Inorg. Chem. **1994**, *33*, 4319−4326

Synthesis, Characterization, and Reactions of [Rh(η^1-DMPP)(μ-σ, η^4-DMPP)(CO)]$_2$(BF$_4$)$_2$ and [Rh(η^1-DMPP)(μ-σ, η^4-DMPP)Cl]$_2$

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Received December 3, 1993[⊗]

trans-(DMPP)$_2$Rh(CO)Cl (DMPP = 1-phenyl-3,4-dimethylphosphole) reacts with AgBF$_4$ to form [Rh(η^1-DMPP)(μ-σ, η^4-DMPP)(CO)]$_2$ (BF$_4$)$_2$, **1**. [(COE)$_2$RhCl]$_2$ (COE = cyclooctene) reacts with DMPP to form [Rh(η^1-DMPP)(μ-σ, η^4-DMPP) Cl]$_2$, **2**. In both **1** and **2** the phospholes are bound to rhodium(I) as 2- and [4 + 2]-electron donors. The 2-electron donor is bound through phosphorus only and the [4 + 2] donor is bound through its diene system to one rhodium and through phosphorus to a second rhodium such that each rhodium atom is pentacoordinate. Substitution of the chloride in **2** by N$_3^-$, OH$^-$, and DMPP (the latter in the presence of AgBF$_4$) produces **3**, **4**, and **5**. Reaction of **2** with diphenylvinylphosphine and 2-vinylpyridine in the presence of AgBF$_4$ produces the [4 + 2] Diels−Alder adducts **6** and **7**, respectively. New complexes were characterized by elemental analyses, infrared and ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{31}P{^{1}H,^{31}P(sel)} and in some cases by ^{1}H{^{31}P} nuclear magnetic resonance spectroscopy. The structure of **7**, [Rh(2-pyridyl-5,6-dimethyl-7-phosphabicyclo[2.2.1]hept-5-ene)(μ-σ, η^4-1-phenyl-3,4-dimethylphosphole]$_2$(BF$_4$)$_2$ was confirmed by X-ray crystallography. It crystallized in the monoclinic $P2_1/c$ space group in a unit cell with the following dimensions: $a = 11.460(3)$ Å, $b = 20.088(6)$ Å, $c = 16.002(4)$ Å, $\beta = 109.46(2)°$, ϱ(calcd) = 1.519 g cm^{-3}, $Z = 2$. Refinement converged to $R(F) = 0.033$ for 4907 independent observed ($I \geq 3\sigma(I)$) reflections. The dirhodium cation is centrosymmetric with considerable differences in the three Rh−P distances (RhP1 = 2.8336 (9) Å, RhP1′ = 2.3173 (9) Å, and RhP2 = 2.2690 (9) Å). These distances do not correlate with the relative magnitudes of the rhodium−phosphorus coupling constants (J(RhP1) = −13.86 Hz, ^1J(RhP1′) = 172.87 Hz, and ^1J(RhP2) = 119.96 Hz. The short P1···P1′ separation (3.352(9) Å) gives rise to a large through-space P···P coupling of 243.93 Hz.

Introduction

Since their discovery, phospholes have been extensively studied as a result of their unusual electronic properties.[1−15] Phospholes exhibit a lower basicity than their phosphine counterparts[1−4] and act as mild reducing agents.[1] Additionally, when coordinated to transition metals, 1-phenyl-3,4-dimethylphosphole (DMPP) can undergo [4 + 2] cycloaddition reactions with a variety of dienophiles to produce conformationally rigid chiral bidentate ligands.[13] These reactions are highly diastereoselective and generally do not occur when DMPP is not coordinated to a transition metal. In the few instances where Diels−Alder cycloaddition does occur in the absence of a metal, the bridging phosphorus eliminates readily to provide a benzenoid ring system.[7]

In the first reactions that were done within our research group, both the phosphole and the dienophile were coordinated to the transition metals Pd or Pt.[16,17] The cycloaddition occurred after ligand redistribution placed the phosphole and vinyl donor ligand in close proximity to each other (reaction 1). Similar reactions have also been reported with DMPP compounds of Ni(II),[18] Fe(II),[19] Ru(II),[20−22] and Mo(0).[23]

Another reaction type that was studied by our research group involved silver induced halide abstraction from *cis*-(DMPP)$_2$MX$_2$

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[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

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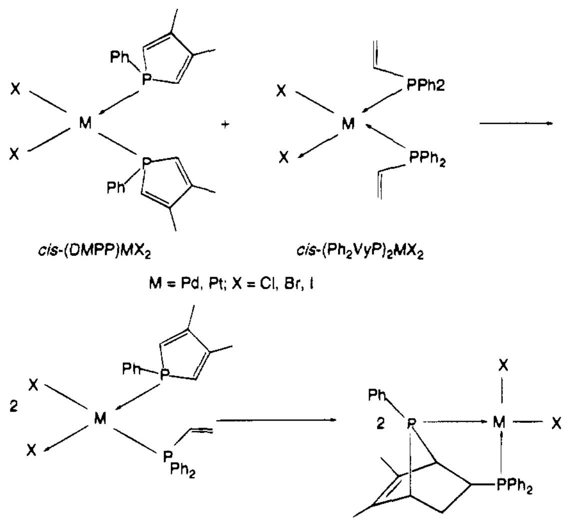
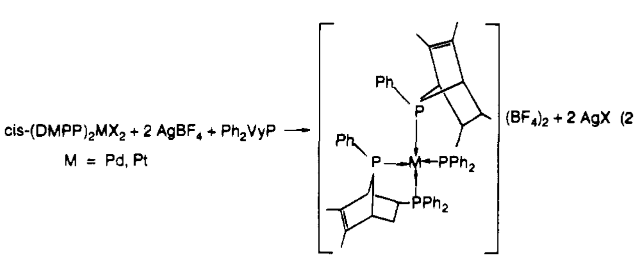


(1)

followed by addition of the desired dienophile (Reaction 2). In these reactions, bis(Diels–Alder products) were obtained[24] (reaction 2).



(2)

Since Rh(I) is isoelectronic with Pd(II), it was believed that Rh(I)–DMPP complexes would undergo ligand redistribution reactions similar to those demonstrated by the Pd and Pt complexes. The ability of Rh(I) to readily undergo both phosphine and halide exchange is well recognized.[25] Therefore, we felt that Rh(I) complexes of DMPP should easily undergo Diels–Alder cycloadditions with various dienophiles, providing a useful method of synthesizing chiral Rh(I) complexes that could be used in the study of asymmetric catalysis. Although we have obtained Diels–Alder adducts on Rh(I) by direct synthesis, the route was not as straightforward as expected and a novel Rh(I) dimer structure was formed and its chemistry investigated.

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. Solvents were dried by standard procedures and stored over Linde type 4-Å molecular sieves. All reactions were conducted under a dry nitrogen atmosphere. The phosphines were obtained from either Strem Chemical or Organometallics, Inc. 1-Phenyl-3,4-dimethylphosphole,[26] $[(COE)_2RhCl]_2$,[27] and $(DMPP)_2Rh(CO)Cl$[28] were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 1800 FT-IR instrument as Nujol mulls on polyethylene thin films. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected.

The solution $^{31}P\{^{1}H\}$ NMR spectra were recorded at 121.66 MHz on a General Electric GN-300 spectrometer on CD_3NO_2 and $CDCl_3$ solutions. The chemical shifts were referenced to 85% H_3PO_4 via external PPh_3 ($\delta = -6.0$ ppm) with shifts to low field (high frequency) being positive. Solution ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 300.16 and 75 MHz, respectively, on a General Electric QE-300 spectrometer on CD_3NO_2 and $CDCl_3$ solutions. The chemical shifts were referenced to $(CH_3)_4Si$ *via* internal CHD_2NO_2 ($\delta(^{1}H) = 4.33$; $\delta(^{13}C) = 62.8$ ppm) or internal $CHCl_3$ ($\delta(^{1}H) = 7.26$; $\delta(^{13}C) = 77.0$ ppm) with shifts to low field (high frequency) being positive. The $^{31}P\{^{31}P(sel)\}$ and $^{1}H\{^{31}P(sel)\}$ spectra were recorded at 202.35 and 500.00 MHz, respectively, on a JEOL JNMA 500 spectrometer in CD_3NO_2 and $CDCl_3$ solutions. The chemical shifts were referenced as above.

