

Syntheses and Reactions of Iron and Ruthenium Complexes of an Optically Pure Fused Cyclopentadienyl Ligand

Debjani Bhaduri and John H. Nelson*

Department of Chemistry, University of Nevada, Reno, Nevada 89557-0020

Tieli Wang and Robert A. Jacobson

Department of Chemistry, Iowa State University, Ames, Iowa 50011

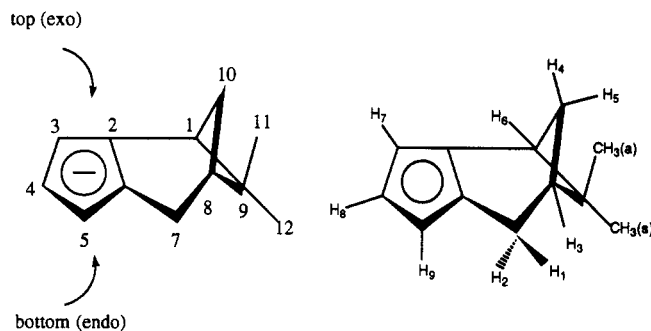
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Optically pure (1*R*)-(-)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (HPCp) reacts with Fe(CO)₅ and Ru₃(CO)₁₂, in the presence of the hydrogen acceptor norbornene, to form the isomorphous and isostructural complexes *cis*-[PCpM(CO)₂]₂ (M = Fe (1), Ru (8)), in which the metal is coordinated exclusively to the *exo* face of PCp. These complexes react with iodine to form PCpM(CO)₂I (M = Fe(2), Ru(9)). Complex 2 reacts with 1-phenyl-3,4-dimethylphosphole (DMPP), diphenylvinylphosphine (DPVP), and phenyldivinylphosphine (DVPP) to form two diastereomers of PCpFe(CO)(DMPP)I (3*a,b*), PCpFe(CO)(DPVP)I (4*a,b*), and PCpFe(CO)(DVPP)I (5*a,b*), respectively. Complex 9 reacts with DMPP to form two diastereomers of PCpRu(CO)(DMPP)I (10*a,b*). Complexes 4*a* and 4*b* react with DPVP and DVPP to undergo sequential ligand substitution and intramolecular [4 + 2] Diels-Alder cycloaddition forming four and five diastereomers of [PCpFe(CO)(DMPP)(DPVP)]I (6*a-d*) and [PCpFe(CO)(DMPP)(DVPP)]I (7*a-e*), respectively. Complexes 10*a* and 10*b* similarly react with DPVP and AgBF₄ BF₄ (11*a-d*). Little asymmetric induction is observed in these metal-promoted intramolecular [4 + 2] Diels-Alder cycloadditions. New complexes were characterized by elemental analyses, infrared spectroscopy, and ¹H, ¹³C{¹H}, and where appropriate ³¹P{¹H} NMR spectroscopy. The structures of 8 and 9 were confirmed by X-ray crystallography. Both compounds crystallized in the acentric space group *P*2₁2₁2₁ in unit cells with the following dimensions. 8: *a* = 12.082(2) Å, *b* = 18.689(5) Å, *c* = 11.156(2) Å, *V* = 2519.0(9) Å³, *Z* = 4. 9: *a* = 20.061(5) Å, *b* = 7.166(2) Å, *c* = 10.323(2) Å, *V* = 1483.9(6) Å³, *Z* = 4. Refinements converged to *R*(*F*) = 0.054 and 0.045 for 3561 and 2185 independent observed (*I* > 4σ(*I*)) reflections. In both compounds ruthenium coordinates to the less sterically hindered *exo* face of the PCp ligand, *anti* to the *gem*-dimethyl group.

Introduction

Asymmetric reactions catalyzed by transition metal complexes containing chiral ligands have shown that the metal can become a chiral center¹ during catalysis.^{2,3} Moreover, the chirality at the metal is believed to play a dominant role in determining the stereochemical outcome of the reactions, particularly when phosphine ligands are involved.^{4,5} We have previously shown that [(η⁵-C₅H₅)Ru(DMPP)_{3-n}(dienophile)_n]PF₆⁶ and [(η⁵-C₅H₅)Fe(DMPP)(CO)I]⁷ complexes [DMPP = 1-phenyl-3,4-dimethylphosphole] undergo [4 + 2] Diels-Alder cycloadditions with various dienophiles to produce conformationally rigid chiral bidentate ligands and have studied the diastereoselectivities of these reactions.⁸ It was of

Chart 1. PCp (1) and Its ¹³C and ¹H Numbering Schemes



interest to determine whether similar reactions would occur with iron and ruthenium complexes of the optically pure cyclopentadienide⁹ (1*R*)-(-)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienide (PCp, 1; Chart 1) and to ascertain the extent of asymmetric induction by the PCp ligand on these metal-promoted intramolecular [4 + 2] Diels-Alder cycloadditions. In order to do this, it was necessary to find methods for coordination of iron and ruthenium to only one of the two diastereotopic faces of PCp. The synthesis, characterization, and reactions of iron and ruthenium complexes of PCp wherein these metals are coordinated specifically to the *exo* face of PCp are reported herein.

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* Author to whom correspondence should be addressed.
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Experimental Section

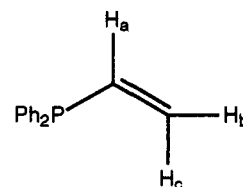
A. Reagents and Physical Measurements. Commercially available reagents were reagent grade and were used as received unless otherwise indicated. Solvents were distilled and dried by standard procedures. $\text{Fe}(\text{CO})_5$ (Strem Chemicals), $\text{Ph}_2\text{PCH}=\text{CH}_2$ (DPVP) and $\text{PhP}(\text{CH}=\text{CH}_2)_2$ (DVPP) (Organometallics Inc.), and $\text{Ru}_3(\text{CO})_{12}$, norbornene, and AgBF_4 (Aldrich) were obtained from the companies indicated. HPCp was prepared by the Salzer and Schmale¹⁰ modification of the Paquette and McLaughlin procedure.⁹ $[\text{PCpFe}(\text{CO})_2]_2$ ¹¹ and DMPP (1-phenyl-3,4-dimethylphosphole)¹² were prepared by literature methods. All reactions were carried out under a dry nitrogen atmosphere. Column chromatography was performed using either silica gel (grade 12, 28–300 mesh, Aldrich) or neutral alumina (Brockman I, standard grade 150 mesh, Aldrich). Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were obtained on Perkin-Elmer 599 and 1800 FT spectrometers. Photochemical reactions were performed with a Philips 100-W high-pressure Hg lamp with quartz immersion wells. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 121.65 MHz on a General Electric GN-300 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, on General Electric GN-300 and QE-300 spectrometers. Proton and carbon chemical shifts are relative to internal $(\text{CH}_3)_4\text{Si}$ while phosphorus chemical shifts are relative to external 85% H_3PO_4 with positive values being downfield of the respective reference.

B. Syntheses. $\text{PCpFe}(\text{CO})_2\text{I}$ (2). To a solution containing 2.71 g (5.00 mmol) of $[\text{PCpFe}(\text{CO})_2]_2$ in 100 mL of chloroform was added 1.98 g (7.80 mmol) of I_2 , and the resulting black solution was brought to reflux. After heating at reflux for 3 h, the red solution was stirred at ambient temperature for an additional 10 h. The solution was washed with a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (4×40 mL); the organic phase was separated from the mixture, dried over anhydrous sodium sulfate, and filtered. The filtrate was reduced to dryness on a rotary evaporator at 40 °C to produce a black crystalline solid. Recrystallization from ether/hexane afforded 3.46 g (87%) of black crystalline solid, mp 106 °C. IR (hexane): ν_{CO} 2032, 1988 cm^{-1} . ^1H NMR (CDCl_3): δ 0.69 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.84 (d, $^2J(\text{H}_4\text{H}_5) = 10.1$ Hz, 1H, H_4), 2.21 (app tt, $^3J(\text{H}_3\text{H}_6) = ^4J(\text{H}_3\text{H}_6) = 5.1$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.7$ Hz, 1H, H_3), 2.54 (app t, $^3J(\text{H}_5\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.1$ Hz, 1H, H_6), 2.62 (dd, $^2J(\text{H}_1\text{H}_2) = 17.4$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.7$ Hz, 1H, H_1), 2.75 (app dt, $^2J(\text{H}_4\text{H}_5) = 10.1$ Hz, $^3J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.1$ Hz, 1H, H_5), 3.02 (dd, $^2J(\text{H}_1\text{H}_2) = 17.4$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.7$ Hz, 1H, H_2), 4.48 (br s, 1H, H_8), 4.57 (br s, 1H, H_7), 5.12 (br s, 1H, H_9). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.49 (C_{12}), 25.91 (C_7), 26.29 (C_{11}), 35.70 (C_{10}), 40.20 (C_1), 40.74 (C_9), 41.70 (C_9), 74.62 (C_5), 76.58 (C_3), 87.65 (C_4), 102.77 (C_6), 115.78 (C_2), 213.82 (CO), 214.14 (CO). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{FeIO}_2$: C, 42.25; H, 3.79. Found: C, 41.91; H, 3.55.

