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Iron-Promoted Intramolecular [4 + 2] Diels–Alder Cycloadditions of 1-Phenyl-3,4-dimethylphosphole with Selected Dienophiles

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The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ reacts with 1-phenyl-3,4-dimethylphosphole (DMPP), diphenylvinylphosphine (DPVP), and divinylphenylphosphine (DVPP) to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)(R_3P)I]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)(R_3P)_2]^+I^-$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(R_3P)]^+I^-$ under different conditions. $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)I]$ (**1**) reacts with the dienophiles: DMPP, DPVP, DVPP, and PhP $(CH_2CH{=}CH_2)_2$ (DAPP) to produce one (**10**), two (**8a,b**), three (**9a–c**), or four (**11a–d**) diastereomers of [4 + 2] Diels–Alder cycloadducts. Complex **1** reacts with $AgBF_4$ and the dienophiles 2-vinylpyridine, $PhSCH{=}CH_2$, and $PhS(O)CH{=}CH_2$ to produce one (**14**), two (**13a,b**), or three (**12a–c**) diastereomers of [4 + 2] Diels–Alder cycloadducts. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DMPP)]^+I^-$ (**4**) reacts with DPVP and DVPP to produce **8a,b** and **9a,b** with greater diastereoselectivities than observed for the analogous reactions of **1** with these same dienophiles but with the same diastereoselectivities as observed in the reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)(DPVP)I]$ (**2**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)(DVPP)I]$ (**3**) with DMPP. New complexes were characterized by elemental analyses, physical properties, cyclic voltammetry, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The structures of $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)_2]I$ (**7**), **9c**, and **8a** were confirmed by X-ray crystallography. They crystallize in the $P2_1/c$, $P2_1/c$, and $Pna2_1$ space groups, respectively, in unit cells of the following dimensions: **7**: $a = 10.710$ (4) Å, $b = 17.983$ (4) Å, $c = 15.490$ (5) Å, $\beta = 103.20$ (4)°, ρ (calcd) = 1.491 g cm^{-3}, $Z = 4$. **9c**: $a = 12.542$ (4) Å, $b = 11.488$ (5) Å, $c = 19.350$ (3) Å, $\beta = 108.22°$, ρ (calcd) = 1.571 g cm^{-3}, $Z = 4$. **8a**: $a = 18.3381$ (3) Å, $b = 9.910$ (1) Å, $c = 16.549$ (6) Å, $\alpha = \beta = \gamma = 90°$, ρ (calcd) = 1.4911 g cm^{-3}, $Z = 4$. Refinements converged to $R(F) = 0.042$, 0.043, and 0.048 for 2930, 2831, and 1082 independent observed ($I \geq 3\sigma(I)$) reflections, respectively.

Introduction

In our studies of the synthesis of conformationally rigid asymmetric bidentate ligands by metal promoted intramolecular [4 + 2] Diels–Alder cycloadditions of phospholes with various dienophilic ligands,[2–9] we have found that the scope of these reactions is metal dependent and that the diastereoselectivity is generally thermodynamically controlled and is a primary function of steric effects within the metals' coordination sphere. The $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_{3-n}(\text{dienophile})_n]PF_6$ system[9] promotes these reactions with the widest variety of dienophiles yet found and in some cases with very high diastereoselectivity. Herein, we report on [4 + 2] Diels–Alder reactions of the similar piano-stool complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)I]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DMPP)]^+I^-$. These reactions were studied in order to increase our understanding of the factors which influence the diastereoselectivity of these unique intramolecular [4 + 2] Diels–Alder cycloadditions.

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 where necessary. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals, Inc. $PhP(CH{=}CH_2)_2$ (DVPP), $Ph_2PCH{=}CH_2$ (DPVP), and $PhP(CH_2CH{=}CH_2)_2$ (DAPP) were obtained from Organometallics, Inc. Both 1-phenyl-3,4-dimethylphosphole (DMPP)[10] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$[11] were prepared by literature methods. Column chromatography was performed using either silica gel (grade 12, 28–200 mesh, Aldrich) or CM-Sephadex (bead size 40–120 μm, Sigma Chemical Co.). All reactions were carried out under a dry nitrogen atmosphere. 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 a Perkin-Elmer 599 or a 1800 FT spectrometer. Cyclic voltammograms were recorded as previously described.[12] $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer or at 121.66 MHz on a General Electric GN-300 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, on a GE GN-300 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4 with a positive value being downfield of the respective reference.

(B) Synthesis. $[(\eta^5\text{-}C_5H_5)Fe(CO)(R_3P)I]$: R_3P = DMPP (1), DPVP (2), and DVPP (3). Method a. A solution containing 6 mmol of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and 0.09 mmol of $[(\eta_5\text{-}C_5H_5)Fe(CO)_2]_2$[13] in 75 mL of dry benzene was heated to reflux under N_2, and 6.6 mmol of R_3P was then added to this solution. Refluxing was continued for 1 h, and the resulting green solution was cooled to ambient temperature and filtered through cellulose. The filtrate was evaporated to dryness on a rotary evaporator at 50 °C, and the residue was purified by column chromatography on silica gel (hexane/benzene 40:60 eluant). Recrystallization from benz-

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[2] Solujic', L.; Milosavljevic', E. B.; Nelson, J. H.; Alcock, N. W.; Fischer, J. *Inorg. Chem.* **1989**, *28*, 3453.

