed as a single diastereomer with the syn-exo stereochemistry for the 7-phosphanorbornene skeleton.[23] This is confirmed by the crystal structures of **5** and **9**.

Crystal Structure of Complex 5. This structure analysis was undertaken not only to confirm the assumed structure but also to characterize the new triphosphine ligand system since suitable single crystals of **1** could not be obtained. The crystal structure of **5** (Figure 3) consists of discrete molecules linked by van der Waals interactions. Selected bond lengths and angles are listed in Tables IV and V, respectively.

The geometry of the Ru(II) coordination sphere is distorted octahedral. The triphosphine ligand is tridentate, coordinating through two 7-phospha phosphorus atoms and a phosphino phosphorus atom. It forms two fused equatorially disposed five-membered chelate rings. Two chlorine atoms are coordinated in mutually trans positions. The sixth coordination position is occupied by triphenylphosphine. The triphosphine has a noncrystallographic mirror plane passing through P2 and thus has the meso, not the *dl*, structure. It creates a "fence" surrounding the ruthenium atom with Cl2 surrounded by phenyl rings and with Cl1 on the fence side of the ligand.

As can be seen from the data in Table IV, the two RuP(bridging) distances are slightly different (Ru–P1 = 2.320 (1) Å; Ru–P3 = 2.350 (1) Å) and are longer than Ru–P(exocyclic) (Ru–P2 = 2.308 (1) Å). The angles made by the bridgehead carbons and the 7-phospha phosphorus are small (79.5 (2) and 79.1 (2)°). These C–P–C angles are similar to the analogous angles found in 7-phosphanorbornene complexes of molybdenum (79.4 (2)°)[14] and chromium 79.0 (1)°).[15] On the other hand, the phosphanorbornene rings in this molecule are more strained than the corresponding rings in (2-phosphino-7-phosphanorbornene)-palladium(II) complexes, which have[2,3] C–P–C angles of 82.5 and 82.3°. The C=C double bonds are well localized with a mean bond length of 1.321 (5) Å.

Table VI. Atom Coordinates and Their Estimated Standard Deviations for $NiC_{26}H_{26}Br_2P_2$ (**9**)

atom	*x*	*y*	*z*
Ni	0.15722 (6)	0.77044 (5)	0.48098 (8)
Br1	0.32688 (5)	0.77498 (5)	0.65141 (7)
Br2	0.04535 (5)	0.81718 (5)	0.68336 (6)
P1	0.00620 (9)	0.75598 (9)	0.3199 (1)
P2	0.23522 (9)	0.75139 (9)	0.2674 (1)
C1	0.0321 (4)	0.6992 (3)	0.1146 (5)
C2	−0.0790 (4)	0.7322 (4)	0.0192 (5)
C3	−0.1240 (4)	0.8300 (4)	0.0846 (6)
C4	−0.0482 (4)	0.8795 (4)	0.2290 (6)
C5	−0.1200 (5)	0.6611 (5)	−0.1291 (7)
C6	−0.2307 (5)	0.9005 (6)	0.0261 (9)
C7	0.1190 (3)	0.7789 (3)	0.1110 (5)
C8	0.0588 (4)	0.8958 (4)	0.1640 (6)
C9	−0.1059 (4)	0.6897 (4)	0.3601 (6)
C10	−0.2094 (5)	0.7489 (5)	0.3917 (8)
C11	−0.2910 (5)	0.6198 (7)	0.4195 (9)
C12	−0.2714 (5)	0.5830 (6)	0.4170 (9)
C13	−0.1725 (5)	0.5237 (4)	0.3848 (8)
C14	−0.0871 (5)	0.5788 (4)	0.3571 (7)
C15	0.3064 (4)	0.6143 (3)	0.2032 (5)
C16	0.2932 (5)	0.5626 (4)	0.0488 (6)
C17	0.3521 (5)	0.4581 (5)	0.0068 (7)
C18	0.4203 (4)	0.4083 (4)	0.1195 (8)
C19	0.4306 (5)	0.4583 (5)	0.2693 (8)
C20	0.3735 (5)	0.5607 (4)	0.3130 (7)
C21	0.3326 (4)	0.8460 (4)	0.2589 (5)
C22	0.3976 (4)	0.8239 (4)	0.1403 (7)
C23	0.4688 (5)	0.8959 (5)	0.1253 (9)
C24	0.4745 (5)	0.9909 (5)	0.2277 (8)
C25	0.4080 (6)	1.0152 (5)	0.3459 (8)
C26	0.3369 (5)	0.9438 (4)	0.3606 (7)