$\text{PCpFe}(\text{CO})(\text{DMPP})\text{I}$ (3a,b). A solution containing 0.99 g (2.5 mmol) of 2 and 10 mg of 1 in 65 mL of benzene was brought to reflux, and 0.51 mL (2.71 mmol) of DMPP was added by syringe to the black solution. After 36 h at reflux, the solution had become green. The solution was cooled to ambient temperature and filtered over cellulose. A small amount of a yellow precipitate remained on the cellulose. This was extracted with CH_2Cl_2 . The CH_2Cl_2 was removed on a rotary evaporator to produce an air- and light-sensitive yellow solid that was identified as $[\text{PCpFe}(\text{CO})_2(\text{DMPP})]_2$, yield <5%. The original green benzene filtrate was reduced in volume and then purified by chromatography on silica gel. Elution with benzene/hexane (10:90) separated the product from the starting materials. Elution with benzene/hexane (50:50) produced a green eluate that was reduced in volume on a rotary evaporator to give a green oil. This oil was dissolved

in ether, and the solution was kept in a freezer at -20 °C overnight. Dark green crystals of a 2:1 diastereomeric ratio of 3a and 3b separated out. They were isolated by filtration, washed with cold ether, and dried under vacuum to yield 0.70 g (50%), mp 130–131 °C dec. IR (CH_2Cl_2): ν_{CO} 2000 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 3a δ 65.48; 3b δ 68.31. ^1H NMR (C_6D_6): 3a δ 0.55 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.54 (s, 3H, DMPP CH_3), 1.65 (s, 3H, DMPP CH_3), 1.92 (app tt, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.1$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 0.3$ Hz, 1H, H_3), 2.09 (d, $^4J(\text{H}_4\text{H}_5) = 16.2$ Hz, 1H, H_4), 2.25 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.1$ Hz, 1H, H_6), 2.47 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_1\text{H}_3) = 0.3$ Hz, 1H, H_1), 2.66 (app dt, $^2J(\text{H}_4\text{H}_5) = 16.2$ Hz, $^3J(\text{H}_5\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.1$ Hz, 1H, H_5), 3.65 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_2\text{H}_3) = 0.3$ Hz, 1H, H_2), 4.07 (br s, 1H, H_7), 4.48 (br s, 1H, H_8), 4.69 (br s, 1H, H_9), 6.09 (d, $^2J(\text{PH}) = 32.4$ Hz, 1H, H_a), 6.71 (d, $^2J(\text{PH}) = 32.1$ Hz, 1H, H_a'), 7.09–7.16 (m, 5H, Ph). 3b δ 0.45 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.54 (s, 3H, DMPP CH_3), 1.65 (s, 3H, DMPP CH_3), 1.85 (app tt, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.1$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 0.3$ Hz, 1H, H_3), 2.56 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_1\text{H}_3) = 0.3$ Hz, 1H, H_1), 2.57 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.1$ Hz, 1H, H_6), 2.79 (app dt, $^2J(\text{H}_4\text{H}_5) = 16.2$ Hz, $^3J(\text{H}_5\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.1$ Hz, 1H, H_5), 3.63 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_2\text{H}_3) = 0.3$ Hz, 1H, H_2), 4.08 (br s, 1H, H_7), 4.48 (br s, 1H, H_8), 4.69 (br s, 1H, H_9), 6.14 (d, $^2J(\text{PH}) = 32.4$ Hz, 1H, H_a), 6.66 (d, $^2J(\text{PH}) = 32.1$ Hz, 1H, H_a'), 7.86–7.91 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 3a δ 16.78 (d, $^3J(\text{PC}) = 12.26$ Hz, DMPP CH_3), 17.26 (d, $^3J(\text{PC}) = 11.47$ Hz, DMPP CH_3), 21.43 (C_{12}), 26.46 (C_7 and C_{11}), 34.89 (C_{10}), 41.00 (C_1), 41.56 (C_9), 41.76 (C_9), 64.29 (C_5), 78.18 (C_3), 82.57 (C_4), 100.92 (d, $^2J(\text{PC}) = 4.82$ Hz, C_6), 109.71 (C_2), 128.39 (d, $^3J(\text{PC}) = 7.20$ Hz, C_m), 128.42 (d, $^3J(\text{PC}) = 7.43$ Hz, C_m), 130.18 (d, $^4J(\text{PC}) = 1.81$ Hz, C_p), 130.25 (d, $^4J(\text{PC}) = 47.22$ Hz, C_a), 130.72 (d, $^4J(\text{PC}) = 46.87$ Hz, C_a'), 132.75 (d, $^2J(\text{PC}) = 8.60$ Hz, C_o), 132.78 (d, $^2J(\text{PC}) = 8.60$ Hz, C_o), 135.00 (d, $^1J(\text{PC}) = 48.43$ Hz, C_i), 148.57 (d, $^2J(\text{PC}) = 8.80$ Hz, C_β), 149.27 (d, $^2J(\text{PC}) = 9.27$ Hz, C_β), 219.57 (d, $^2J(\text{PC}) = 28.23$ Hz, CO); 3b δ 16.81 (d, $^3J(\text{PC}) = 12.53$ Hz, DMPP CH_3), 17.26 (d, $^3J(\text{PC}) = 11.47$ Hz, DMPP CH_3), 21.51 (C_{12}), 26.58 (C_7 and C_{11}), 38.02 (C_{10}), 40.63 (C_1), 40.74 (C_9), 42.07 (C_9), 61.28 (C_5), 81.97 (C_3), 82.30 (C_4), 97.50 (C_6), 113.24 (d, $^2J(\text{PC}) = 4.98$ Hz, C_6), 128.34 (d, $^3J(\text{PC}) = 7.2$ Hz, C_m), 128.37 (d, $^3J(\text{PC}) = 7.4$ Hz, C_m), 130.12 (d, $^4J(\text{PC}) = 2.64$ Hz, C_p), 130.26 (d, $^4J(\text{PC}) = 47.25$ Hz, C_a), 130.72 (d, $^4J(\text{PC}) = 46.72$ Hz, C_a'), 132.75 (d, $^2J(\text{PC}) = 8.60$ Hz, C_o), 132.78 (d, $^2J(\text{PC}) = 8.60$ Hz, C_o), 134.59 (d, $^2J(\text{PC}) = 48.46$ Hz, C_i), 148.66 (d, $^2J(\text{PC}) = 8.23$ Hz, C_β), 149.03 (d, $^2J(\text{PC}) = 9.36$ Hz, C_β), 221.28 (d, $^2J(\text{PC}) = 28.76$ Hz, CO). Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{FeIOP}$: C, 53.79; H, 5.06. Found: C, 53.76; H, 5.06.

$\text{PCpFe}(\text{CO})(\text{DPVP})\text{I}$ (4a,b). In the same manner as for 3a,b dark green crystals as a 5:1 diastereomeric ratio of 4a and 4b were obtained (1.00 g, 69%), mp 145–146 °C. IR (CH_2Cl_2): ν_{CO} 1945 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 4a δ 60.06; 4b δ 61.73.



^1H NMR (toluene- d_6): 4a δ 0.55 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.94 (app tt, $^3J(\text{H}_3\text{H}_6) = ^4J(\text{H}_3\text{H}_6) = 5.55$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.0$ Hz, 1H, H_3), 2.21 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 2.0$ Hz, 1H, H_6), 2.47 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.0$ Hz, 1H, H_1), 2.59 (app dt, $^2J(\text{H}_4\text{H}_5) = 9.7$ Hz, $^3J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.5$ Hz, 1H, H_5), 3.69 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.0$ Hz, 1H, H_2), 3.85 (app dt, $^2J(\text{PH}) = 6.6$ Hz, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.1$ Hz, 1H, H_8), 4.51 (br s, 2H, H_7 and H_9), 5.31 (app t, $^2J(\text{PH}) = ^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, 1H, H_a), 5.52 (dd, $^3J(\text{PH}) = 36.3$ Hz, $^2J(\text{H}_a\text{H}_b) = 12.0$ Hz, 1H, H_b), 6.72 (ddd, $^2J(\text{PH}) = 22.5$ Hz, $^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^3J(\text{H}_a\text{H}_b) = 12.0$ Hz, 1H, H_a), 7.46–7.80 (m, 10H, Ph); 4b δ 0.55 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.30 (app tt, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_3\text{H}_6) = 5.5$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.0$ Hz,