B. Syntheses. $[Rh(\eta^{1}\text{-DMPP})(\mu\text{-}\sigma,\ \eta^{4}\text{-DMPP})(CO)]_2(BF_4)_2$, 1 (*syn, anti*). To a solution containing 206 mg (0.380 mmol) of *trans*-$(DMPP)_2Rh(CO)Cl$ in 50 mL of C_6H_6 was added 1 molar equiv of $AgBF_4$ (73.98 mg, 0.380 mmol). This mixture was shielded from light and stirred at room temperature for 1 day. The solid was collected by filtration and extracted with CH_2Cl_2 to separate AgCl. The CH_2Cl_2 was removed by evaporation to yield 225 mg (77%) of a dull yellow powder that was shown by $^{31}P\{^{1}H\}$ NMR spectroscopy to be a 4:1 mixture of *anti* and *syn* isomers. The *anti* isomer was separated from the *syn* isomer by fractional crystallization from CH_3NO_2/ether (172 mg). The *syn* isomer could not be obtained completely free of the *anti* isomer and was characterized as a 10:1 isomeric mixture; mp 200 °C dec (*anti*). IR (Nujol) υ_{CO} 2046 (s) cm^{-1} (*anti*); 2067 (sh), 2046 (s) cm^{-1} (*syn*). $\upsilon_{BF_4} = 1046$ cm^{-1} (b, s) for both isomers. ^{1}H NMR (500 MHz, CD_3NO_2): *anti* isomer, δ 1.89 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 2.22 (m, 6H, CH_3), 2.41 (m, 6H, CH_3), 3.57 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 4.87 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 5.79 (d, $^{2}J(PH) = 37.0$ Hz, 2H, =CH, η^{1}-DMPP), 6.15 (d, $^{2}J(PH) = 38.0$ Hz, 2H, =CH, η^{1}-DMPP), 7.3–7.6 (m, 20H, Ph); *syn* isomer, δ 1.70 (m, 6H, CH_3), 1.77 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.70 (m, 6H, CH_3), 4.08 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 4.56 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 5.95 (d, $^{2}J(PH) = 37.0$ Hz, 2H, =CH, η^{1}-DMPP), 6.01 (d, $^{2}J(PH) = 37.5$ Hz, 2H, =CH, η^{1}-DMPP), 7.3–7.6 (m, 20H, Ph). $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3NO_2): δ 15.24 (s, CH_3, η^{4}-DMPP), 15.91 (s, CH_3, η^{4}-DMPP) 17.75 (d, $^{3}J(PC) = 13.35$ Hz, CH_3, η^{1}-DMPP), 17.84 (d, $^{3}J(PC) = 13.21$ Hz, CH_3, η^{1}-DMPP), 52.63 (m, C_α and C_β, η^{4}-DMPP) 52.84 (m, C_α and C_β, η^{4}-DMPP), 119.17 (m, C_m, η^{4}-DMPP), 121.12 (m, C_m, η^{4}-DMPP), 123.75 (d, $^{1}J(PC) = 51.17$ Hz, C_α, η^{1}-DMPP), 124.43 (d, $^{1}J(PC) = 51.63$ Hz, C_α, η^{1}-DMPP), 127.43 (d, $^{1}J(PC) = 47.86$ Hz, C_i, η^{1}-DMPP), 128.50 (m, C_o, η^{4}-DMPP), 128.50 (m, C_o, η^{4}-DMPP), 128.50 (d, $^{3}J(PC) = 10.27$ Hz, C_m, η^{1}-DMPP), 130.63 (m, C_o, η^{4}-DMPP), 130.63 (d, $^{3}J(PC) = 10.57$ Hz, C_m, η^{1}-DMPP), 130.89 (d, $^{2}J(PC) = 11.02$ Hz, C_o, η^{1}-DMPP), 132.06 (s, C_p, η^{4}-DMPP), 132.68 (d, $^{2}J(PC) = 10.87$ Hz, C_o, η^{1}-DMPP), 133.05 (d, $^{4}J(PC) = 2.11$ Hz, C_p, η^{1}-DMPP), 147.33 (m, C_i, η^{4}-DMPP), 155.38 (d, $^{2}J(PC) = 10.04$ Hz, C_β, η^{1}-DMPP), 156.73 (d, $^{2}J(PC) = 10.11$ Hz, C_β, η^{1}-DMPP), 186.84 (ddd, $^{1}J(RhC) = 62.12$ Hz, $^{2}J(PC) = 12.38$ Hz, $^{2}J(P'C) = 3.70$ Hz, CO). Anal. Calcd for $C_{50}H_{52}B_2F_8O_2P_4Rh_2$: C, 50.51; H, 4.42. Found (anti): C, 50.44; H, 4.40. Found (*syn*:*anti* = 10:1) C, 50.53; H, 4.47.

$[Rh(\eta^{1}\text{-DMPP})(\mu\text{-}\sigma,\ \eta^{4}\text{-DMPP})Cl]_2$, 2. To a solution containing 514 mg (0.716 mmol) of $[(COE)_2RhCl]_2$ in 50 mL of toluene was added 1.34 g of DMPP (7.13 mmol). The solution was refluxed for 2 h and cooled gradually to ambient temperature. The resultant precipitate was collected by filtration, washed with toluene and vacuum dried at room temperature. The product was obtained as an orange powder (650 mg; 88% based on rhodium), mp 270 °C dec. IR (Nujol): $\upsilon_{RhCl} = 269$ cm^{-1} (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (m, 6H, CH_3), 1.29 (m, 6H, CH_3), 1.92 (s, 6H, CH_3), 2.21 (m, 6H, CH_3), 2.94 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 3.21 ($[AMX]_2$, 2H, =CH, η^{4}-DMPP), 5.64 (d, $^{2}J(PH) = 33.2$ Hz, 2H, =CH, η^{1}-DMPP), 5.89 (d, $^{2}J(PH) = 33.7$ Hz, 2H, =CH, η^{1}-DMPP), 7.1–7.5 (m, 20H, Ph). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 13.87 (s, CH_3, η^{4}-DMPP), 14.28 (s, CH_3, η^{4}-DMPP), 17.40 (d, $^{3}J(PC) = 11.34$ Hz, CH_3, η^{1}-DMPP), 17.74 (d, $^{3}J(PC) = 10.88$ Hz, CH_3, η^{1}-DMPP), 45.90 (m, C_β, η^{4}-DMPP), 47.63 (m, C_α, η^{4}-DMPP), 48.05 (m, C_α, η^{4}-DMPP), 50.26 (m, C_β, η^{4}-DMPP), 103.92 (m, C_m, η^{4}-DMPP), 116.34 (m, C_m, η^{4}-DMPP), 123.71 (d, $^{1}J(PC) = 43.68$ Hz, C_α, η^{1}-DMPP), 127.60 (m, C_o, η^{4}-DMPP), 127.60 (d, $^{3}J(PC) = 6.88$ Hz, C_m, η^{1}-DMPP), 127.92 (s, C_p, η^{4}-DMPP), 128.08 (d, $^{2}J(PC) = 9.75$

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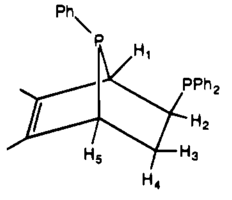
Hz, C_o, η^1-DMPP), 129.17 (d, ^1J(PC) = 44.06 Hz, C_α, η^1-DMPP), 129.29 (m, C_o, η^4-DMPP), 129.29 (d, ^3J(PC) = 9.14 Hz, C_m, η^1-DMPP), 129.65 (d, ^4J(PC) = 1.51 Hz, C_p, η^1-DMPP), 129.92 (d, ^1J(PC) = 39.80 Hz, C_i, η^1-DMPP), 131.79 (d, ^2J(PC) = 10.20 Hz, C_o, η^1-DMPP), 147.58 (d, ^2J(PC) = 7.41 Hz, C_β, η^1-DMPP), 148.18 (m, C_i, η^4-DMPP), 152.70 (d, ^2J(PC) = 9.52 Hz, C_β, η^1-DMPP). Anal. Calcd for $C_{48}H_{52}Cl_2P_4Rh_2$: C, 55.97; H, 5.10; Cl, 6.89. Found: C, 56.03; H, 5.25; Cl, 6.69.