[3] Holt, M. S.; Nelson, J. H.; Savignac, P.; Alcock, N. W. *J. Am. Chem. Soc.* **1985**, *107*, 6939.

[4] Rahn, J. A.; Holt, M. S.; Gray, G. A.; Alcock, N. W.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 217.

[5] Rahn, J. A.; Holt, M. S.; Nelson, J. H. *Polyhedron* **1989**, *8*, 897.

[6] Green, R. L.; Nelson, J. H.; Fischer, J. *Organometallics* **1987**, *6*, 2256.

[7] Vac, R.; Nelson, J. H.; Milosavljevic', E. B.; Solujic', L.; Fischer, J. *Inorg. Chem.* **1989**, *28*, 4132.

[8] Affandi, S.; Nelson, J. H.; Fischer, J. *Inorg. Chem.* **1989**, *28*, 4536.

[9] Ji, H. L.; Nelson, J. H.; DeCian, A.; Fischer, J.; Solujic', L.; Milosavljevic', E. B. *Organometallics* **1992**, *11*, 1840.

[10] Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1991**, 983.

[11] Piper, T. S.; Wilkinson, J. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38.

[12] Milosavljevic', E. B.; Solujic', L.; Krassowski, D. W.; Nelson, J. H. *J. Organomet. Chem.* **1988**, *352*, 177.

[13] Coville, N. J.; Darling, E. A.; Hearn, A. W.; Johnston, P. *J. Organomet. Chem.* **1987**, *328*, 375.

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ene/hexane afforded the product as dark green crystals. **1**: 80% yield, mp 126 °C (dec). IR (Nujol) ν_{CO} 1962 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 63.39. ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3 H, CH_3) 2.13 (s, 3 H, CH_3), 4.54 (s, 5 H, C_5H_5), 6.42 (d, ^2J(PH) = 31.86 Hz, 1 H, H_α), 6.56 (d, ^2J(PH) = 32.46 Hz, 1 H, H_α), 7.2–7.9 (m, 5 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.23 (d, ^3J(PC) = 12.23 Hz, CH_3), 17.53 (d, ^3J(PC) = 11.92 Hz, CH_3), 81.0 (s, C_5H_5), 128.34 (d, ^3J(PC) = 9.67, Hz, C_m), 129.82 (d, ^1J(PC) = 51.01 Hz, C_α), 130.16 (s, Cp), 131.91 (d, ^1J(PC) = 44.06 Hz, C_i), 131.99 (d, ^2J(PC) = 8.99 Hz, C_o), 132.85 (d, ^1J(PC) = 49.05 Hz, C_α), 149.39 (d, ^2J(PC) = 8.92 Hz, C_β) 149.76 (d, ^2J(PC) = 8.84 Hz, C_β), 218.39 (d, ^2J(PC) = 29.70 Hz, CO). Anal. Calcd for $C_{18}H_{18}FeIOP$: C, 46.58; H, 3.90. Found: C, 45.96; H, 3.85. **2**: 93% yield, mp 152 °C (dec). IR (Nujol) ν_{CO} 1936 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 59.40. ^{1}H NMR ($CDCl_3$) δ 4.49 (s, 5 H, C_5H_5), 5.38 (apparent td, ^2J(PH) = ^3J(ac) = 18.15, ^2J(bc) = 1.47 Hz, 1 H, H_b), 6.74 (ddd, ^2J(PH) = 22.80, ^3J(ac) = 18.15, ^3J(ab) = 12.06 Hz, 1 H, H_a), 7.3–7.9 (m, 10 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 82.24 (s, C_5H_5), 128.31 (d, ^3J(PC) = 9.75 Hz, C_m), 129.39 (s, C_β), 130.20 (s, C_p), 130.39 (s, C_p), 132.98 (d, ^2J(PC) = 10.05 Hz, C_o), 133.54 (d, ^2J(PC) = 9.67 Hz, C_o), 133.84 (d, ^1J(PC) = 41.79 Hz, C_i), 135.02 (d, ^1J(PC) = 46.55 Hz, C_i), 135.76 (d, ^1J(PC) = 43.91 Hz, C_α), 219.74 (d, ^2J(PC) = 30.51 Hz, CO). Anal. Calcd for $C_{20}H_{18}FeIOP$: C, 49.22; H, 3.72. Found: C, 48.83; H, 3.81. **3**: 80% yield, mp 92 °C (dec). IR (Nujol) ν_{CO} 1955 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 53.08. ^{1}H NMR ($CDCl_3$) δ 4.43 (s, 5 H, C_5H_5), 5.38 (apparent t, ^3J(PH) = ^3J(ac) = 17.13 Hz, 1 H, H_c), 5.69 (apparent t, ^3J(PH) = ^3J(a′c′) = 18.63 Hz, 1 H, $H_{c'}$), 5.82 (dd, ^3J(PH) = 27.95, ^3J(ab) = 15.93 Hz, 1 H, H_b), 5.99 (dd, ^3J(PH) = 27.65, ^3J(a′b′) = 12.02 Hz, 1 H, $H_{b'}$), 6.48 (ddd, ^2J(PH) = 18.33, ^3J(ac) = 17.13, ^3J(ab) = 15.93 Hz, 1 H, Ha), 6.48 (ddd, ^2J(PH) = 18.33, ^3J(a′c′) = 18.63, ^3J(a′b′) = 12.02 Hz, 1 H, $H_{a'}$), 7.3–7.7 (m, 5 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 81.84 (s, C_5H_5), 128.50 (d, ^3J(PC) = 9.75 Hz, C_m), 130.38 (s, C_β), 130.46 (s, C_β), 130.54 (s, C_p), 132.39 (d, ^2J(PC) = 9.37 Hz, C_o), 133.56 (d, ^1J(PC) = 45.35 Hz, C_i), 133.93 (d, ^1J(PC) = 42.62 Hz, C_α), 134.51 (d, ^1J(PC) = 44.14 Hz, C_α), 219.21 (d, ^2J(PC) = 31.44 Hz, CO). Anal. Calcd for $C_{16}H_{16}FeIOP$: C, 43.87; H, 3.68. Found: C, 44.34; H, 3.83.