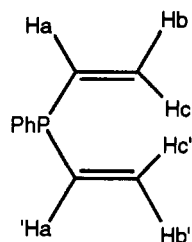
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^1H , H_3), 2.47 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.0$ Hz, 1H, H_1), 2.70 (app dt, $^2J(\text{H}_4\text{H}_5) = 9.7$ Hz, $^3J(\text{H}_3\text{H}_5) = ^3J(\text{H}_5\text{H}_6) = 5.5$ Hz, 1H, H_5), 2.83 (d, $^2J(\text{H}_4\text{H}_5) = 9.7$ Hz, 1H, H_4), 3.69 (dd, $^2J(\text{H}_1\text{H}_2) = 16.8$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.0$ Hz, 1H, H_2), 4.00 (app dt, $^2J(\text{PH}) = 6.6$ Hz, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.1$ Hz, 1H, H_8), 4.86 (br s, 2H, H_7 and H_9), 5.31 (app t, $^2J(\text{PH}) = ^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, 1H, H_c), 5.53 (dd, $^3J(\text{PH}) = 36.3$ Hz, $^2J(\text{H}_a\text{H}_b) = 12.0$ Hz, 1H, H_b), 6.66 (ddd, $^2J(\text{PH}) = 22.5$ Hz, $^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^3J(\text{H}_a\text{H}_b) = 12.0$ Hz, 1H, H_a), 7.46–7.80 (m, 10H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_6): **4a**: δ 21.39 (C_{12}), 26.47 (C_{11}), 26.64 (C_7), 34.52 (C_{10}), 40.56 (C_9), 41.73 (C_6), 41.92 (C_1), 64.33 (C_5), 83.35 (C_3 and C_4), 98.89 (C_8), 111.72 (C_2), 129.81 (d, $^4J(\text{PC}) = 1.5$ Hz, C_p), 130.24 (d, $^2J(\text{PC}) = 1.5$ Hz, C_β), 133.28 (d, $^3J(\text{PC}) = 9.3$ Hz, C_m), 133.29 (d, $^3J(\text{PC}) = 9.3$ Hz, C_m), 134.22 (d, $^2J(\text{PC}) = 9.4$ Hz, C_o), 134.55 (d, $^2J(\text{PC}) = 9.4$ Hz, C_o), 134.78 (d, $^1J(\text{PC}) = 40.0$ Hz, C_a), 136.46 (d, $^1J(\text{PC}) = 37.4$ Hz, C_i), 136.95 (d, $^1J(\text{PC}) = 37.4$ Hz, C_i), 220.82 (d, $^2J(\text{PC}) = 30.1$ Hz, CO); **4b** δ 21.55 (C_{12}), 26.33 (C_7), 26.59 (C_{11}), 38.56 (C_8 and C_{10}), 41.02 (C_1), 42.27 (C_9), 62.37 (C_5), 81.03 (C_3), 84.97 (C_3), 98.38 (C_6), 113.01 (C_2), 129.79 (d, $^4J(\text{PC}) = 1.5$ Hz, C_p), 130.22 (d, $^2J(\text{PC}) = 1.5$ Hz, C_β), 133.28 (d, $^3J(\text{PC}) = 9.3$ Hz, C_m), 133.29 (d, $^3J(\text{PC}) = 9.3$ Hz, C_m), 134.22 (d, $^2J(\text{PC}) = 9.4$ Hz, C_o), 134.55 (d, $^2J(\text{PC}) = 9.4$ Hz, C_o), 135.00 (d, $^1J(\text{PC}) = 40.0$ Hz, C_a), 136.60 (d, $^1J(\text{PC}) = 37.4$ Hz, C_i), 137.05 (d, $^1J(\text{PC}) = 37.4$ Hz, C_i), 222.77 (d, $^2J(\text{PC}) = 30.70$ Hz, CO). Anal. Calcd for $\text{C}_{27}\text{H}_{23}\text{FeIOP}$: C, 55.70; H, 4.85. Found: C, 55.75; H, 4.85.

PCpFe(CO)(DVPP)I (5a,b). In the same manner as for **3a,b** a dark green oil as a 3:2 diastereomeric ratio of **5a** and **5b** was obtained (0.86 g, 65%). IR(CH_2Cl_2): ν_{CO} 1945 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): **5a** δ 54.13; **5b** δ 55.85.



^1H NMR (toluene- d_6): **5a** δ 0.57 (s, 3H, $\text{CH}_3(\text{a})$), 1.16 (s, 3H, $\text{CH}_3(\text{a})$), 1.95 (app tt, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_3\text{H}_5) = 5.6$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.4$ Hz, 1H, H_3), 2.25 (app t, $^3J(\text{H}_5\text{H}_6) = ^4J(\text{H}_5\text{H}_6) = 5.6$ Hz, 1H, H_6), 2.56 (app dt, $^1J(\text{H}_4\text{H}_5) = 10.2$ Hz, $^3J(\text{H}_3\text{H}_5) = ^3J(\text{H}_5\text{H}_6) = 5.6$ Hz, 1H, H_5), 2.57 (dd, $^2J(\text{H}_1\text{H}_2) = 15.3$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.4$ Hz, 1H, H_1), 2.86 (dd, $^2J(\text{H}_1\text{H}_2) = 15.3$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.4$ Hz, 1H, H_2), 2.86 (d, $^2J(\text{H}_4\text{H}_5) = 10.2$ Hz, 1H, H_4), 3.68 (br s, 1H, H_7), 3.70 (app dt, $^3J(\text{PH}) = 6.3$ Hz, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.4$ Hz, 1H, H_8), 4.39 (app dt, $^3J(\text{H}_8\text{H}_9) = 2.4$ Hz, $^3J(\text{PH}) = ^4J(\text{H}_7\text{H}_9) = 1.2$ Hz, 1H, H_9), 5.25 (app td, $^3J(\text{PH}) = ^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^2J(\text{H}_b\text{H}_c) = 1.5$ Hz, 1H, H_c), 5.47 (ddd, $^3J(\text{PH}) = 36.0$ Hz, $^3J(\text{H}_a\text{H}_b) = 12.0$ Hz, $^2J(\text{H}_b\text{H}_c) = 1.5$ Hz, 1H, H_b), 5.57 (app td, $^3J(\text{PH}) = ^3J(\text{H}_a'\text{H}_c') = 18.1$ Hz, $^2J(\text{H}_b'\text{H}_c') = 1.5$ Hz, 1H, H_c'), 5.61 (ddd, $^3J(\text{PH}) = 36.0$ Hz, $^3J(\text{H}_a'\text{H}_b') = 12.0$ Hz, $^2J(\text{H}_b'\text{H}_c') = 1.5$ Hz, 1H, H_b'), 6.33 (ddd, $^2J(\text{PH}) = 21.6$ Hz, $^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^3J(\text{H}_a\text{H}_b) = 12.0$ Hz, 1H, H_a), 6.40 (ddd, $^2J(\text{PH}) = 21.6$ Hz, $^3J(\text{H}_a'\text{H}_c') = 18.1$ Hz, $^3J(\text{H}_a'\text{H}_b') = 12.0$ Hz, 1H, H_a'), 6.98–7.77 (m, 5H, Ph); **5b** δ 0.27 (s, 3H, $\text{CH}_3(\text{a})$), 1.20 (s, 3H, $\text{CH}_3(\text{a})$), 1.87 (app tt, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_3\text{H}_5) = 5.6$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.4$ Hz, 1H, H_3), 2.49 (dd, $^2J(\text{H}_1\text{H}_2) = 15.3$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.4$ Hz, 1H, H_1), 2.57 (dd, $^2J(\text{H}_1\text{H}_2) = 15.3$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.4$ Hz, 1H, H_2), 2.61 (d, $^2J(\text{H}_4\text{H}_5) = 10.2$ Hz, 1H, H_4), 2.68 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.6$ Hz, 1H, H_6), 2.70 (app dt, $^2J(\text{H}_4\text{H}_5) = 10.2$ Hz, $^3J(\text{H}_3\text{H}_5) = ^3J(\text{H}_5\text{H}_6) = 5.6$ Hz, 1H, H_5), 3.73 (m, 1H, H_7), 3.84 (app dt, $^3J(\text{PH}) = 6.3$ Hz, $^3J(\text{H}_8\text{H}_9) = ^3J(\text{H}_7\text{H}_8) = 2.4$ Hz, 1H, H_8), 4.67 (app dt, $^3J(\text{H}_8\text{H}_9) = 2.4$ Hz, $^3J(\text{PH}) = ^4J(\text{H}_7\text{H}_9) = 1.2$ Hz, 1H, H_9), 5.27 (app td, $^3J(\text{PH}) = ^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^2J(\text{H}_b\text{H}_c) = 1.5$ Hz, 1H, H_c), 5.59 (ddd, $^3J(\text{PH}) = 36.0$ Hz, $^3J(\text{H}_a\text{H}_b) = 12.0$ Hz, $^2J(\text{H}_b\text{H}_c) = 1.5$ Hz, 1H, H_b), 5.61 (ddd, $^3J(\text{PH}) = 36.0$ Hz, $^3J(\text{H}_a'\text{H}_b') = 12.0$ Hz, $^2J(\text{H}_b'\text{H}_c') = 1.5$ Hz, 1H, H_b'), 5.65 (app td, $^3J(\text{PH}) = ^3J(\text{H}_a'\text{H}_c') = 18.1$ Hz, $^2J(\text{H}_b'\text{H}_c') = 1.5$ Hz, 1H, H_c'), 6.32 (ddd, $^2J(\text{PH}) = 21.6$ Hz, $^3J(\text{H}_a\text{H}_c) = 18.0$ Hz, $^3J(\text{H}_a\text{H}_b) =$

12.0 Hz, 1H, H_a), 6.40 (ddd, $^2J(\text{PH}) = 21.6$ Hz, $^3J(\text{H}_a'\text{H}_c') = 18.1$ Hz, $^3J(\text{H}_a'\text{H}_b') = 12.0$ Hz, 1H, H_a'), 6.98–7.77 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_6): **5a** δ 20.59 (C_{12}), 25.88 (C_{11}), 26.03 (C_7), 34.01 (C_{10}), 39.96 (C_9), 41.35 (C_9), 63.60 (C_6), 79.28 (C_3), 82.83 (C_4), 100.37 (C_6), 110.81 (C_2), 128.62 (s, C_β), 128.93 (d, $^3J(\text{PC}) = 8.98$ Hz, C_m), 129.56 (s, C_β), 129.72 (s, C_β), 132.35 (d, $^2J(\text{PC}) = 8.1$ Hz, C_o), 134.36 (d, $^1J(\text{PC}) = 44.34$ Hz, C_i), 134.36 (d, $^1J(\text{PC}) = 42.35$ Hz, C_a), 135.25 (d, $^1J(\text{PC}) = 42.34$ Hz, C_a), 219.66 (d, $^2J(\text{PC}) = 31.39$ Hz, CO); **5b** δ 21.08 (C_{12}), 26.03 (C_{11}), 29.66 (C_7), 37.89 (C_{10}), 40.11 (C_9), 41.12 (C_1), 41.73 (C_8), 61.52 (C_6), 82.91 (C_4), 83.18 (C_3), 97.92 (C_6), 112.67 (C_2), 127.98 (d, $^3J(\text{PC}) = 8.9$ Hz, C_m), 128.62 (s, C_β), 129.56 (s, C_β), 129.72 (s, C_β), 132.41 (d, $^2J(\text{PC}) = 8.0$ Hz, C_o), 134.10 (d, $^1J(\text{PC}) = 44.2$ Hz, C_i), 134.20 (d, $^1J(\text{PC}) = 42.10$ Hz, C_a), 135.08 (d, $^1J(\text{PC}) = 42.3$ Hz, C_a), 221.49 (d, $^2J(\text{PC}) = 30.70$ Hz, CO). Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{FeIOP}$: C, 53.85; H, 4.48. Found: C, 53.69; H, 4.53.