[Rh(η^1-DMPP)(μ-σ, η^4-DMPP)(N_3)]$_2$, 3. To a suspension of 206 mg (0.200 mmol) of [Rh(η'-DMPP) (μ-σ, η^4-DMPP) Cl]$_2$ in 50 mL of CH_2Cl_2 was added a solution of 26.4 mg (0.406 mmol) of NaN_3 in 5 mL of absolute EtOH. The reaction mixture was stirred at room temperature for 1 day and then allowed to sit without stirring for 2 days. The resultant precipitate was collected by filtration, washed with CH_2Cl_2 followed by Et_2O, and vacuum dried at room temperature. The product was obtained as a bright yellow powder (195 mg; 93%), mp 208 °C dec. IR (Nujol): $\upsilon_{N_3} = 2030$ cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (m, 6H, CH_3), 1.47 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 2.29 (m, 6H, CH_3), 2.9 ([AMX]$_2$, 2H, =CH, η^4-DMPP), 3.41 ([AMX]$_2$, 2H, =CH, η^4-DMPP), 5.61 (d, ^2J(PH) = 34.4 Hz, 2H, =CH, η^1-DMPP), 5.78 (d, ^2J(PH) = 34.5 Hz, 2H, =CH, η^1-DMPP), 7.1−7.4 (m, 20H, Ph). ^{13}C{^{1}H} NMR (125.65 MHz, $CDCl_3$): δ 13.55 (s, CH_3, η^4-DMPP), 14.00 (s, CH_3, η^4-DMPP), 17.47 (d, ^3J(PC) = 11.40 Hz, CH_3, η^1-DMPP), 17.70 (d, ^3J(PC) = 10.40 Hz, CH_3, η^1-DMPP), 42.50 (m, C_β, η^4-DMPP), 49.30 (m, C_α, η^4-DMPP), 105.88 (m, C_m, η^4-DMPP), 113.57 (s, C_m, η^4-DMPP), 123.79 (d, ^1J(PC) = 45.5 Hz, C_α, η^1-DMPP), 123.86 (d, ^1J(PC) = 42.4 Hz, C_α, η^1-DMPP), 127.34 (d, ^1J(PC) = 43.5 Hz, C_i, η^1-DMPP), 127.64 (s, C_p, η^4-DMPP), 128.00 (m, C_o, η^4-DMPP), 128.49 (d, ^3J(PC) = 10.00 Hz, C_m, η^1-DMPP), 128.50 (d, ^3J(PC) = 9.80 Hz, C_m, η^1-DMPP), 129.89 (m, C_o, η^4-DMPP), 131.59 (d, ^2J(PC) = 11.40 Hz, C_o, η^1-DMPP), 131.78 (d, ^2J(PC) = 10.30 Hz, C_o, η^1-DMPP), 147.77 (m, C_i, η^4-DMPP), 148.89 (d, ^2J(PC) = 7.30 Hz, C_β, η^1-DMPP), 152.89 (d, ^2J(PC) = 9.40 Hz, C_β, η^1-DMPP). Anal. Calcd for $C_{48}H_{52}N_6P_4Rh_2{\cdot}2CH_2Cl_2$: C, 49.50; H, 4.67. Found: C, 49.89; H, 4.55. CH_2Cl_2 was detected in approximately the correct ratio in the ^{1}H NMR spectrum.

[Rh(η^1-DMPP)(μ-σ, η^4-DMPP)(OH)]$_2$, 4. In a reaction similar to the synthesis of **3**, using 211 mg (0.205 mmol) of [Rh(η^1-DMPP) (μ-σ, η^4-DMPP) Cl]$_2$ and 1.1 mL of 1 M NaOH solution, 192 mg (94%) of **4** was obtained; mp 252 °C dec. The infrared spectrum shows the absence of υ_{RhCl}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (m, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.50 (s, 2H, OH), 1.98 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 3.00 ([AMX]$_2$, 2H, =CH, η^4-DMPP), 3.28 ([AMX]$_2$, 2H, =CH, η^4-DMPP), 5.70 (d, ^2J(PH) = 35.40 Hz, 2H, =CH, η^1-DMPP), 5.96 (d, ^2J(PH) = 35.40 Hz, 2H, =CH, η^1-DMPP), 7.3−7.6 (m, 20H, Ph).

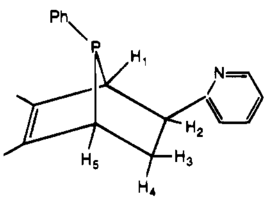
[Rh(η^1-DMPP)$_2$(μ-σ, η^4-DMPP)]$_2$(BF$_4$)$_2$, 5. To a suspension containing 114 mg (0.111 mmol) of [Rh(η^1-DMPP)$_2$(μ-σ, η^4-DMPP)Cl]$_2$, in 15 mL of CH_2Cl_2 were added 0.05 mL (0.266 mmol) of DMPP and 43.2 mg (0.222 mmol) of $AgBF_4$. The reaction mixture was shielded from light and stirred at ambient temperature for 1 day. The resultant precipitate was removed by filtration and extracted with CH_2Cl_2. The filtrate and extract were combined, and the volume was reduced on a rotary evaporator until a precipitate formed. The precipitate was collected by filtration, washed with Et_2O, and vacuum dried at ambient temperature. The product was obtained as 136 mg (77%) of a dull yellow powder, mp 210 °C dec. ^{1}H NMR (500 MHz, CD_3NO_2): δ 1.89 (s, 12H, CH_3), 2.01 (s, 12H, CH_3), 2.07 (s, 12H, CH_3), 3.69 [(AMX$_2$]$_2$, 4H, =CH, η^4-DMPP), 5.79 ([AX]$_2$, $|^2J(PH) + {}^4J(PH)|$ = 35.46 Hz, 4H, =CH, η^1-DMPP), 6.17 ([AX]$_2$, $|^2J(PH) + {}^4J(PH)|$ = 35.46 Hz, 4H, =CH, η^1-DMPP), 7.1−7.6 (m, 30H, Ph). ^{13}C{^{1}H} NMR (75 MHz, CD_3NO_2): δ 14.35 (s, CH_3, η^4-DMPP), 16.13 (T, $|^3J(PC) + {}^5J(PC)|$ = 11.49 Hz, CH_3, η^1-DMPP), 16.44 (T, $|^3J(PC) + {}^5J(PC)|$ = 11.64 Hz, CH_3, η^1-DMPP), 53.1 (m, C_α and C_β, η^4-DMPP), 113.00 (m, C_m, η^4-DMPP), 125.51 (5L, AXX′, ^2J(PP′) = 31.40 Hz, ^2J(PC) = 43.14 Hz, ^4J(P′C) = 2.28 Hz, C_α, η^1-DMPP), 126.51 (6L, AXX′, ^2J(PP′) = 31.40 Hz, ^2J(PC) = 37.00 Hz, ^4J(P′C) = 10.23 Hz, C_α, η^1-DMPP), 127.60 (T, $|^2J(PC) + {}^4J(PC)|$ = 9.45 Hz, C_o, η^4-DMPP), 127.89 (m, C_i, η^1-DMPP), 128.10 (m, C_i, η^4-DMPP), 128.85 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.05 Hz, C_m, η^1-DMPP), 129.33 (s, C_p, η^4-DMPP), 130.83 (s, C_p, η^1-DMPP), 131.53 (T, $|^2J(PC) + {}^4J(PC)|$ = 10.88 Hz, C_o, η^1-DMPP), 152.61 (T, $|^2J(PC) + {}^4J(PC)|$ = 8.24 Hz, C_β, η^4-DMPP), 153.20 (T, $|^2J(PC) + {}^4J(PC)|$ = 7.56 Hz, C_β, η^1-DMPP). Anal. Calcd for $C_{72}H_{78}B_2F_8P_6Rh_2{\cdot}1.5CH_2Cl_2$: C, 53.93; H, 4.87. Found: C, 53.95; H, 4.98. CH_2Cl_2 was detected in approximately the correct ratio in the ^{1}H NMR spectrum.