Method b. A solution containing 1 mmol of [(η^5-C_5H_5)Fe($CO)_2$]$_2$ in 50 mL of dry benzene was heated to reflux under N_2, and 2 mmol of R_3P was added by syringe. This mixture was heated at reflux for 1 h, and a solution containing 2.2 mmol of I_2 in 25 mL of dry benzene was slowly added (addition of solid I_2 results in vigorous effervescence). The reaction mixture immediately turns dark green. Refluxing was continued for an additional 4 h. The solution was cooled to ambient temperature and filtered through cellulose. The filtrate was evaporated to dryness on a rotary evaporator at 50 °C, and the residue was purified by column chromatography on silica gel (hexane/benzene 40:60 eluant). Recrystallization from benzene/hexane afforded **1** and **2** as dark green crystals in 96–99% yield.

[(η^5-C_5H_5)Fe(CO)$_2$(R_3P)]$^+$I$^-$: R_3P = DMPP (4), DPVP (5), and DVPP (6). A solution containing 6 mmol of (η^5-C_5H_5)Fe(CO)$_2$I, 0.09 mmol of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, and 6.6 mmol of R_3P in 60 mL of benzene was heated at reflux under a CO atmosphere for 12 h. The color changed to yellow, and a yellow precipitate formed. The reaction mixture was cooled to ambient temperature and filtered through cellulose. The yellow precipitate was extracted from the cellulose with CH_2Cl_2, the volume of the solvent was reduced on a rotary evaporator, and diethyl ether was added to induce crystallization. The product was isolated by filtration, washed with ether, and vacuum dried at ambient temperature. **4**: 70% yield, mp 270 °C (dec). IR (Nujol) ν_{CO} 2025, 2050 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 59.67. ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6 H, CH_3), 5.44 (s, 5 H, C_5H_5), 7.10 (d, ^2J(PH) = 36.32 Hz, 2 H, H_α) 7.3–7.7 (m, 5 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.56 (d, ^3J(PC) = 14.27 Hz, CH_3), 87.91 (s, C_5H_5), 125.78 (d, ^1J(PC) = 52.76 Hz, C_α), 127.91 (d, ^1J(PC) = 51.85 Hz C_i), 129.65 (d, ^3J(PC) = 11.40 Hz, C_m), 131.12 (d, ^2J(PC) = 10.19 Hz, C_o), 131.79 (d, ^4J(PC) = 2.42 Hz, C_p), 153.48 (d, ^2J(PC) = 11.47 Hz, C_β), 208.35 (d, ^2J(PC) = 23.78 Hz, CO). Anal. Calcd for $C_{19}H_{18}FeO_2PI\cdot1.25C_6H_6$: C, 53.99; H, 4.33. Found: C, 54.11; 4.00. **5**: 74% yield, mp 188 °C (dec). IR (Nujol) ν_{CO} 1985, 2050 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 54.13. ^{1}H NMR ($CDCl_3$) δ 5.51 (s, 5 H, C_5H_5), 5.51 (apparent t, ^2J(PH) = ^3J(ac) = 18.31 Hz, 1 H, H_c), 6.34 (dd, ^3J(PH) = 43.37, ^3J(ab) = 11.86 Hz, 1 H, H_b), 7.32 (m, 1 H, H_a), 7.5–7.7 (m, 10 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 86.64 (s, C_5H_5), 129.69 (d, ^1J(PC) = 54.50 Hz, C_l), 129.87 (d, ^3J(PC) = 11.10 Hz, C_m), 131.95 (d, ^1J(PC) = 47.10 Hz, C_α), 132.38 (s, C_β), 132.45 (d, ^2J(PC) = 9.89 Hz, C_o), 133.63 (s, C_p), 208.95 (d, ^2J(PC) = 24.46 Hz, CO). This compound is photochemically unstable and is slowly converted by room light to compound **2**. **6**: This compound was always obtained as an inseparable mixture with **3**. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 45.60. IR (Nujol) ν_{CO} 1985, 2025 cm^{-1}.