Direct "One-Pot" Syntheses of 3a,b, 4a,b, and 5a,b. All these complexes could be conveniently synthesized in the following way. To a solution containing 0.50 g (0.92 mmol) of **1** in 20 mL of benzene was added 2.50 mmol of the appropriate phosphine, and the solution was brought to reflux. After 1 h, a solution containing 0.23 g (0.92 mmol) I_2 in 50 mL of benzene was added slowly. Some effervescence was observed. The resulting solution was heated at reflux for 48 h, during which time the color changed from black to dark green. The solution was cooled to ambient temperature and filtered, and the solvent was removed on a rotary evaporator. Purification by column chromatography on silica gel (benzene:hexane = 50:50) gave a green eluate containing the product. The solvent was removed on a rotary evaporator, and the residue was crystallized from ether to afford green crystals of the product in 30–40% yields.

Intramolecular [4 + 2] Cycloaddition of [PCpFe(CO)-(DMPP)(DPVP)]I (6a–d). A solution containing a mixture of **3a** and **3b** (2:1 ratio, 0.56 g, 1 mmol) and 5 mg of **1** in 50 mL of dry benzene was brought to reflux, and 0.23 mL (1.1 mmol) of DPVP was added by syringe. The green solution was heated at reflux for 48 h, during which time a small amount of yellow precipitate formed. After cooling to ambient temperature, the reaction mixture was filtered over cellulose. The green benzene filtrate contained mainly unreacted starting materials, which could be separated and recovered by column chromatography on silica gel. The yellow precipitate was extracted from the cellulose with 100 mL of CH_2Cl_2 . Evaporation of the solvent at room temperature produced yellow-brown crystals consisting of a 2:1:2:2 mixture of four diastereomers of the [4 + 2] Diels–Alder cycloadducts. Total yield: 340 mg, 44%. All attempts to separate the diastereomers by column chromatography (silica gel, Sephadex) or fractional crystallization failed. These compounds were characterized only by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Intramolecular [4 + 2] Cycloaddition of [PCpFe(CO)-(DMPP)(DVPP)]I (7a–e). These were prepared in the same way as described above for **6a–d**. The yellow precipitate consisted of a mixture of five diastereomers of the [4 + 2] Diels–Alder cycloadduct in a 2:2:1:2:2 ratio. Total yield: 430 mg, 60%. All attempts to separate the diastereomers by either column chromatography (silica gel, Sephadex) or fractional crystallization failed. These compounds were characterized only by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

[PCpRu(CO)]₂ (8). To a suspension of 1.278 g (2.00 mmol) of $\text{Ru}_3(\text{CO})_{12}$ in 75 mL of isooctane were added 0.96 g (6.00 mmol) of PCpH and 0.62 g (6.6 mmol) of norbornene. The resulting mixture was heated at reflux for 12 h. The reaction mixture turned dark red within 15 min. The solution was filtered while hot, and the filtrate was cooled to -10°C , whereupon red crystals (0.85 g) of the product precipitated. These were isolated by filtration, washed with hexane, and air-dried. The remaining filtrate was reduced in volume on a rotary evaporator and again cooled to -10°C to afford an additional 0.70 g of product. These products were combined and purified by column chromatography on neutral alumina by elution with hexane followed by ether. The ether eluate was reduced in volume, hexane was added, and the mixture was kept in the freezer at -10°C overnight. The

red-orange crystals were isolated by filtration and air-dried to yield 1.5 g (79%); mp 174 °C dec. $^1\text{H NMR}$ (CDCl_3): δ 0.65 (s, 6H, $\text{CH}_3(\text{a})$), 1.40 (s, 6H, $\text{CH}_3(\text{a})$), 1.87 (d, $^2J(\text{H}_4\text{H}_5) = 10.0$ Hz, 2H, H_4), 2.27 (app tt, $^3J(\text{H}_3\text{H}_5) = ^4J(\text{H}_3\text{H}_6) = 6.0$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 3.0$ Hz, 2H, H_3), 2.50 (dd, $^2J(\text{H}_1\text{H}_2) = 16.0$ Hz, $^3J(\text{H}_1\text{H}_3) = 3.0$ Hz, 2H, H_1), 2.59 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 6.0$ Hz, 2H, H_6), 2.78 (app dt, $^2J(\text{H}_4\text{H}_5) = 10.0$ Hz, $^3J(\text{H}_3\text{H}_5) = ^3J(\text{H}_5\text{H}_6) = 6.0$ Hz, 2H, H_5), 2.97 (dd, $^2J(\text{H}_1\text{H}_2) = 16.0$ Hz, $^3J(\text{H}_2\text{H}_3) = 3.0$ Hz, 2H, H_2), 4.44 (dd, $^3J(\text{H}_7\text{H}_8) = 3.0$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.0$ Hz, 2H, H_7), 4.78 (app t, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 3.0$ Hz, 2H, H_8), 5.08 (dd, $^3J(\text{H}_8\text{H}_9) = 3.0$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.0$ Hz, 2H, H_9). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.48 (C_{12}), 24.71 (C_7), 26.51 (C_{11}), 36.59 (C_{10}), 40.89 (C_8), 40.95 (C_1), 41.60 (C_9), 83.05 (C_5), 83.19 (C_3), 91.50 (C_4), 105.75 (C_6), 121.05 (C_{12}), 224.56 (CO). Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{Ru}_2\text{O}_4$: C, 53.17; H, 4.78. Found: C, 53.11; H, 4.86.

PCpRu(CO) $_2$ I (9). A mixture containing 0.632 g (1.00 mmol) of 8 and 0.380 g (1.50 mmol) of I_2 in 50 mL of chloroform was heated at reflux for 3 h and then stirred at ambient temperature for another 12 h. The dark red solution was washed with a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (4 \times 10 mL) to remove excess I_2 . The organic phase was collected, dried over anhydrous Na_2SO_4 , filtered, and reduced to about 10 mL on a rotary evaporator. Hexane (10 mL) was added, and the mixture was kept in the freezer at -10 °C overnight. The orange-red crystals that formed were isolated by filtration and air-dried. Yield: 0.85 g (96%). Mp: 115 °C. IR (CH_2Cl_2) ν_{CO} 1990, 2050 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): δ 0.75 (s, 3H, $\text{CH}_3(\text{a})$), 1.40 (s, 3H, $\text{CH}_3(\text{a})$), 1.66 (d, $^2J(\text{H}_4\text{H}_5) = 10.21$ Hz, 1H, H_4), 2.24 (app tt, $^3J(\text{H}_3\text{H}_5) = ^4J(\text{H}_3\text{H}_6) = 5.40$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 3.0$ Hz, 1H, H_3), 2.56 (app t, $^4J(\text{H}_3\text{H}_6) = ^4J(\text{H}_5\text{H}_6) = 5.40$ Hz, 1H, H_6), 2.70 (dd, $^2J(\text{H}_1\text{H}_2) = 17.11$ Hz, $^3J(\text{H}_1\text{H}_3) = 3.0$ Hz, 1H, H_1), 2.73 (app dt, $^2J(\text{H}_4\text{H}_5) = 10.21$ Hz, $^3J(\text{H}_2\text{H}_3) = 5.40$ Hz, 1H, H_5), 3.09 (dd, $^2J(\text{H}_1\text{H}_2) = 17.11$ Hz, $^3J(\text{H}_1\text{H}_3) = 3.0$ Hz, 1H, H_2), 4.96 (dd, $^3J(\text{H}_7\text{H}_8) = 2.70$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.50$ Hz, 1H, H_7), 5.00 (dd, $^3J(\text{H}_8\text{H}_9) = 3.0$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.50$ Hz, 1H, H_9), 5.38 (app t, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.70$ Hz, 1H, H_8). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.58 (C_{12}), 26.01 (C_7), 26.19 (C_{11}), 36.81 (C_{10}), 40.40 (C_1), 41.05 (C_8), 41.15 (C_9), 77.26 (C_5), 79.23 (C_3), 88.55 (C_4), 107.63 (C_6), 121.51 (C_2), 196.20 (CO), 196.55 (CO). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{RuO}_2$: C, 37.95; H, 3.39. Found: C, 37.41; H, 2.97.