[Rh(2-(diphenylphosphino)-5,6-dimethyl-7-phenylphosphabicyclo[2.2.1]hept-5-ene)(μ-σ, η^4-DMPP)]$_2$(BF$_4$)$_2$, 6. To a solution containing 435 mg (0.441 mmol) of [Rh(η^1-DMPP)$_2$(μ-σ, η^4-DMPP) (CO)](BF$_4$)$_2$ (as a mixture of *syn* and *anti* isomers) in 15 mL of CH_3NO_2 was added 0.17 mL (0.855 mmol) of diphenylvinylphosphine. The solution was stirred at room temperature for 1 day and the solvent was removed in vacuo. The ^{31}P{^{1}H} NMR spectrum of the crude product showed overlapping second order patterns for the two isomers that had formed in a 1:1 ratio in about an 80% overall yield. These isomers are believed to be the *syn* and *anti* isomers of the Diels−Alder adduct. The *anti* isomer was isolated by fractional crystallization by slow evaporation of a CH_2Cl_2 solution of the crude product. The *syn* isomer could not be obtained free of the *anti* isomer. Yield: 49.3 mg (17%) of pure *anti* isomer. Mp: 222 °C dec. ^{31}P{^{1}H} NMR (121.66 MHz, CD_3NO_2): *anti* isomer, δ 38.95 (apparent dd, ^1J(RhP) = 114.24 Hz, ^2J(PP) = 37.67 Hz, 2P, PPh$_2$), 64.12 (m, ^1J(RhP) = 160.35 Hz, J(PP′) = 261.21 Hz, ^1J(RhP′) = −12.17 Hz, J(RhRh) = 0, 2P, η^4-DMPP), 132.18 (m, ^1J(RhP) = 113.75 Hz, ^2J(PP) = 37.67 Hz, $|J(P_AP_X) + J(P_AP_{X'})|$ = 19.20 Hz, 2P, 7-PPh); *syn* isomer, δ 38.03 (apparent dd, ^1J(RhP) = 115.94 Hz, ^2J(PP) = 34.95 Hz, 2P, PPh$_2$), 63.38 (m, ^1J(RhP) = 160.70 Hz, J(PP′) = 279.49 Hz, ^1J(RhP′) = −13.74 Hz, J(RhRh) = 0, 2P, η^4-DMPP), 130.29 (m, ^2J(PP) = 34.95 Hz, ^1J(RhP) = 113.02 Hz, $|J(P_AP_X) + J(P_AP_{X'})|$ = 9.36 Hz, 2P, 7-PPh).



^{1}H NMR (500 MHz, CH_3NO_2), *anti* isomer: δ 0.80 (m, ^3J(PH) = 24.0 Hz, $^2J(H_3H_4)$ = 13.50 Hz, $^3J(H_2H_4)$ = 10.15 Hz, 2H, H_3), 1.09 (s, 6H, CH_3), 1.17 (m, ^3J(PH) = 25.00 Hz, $^2J(H_3H_4)$ = 13.50 Hz, $^3J(H_2H_4)$ = 10.15 Hz, 2H, H_4), 1.32 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.83 (s, 6H, CH_3), 2.64 (s, 2H, H_1), 2.90 (apparent dt, ^3J(PH) = 42.62 Hz, $^3J(H_2H_4)$ = ^2J(PH) = 10.15 Hz, 2H, H_2), 3.29 ([AX]$_2$, 4H, =CH, η^4-DMPP), 3.71 (s, 2H, H_5), 7.0−7.8 m, 40H, Ph). Anal. Calcd for $C_{74}H_{78}B_2F_8P_6Rh_2{\cdot}H_2O$: C, 57.34; H, 5.16. Found (*anti*): C, 57.24; H, 4.64. Found: (isomeric mixture) C, 57.45; H, 4.97.

[Rh(2-pyridyl-5,6-dimethyl-7-phosphabicyclo[2.2.1]hept-5-ene)(μ-σ, η^4-DMPP)]$_2$(BF$_4$)$_2$, 7. To a suspension containing 319 mg (0.310 mmol) of [Rh(η^1-DMPP)(η^4-DMPP)Cl]$_2$ in 15 mL of C_6H_6 were added 0.04 mL (0.371 mmol) of 2-vinylpyridine and 120.7 mg (0.62 mmol) of $AgBF_4$. The reaction mixture was shielded from light and stirred at ambient temperature for 1 day. A ^{31}P NMR spectrum of the crude reaction mixture indicated that about 75% of **2** was converted into a 2:1:1 isomeric mixture of **7**. The reaction mixture was filtered, and the filtrate was layered with hexanes. The resulting precipitate was collected by filtration, washed with Et_2O, and dried at ambient temperature under vacuum. A total of 31.2 mg (8%) of the major isomer was obtained and shown by ^{31}P{^{1}H} NMR to be isomerically pure; mp 200 °C dec. ^{31}P{^{1}H} (121.66 MHz, $CDCl_3$): δ 42.67 (m, ^1J(RhP) = 172.87 Hz, J(PP′) = 243.93 Hz, ^1J(RhP′) = −13.86 Hz, J(RhRh) = 0, 2P, η^4-DMPP), 113.58 (m, ^1J(RhP) = 119.96 Hz, $|J(P_AP_X) + J(P_AP_{X'})|$ = 27.86 Hz, 2P, 7-PPh).



^{1}H NMR (300 MHz, CD_3NO_2): δ 1.42 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.90 (s, 6H, CH_3), 2.1 (m, 2H, H_4), 2.38 (m, 2H, H_1), 2.54 (m, 2H, H_3), 3.17 (m, 2H, H_2), 3.37 ([AX]$_2$, 4H, =CH, η^4-DMPP), 3.61 (s, 2H,

Table 1. Crystallographic Data for **7**

chem formula	$C_{62}H_{66}B_2F_8N_2P_4Rh_2{\cdot}2C_6H_5NO_2$	T (°C)	20 ± 1
		λ (Å)	0.7107
fw	1588.8	ϱ_{calcd} (g cm^{-3})	1.519
a (Å)	11.460(3)	μ (cm^{-1})	6.299
b (Å)	20.088(6)	no. of data with $I > 3\sigma(I)$	4907
c (Å)	16.002(4)		
β (deg)	109.46(2)	abs min/max	0.96/1.00
V (Å^3)	3473.4	$R(F)^a$	0.033
Z	2	$R_w(F)^b$	0.049
space group	$P2_1/c$		

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w(|F_o|^2]^{1/2}$; $w = 1/(\sigma^2(F^2) + (pI)^2)$.