[(η^5-C_5H_5)Fe(CO)(DMPP)$_2$]$^+$I$^-$ (7). A solution containing 1 mmol of **1**, 2.2 mmol of DMPP, and 10 mg of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ in 45 mL, of benzene was heated under N_2 at reflux overnight. The solution color changed from dark green to yellow, and a large quantity of yellow precipitate formed. The mixture was cooled to ambient temperature and filtered over cellulose. The yellow precipitate was extracted from the cellulose with CH_2Cl_2 and the volume of the solvent was reduced on a rotary evaporator. Addition of diethyl ether afforded orange crystals that were isolated by filtration and vacuum dried at ambient temperature; 90% yield, mp 204 °C. IR (Nujol) ν_{CO} 1970 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 60.91. ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6 H, CH_3), 1.93 (s, 6 H, CH_3), 4.79 (s, 5 H, C_5H_5), 6.27 (D, $|^2J(PH) + {}^4J(PH)|$ = 35.16 Hz, 2 H, H_α), 6.66 (D, $|^2J(PH) + {}^4J(PH)|$ = 34.86 Hz, 2 H, H_α), 7.2–7.5 (m, 10 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.01 (T, $|^3J(PC) + {}^5J(PC)|$ = 12.92 Hz, CH_3), 16.09 (T, $|^3J(PC) + {}^5J(PC)|$ = 12.70 Hz, CH_3), 83.64 (s, C_5H_5), 126.09 (T, $|^1J(PC) + {}^3J(PC)|$ = 49.73 Hz, C_i), 126.76 (s, C_β), 127.56 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.43 Hz, C_m), 129.18 (s, C_p), 129.53 (T, $|^2J(PC) + {}^4J(PC)|$ = 9.45 Hz, C_o), 149.74 (T, $|^1J(PC) + {}^3J(PC)|$ = 9.30 Hz, C_α), 150.53 (T, $|^1J(PC) + {}^3J(PC)|$ = 8.54 Hz, C_α), 215.26 (t, ^2J(PC) = 26.37 Hz, CO). Anal. Calcd for $C_{30}H_{31}FeIOP_2$: C, 55.24; H, 4.79. Found: C, 54.90; H, 5.08.

Reactions of 1 with Dienophilic Ligands. A solution containing 2 mmol of **1**, 2.2 mmol of the dienophilic ligand, and 25 mg of [(η^5-C_5H_5Fe(CO)$_2$]$_2$ in 50 mL benzene was heated under nitrogen at reflux overnight. Over 45 min the solution color changed from green to brownish-yellow and a brownish yellow precipitate formed. The mixture was cooled to ambient temperature and filtered over cellulose. The precipitate was extracted from the cellulose with CH_2Cl_2 and the solvent was removed on a rotary evaporator. The product was then placed on a Sephadex column which had been prepared with hexane and was successively eluted with hexane:CH_2Cl_2 (80:20), hexane:CH_2Cl_2:CH_3OH (70:10:20), and finally with hexane:CH_3OH (60:40). The separation was monitored by ^{31}P NMR spectroscopy. **8a,b** [(η^5-C_5H_5)Fe(CO)(DMPP)(DPVP)]$^+$I$^-$: These two diastereomeric [4 + 2] Diels–Alder adducts were formed in an overall 77% yield in a 3:2 ratio. **8a** was isolated by fractional crystallization from CH_2Cl_2/ether, mp 270 °C (dec). IR (Nujol) ν_{CO} 1964 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 70.47 (d, ^2J(PP) = 50.98 Hz), 173.10 (d, ^2J(PP) = 50.98 Hz). ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3 H, CH_3), 1.71 (m, 2 H, H_3, H_4), 1.84 (s, 3 H, CH_3), 2.80 (s, 1 H, H_1), 3.02 (apparent t, ^2J(PH) = $^3J(H_2H_4)$ = 8.11 Hz, 1 H, H_2), 4.65 (s, 5 H, C_5H_5), 4.96 (s, 1 H, H_5), 7.2–8.0 (m, 15 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 13.8 (s, CH_3), 15.4 (s, CH_3), 31.38 (d, ^2J(PC) = 13.23 Hz, C_3), 33.70 (dd, ^1J(PC) = 36.81, ^2J(PC) = 27.51 Hz, C_2), 50.04 (d, ^1J(PC) = 31.13 Hz, C_4), 57.96 (dd, ^1J(PC) = 31.97, ^2J(PC) = 12.02 Hz, C_1), 84.80 (s, C_5H_5), 129.29 (d, ^3J(PC) = 10.43 Hz, C_m), 129.34 (d, ^3J(PC) = 9.90 Hz, C_m), 129.59 (d, ^1J(PC) = 9.98 Hz, C_i), 130.15 (d, ^3J(PC) = 9.98 Hz, C_m), 131.07 (d, ^4J(PC) = 2.65 Hz, C_p), 131.11 (d, ^4J(PC) = 3.70 Hz, C_p), 131.80 (d, ^3J(PC) = 1.81 Hz, C_p), 132.06 (d, ^2J(PC) = 9.60 Hz, C_o), 132.37 (d, ^1J(PC) = 15.12 Hz, C_i), 134.04 (d, ^2J(PC) = 9.90 Hz, C_o), 138.77 (s, C_5), 138.80 (s, C_6), 215.56 (dd, ^2J(PC) = 26.60; ^2J(PC) = 22.22 Hz, CO). Anal. Calcd for $C_{32}H_{31}FeIOP_2\cdot0.5C_6H_6$: C, 58.76; H, 4.79. Found: C, 59.19; H, 5.52. **8b** was isolated by fractional crystallization from CH_2Cl_2/ether, mp 274 °C (dec). IR (Nujol) ν_{CO} 1964 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 88.09 (d, ^2J(PP) = 51.16 Hz), 171.27 (d, ^2J(PP) = 51.16 Hz). ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 2.31 (m, ^3J(PH) = 24.94, ^3J(PH) = 24.54, $^2J(H_3H_4)$ = 12.92, $^3J(H_3H_4)$ = 8.71 Hz, 1 H, H_4), 2.67 (dddd, ^3J(PH) = 21.64, $^1J(H_3H_4)$ = 12.92, ^3J(PH) = 1.80, $^3J(H_2H_3)$ = 1.65 Hz, 1 H, H_3), 2.81 (d, $^3J(H_1H_2)$ = 1.65 Hz, 1 H, H_1), 3.43 (apparent dtt, ^3J(PH) = 38.47, ^2J(PH) = $^3J(H_2H_4)$ = 8.71, $^3J(H_1H_2)$ = $^3J(H_2H_3)$ = 1.65 Hz, 1 H, H_2), 4.55 (s, 1 H, H_5), 4.96 (t, ^4J(PH) = 1.20 Hz, C_5H_5), 7.4–7.8 (m, 15 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.01 (s, CH_3), 15.01 (s, CH_3), 31.17 (dd, ^2J(PC) = 18.14, ^3J(PC) = 13.83 Hz, C_3), 31.43 (dd, ^1J(PC) = 38.47, ^2J(PC) = 29.85 Hz, C_2), 51.69 (d, ^1J(PC) = 26.22 Hz, C_4), 54.26 (dd, ^1J(PC) = 34.92, ^2J(PC) = 10.51 Hz,