PCpRu(CO)(DMPP)I (10a,b). A solution containing 0.300 g (0.677 mmol) of 9 and 0.127 g (0.667 mmol) of DMPP in 300 mL of toluene was photolyzed under N_2 for 18 h. After cooling to ambient temperature, the red solution was reduced to dryness on a rotary evaporator to give an orange oil. The oil was purified by column chromatography on silica gel. Elution with hexane afforded unreacted 9. Elution with benzene/hexane (80:20) followed by reduction in volume of the eluate afforded 0.285 g (70%) of a pale orange waxy solid (mp >200 dec) containing 10a and 10b in a 3:2 diastereomeric ratio. All attempts to separate 10a from 10b by fractional crystallization and column chromatography were unsuccessful. IR (CH_2Cl_2): ν_{CO} 1975 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 10a δ 41.91; 10b δ 39.74. $^1\text{H NMR}$ (CDCl_3): 10a δ 0.72 (s, 3H, $\text{CH}_3(\text{a})$), 1.36 (s, 3H, $\text{CH}_3(\text{a})$), 1.87 (d, $^2J(\text{H}_4\text{H}_5) = 9.61$ Hz, 1H, H_4), 2.10 (s, 6H, DMPP CH_3), 2.17 (app tt, $^3J(\text{H}_3\text{H}_5) = ^4J(\text{H}_3\text{H}_6) = 5.70$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.10$ Hz, 1H, H_3), 2.40 (app t, $^3J(\text{H}_5\text{H}_6) = ^4J(\text{H}_5\text{H}_6) = 5.70$ Hz, 1H, H_6), 2.50 (app dt, $^2J(\text{H}_4\text{H}_5) = 9.61$ Hz, $^3J(\text{H}_2\text{H}_3) = ^3J(\text{H}_5\text{H}_6) = 5.70$ Hz, 1H, H_5), 2.61 (dd, $^2J(\text{H}_1\text{H}_2) = 17.11$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.10$ Hz, 1H, H_1), 3.10 (dd, $^2J(\text{H}_1\text{H}_2) = 17.11$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.10$ Hz, 1H, H_2), 4.41 (dd, $^3J(\text{H}_8\text{H}_9) = 2.40$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.20$ Hz, 1H, H_9), 4.54 (dd, $^3J(\text{H}_7\text{H}_8) = 2.40$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.20$ Hz, 1H, H_7), 4.69 (app t d, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.40$ Hz, $^3J(\text{PH}) = 1.50$ Hz, 1H, H_8), 6.55 (d, $^2J(\text{PH}) = 33.02$ Hz, 1H, H_α), 6.70 (d, $^2J(\text{PH}) = 33.34$ Hz, 1H, H_α), 7.30–7.70 (m, 5H, Ph); 10b δ 0.69 (s, 3H, $\text{CH}_3(\text{a})$), 1.33 (s, 3H, $\text{CH}_3(\text{a})$), 1.76 (d, $^2J(\text{H}_4\text{H}_5) = 9.91$ Hz, 1H, H_4), 2.10 (s, 6H, DMPP CH_3), 2.17 (app tt, $^3J(\text{H}_3\text{H}_5) = ^4J(\text{H}_3\text{H}_6) = 5.40$ Hz, $^3J(\text{H}_1\text{H}_3) = ^3J(\text{H}_2\text{H}_3) = 2.40$ Hz, 1H, H_3), 2.30 (app t, $^4J(\text{H}_3\text{H}_6) = ^3J(\text{H}_5\text{H}_6) = 5.40$ Hz, 1H, H_6), 2.62 (app dt, $^2J(\text{H}_4\text{H}_5) = 9.91$ Hz, $^3J(\text{H}_2\text{H}_3) = ^3J(\text{H}_5\text{H}_6) = 5.40$ Hz, 1H, H_5), 2.90 (dd, $^2J(\text{H}_1\text{H}_2) = 16.81$ Hz, $^3J(\text{H}_1\text{H}_3) = 2.40$ Hz, 1H, H_1), 3.11 (dd, $^2J(\text{H}_1\text{H}_2) = 16.81$ Hz, $^3J(\text{H}_2\text{H}_3) = 2.40$ Hz, 1H, H_2), 4.45 (dd, $^3J(\text{H}_7\text{H}_8) = 2.40$

Table 1. Crystallographic Data for 8 and 9

	8	9
chem formula	$\text{Ru}_2(\text{CO})_4\text{C}_{24}\text{H}_{30}$	$\text{Ru}(\text{CO})_2\text{C}_{15}\text{H}_{15}\text{I}$
fw	632.68	443.25
<i>a</i> (Å)	12.082(2)	20.061(5)
<i>b</i> (Å)	18.689(5)	7.166(2)
<i>c</i> (Å)	11.156(2)	10.323(2)
<i>V</i> (Å ³)	2519.0(9)	1483.9(6)
<i>Z</i>	4	4
space group	$P2_12_12_1$	$P2_12_12_1$
<i>T</i> (°C)	23 \pm 1	23 \pm 1
λ (Å)	0.710 69	0.710 69
ρ_{calcd} (g cm^{-3})	1.668	1.984
μ (cm^{-1})	12.1	30.875
<i>R</i> (<i>F</i>) ^a	0.054	0.045
<i>R</i> _w (<i>F</i>) ^b	0.065	0.058

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F) = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}.$$

Hz, $^4J(\text{H}_7\text{H}_9) = 1.2$ Hz, 1H, H_7), 4.60 (dd, $^3J(\text{H}_8\text{H}_9) = 2.40$ Hz, $^4J(\text{H}_7\text{H}_9) = 1.20$ Hz, 1H, H_9), 4.76 (app t, $^3J(\text{H}_7\text{H}_8) = ^3J(\text{H}_8\text{H}_9) = 2.40$ Hz, 1H, H_8), 6.43 (d, $^2J(\text{PH}) = 34.82$ Hz, 1H, H_α), 6.66 (d, $^2J(\text{PH}) = 32.72$ Hz, 1H, H_α), 7.30–7.70 (m, 5H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 10a δ 17.16 (d, $^3J(\text{PC}) = 12.08$ Hz, DMPP CH_3), 17.32 (d, $^3J(\text{PC}) = 11.47$ Hz, DMPP CH_3), 21.70 (C_{12}), 25.81 (C_7), 26.59 (C_{11}), 36.62 (C_{10}), 40.90 (C_9), 41.03 (C_1), 41.57 (C_8), 76.45 (C_6), 78.00 (C_3), 86.45 (C_4), 104.55 (d, $^2J(\text{PC}) = 1.66$ Hz, C_6), 128.13 (C_2), 129.81 (d, $^3J(\text{PC}) = 7.02$ Hz, C_m), 129.84 (C_p), 130.03 (d, $^3J(\text{PC}) = 7.70$ Hz, C_m), 130.89 (d, $^1J(\text{PC}) = 50.42$ Hz, C_α), 131.11 (d, $^1J(\text{PC}) = 52.84$ Hz, C_α'), 131.86 (d, $^2J(\text{PC}) = 10.11$ Hz, C_o), 131.89 (d, $^1J(\text{PC}) = 35.40$ Hz, C_i), 132.11 (d, $^2J(\text{PC}) = 10.49$ Hz, C_o), 149.01 (d, $^2J(\text{PC}) = 9.89$ Hz, C_β), 149.09 (d, $^2J(\text{PC}) = 10.49$ Hz, C_β); 10b δ 17.25 (d, $^3J(\text{PC}) = 12.38$ Hz, DMPP CH_3), 17.34 (d, $^3J(\text{PC}) = 12.59$ Hz, DMPP CH_3), 21.57 (C_{12}), 26.28 (C_7), 26.54 (C_{11}), 36.48 (C_{10}), 40.73 (C_9), 40.80 (C_1), 41.25 (C_8), 72.36 (C_6), 73.83 (C_3), 84.20 (C_4), 104.74 (C_6), 128.27 (C_2), 130.01 (C_p), 130.03 (d, $^3J(\text{PC}) = 7.70$ Hz, C_m), 130.56 (d, $^3J(\text{PC}) = 9.13$ Hz, C_m), 130.89 (d, $^1J(\text{PC}) = 50.42$ Hz, C_α), 131.11 (d, $^1J(\text{PC}) = 52.84$ Hz, C_α'), 131.89 (d, $^1J(\text{PC}) = 35.40$ Hz, C_i), 131.98 (d, $^2J(\text{PC}) = 8.83$ Hz, C_o), 132.11 (d, $^2J(\text{PC}) = 10.49$ Hz, C_o), 149.04 (d, $^2J(\text{PC}) = 9.89$ Hz, C_β), 149.23 (d, $^2J(\text{PC}) = 10.72$ Hz, C_β).

Intramolecular [4 + 2] Cycloaddition of [PCpRu(CO)(DMPP)(DPVP)]BF₄ (11a–d). A solution containing a 3:2 mixture of 10a and 10b (0.360 g, 0.596 mmol) in 65 mL of 1,2-dichloroethane was brought to reflux, and 0.148 g (0.745 mmol) of DPVP was added via syringe. To this mixture was added rapidly 0.115 g (0.596 mmol) of AgBF_4 . A white precipitate of AgI formed, and the solution color changed from orange to yellow. The reaction mixture was heated at reflux for 36 h, cooled to ambient temperature, and filtered through Celite. The yellow filtrate was concentrated to an oil on a rotary evaporator, and the oil was washed with hexane (4 \times 10 mL). The oil was dissolved in CH_2Cl_2 , and ether was added. The brown solid that formed was isolated by filtration, washed with ether, and air-dried to yield 0.25 g (50%) (mp >250 °C) containing 11a–d in a 2:3:2:3 diastereomeric ratio. No attempts were made to separate the four diastereomers.