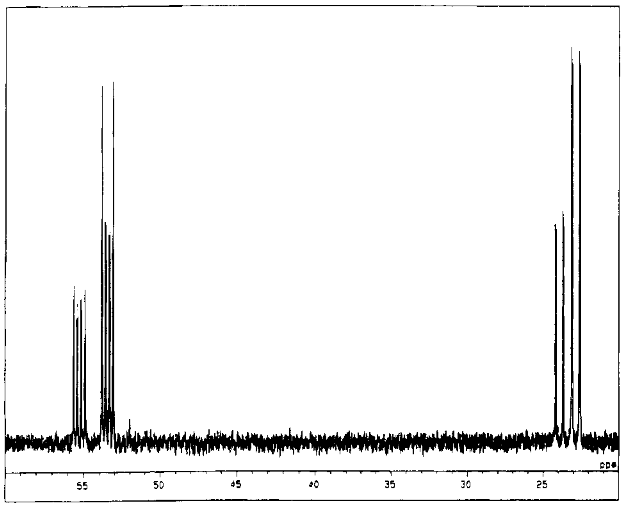


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a mixture of the *syn* and *anti* isomers of **1** in CD_3NO_2 at 293 K. The less intense, more downfield multiplets represent the *syn* isomer.

H_5), 6.40–8.30 (m, 18H, Ph, Py). Anal. Calcd for $C_{62}H_{66}B_2N_2F_8P_4Rh_2$: C, 55.56; H, 4.92. Found: C, 55.35; H, 5.06.

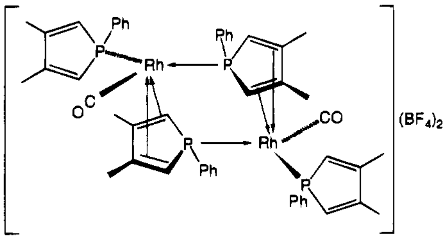
C. X-ray Data Collection and Processing. Yellow crystals of **1** and **7** were obtained by slow evaporation of CH_3NO_2/Et_2O and $C_6H_5NO_2$ solutions respectively. Crystal data for **1**: monoclinic, a = 15.321(5) Å, b = 11.982(4) Å, c = 15.460(6) Å, β = 91.81 (3)°, Z = 4, space group $P2_1/n$. Crystal data and details of data collection for **7** are given in Table 1. For both compounds, single crystals were cut out from a cluster of crystals and mounted on a rotation-free goniometer head. Systematic searches in reciprocal space with an Enraf-Nonius CAD4-F diffractometer showed that crystals of both complexes belong to the monoclinic system.

Quantitative data were obtained at room temperature. The resulting data sets were transferred from the X-ray instrument computer to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[29] was used. Three standard reflections measured every 1 h during the entire data collection period showed a decay of 49% for **1** and no significant trends for **7**. For **1**, linear time-dependent decay corrections were applied. The raw data were converted to intensities and corrected for Lorentz and polarization factors. Absorption corrections from ψ scans of four reflections were applied.

The structures were solved by the heavy atom method. For **1**, after location of all non hydrogen atoms of the anionic and cationic parts, residual electronic density maxima appeared which were assigned to carbon atoms. The coordinates and temperature factors of these atoms converged by least-squares refinements, but no chemical moiety could be built, even by assuming positional disorder. Therefore, refinement was stopped with an R value of 0.097. All attempts to grow better single crystals failed and consequently no low temperature data were collected. Despite these problems, the connectivity and bond distances found in the anionic and cationic parts of **1** should be in the correct range. For **7**, after refinement of the non-hydrogen atoms, difference-Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in the structure factor calculations by their computed coordinates (CH = 0.95 Å) with isotropic temperature factors such as B(H) = 1.3B (C) Å^2 but were not refined. Otherwise, solutions were obtained with full least-squares refinements with the weighting schemes given in Table 1. Final difference maps revealed no significant maxima (0.32 e Å^{-3}). The scattering factors coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 30. Final atom coordinates are given in Table 2, and selected bond lengths and angles are given in Tables 3 and 4 respectively.

Results and Discussion

Syntheses of [Rh(η^1-DMPP)$_2$(μ-σ, η^4-DMPP) L]$_2$(BF$_4$)$_n$, n = 0, 2. The first reactions in which we attempted to form the Diels–Alder adduct directly on the rhodium center paralleled the initial palladium/platinum cycloaddition reaction (1) in which *trans*-$(DMPP)_2Rh(CO)Cl$ and *trans*-$(Ph_2VyP)_2Rh(CO)Cl$[28] were the starting materials. Phosphine exchange occurred rapidly[25] at room temperature but the phosphole and vinylphosphine did not undergo the desired Diels–Alder reaction. Instead only *trans*-(DMPP)(Ph_2VyP)Rh(CO)Cl [$^{31}P\{^1H\}$ NMR (121.66 MHz, C_6D_6): δ 21.92 (dd, ^1J(RhP) = 124.5 Hz, ^2J(PP) = 83.0 Hz, 1P, DMPP), 25.61 (dd, ^1J(RhP) = 117.2 Hz, ^2J(PP) = 83 .0 Hz, 1P, Ph_2VyP)] was formed. A subsequent attempt involved a halide abstraction reaction similar to reaction 2; again, using *trans*-$(DMPP)_2Rh(CO)Cl$ and Ph_2VyP as L′. This one-pot preparation resulted in an intractable mixture of cycloaddition products. However, recovery of the halide abstraction product, prior to the addition of the dienophile (Ph_2VyP) yielded compound **1**.



This compound is unusual in that one of the phospholes on each Rh center is tridentate; coordinating as a diene to one rhodium while also serving as a bridging ligand to a second rhodium. The most common bonding mode for a phosphole, when coordinated to a transition metal, is through the phosphorus atom only.[10] However, coordination of a phosphole as a diene has been previously reported for complexes of Mn, Mo, Co, and Fe,[31–36] and has been proposed for a Rh(I) system.[1] To our knowledge, this is the first example of this phosphole bonding mode having been demonstrated for a rhodium system. In all of these species, the metal centers are relatively electron rich. Compound **1** forms as two geometric isomers, *syn* (**1a**)

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

(30) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* Kynoch: Birmingham, England, 1974; Vol. IV: (a) Table 2.2.b; (b) Table 2.3.1.

(31) Mathey, F.; Thavard, D. *Can. J. Chem.* **1978**, *56*, 1952.

(32) Santini, C. C.; Mathey, F. *J. Organomet. Chem.* **1984**, *266*, 285.

(33) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *Inorg. Chem.* **1981**, *20*, 2848.

(34) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

(35) Mathey, F.; Muller, G. *J. Organomet. Chem.* **1977**, *136*, 241.

(36) Holland, S.; Mathey, F.; Fischer, J.; Mitschler, A. *Organometallics* **1983**, *2*, 1234.