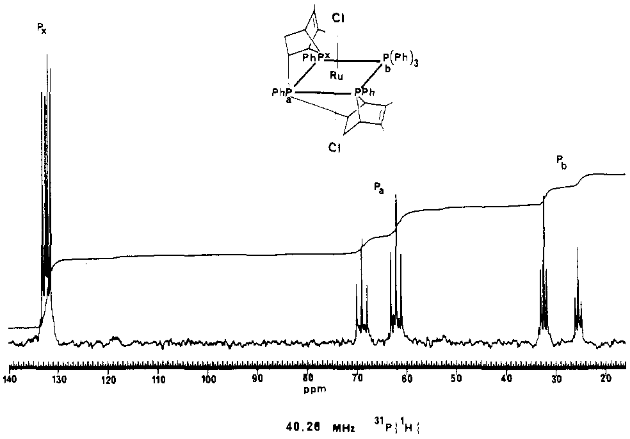

Figure 1. 40.26-MHz $^{31}P\{^1H\}$ NMR spectrum of complex **5** in $CDCl_3$ at 300 K.

The two Ru–Cl bond lengths of 2.470 (1) and 2.420 (1) Å are in the normal range. The Ru–P(Ph_3P) bond (2.429 (1) Å) is, as expected, the longest Ru–P bond. The bond distances and angles in the triphosphine ligand are unexceptional.

Crystal Structure of Complex 9. The structure of **9** (Figure 4) also consists of discrete molecules linked only by van der Waals interactions. The bond lengths and angles are listed in Tables VII and VIII, respectively.

The coordination polyhedron of the Ni atom is a nearly square plane with two cis bromine atoms, and the two phosphorus atoms of the diphosphine ligand also mutually cis. The two phosphorus atoms, P1 and P2, of the ligand are out of the Ni–Br1–Br2 mean plane by 0.111 (1) and 0.311 (1) Å, respectively. Of the carbon

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(23) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

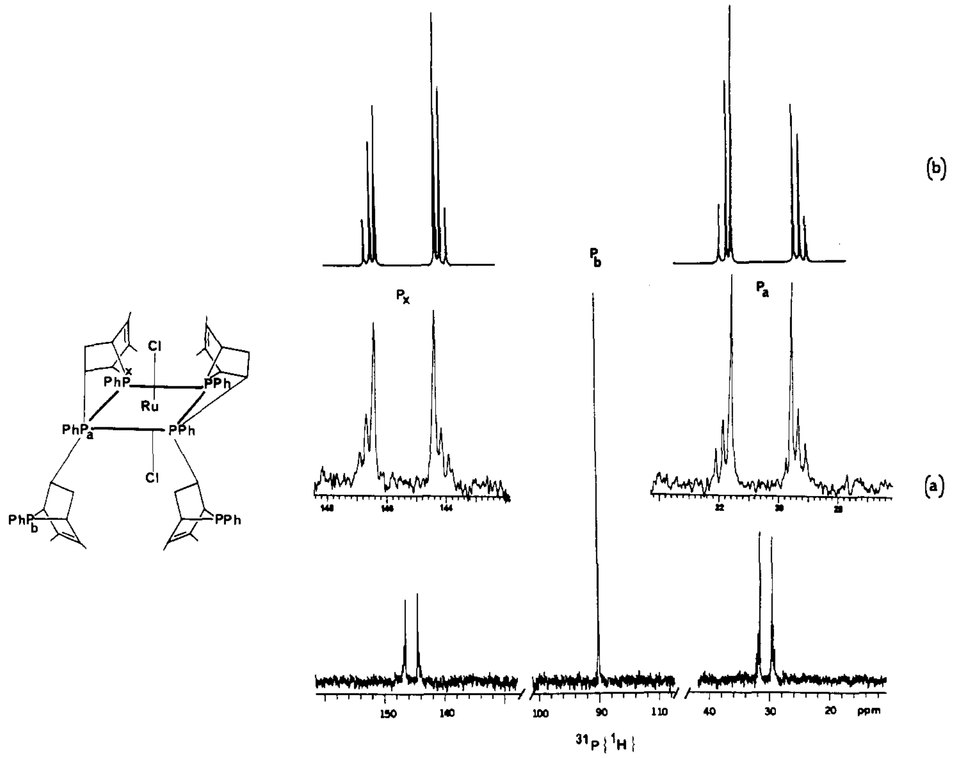


Figure 2. (a) 121.48-MHz $^{31}P\{^1H\}$ NMR spectrum of complex **6** in $CDCl_3$ at 300 K. (b) Simulation from data given in Table I. This spectrum is field independent, being the same at 32.2, 40.26, and 121.48 MHz.