C. X-ray Data Collection and Processing. Crystals of 8 (red-orange) and 9 (brown) were isolated from ether/hexane and CHCl_3 /hexane solutions, respectively, at room temperature. Crystal data and details of data collection are given in Table 1. The crystals were indexed, and data were collected on a Hilger Watts diffractometer on a Rigaku rotating-anode generator using graphite-monochromated $\text{Mo K}\alpha$ radiation. On the basis of the systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) and the successful solution and refinements of the structures, the space group in each case was determined to be $P2_12_12_1$. The data were collected at 23 \pm 1 °C using the ω -scan technique. Three standard reflections measured after every 200 reflections during the entire data collection period showed a 1.5% decrease for 8 and no significant trends for 9. Empirical absorption corrections, based on azimuthal scans of several reflections, were applied, and the data were corrected for Lorentz and polarization effects.

Table 2. Atom Coordinates for 8

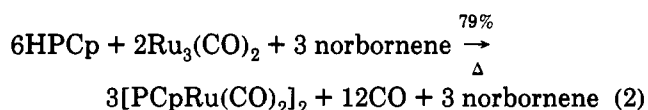
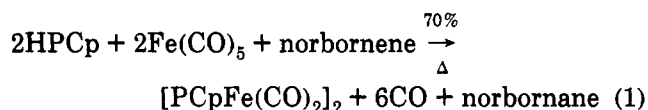
atom	x	y	z	B(eq) ^a (Å ²)
Ru1	0.1090(1)	0.12248(8)	0.7286(1)	2.80(7)
Ru2	0.3175(1)	0.16780(8)	0.6710(1)	2.91(7)
O1	0.209(1)	0.2374(8)	0.883(1)	4.0(7)
O2	0.196(1)	0.0799(8)	0.488(1)	5.1(8)
O3	0.256(1)	0.2960(7)	0.519(1)	6.0(9)
O4	-0.020(1)	0.2464(9)	0.629(1)	6(1)
C1	0.202(2)	0.198(1)	0.801(2)	4(1)
C2	0.204(2)	0.109(1)	0.576(2)	4(1)
C3	0.278(1)	0.248(1)	0.572(2)	2.7(9)
C4	0.031(2)	0.202(1)	0.664(2)	4(1)
C5	0.487(2)	0.140(1)	0.607(2)	4(1)
C6	0.429(2)	0.093(1)	0.783(2)	4(1)
C7	0.443(2)	0.080(1)	0.662(2)	5(1)
C8	0.497(2)	0.195(1)	0.695(2)	3(1)
C9	0.463(2)	0.165(1)	0.803(2)	5(1)
C10	0.479(2)	0.213(1)	0.918(2)	4(1)
C11	0.539(2)	0.284(1)	0.877(2)	3(1)
C12	0.480(2)	0.316(1)	0.772(2)	4(1)
C13	0.552(2)	0.267(1)	0.690(2)	4(1)
C14	0.638(2)	0.269(1)	0.795(2)	4(1)
C15	0.713(2)	0.204(1)	0.818(2)	4(1)
C16	0.711(2)	0.334(1)	0.794(2)	5(1)
C17	-0.036(2)	0.047(1)	0.749(2)	4(1)
C18	-0.010(2)	0.080(1)	0.863(2)	4(1)
C19	0.094(2)	0.058(1)	0.899(2)	4(1)
C20	0.137(2)	0.012(1)	0.807(2)	5(1)
C21	0.055(2)	0.0050(9)	0.721(2)	3(1)
C22	0.040(2)	-0.046(1)	0.613(2)	4(1)
C23	-0.078(2)	-0.036(1)	0.561(2)	4(1)
C24	-0.102(2)	0.045(1)	0.539(2)	6(1)
C25	-0.136(2)	0.044(1)	0.675(2)	5(1)
C26	-0.165(2)	-0.038(1)	0.660(2)	5(1)
C27	-0.153(2)	-0.089(1)	0.765(2)	6(1)
C28	-0.282(2)	-0.047(1)	0.604(3)	7(2)

$${}^a B(\text{eq}) = (\pi^3/8) \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j.$$

The structures were solved by direct methods.^{13a} The non-hydrogen atoms were refined anisotropically. The hydrogen atoms are in calculated positions. Full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o)^2$ converged to the values given in Table 1.^{13b} The maximum and minimum peaks on the final difference maps occurred close to the ruthenium atoms and corresponded to 0.998 and -0.941 e/Å³ for 8 and 1.018 and -1.487 e/Å³ for 9 respectively. The scattering factor coefficients and anomalous dispersion coefficients were taken respectively from parts a and b of ref ¹⁴. Final atom coordinates for 8 and 9 are given in Tables 2 and 5, and selected bond lengths and angles are given in Tables 3 and 6, respectively.

Results and Discussion

HPCp reacts¹¹ with Fe(CO)₅ (reaction 1) and Ru₃(CO)₁₂ (reaction 2) in the presence of the hydrogen acceptor norbornene to form the isomorphous and isostructural



complexes [PCpFe(CO)₂]₂ (1) and [PCpRu(CO)₂]₂ (8) in

(13) (a) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) All calculations were performed using the TEXAN-TEXRAY Crystallographic software package of Molecular Structure Corp., 1985.

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

Table 3. Selected Bond Lengths and Angles for [PCpM(CO)₂]₂

	bond lengths (Å)		bond lengths (Å)	
	M = Fe ^a	M = Ru	M = Fe ^a	M = Ru
M1-M2	2.543(2)	2.735(2)	M2-C3 or -C4 ^b	1.76(3) 1.96(2)
M1-C1	1.94(2)	1.99(2)	C1-O1	1.17(3) 1.17(2)
M1-C2	1.91(2)	2.06(2)	C2-O2	1.17(3) 1.14(2)
M2-C1	1.92(2)	2.09(2)	C3-O3	1.14(3) 1.11(2)
M2-C2	1.94(3)	2.04(2)	C4-O4	1.13(4) 1.11(2)
M1-C3 or -C4 ^b	1.76(3)	1.90(2)	M-PCp (av)	2.12(3) 2.26(2)

	bond angles (deg)	
	M - Fe ^a	M = Ru
M1-C1-M2	82(1)	84.2(8)
M1-C2-M2	83(1)	83.5(8)
C1-M1-C2	96.6(9)	96.0(9)
C1-M2-C2	96(1)	93.3(8)
M1-C1-O1	137(1)	143(2)
M1-C2-O2	141(2)	137(2)
M1- or M2-C3-O3 ^b	179(1)	177(2)
M2- or M1-C4-O4 ^b	176(2)	176(2)

^a Reference 15. ^b The atom-numbering schemes differ slightly for the two molecules; equivalent distances and angles are listed.

good yield. The crystal structure of 1 has been reported previously,¹⁵ and that of 8 is shown in Figure 1. For both 1 and 8 the metal is coordinated only to the *exo* face of PCp (Chart 1), and both molecules adopt the less common *cis* geometry.¹⁶ Both molecules crystallize as discrete molecular entities with no unusual intermolecular contacts. Their structures differ only in their metrical parameters in the expected direction (Table 3).

Ever since the discovery that [CpFe(CO)₂]₂ is dynamic in solution undergoing rapid *cis-trans* isomerization,^{17,18} every other cyclopentadienylmetal carbonyl dimer has been similarly examined. There is now reasonable agreement as to the predominant structure in solution, the intimate mechanism of isomerization, and the spectroscopic characterization of these complexes.¹⁹⁻²¹ In general, there are believed to be four different isomers that exist in solution, the relative abundances of which are solvent and temperature dependent. These are the *cis* and *trans* carbonyl-bridged isomers and the *cis* and *trans* nonbridged isomers. For [CpRu(CO)₂]₂ in nonpolar solvents all four isomers are present with the *cis* bridged isomer predominating.²² As the steric bulk of the cyclopentadienyl ligand increases, the stability of the *cis* bridged isomer decreases such that for [(C₅Me₅)Ru(CO)₂]₂ and [(C₅Me₄Et)Ru(CO)₂]₂ only the *trans* bridged isomer is observed.^{23,24} As a means of comparison, a survey of infrared data in the ν_{CO} region (1700-2200 cm⁻¹) for different cyclopentadi-

(15) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599.

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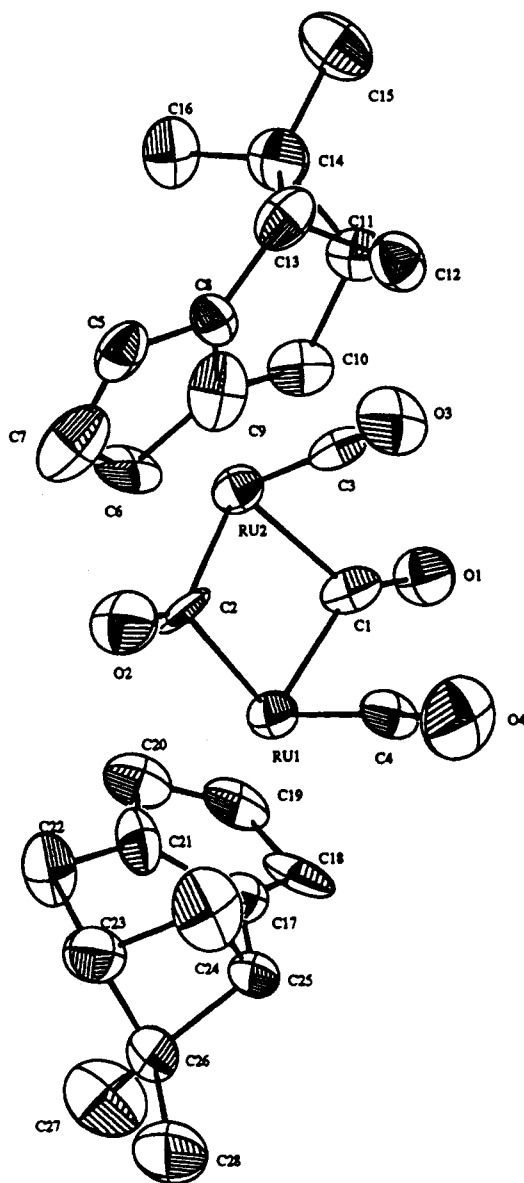


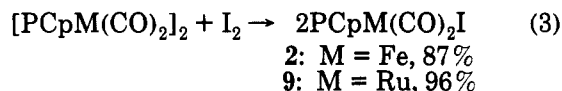
Figure 1. ORTEP drawing of **8** showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

enylruthenium carbonyl dimers was undertaken (Table 4). The solid-state infrared data (Nujol) for $[\text{PCpRu}(\text{CO})_2]_2$ are consistent with the X-ray crystal structure, as two bridging and two terminal ν_{CO} stretching vibrations are expected for the *cis* carbonyl-bridged dimer. The additional vibration most probably results from correlation field effects.^{25,26} The *cis* carbonyl-bridged dimer is probably also the predominant species present in the solvents hexane, isooctane, and CH_2Cl_2 .