C_1), 84.02 (s, C_5H_5), 128.76 (d, $^1J(PC) = 14.21$ Hz, C_i), 129.24 (d, $^3J(PC) = 10.43$ Hz, C_m), 129.37 (d, $^3J(PC) = 10.05$ Hz, C_m), 129.62 (d, $^3J(PC) = 9.82$ Hz, C_m), 130.83 (d, $^2J(PC) = 8.99$ Hz, C_o), 131.20 (d, $^2J(PC) = 8.99$ Hz, C_o), 131.20 (s, C_p), 131.23 (s, C_p), 131.31 (s, C_p), 131.53 (d, $^2J(PC) = 9.90$ Hz, C_o), 133.75 (d, $^1J(PC) = 40.89$ Hz, C_i), 139.53 (s, C_5), 139.55 (s, C_6), 214.96 (dd, $^2J(PC) = 24.71$, $^2J(PC) = 21.09$ Hz, CO). Anal. Calcd for $C_{32}H_{31}FeIOP_2$: C, 56.85; H, 4.59. Found: C, 56.53; H, 4.71. **9a–c** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(DVPP)]^+I^-$: These three diastereomers were formed in an overall 70% yield in a 1:1:1 ratio. Pure **9c** was isolated from the mixture by fractional crystallization from CH_2Cl_2. However, **9a** and **9b** could not be separated from each other and were characterized only by ^{31}P NMR spectroscopy. **9a**: δ 64.42 (d, $^2J(PP) = 52.13$ Hz), 171.19 (d, $^2J(PP) = 52.13$ Hz). **9b**: δ 66.86 (d, $^2J(PP) = 51.95$ Hz), 174.43 (d, $^2J(PP) = 51.95$ Hz). **9c**: δ 83.39 (d, $^2J(PP) = 54.87$ Hz), 168.55 (d, $^2J(PP) = 54.87$ Hz). Mp 101 °C (dec). IR (Nujol) ν_{CO} 1965 cm^{-1}. ^1H NMR ($CDCl_3$) 1.44 (s, 3 H, CH_3), 1.70 (m, 2 H, H_3, H_4), 1.81 (s, 3 H, CH_3), 2.78 (s, 1 H, H_5), 2.88 (apparent dt, $^3J(PH) = 39.97$, $^2J(PH) = {}^3J(H_2H_4) = 10.21$ Hz, 1 H, H_2), 4.84 (s, 5 H, C_5H_5), 4.94 (dd, $^3J(PH) = 20.74$, $^3J(H_aH_b) = 18.03$ Hz, 1 H, H_c), 6.03 (dd, $^3J(PH) = 39.07$, $^3J(H_aH_b) = 12.18$ Hz, 1 H, H_b), 7.4–7.7 (m, 10 H, Ph), 7.80 (ddd, $^2J(PH) = 30.05$, $^3J(H_aH_c) = 18.03$, $^3J(H_aH_b) = 12.18$ Hz, 1 H, H_a). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.54 (d, $^3J(PC) = 2.27$ Hz, CH_3), 14.78 (s, CH_3), 29.68 (d, $^2J(PC) = 14.89$ Hz, C_3), 32.22 (dd, $^1J(PC) = 36.28$, $^2J(PC) = 32.42$ Hz, C_2), 49.63 (d, $^1J(PC) = 30.68$ Hz, C_1), 56.08 (dd, $^1J(PC) = 31.59$, $^3J(PC) = 12.17$ Hz, C_4), 84.40 (s, C_5H_5), 127.26 (d, $^1J(PC) = 47.16$ Hz, C_α), 128.95 (d, $^3J(PC) = 9.98$ Hz, C_m), 129.08 (d, $^3J(PC) = 10.35$ Hz, C_m), 130.07 (d, $^4J(PC) = 4.53$ Hz, C_p), 130.64 (d, $^4J(PC) = 1.28$ Hz, C_p), 131.42 (dd, $^1J(PC) = 37.30$, $^2J(PC) = 3.52$ Hz, C_i), 131.96 (d, $^2J(PC) = 1.81$ Hz, C_β), 132.18 (d, $^2J(PC) = 15.64$ Hz, C_o), 133.93 (d, $^2J(PC) = 10.20$ Hz, C_o), 135.25 (d, $^1J(PC) = 33.40$ Hz, C_i), 137.95 (s, C_5), 137.97 (s, C_6), 215.26 (dd, $^2J(PC) = 25.77$, $^2J(PC) = 21.99$ Hz, CO). Anal. Calcd for $C_{28}H_{29}FeIOP_2$: C, 53.70; H, 4.67. Found: C, 53.63; H, 4.61. **10** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)_2]^+I^-$ [4 + 2] Diels–Alder adduct: Compound **7** was heated at reflux for 24 h in a $Cl_2CHCHCl_2$ solution and was 80% converted to **10**. It could not be isolated in pure form and was characterized only by ^{31}P NMR spectroscopy: δ 86.76 (d, $^2J(PP) = 52.50$ Hz), 183.24 (d, $^2J(PP) = 52.50$ Hz). **11a–d** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(DAPP)]^+I^-$: These four diastereomers were formed as an inseparable mixture in an overall 62% yield in a 3.5:2.8:1.3:1 ratio. They were characterized only by ^{31}P NMR spectroscopy. **11a**: δ 38.31 (d, $^2J(PP) = 53.71$ Hz), 144.57 (d, $^2J(PP) = 53.71$ Hz). **11b**: δ 34.43 (d, $^2J(PP) = 58.61$ Hz), 144.27 (d, $^2J(PP) = 58.61$ Hz). **11c**: δ 38.79 (d, $^2J(PP) = 53.71$ Hz), 145.30 (d, $^2J(PP) = 53.71$ Hz). **11d**: 30.34 (d, $^2J(PP) = 56.17$ Hz), 141.57 (d, $^2J(PP) = 56.17$ Hz). Similar reactions of **1** with $Me_2NC(O)CH{=}CH_2$, $EtOC(O)CH{=}CH_2$, 2-vinylpyridine, $PhSCH{=}CH_2$, $PhS(O)CH{=}CH_2$, and $PhS(O)_2CH{=}CH_2$ all produced approximately 40% yields of **7** by ligand redistribution reactions.