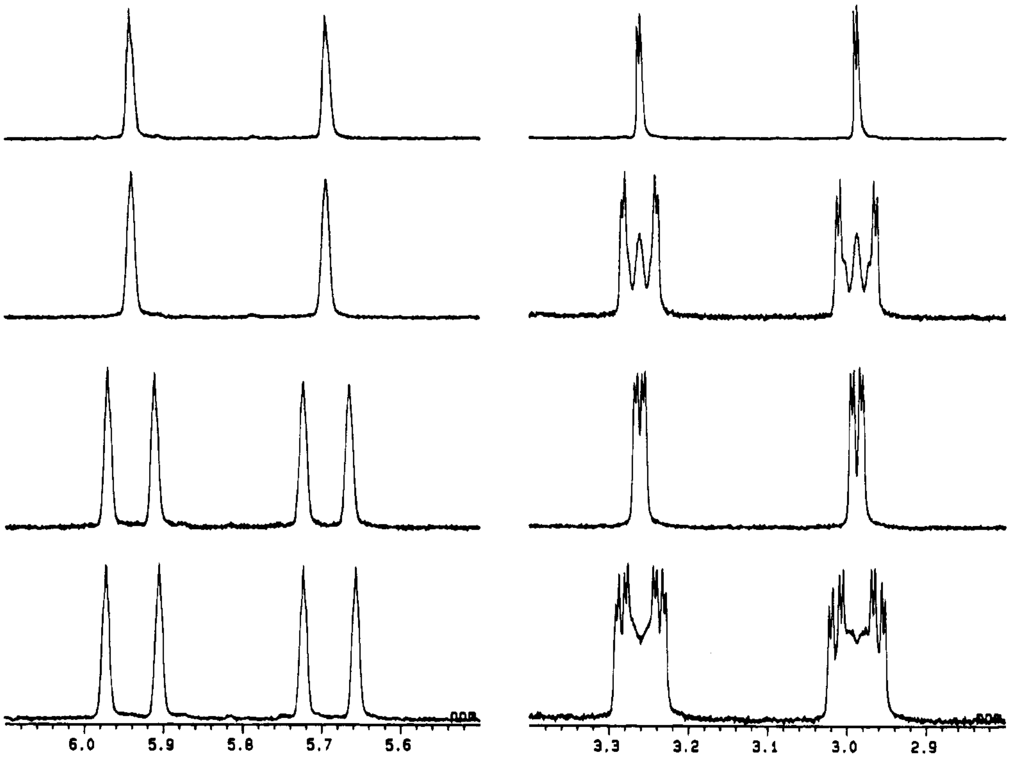
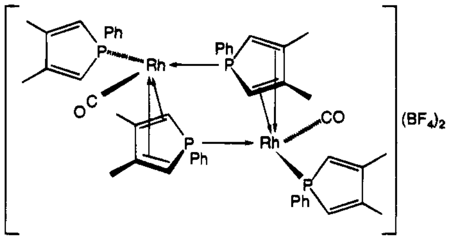
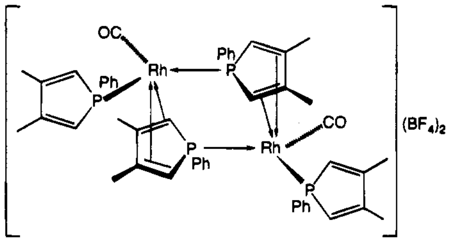


Figure 2. Expansions of the 500-MHz ^1H NMR spectrum (bottom), selectively decoupled $^1H\{^{31}P\}$ NMR spectra with P2 (lower) and P1 (upper) decoupling, and $^1H\{^{31}P_{BB}\}$ NMR spectrum (top) of **2** in $CDCl_3$ at 293 K. The =CH resonances of the η^4- and η^1-DMPP ligands appear at 3.13 and 5.82 ppm respectively.

and *anti* (**1b**), in a 1:4 ratio with the *anti* isomer predominating, as evidenced by ^1H and 202-MHz $^{31}P\{^1H\}$ NMR spectroscopy (Figure 1). Characterization of the *anti* isomer **1b** by preliminary X-ray crystallography, despite the poor quality of the data, showed the complex to possess an inversion center with both Rh–P distances equal to about 2.3 Å, and with a P2⋯P2′ separation of about 3.292 Å. The tridentate phospholes were determined to be slightly puckered and the penta-coordinate rhodium centers to possess distorted trigonal-bipyramidal geometry.

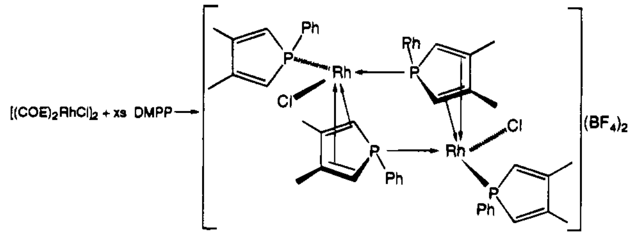


1b (anti)



1a (syn)

In attempting to synthesize the DMPP analog of Wilkinson's catalyst $(Ph_3P)_3RhCl$, [37] as another possible route to the Diels-Alder adduct (reaction 3), a molecular species with a similar dimeric structure to **1** was obtained (compound **2**). Whereas **1** forms as a mixture of *syn* and *anti* isomers, **2** forms only as the *anti* isomer.



We thought that the formation of **1** during the halide abstraction may have resulted from the relative insolubilities of the reactants in benzene. Repeating the reaction in acetonitrile did not change the outcome. We thought that the DMPP analog of Wilkinson's catalyst could be better obtained from ligand substitution of Ph_3P by DMPP in $(Ph_3P)_3RhCl$. However, compound **2** was also formed in this reaction. Thus, it appears that the dimeric $[(\mu\text{-}\sigma,\eta^4\text{-DMPP})Rh]_2$ moiety represents a thermodynamic sink.

Reactions of 1 and 2. The *syn* and *anti* isomers of $[Rh(\eta^1\text{-DMPP})(\mu\text{-}\sigma,\ \eta^4\text{-DMPP})(CO)]_2(BF_4)_2$, **1**, are configurationally stable and do not readily interconvert as shown by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy in CD_3NO_2 in the 0–100 °C temperature range. Hence, dissociation of CO is slow on the NMR time scale. However, the CO groups are easily replaced by other ligands. Reaction of **1**, as a *syn–anti* mixture of isomers, with Ph_2VyP leads to substitution of CO followed immediately by [4 + 2] Diels–Alder cycloaddition between the coordinated DMPP and Ph_2VyP to produce **6** as a 1:1 mixture of *syn-* and *anti-* isomers. The *anti* isomer was separated by fractional crystallization and completely characterized. Similarly, **1** reacts with 2-vinylpyridine to yield the Diels–Alder adduct **7** as three diastereomers in a 2:1:1 ratio. An *anti*

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[37] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

Table 2. Atom Coordinates for **7**[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Rh	0.34789(2)	0.00081(1)	0.39556(1)	1.337(4)
P1	0.49650(7)	0.07602(4)	0.54224(5)	1.47(2)
C1	0.4630(3)	0.0932(2)	0.4265(2)	1.74(6)
C2	0.3347(3)	0.1104(2)	0.3850(2)	1.94(7)
C3	0.2611(3)	0.0864(2)	0.4344(2)	1.93(7)
C4	0.3386(3)	0.0485(2)	0.5108(2)	1.66(6)
C5	0.2860(4)	0.1486(2)	0.2999(3)	2.83(9)
C6	0.1283(3)	0.1032(2)	0.4175(3)	2.75(8)
C7	0.5017(3)	0.1556(2)	0.5997(2)	1.90(7)
C8	0.4822(4)	0.1559(2)	0.6823(2)	2.60(8)
C9	0.4905(4)	0.2160(2)	0.7277(3)	3.54(9)
C10	0.5191(4)	0.2738(2)	0.6932(3)	3.6(1)
C11	0.5360(4)	0.2740(2)	0.6124(3)	3.3(1)
C12	0.5277(3)	0.2150(2)	0.5657(3)	2.42(8)
P2	0.19310(7)	−0.07411(5)	0.37693(5)	1.53(2)
C13	0.0363(3)	−0.0461(2)	0.3117(2)	1.96(7)
C14	0.0628(3)	−0.0225(2)	0.2272(2)	2.15(7)
C15	0.1451(3)	−0.0778(2)	0.2068(2)	1.83(6)
C16	0.1647(3)	−0.1312(2)	0.2822(2)	1.67(6)
C17	−0.0337(3)	−0.1114(2)	0.2905(2)	2.16(7)
C18	0.0365(3)	−0.1587(2)	0.2724(2)	1.94(7)
C19	−0.1660(4)	−0.1137(2)	0.2867(3)	3.4(1)
C20	0.0032(4)	−0.2277(2)	0.2402(3)	3.03(9)
C21	0.2623(3)	−0.0527(2)	0.1954(2)	1.87(7)
N1	0.3463(3)	−0.0173(1)	0.2607(2)	1.77(6)
C22	0.4462(3)	0.0062(2)	0.2430(2)	2.31(7)
C23	0.4683(3)	−0.0034(2)	0.1646(2)	2.82(8)
C24	0.3855(4)	−0.0407(2)	0.0995(2)	2.98(9)
C25	0.2816(4)	−0.0647(2)	0.1152(2)	2.63(8)
C26	0.1887(3)	−0.1213(2)	0.4720(2)	2.10(7)
C27	0.2116(4)	−0.1891(2)	0.4786(3)	2.84(8)
C28	0.2218(4)	−0.2224(3)	0.5575(3)	4.1(1)
C29	0.2083(4)	−0.1867(3)	0.6282(3)	4.7(1)
C30	0.1818(4)	−0.1210(3)	0.6204(3)	3.8(1)
C31	0.1710(3)	−0.0874(2)	0.5428(2)	2.98(9)
B	0.8032(5)	0.0992(3)	0.1366(3)	3.1(1)
F1	0.8307(3)	0.0500(1)	0.0856(2)	5.67(7)
F2	0.9086(3)	0.1127(1)	0.2070(2)	4.16(6)
F3	0.7729(3)	0.1552(2)	0.0818(2)	5.69(8)
F4	0.7090(3)	0.0835(2)	0.1648(2)	7.02(9)
C32	0.2321(4)	0.1557(2)	0.9836(3)	2.91(9)
C33	0.2066(4)	0.2178(2)	1.0083(3)	3.6(1)
C34	0.1183(5)	0.2234(3)	1.0491(4)	4.5(1)
C35	0.0589(4)	0.1681(3)	1.0645(3)	4.4(1)
C36	0.0869(5)	0.1059(3)	1.0390(3)	4.2(1)
C37	0.1759(4)	0.0994(2)	0.9984(3)	3.6(1)
N2	0.3242(4)	0.1499(2)	0.9387(3)	4.2(1)
O1	0.3712(4)	0.0952(2)	0.9381(3)	6.8(1)
O2	0.3508(3)	0.1996(2)	0.9051(2)	5.4(1)