The ^1H NMR spectra of **11** and **8** in CD_3COCD_3 and CDCl_3 , respectively, each exhibit only two methyl resonances, showing that only one face of PCp is coordinated to either iron or ruthenium. The chemical shifts of these resonances (δ 0.68 and 1.42, Fe; δ 0.65 and 1.40, Ru) show that both metals are coordinated to the *exo* face of PCp as they are in the solid state. This conclusion is based on the different chemical shifts of the methyl resonances for

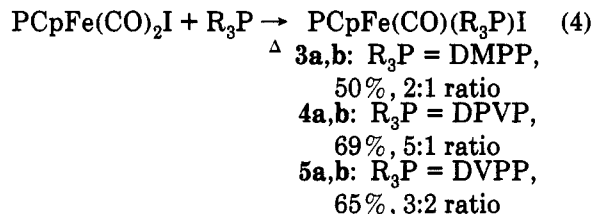
the *exo* and *endo* isomers of $[\text{PCpRu}(\text{C}_6\text{H}_8)]\text{PF}_6$ (δ 0.56 and 1.36, *exo*; δ 1.19 and 1.34, *endo*).²⁷ Similar chemical shift differences are observed for other isomeric pairs of $[(\text{PCp})\text{Ru}(\text{arene})]\text{PF}_6$ complexes. The *exo* and *endo* isomers are readily distinguished on the basis that the resonance for the methyl group proximate to the Cp ring in the *exo* isomer is shifted considerably upfield by the diamagnetic anisotropy of the Cp ring. $[\text{PCpRu}(\text{CO})_2]_2$ is dynamic in solution, as only one carbonyl carbon resonance (δ 224.56) is observed, appearing at an average value of what would be expected²⁸ for bridging ($\delta \sim 250$) and terminal ($\delta \sim 200$) carbonyl chemical shifts for such species.

Complexes **1** and **8** react with iodine in chloroform (reaction 3) to form **2** and **9**, respectively, in high yields.

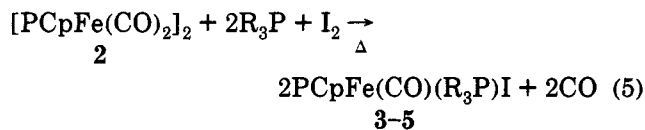


These compounds are air-stable crystalline solids. The crystal structure of **9** (Figure 2) demonstrates that the metal remains coordinated to the *exo* face of PCp as expected. This molecule crystallizes as a discrete molecular entity with no unusual intermolecular contacts. The bond lengths and angles (Table 6) are normal.

The proton and carbon NMR spectral data for **2** and **9** show that only one isomer of each species is present in solution and that the metal is coordinated to the *exo* face of PCp. When **2** is reacted with 1 equiv of a phosphine at reflux temperatures in benzene for a period of 44 h, one of the carbonyl groups is replaced by the phosphine and two inseparable diastereomers of the green neutral monophosphine complexes of general formula $\text{PCpFe}(\text{CO})(\text{R}_3\text{P})\text{I}$ are obtained (reaction 4). These reactions proceed



in lower overall yield compared to the analogous reactions of $\text{CpFe}(\text{CO})_2\text{I}$ with these same phosphines,⁷ where the yields ranged from 80 to 93%. Complexes **3–5** are very soluble in both nonpolar and polar solvents and are moderately air and light sensitive in solution, with halocarbon solvents hastening the decomposition process. The diastereomeric ratios, which are readily determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy,²⁹ increase with increasing steric bulk of the phosphine. Compounds **3–5** could also be prepared directly from **1** via reaction 5. The diaster-



eomeric ratios were the same in both preparative routes, suggesting that they are thermodynamically controlled. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data show that iron is

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Table 4. ν_{CO} (cm⁻¹) Vibrational Frequencies for [CpRu(CO)₂]₂ Complexes

Cp	solvent	A	B	C	D	E	F	G	ref
C ₅ H ₅	heptane	1794	1814	1944	1965	1973	2010	2020	21
C ₅ H ₅	CHCl ₃	1773	1806	1936	1968	1951	2009	2014	21
C ₅ H ₄ Me	heptane	1790	1813	1941	1960	1969	2006	2015	21
C ₅ H ₄ Me	CHCl ₃	1779	1809	1937	1959	1964	2003		21
indenyl	heptane	1798	1837		1964		2006		21
indenyl	CHCl ₃	1779			1961		2003		21
C ₅ Me ₅	CH ₂ Cl ₂	1744		1925					22
C ₅ Me ₄ Et	cyclohexane	1765		1937					23
MCp ^a	pentane	1785		1935	1955	1965	2000	2010	24
NMCp ^a	pentane	1785		1935	1955	1965	2000		24
PCp	hexane	1770		1925	1945	1990			b
PCp	isooctane	1730	1770	1930	1950	1995			b
PCp	CH ₂ Cl ₂	1750			1945	1980			b
PCp	Nujol	1730	1760	1935	1940	1990			b

^a MCp = menthylcyclopentadienyl; NMCp = neomenthylcyclopentadienyl. ^b This work.

Table 5. Atom Coordinates for 9^a

atom	x	y	z	B(eq) ^a (Å ²)
I1	0.66775(3)	0.1896(1)	0.45763(8)	5.36(3)
Ru1	0.79890(3)	0.1002(1)	0.45386(7)	3.49(3)
O1	0.8296(5)	0.367(2)	0.242(1)	6.9(5)
O2	0.8217(5)	0.388(1)	0.661(1)	6.9(5)
C1	0.8761(4)	-0.097(1)	0.5259(8)	3.4(3)
C2	0.8109(5)	-0.161(1)	0.569(1)	4.3(5)
C3	0.7749(5)	-0.203(1)	0.458(1)	5.1(5)
C4	0.8128(7)	-0.167(2)	0.347(1)	5.2(5)
C5	0.8754(5)	-0.102(2)	0.3866(8)	3.6(4)
C6	0.9406(6)	-0.079(2)	0.317(1)	5.7(6)
C7	0.9956(5)	-0.050(1)	0.416(1)	5.2(5)
C8	0.9947(5)	-0.188(1)	0.528(1)	4.6(4)
C9	0.9407(5)	-0.055(1)	0.590(1)	3.8(4)
C10	0.9762(5)	0.102(1)	0.513(1)	5.0(5)
C11	0.9735(6)	-0.390(2)	0.507(1)	5.4(5)
C12	1.0590(6)	-0.186(2)	0.608(2)	6.9(7)
C13	0.8158(6)	0.278(2)	0.318(1)	5.0(5)
C14	0.8132(6)	0.285(2)	0.581(1)	4.6(5)

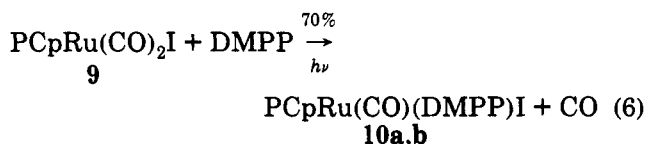
^a B(eq) = $(\pi^3/8) \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \tilde{a}_i \tilde{a}_j$.

Table 6. Selected Bond Lengths and Angles for 9

Bond Lengths (Å)			
Ru1-I1	2.708(1)	Ru1-C5	2.22(1)
Ru1-C1	2.22(1)	Ru1-C13	1.93(1)
Ru1-C2	2.33(1)	Ru1-C14	1.89(1)
Ru1-C3	2.33(1)	C13-O1	1.05(1)
Ru1-C4	2.23(1)	C14-O2	1.12(1)
Bond Angles (deg)			
I1-Ru1-C13	91.4(3)	Ru1-C13-O1	174(1)
I1-Ru1-C14	88.4(3)	Ru1-C14-O2	177(1)
C13-Ru1-C14	90.8(4)		

coordinated only to the *exo* face of the PCp ligand. Hence, the diastereomers differ only in the absolute configuration at the iron stereocenter.