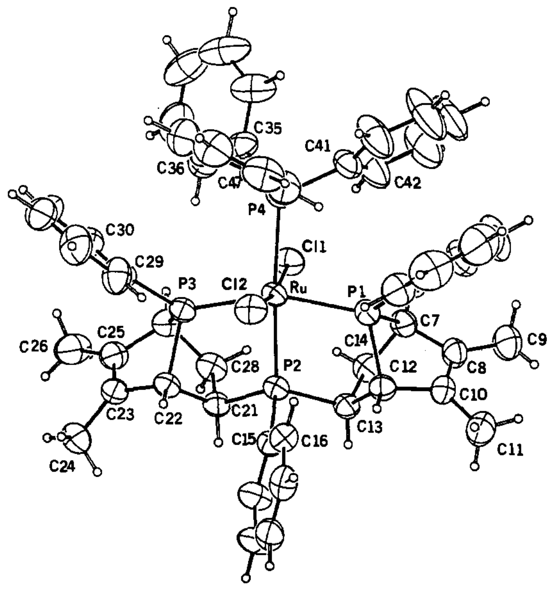


Figure 3. ORTEP plot of the structure of *mer*-dichloro(triphenylphosphine)[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine]ruthenium(II) (**5**) showing the atom-labeling scheme (50% probability ellipsoids).

Table VII. Selected Bond Distances (Å) for Complex **9**

Ni-Br1	2.3433 (8)	P2-C21	1.814 (4)
Ni-Br2	2.3230 (8)	C1-C2	1.511 (5)
Ni-P1	2.135 (1)	C1-C7	1.567 (5)
Ni-P2	2.169 (1)	C2-C3	1.317 (6)
P1-C1	1.843 (4)	C2-C5	1.479 (7)
P1-C4	1.843 (4)	C3-C4	1.522 (7)
P1-C9	1.809 (5)	C3-C6	1.524 (7)
P2-C7	1.837 (4)	C4-C8	1.555 (6)
P2-C15	1.821 (4)	C7-C8	1.546 (5)

atoms, C1 is on one side and C4, C7 and C8 are on the other side of this plane.

The two Ni-Br bond lengths of 2.3433 (8) and 2.3230 (8) Å are significantly different, the longer being trans to the 7-phospha phosphorus atom. The phosphorus donors have quite different donor abilities (Ni-P1 = 2.135 (1) Å; Ni-P2 = 2.169 (1) Å). The C1-C4 moiety of the phospholene ring is planar within experi-

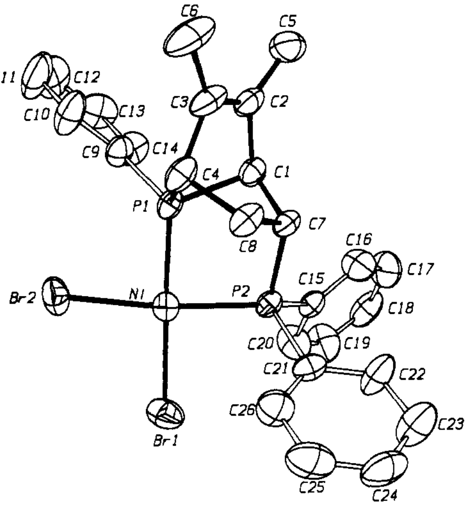


Figure 4. ORTEP plot of the structure of dibromo[2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]nickel(II) (**9**) showing the atom-labeling scheme (50% probability ellipsoids).