Direct Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(DMPP)(DPVP)]^+I^-$ Diels–Alder Adducts (8a,b). A solution containing 3 mmol of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in 50 mL of dry benzene was stirred at room temperature under CO for 30 min, and 6 mmol each of DMPP and DPVP were successively added. The solution was heated at reflux for 1 h, and then a solution containing 3.3 mmol of I_2 in 25 mL of dry benzene was slowly added. Over 15 min the solution color changed from a reddish-brown to a brownish yellow and a brownish yellow preciptiate formed. The mixture was heated at reflux overnight, cooled to ambient temperature, and filtered over cellulose. The precipitate was extracted from the cellulose with CH_2Cl_2 and the solvent was removed on a rotary evaporator. The two diastereomeric [4 + 2] Diels–Alder adducts were separated by repeated fractional crystallization from CH_2Cl_2. The overall yield was 95% and the ratio of the diastereomers was 2:1.

Reactions of 1 with $AgBF_4$ and Dienophilic Ligands. To a solution containing 3.0 mmol of **1**, 0.05 mmol of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, and 3.6 mmol of the dienophilic ligand in 50 mL of benzene was added 3.3 mmol of solid $AgBF_4$. Immediate precipitation of AgI occurred. The reaction mixture was heated at reflux under nitrogen overnight, cooled to ambient temperature, and filtered over cellulose. The residue was extracted from the cellulose with CH_2Cl_2, and then the solution was repeatedly filtered through Celite until a clear yellow solution was obtained (complete precipitation of AgI is slow). This solution was evaporated to dryness on a rotary evaporator, and the product was purified by chromatography on Sephadex as described previously for **8a,b**; **12a–c** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(PhS(O)CH{=}CH_2)]^+BF_4^-$: These three diastereomers were formed as an inseparable mixture in an overall 49% yield in a 1:1:1 ratio. They were characterized only by ^{31}P NMR spectroscopy: **12a** δ 174.2, **12b** δ 169.8, **12c** δ 165.8. **13a,b** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(PhSCH{=}CH_2)]^+BF_4^-$: These two diastereomers were formed as an inseparable mixture in an overall 28% yield in a 1:1 ratio. They were characterized only by ^{31}P NMR spectroscopy: **13a** δ 170.1, **13b** δ 166.9. **14** $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(2\text{-vinylpyridine})]^+BF_4^-$ formed in 24% yield as a single diastereomer but could not be isolated in pure form. It was characterized only by ^{31}P NMR spectroscopy, δ 155.4.