In contrast to 2, 9 does not undergo thermal carbonyl substitution by phosphines. This result is somewhat surprising, since such reactions occur readily for (menthyl-Cp)Ru(CO)₂I,¹² (neomenthyl-Cp)Ru(CO)₂I,¹² and (η^5 -Me₅C₅)Ru(CO)₂I.³⁰ However, photolysis of 9 in toluene in the presence of DMPP produces an inseparable mixture of the two diastereomers of PCpRu(CO)(DMPP)I (10a,b) (reaction 6). The diastereomeric ratio (3:2) was determined



by ³¹P{¹H} NMR spectroscopy and is lower than that found

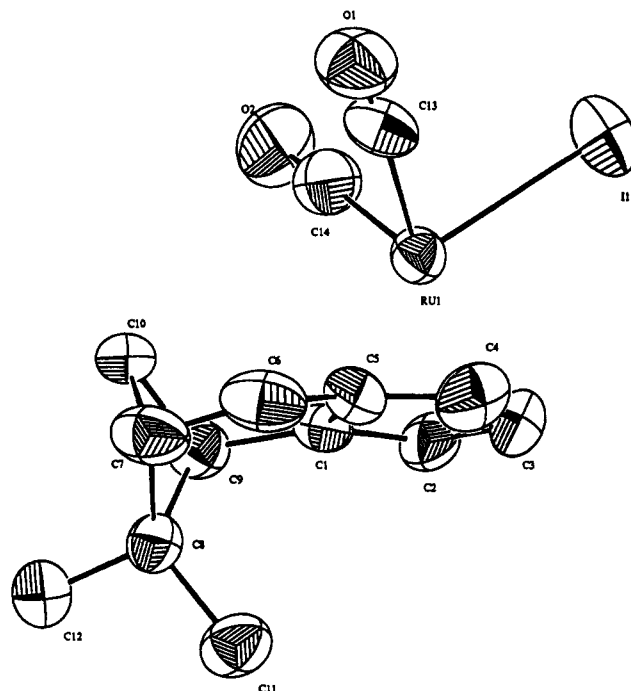
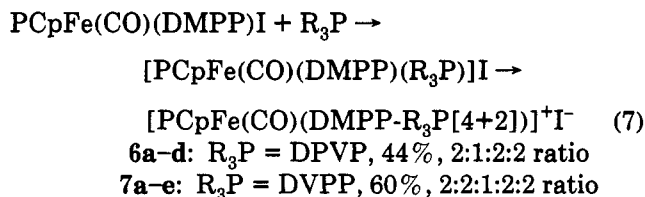


Figure 2. ORTEP drawing of 9 showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

for PCpFe(CO)(DMPP)I (2:1), probably as a result of the greater metal-to-PCp distance in the ruthenium than in the iron complex. The ¹H and ¹³C{¹H} NMR spectral data show that ruthenium is coordinated only to the *exo* face of the PCp ligand.

Complex 3 (as a 2:1 mixture of diastereomers) reacts with the phosphines DPVP and DVPP, which are capable of behaving as dienophiles toward the coordinated DMPP to replace the coordinated iodide and undergo a metal-promoted intramolecular [4 + 2] Diels-Alder cycloaddition⁸ (reaction 7). The ligand substitution products,



[PCpFe(CO)(DMPP)(R₃P)]⁺I⁻, could neither be isolated

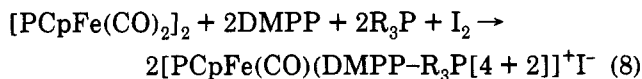
Table 7. 121.66-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR Data for the [4 + 2] Diels-Alder Adducts and Ligand Structure Assignments^a

cmpd	$\delta(\text{P}_7)$	$\delta(\text{P}_2)$	$^2J(\text{P}_7\text{P}_2)$	$\Delta\delta = \delta(\text{P}_7) - \delta(\text{P}_2)$	ligand structure
6a	171.57	69.97	47.99	101.60	A
6b	172.23	88.49	50.60	83.74	B
6c	171.42	70.58	47.02	100.84	A
6d	171.23	87.70	48.18	83.53	B
7a	175.79	66.16	48.97	109.63	A
7b	175.36	65.62	48.97	109.74	A
7c	172.19	64.00	50.37	108.19	A
7d	171.73	63.14	50.13	108.59	A
7e	170.77	82.95	50.49	87.82	B
11a	144.77	71.38	36.98	73.39	B
11b	143.80	54.26	32.18	89.54	A
11c	143.70	70.53	36.80	73.17	B
11d	143.35	53.96	32.60	89.39	A

^a In C_6D_6 ; δ in ppm; J in Hz; P_7 is the 7-phospha phosphorus atom, and P_2 is the exocyclic 2-phosphino phosphorus atom.

nor spectroscopically detected in these reactions. This suggests that the [4 + 2] Diels-Alder cycloaddition is faster than the ligand substitution, as has been observed for all other similar reactions.⁸

These same complexes were also prepared, with the same diastereomeric ratios, by the direct "one-pot" reaction (reaction 8). Small amounts of $\text{PCpFe}(\text{CO})(\text{DMPP})\text{I}$ and



$\text{PCpFe}(\text{CO})(\text{R}_3\text{P})\text{I}$ were also formed in reaction 8. These same complexes were also prepared by reaction of $\text{PCpFe}(\text{CO})(\text{DPVP})\text{I}$ and $\text{PCpFe}(\text{CO})(\text{DVPP})\text{I}$ with DMPP. The ratios of the diastereomeric Diels-Alder products were the same as those prepared by the other two routes. Hence, the diastereomeric ratios are thermodynamically controlled. The diastereomers could not be separated and were characterized only by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Table 7).

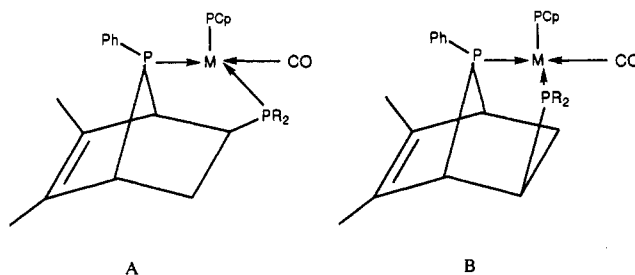
$\text{PCpFe}(\text{CO})(\text{DMPP})\text{I}$ was reacted with 2-vinylpyridine, phenyl vinyl sulfoxide, phenyl vinyl sulfide, diphenylallylphosphine, and diallylphenylphosphine. In all cases, neither ligand substitution nor Diels-Alder cycloaddition occurred and $\text{PCpFe}(\text{CO})(\text{DMPP})\text{I}$ was recovered unchanged from these reactions. This contrasts with the reactions of $\text{CpFe}(\text{CO})(\text{DMPP})\text{I}$, where Diels-Alder cycloadditions occurred with most of these dienophiles.⁷

Complex 10 (as a 3:2 mixture of diastereomers) reacts with the phosphine DPVP and AgBF_4 to form the [4 + 2] Diels-Alder adduct $[\text{PCpRu}(\text{CO})(\text{DMPP}-\text{DPVP})]^+\text{BF}_4^-$ as an inseparable mixture of four diastereomers (11a-d) in a 2:3:2:3 ratio. They were characterized only by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Table 7).

Structures of the Diels-Alder Adducts

The vinyl groups of DPVP and DVPP possess diastereotopic faces, and [4 + 2] cycloaddition with DMPP within the coordination sphere of the $\text{PCpM}(\text{CO})$ moiety leads to diastereomers because the PCp ligand is chiral,

the metal is a stereocenter, and the [4 + 2] Diels-Alder adducts form as the enantiomers A and B. For DPVP



adducts four diastereomers are possible: $R_m(\text{A})$, $S_m(\text{A})$, $R_m(\text{B})$, $S_m(\text{B})$. $R_m(\text{A})$ and $S_m(\text{B})$ are not enantiomers because the PCp absolute configuration does not change. For DVPP adducts the exocyclic 2-phosphino phosphorus is also a stereocenter and eight diastereomers are possible: $R_m(\text{A})R_p$, $R_m(\text{B})R_p$, $R_m(\text{A})S_p$, $R_m(\text{B})S_p$, $S_m(\text{A})R_p$, $S_m(\text{A})S_p$, $S_m(\text{B})R_p$, and $S_m(\text{B})S_p$. We have previously shown²⁹ that $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy is capable of distinguishing diastereomers that contain ligand structures A and B. Diastereomers containing ligand structure A exhibit a greater difference in the chemical shifts of the two phosphorus atoms of the five-membered chelate ring than do diastereomers possessing ligand structure B. For example, for $[(\eta^5\text{-C}_5\text{H}_5)\text{FeLL}'(\text{CO})]\text{BF}_4$ diastereomers⁷ the chemical shift differences are 102.63 ppm (A) and 83.18 ppm (B). For $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{DMPP})\text{LL}']\text{PF}_6$ diastereomers⁶ the chemical shift differences are 97.02 ppm (A) and 82.88 ppm (B). In both of these examples LL' is the [4 + 2] Diels-Alder adduct of DMPP and DPVP. Using this criterion, we have made the ligand structure assignments given in Table 7.

The ratio of the diastereomers 6a:6b:6c:6d is 2:1:2:2. Hence, ligand structure A in this series is favored over B by a ratio of 4:3. For the ruthenium analogs the ratio of the diastereomers 11a:11b:11c:11d is 2:3:2:3. Hence, ligand structure A is favored over B by a ratio of 3:2. In both cases, the extent of asymmetric induction is small. For 7a-e the asymmetric induction is greater (A:B:7:2), but we do not know the phosphorus absolute configuration for any of these diastereomers though the ratio is 4:3.

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Supplementary Material Available: For the two structures, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (U) (12 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors ($\times 10$) (24 pages) are available from the authors.

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