Table VIII. Selected Angles (deg) for Complex **9**

Br1-Ni-Br2	94.79 (3)	C1-C2-C3	109.9 (4)
Br1-Ni-P1	176.45 (5)	C1-C2-C5	120.9 (4)
Br1-Ni-P2	94.31 (4)	C3-C2-C5	129.1 (4)
Br2-Ni-P1	87.15 (4)	C2-C3-C4	111.9 (4)
Br2-Ni-P2	167.72 (4)	C2-C3-C6	129.2 (5)
P1-Ni-P2	84.22 (4)	C4-C3-C6	118.5 (6)
C1-P1-C4	81.4 (2)	P1-C4-C3	100.6 (3)
C1-P1-C9	107.2 (2)	P1-C4-C8	99.6 (2)
C4-P1-C9	111.7 (2)	C3-C4-C8	105.1 (4)
C7-P2-C15	107.0 (2)	P2-C7-C1	106.2 (2)
C7-P2-C21	104.4 (2)	P2-C7-C8	107.3 (3)
P1-C1-C2	102.7 (3)	C1-C7-C8	104.8 (3)
P1-C1-C7	95.0 (2)	C4-C8-C7	106.3 (4)
C2-C1-C7	111.0 (4)		

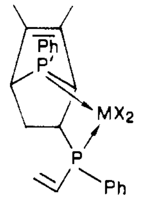
Table IX. Redox Characteristics of the Synthesized Complexes[a]

compd	M(II)/M(III) $E_{1/2}$ (ΔE_p)	M(III)/M(IV) E_{p_a}	M(II)/M(I) E_{p_c}
1	0.21 (80)		-1.52
2	0.38[b]		-1.79
5	0.09 (65)	0.64	
6	-0.03 (65)	0.61	
7			-1.82
8	1.01[b]		-1.79
9	0.56[b]		-1.70
10	0.69[b]		-1.39

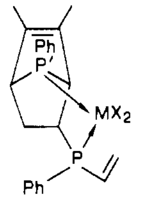
[a] In CH_2Cl_2 containing 0.1 M TBAP at 25 °C; v = 200 mV s^{-1}; E values in units of volts vs Fc^+/Fc; ΔE values in units of millivolts. [b] E_{p_a} only.

mental error, and its mean plane makes a dihedral angle of 127.9 (2)° with the P1–C1–C4 mean plane. The C=C double bond of the phosphole ring is, as expected, localized between C2 and C3. The two P–C intracyclic bond lengths are equivalent, with a mean value of 1.843 (3) Å, and the C1–P1–C4 bond angle (81.4 (2)°) is smaller than this angle in the $PdCl_2$ complex (82.5°).[2] Thus, all geometrical data of the 2-phosphino-7-phosphanorbornene moiety coordinated to Ni(II) are in the ranges of those found in related compounds.

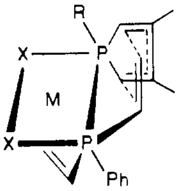
Reaction Mechanism for the Diastereoselective Formation of the [4 + 2] Diels–Alder Products. Detailed analysis of the NMR spectral data for these compounds shows that a single diastereomer was formed in each case. We have previously observed[2,3] a similar result for intramolecular [4 + 2] Diels–Alder cycloadditions within the coordination spheres of palladium(II) and platinum(II). We then argued[2,3] that this diastereoselectivity is caused by steric factors within the coordination sphere. Cycloaddition of DMPP with divinylphenylphosphine coordinated to palladium(II) and platinum(II) in mutually cis positions led to the formation of diastereomers A and B in an approximately 20:1 ratio. This was suggested to occur by way of the transition state



A



B



The smaller of the two substituents on phosphorus (Vy) occupies the more sterically congested site near the coordination plane. Cycloaddition from this conformer then led to diastereomer A and then, when M = Ni(II), to formation of a compound structurally analogous to compound **9**. With both palladium(II) and platinum(II) an additional cycloaddition with the remaining vinyl group cannot be effected under any conditions explored. However, nickel(II) has a greater propensity than either palladium(II) or platinum(II) toward pentacoordination, and as a result coordination of a second molecule of DMPP cis to the vinylphosphino group occurs, leading to the triphosphine complex **1** via a second sequential [4 + 2] Diels–Alder cycloaddition. These two sequential cycloadditions are highly stereoselective, as only the meso triphosphine is formed. None of the corresponding *dl* triphosphine was formed, even though it can be formed[24] via similar reactions within the coordination sphere of Mo(0).