Table I. Crystallographic Data for 7, 8a, and 9c

	7	8a	9c
chemical formula	$[FeP_2OC_{30}H_{31}]$ I	$[FeP_2OC_{32}H_{31}]$ I	$[FeP_2OC_{28}H_{29}]$ I
formula wt	652.27	676.29	626.24
a (Å)	10.710 (4)	18.338 (3)	12.542 (4)
b (Å)	17.983 (4)	9.910 (3)	11.488 (5)
c (Å)	15.490 (5)	16.549 (6)	19.350 (3)
β (deg)	103.20 (4)	$\alpha = \beta = \gamma = 90$	108.22
V (Å^3)	2905 (2)	3007 (6)	2648 (1)
Z	4	4	4
space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)
T (°C)	23	25	23
λ (Å)	0.710 69	0.710 98	0.710 69
ρ(calcd) (g cm^{-3})	1.491	1.4911	1.571
μ (cm^{-1})	16.99	16.43	18.59
abs min/max	0.79–1.00	1.0	0.94–1.00
$R(F)^a$	0.042	0.048	0.043
$R_w(F)$	0.049	0.052	0.047

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

Reactions of 4($[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DMPP)]^+I^-$) with DPVP and DVPP. These reactions were performed in the same fashion as the analogous reactions of **1** with these two phosphines except that a CO rather than an N_2 atmosphere was used. **8a,b** were formed in 77% overall yield in a 7:1 ratio. **8a** was isolated by crystallization from CH_2Cl_2/ether but **8b** could not be obtained free of **8a**. **9c,b** were formed in an overall 63% yield in an 11:1 ratio. **9c** was isolated by crystallization from CH_2Cl_2, but **9b** could not be obtained free of **9c**.

Compounds **8a,b** and **9a–c** were also prepared by reacting **2** and **3** respectively with DMPP in refluxing benzene. They were obtained in 76% and 63% overall yields. The ratios of the diastereomers formed were the same as observed in the reactions of **1** with DPVP and DVPP, respectively.

Conversion of 8a, 9c, and 10 into PF_6 Salts. A solution containing an excess of NH_4PF_6 in H_2O was added to solutions of **8a**, **9c**, or **10** in CH_2Cl_2. The mixtures were stirred vigorously for 10 min, the CH_2Cl_2 layer was separated, dried over anhydrous $MgSO_4$, and reduced in volume on a rotary evaporator, and ether was added. The yellow-brown crystalline products were isolated by filtration and dried under vacuum. The products were obtained in 90–95% yield.

(C) X-ray Data Collection and Processing. Crystals of **7** (orange), **8a** (yellow), and **9c** (brown) were isolated from CH_2Cl_2/ether solutions at room temperature. Crystal data and details of data collection are given in Table I. Systematic searches in reciprocal space with a Rigaku AFC6R diffractometer equipped with a 12-kW rotating anode generator showed that crystals of **7** and **9c** belong to the monoclinic system while crystals of **8a** belong to the orthorhombic system. Data were obtained at room temperature using the ω–2θ scan technique on a Rigaku AFC6R diffractometer. Three standard reflections measured after every 150 reflections during the entire data collection periods showed no significant trends. Empirical absorption corrections, based on azimuthal scans of several reflections, were applied, and the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods.[14a] The non-hydrogen

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

Table II. Atom Coordinates for 7[a]

atom	*x*	*y*	*z*	*B*(eq), Å^2
I	0.21598 (5)	0.03938 (4)	0.76217 (4)	6.38 (3)
Fe	0.25923 (8)	0.06839 (5)	0.13096 (6)	2.79 (4)
P(1)	0.3486 (1)	0.10112 (9)	0.2678 (1)	2.61 (6)
P(2)	0.3076 (1)	0.1744 (1)	0.0724 (1)	2.93 (7)
O	0.0125 (4)	0.1307 (3)	0.1368 (4)	6.5 (3)
C	0.1104 (6)	0.1073 (4)	0.1359 (4)	3.7 (3)
C(1)	0.3914 (7)	−0.0162 (4)	0.1213 (5)	4.1 (3)
C(2)	0.2979 (8)	−0.0421 (4)	0.1628 (5)	5.1 (4)
C(3)	0.1758 (8)	−0.0373 (4)	0.1029 (6)	5.5 (4)
C(4)	0.1969 (7)	−0.0058 (4)	0.0258 (6)	5.4 (4)
C(5)	0.3296 (8)	0.0073 (4)	0.0360 (5)	4.9 (4)
C(10)	0.2886 (6)	0.0557 (3)	0.3553 (4)	3.0 (3)
C(11)	0.3592 (6)	0.0584 (4)	0.4422 (4)	3.9 (3)
C(12)	0.3124 (7)	0.0284 (4)	0.5101 (5)	4.8 (4)
C(13)	0.1975 (8)	−0.0076 (4)	0.4921 (6)	5.2 (4)
C(14)	0.1257 (7)	−0.0115 (4)	0.4062 (6)	5.3 (4)
C(15)	0.1706 (6)	0.0204 (4)	0.3385 (5)	4.3 (3)
C(16)	0.5187 (5)	0.0936 (4)	0.2982 (4)	3.1 (3)
C(17)	0.5709 (5)	0.1613 (4)	0.3195 (4)	3.3 (3)
C(17A)	0.7117 (6)	0.1760 (5)	0.3413 (5)	5.6 (4)
C(18)	0.4781 (6)	0.2206 (3)	0.3194 (4)	3.5 (3)
C(18A)	0.5178 (7)	0.2991 (4)	0.3417 (5)	5.6 (4)
C(19)	0.3559 (6)	0.1975 (3)	0.2966 (4)	3.1 (3)
C(21)	0.4735 (6)	0.2037 (4)	0.0852 (4)	3.4 (3)
C(22)	0.5009 (7)	0.2777 (4)	0.0797 (5)	5.4 (4)
C(23)	0.6260 (8)	0.3025 (5)	0.0869 (6)	7.0 (5)
C(24)	0.7249 (7)	0.2509 (6)	0.1012 (6)	6.5 (5)
C(25)	0.6976 (7)	0.1774 (6)	0.1067 (5)	6.0 (5)
C(26)	0.5726 (6)	0.1528 (4)	0.0994 (5)	4.3 (3)
C(27)	0.2298 (6)	0.1765 (4)	−0.0433 (4)	3.6 (3)
C(28)	0.1384 (6)	0.2276 (4)	−0.0595 (4)	3.8 (3)
C(28A)	0.0461 (7)	0.2393 (5)	−0.1468 (5)	6.3 (4)
C(29)	0.1344 (5)	0.2739 (3)	0.0185 (4)	3.4 (3)
C(29A)	0.0390 (7)	0.3345 (4)	0.0148 (5)	5.5 (4)
C(30)	0.2212 (6)	0.2557 (3)	0.0920 (4)	3.4 (3)