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

Table 3. Selected Bond Distances (Å) for **7**

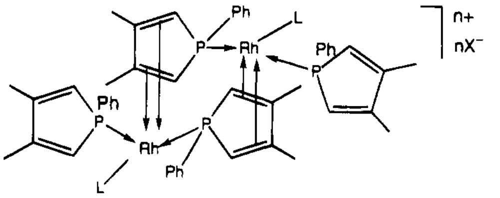
Rh—P1	2.8336(9)	P1—C1	1.796(4)
Rh—P1′	2.3173(9)	P1—C4	1.797(4)
Rh—C1	2.234(3)	C1—C2	1.439(5)
Rh—C2	2.210(4)	C2—C3	1.420(5)
Rh—C3	2.178(3)	C3—C4	1.463(5)
Rh—C4	2.112(3)	P2—C13	1.840(4)
Rh—P2	2.2690(9)	P2—C16	1.841(3)
Rh—N1	2.183(3)		

Table 4. Selected Bond Angles (deg) for **7**

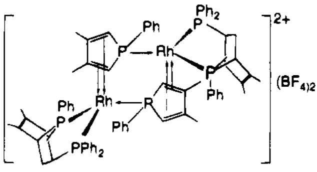
P1—Rh—P1′	80.51(3)	P1—Rh—N1′	93.77(8)
P1—Rh—P2	133.66(3)	C1—P1—C4	85.5(2)
P1—Rh—N1	135.44(8)	C13—P2—C16	81.5(2)
P1—Rh—P2′	94.06(3)		

isomer was separated by fractional crystallization and completely characterized. Analogous reactions of **1** with other dienophiles known to undergo Diels—Alder cycloadditions with DMPP on other metal centers[13] led to a simple ligand substitution product (DMPP, **5**), an inseparable mixture of Diels—Alder products ($PhVy_2P$), or no reaction ($PhS(O)CH{=}CH_2$, $Me_2NC(O)$-$CH{=}CH_2$, allyldiphenylphosphine).

Compound **2** readily undergoes halide exchange with N_3^- and OH^- to produce the *anti* isomers of **3** and **4**. Reaction of **2** with $AgBF_4$ and CO, DMPP, Ph_2VyP, and 2-vinylpyridine produces **1**, **5**, **6**, and **7** respectively. In the reaction of pure *anti*-**2** with $AgBF_4$ and CO only the *anti* isomer of **1** was formed, showing that ligand substitution of **2** is regiospecific. Thus, the *syn* and *anti* isomers of **1** most likely derive from two different modes of dimerization of $[(DMPP)_2Rh(CO)]^+$ that is formed as an intermediate in the $AgBF_4$ induced chloride abstraction from *trans*-$(DMPP)_2Rh(CO)Cl$.



1. L = CO, X = BF_4, n = 2
2. L = Cl, n = 0
3. L = N_3, n = 0
4. L = OH, n = 0
5. L = DMPP, X = BF_4, n = 2



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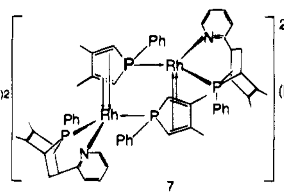


7

NMR Spectroscopy. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra are diagnostic of these dimeric structures and exhibit complicated symmetrical second order multiplets. Coordination of DMPP as a [4 + 2]-electron donor to two different rhodium centers causes a shielding of the proton and carbon nuclei of the coordinated diene and a deshielding of the phosphorus nucleus relative to an η^1-bound DMPP. In the proton NMR spectra (Figure 2) the =CH resonances of the η^4-DMPP ligands are shifted about 2—3 ppm upfield of the =CH resonances of the η^1-DMPP ligands and exhibit complex $[AMX]_2$ (A = ^{31}P, M = ^{103}Rh, X = H) multiplets. As can be seen from the selective and broad band phosphorus decoupling experiments, coupling of these protons to the η^1-DMPP phosphorus and rhodium nuclei is quite small but not zero. In the $^{13}C\{^1H\}$ NMR spectra the C_α and C_β resonances of the η^4-DMPP appear 80—100 ppm upfield of those of the η^1-DMPP and are likewise highly complex multiplets. The $^{31}P\{^1H\}$ NMR spectra exhibit complex $[AMX]_2$ (A, M = ^{31}P, X = ^{103}Rh) spin systems (Figure 3). The ^{31}P chemical shifts and most of the coupling constants (Table 5) were obtained by spin system analyses of the $[AX]_2$ and $[MX]_2$ spin systems that result from selective $^{31}P\{^1H,^{31}P\}$ decoupling experiments. Because of the breadth of the phosphorus multiplet the homonuclear (P—P) decoupling was accomplished by frequency hopping the decoupler frequency. The ^{31}P resonance of the η^4-DMPP appears downfield of that of the η^1-DMPP resonance by 17—38 ppm. The magnitude of $^1J(RhP)$ to the η^1-DMPP (103.20—121.41 Hz) is considerably smaller than that to the μ-σ, η^4-DMPP (158.24—180.47 Hz). The Diels—Alder adducts are characterized by a very low field ^{31}P chemical shift for the 7-phospha phosphorus nucleus.[13]

Of particular interest are the large values obtained for the

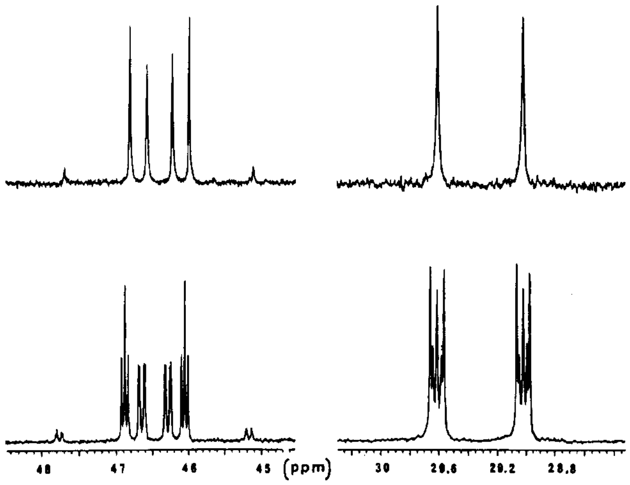


Figure 3. Expansions of the $^{31}P\{^{1}H\}$ (bottom) and $^{31}P\{^{1}H,^{31}P(sel)\}$ (top) NMR spectra of **2** in $CDCl_3$ at 293 K.