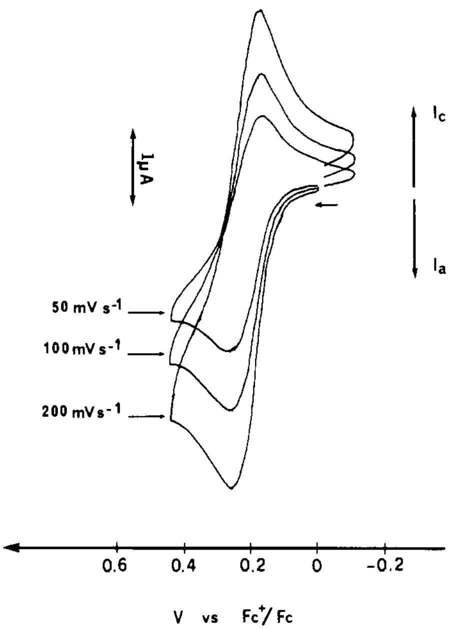


Figure 5. Cyclic voltammograms of complex **1** in CH_2Cl_2 containing 0.1 M TBAP at 25 °C showing the reversible Ni(II)/Ni(III) process.

Electrochemistry. The cyclic voltammograms of all the complexes synthesized were recorded in dichloromethane with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Pertinent data are summarized in Table IX. All the Ni(II) complexes are irreversibly reduced to Ni(I) and oxidized to Ni(II) species. The only exception is complex **1**, the complex of the triphosphine for which the Ni(II) $\rightleftarrows$ Ni(III) + e^- process is chemically reversible ($i_{p_c}/i_{p_a} \approx 1$) and approaches electrochemical reversibility (ΔE_p = 80 mV) (Figure 5).

Both ruthenium complexes with the triphosphine ligand show a reversible Ru(II)/Ru(III) process and an irreversible Ru(III)/Ru(IV) oxidation. No reduction of Ru(II) was seen in the potential range accessible with the electrode/electrolyte/solvent system used. The Ru(II)/Ru(III) potentials are near those observed for other *trans*-P_4RuCl_2 chromophores,[25] suggesting that the triphosphine does not impart any unusual stability to Ru(III), though complex **6** is easier to oxidize than any of the other compounds.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No. **1**, 121935-47-5; [**1**]Br, 121935-34-0; $\mathbf{1}^{2+}$, 121935-39-5; **2**, 121935-48-6; [**2**]Br, 121935-35-1; $\mathbf{2}^{2+}$, 121935-40-8; **3**, 121920-79-4; **4**, 121920-80-7; **5**, 121962-48-9; $\mathbf{5}^{+}$, 121935-41-9; $\mathbf{5}^{2+}$, 121935-45-3; **6**, 121935-36-2; $\mathbf{6}^{+}$, 121962-49-0; $\mathbf{6}^{2+}$, 121935-46-4; [**7**]Cl, 121935-52-2; **7**, 121935-53-3; **8**, 121962-50-3; [**8**]Cl, 121935-51-1; $\mathbf{8}^{2+}$, 121935-42-0; **9**, 121935-37-3; $\mathbf{9}^{+}$, 121935-43-1; $\mathbf{9}^{-}$, 121935-49-7; **10**, 121935-50-0; [**10**]Br, 121935-38-4; $\mathbf{10}^{2+}$, 121935-44-2; DMPP, 30540-36-4; $(Ph_3P)_3RuCl_2$, 34076-51-2; $(PhCN)_2PdCl_2$, 14220-64-5; $(PhCN)_2PtCl_2$, 14873-63-3; divinylphenylphosphine, 26681-88-9; vinyldiphenylphosphine, 2155-96-6.

Supplementary Material Available: For the two structure studies, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (11 pages); listings of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

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(24) Affandi, S. Ph.D. Dissertation, University of Nevada, Reno, NV, 1988.

(25) Under these same conditions $E_{1/2}$ values for the Ru(II)/Ru(III) oxidations were as follows: *trans*-$Ru(DPPM)_2Cl_2$, 0.03 V; *trans*-$Ru(dpple)_2Cl_2$,[26] 0.02 V; *trans*-$(DBP)_4RuCl_2$,[27] 0.22 V; *trans*-$(DMPP)_4RuCl_2$,[27] 0.05 V). DPPM = bis(diphenylphosphino)methane; dpple = 2,2'-bis(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole); DBP = 1-phenyldibenzophosphole; DMPP = 1-phenyl-3,4-dimethylphosphole.

(26) Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.* **1985**, *24*, 4141.

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