Table 5. $^{31}P\{^{1}H\}$ NMR Data for Compounds **1–5**[a]

complex	$\delta(^{31}P)$ (ppm)	$^{1}J(RhP)$ (Hz)	$J(RhP')$ (Hz)	$J(PP')$ (Hz)	$\lvert J(P_1P_2) + J\,P_1P_2)$ (Hz)
1 (anti)	P1: 22.88	103.20	0	0	12.14
	P2: 53.46	158.24	−12.55	263.06	
1 (syn)	P1: 23.95	103.20	0	0	12.04
	P2: 55.27	158.55	−12.86	265.08	
2	P1: 29.31	119.39	0	0	20.24
	P2: 46.41	180.47	−14.54	224.61	
3	P1: 29.26	121.41	0	0	18.21
	P2: 45.09	175.34	−13.46	224.61	
4	P1: 28.79	119.72	0	0	18.73
	P2: 45.92	180.31	−12.54	224.65	
5	P1: 23.00	111.29	0	0	10.12
	P2: 61.10	159.57	−11.85	265.08	

[a] P1 and P2 are the η^1-DMPP and η^4-DMPP phosphorus nuclei, respectively. Data were acquired at 202.35 MHz on CD_3NO_2 solutions at 293 K.

P2–P2′ coupling constants. The magnitude of this coupling is too great to be simply a four-bond Fermi contact interaction, especially considering that the interaction would be required to pass through a 90° angle. This indicates that through-space coupling is most likely involved. Through-space P–P coupling has been observed in a variety of molecules.[33,36,38–41] Since dipolar through-space coupling is inversely proportional to the cube of the internuclear separation (r^3),[42] a linear correlation between the P···P′ coupling constant and $1/r^3$ might be expected. However, such a plot of all the available data is not linear.

Structures of the Diels–Alder Adducts. The rhodium atoms in complexes **1** and **2** are stereocenters[43] being coordinated to four different entities. As a result they could potentially cause some diastereoselection in the metal-promoted [4 + 2] Diels–Alder cycloadditions of DMPP with the dienophiles Ph_2-VyP and 2-vinylpyridine.[13] The vinyl groups of these two dienophiles possess diastereotopic faces and [4 + 2] cycloaddition can lead to diastereomeric complexes containing the enantioneric ligand structures A and B. When the donor group, D, is Ph_2P we have shown that ^{31}P NMR spectroscopy is capable of distinguishing these diastereomeric complexes[44] on the basis of the magnitude of the chemical shift difference of the chemical shifts for the two phosphorus atoms of the five-membered chelate ring. Diastereomers containing ligand structure **A** exhibit greater chemical shift differences than do diastereomers possessing ligand structure **B**. For example, for the structurally similar $[(\eta^5\text{-}C_5H_5)Ru(DMPP)L]$ PF_6, **8**, diastereomers[22] the chemical shift differences are 97.02 ppm (**A**) and 82.88 ppm (**B**). For the $[(\eta^5\text{-}C_5H_5)FeL(CO)]$ BF_4, **9**, diastereomers[19] the chemical shift differences are 102.63 ppm (**A**) and 83.18 ppm (**B**). For the two isomers of **6** the chemical shift differences are 93.23 ppm (*anti*) and 92.26 (*syn*). Thus, we conclude that both isomers contain the ligand structure **A**. The major diastereomer of **7** (Figure 4) also has ligand structure **A**. Thus,

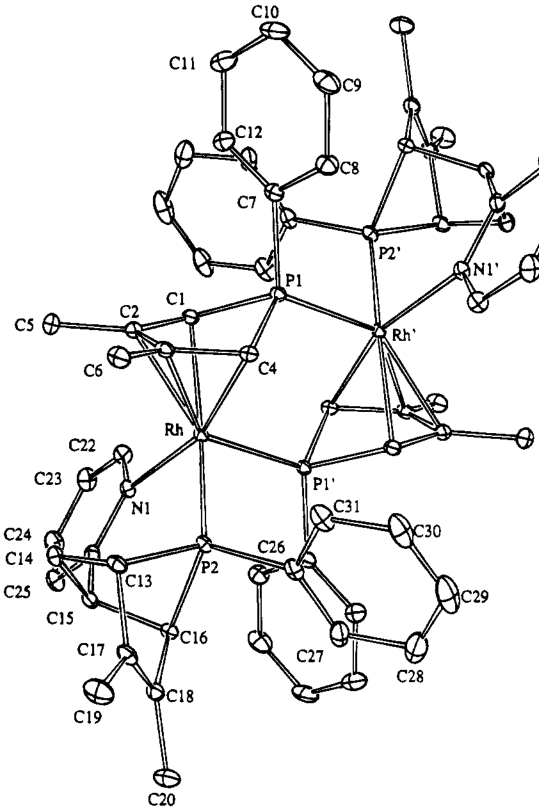
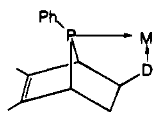
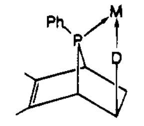


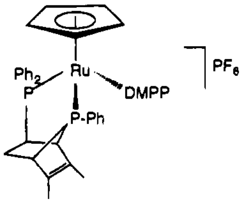
Figure 4. ORTEP drawing of the cation of **7** showing the atom numbering scheme. (50% probability ellipsoids). Hydrogen atoms are omitted.



A



B



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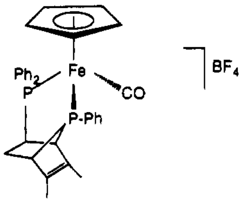

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these Diels–Alder cycloadditions proceed with moderate diastereoselectivity that most likely results from intramolecular steric effects.

The structure of **7** consists of discrete cations and anions with no unusual interionic contacts. The cation lies on a crystallographic inversion center and contains pentacoordinate rhodium(I) atoms bound to a diene, two phosphorus and one nitrogen atom. The μ, σ-η^4-DMPP ring is puckered with the four diene carbons essentially coplanar, the methyl carbons are only slightly out of this plane, and the phosphorus atom deviates considerably from this plane. The deviations from the plane are as follows: C1, 0.008(3) Å; C2, 0.014(3) Å; C3, −0.014(3) Å; C4, 0.008(3) Å; P1, −0.677(1) Å; C5, 0.068(4) Å; C6, −0.190(4) Å. The RhP distance to the η^4-DMPP phosphorus (2.8336(9) Å) is longer than that to P1′ (2.3173(9) Å). The rhodium to carbon distances vary from 2.112(3) Å (C4) to 2.234(3) Å (C1) probably as a result of the influence of the N and P atoms trans to the diene. The C1–C2 (1.439(5) Å) and C3–C4 (1.463(5) Å) distances have been lengthened as expected and are similar to the C2–C3 (1.420(5) Å) distance. The P1–P1′ (3.352 Å) and Rh–Rh′ (3.946 Å) separations are short and long respectively. The former is comparable to the P1–P2′ (3.357 Å) distance, yet the P1–P1′ coupling constant is quite large (243.93 Hz) and the P1–P2′ coupling constant is much smaller (less than 27.86 Hz). The P1–P1′ coupling is mainly a through-space interaction while the P1–P2′ coupling is a through-bond interaction.

The Rh–Rh′ separation may be compared with those found in $Rh_2(Ph_2PCH_2PPh_2)_2$ species.[45] In the latter the Rh–Rh separation ranges from about 2.8 Å for compounds containing a Rh–Rh bond to about 3.35 Å for compounds that do not contain a Rh–Rh bond.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support and to Johnson Matthey Aesar/Alfa for their generous loan of $RhCl_3{\cdot}3H_2O$.

Supplementary Material Available: Listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*) (10 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors (×10) (21 pages) are available from the authors upon request.

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