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

atoms were refined anisotropically. The hydrogens are in calculated positions. Full-matrix least-squares refinements minizing $\sum\omega(|F_o| - |F_c|)^2$ with $\sigma^2(F)^2 = \sigma^2(\text{counts}) + (pI)^2$ converged to the values given in Table I.[14b] Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 15. Final atom coordinates for **7**, **8a**, and **9c** are given in Tables II, V, and VIII, and selected bond lengths and angles are given in Tables III, IV, VI, VII, IX, and X respectively.

Results

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$-catalyzed ligand substitution of carbon monoxide by R_3P in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ occurs more readily than substitution of iodide unless R_3P is strongly nucleophilic.[16-18] Thus, under an N_2 atmosphere in refluxing benzene $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ reacts with 1 mol equiv of DMPP, DPVP, or DVPP to produce dark green crystals of $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)I]$ (**1**), $[(\eta^5\text{-}C_5H_5)Fe(CO)(DPVP)I]$ (**2**), and $[(\eta^5\text{-}C_5H_5)Fe(CO)(DVPP)I]$ (**3**), respectively, in good yield. When these same reactions are conducted under a carbon monoxide atmosphere, the yellow complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DMPP)]I$ (**4**), $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DPVP)]I$ (**5**), and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DVPP)]I$ (**6**), respectively, are obtained also in good yield. Complex **6** could not be obtained pure and was always obtained as a mixture with **3**. Under an N_2 atmosphere in refluxing benzene $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ reacts with 2 mol equiv of DMPP to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)_2]I$ (**7**) in high yield. Complexes **1**–**7** were fully characterized by elemental analyses, infrared, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy (see Experimental Section). These data show that all these complexes are three-legged piano stool molecules with the expected structures. The relative energies of the ν_{CO} vibrations for complexes **1**–**3** suggest that toward Fe(II) the donor abilities of the three phosphines decrease in the sequence DPVP (ν_{CO} = 1936 cm^{-1}) > DVPP (ν_{CO} = 1955 cm^{-1}) > DMPP (ν_{CO} = 1962 cm^{-1}). The ^{31}P coordination chemical shifts; $\Delta\delta\ ^{31}P = \delta^{31}P$ (complex) − $\delta^{31}P$ (ligand) fall in the same sequence: DPVP (70.8 ppm) > DVPP (70.08 ppm) > DMPP (65.89 ppm). The ^{31}P coordination chemical shifts for the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(R_3P)]I$ complexes **4**–**6** are smaller and also fall in the same sequence: DPVP (65.53 ppm) > DVPP (62.6 ppm) > DMPP (62.17 ppm). The ν_{CO} vibrational frequencies are higher for complexes **1**–**3** than for **4**–**6**. Thus, it appears that the Fe–CO bonds and Fe–PR$_3$ bonds are somewhat weaker in the dicarbonyl complexes than in the monocarbonyl complexes. The ^{31}P coordination chemical shift for complex **7** is greater than that for complex **4** but less than that for complex **1**. By way of comparison, $\Delta\delta^{31}P$ = 50.2 ppm for $(DMPP)Fe(CO)_4$.[19]

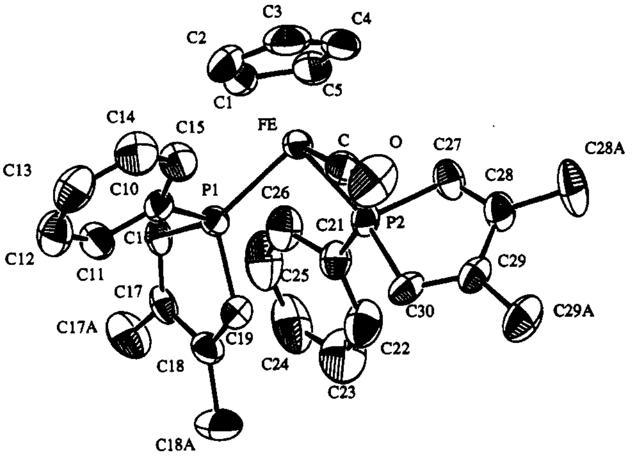

Figure 1. ORTEP drawing of the cation of **7** showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

Table III. Selected Bond Distances (Å) for 7

atom	atom	dist	atom	atom	dist
Fe	P1	2.198 (2)	O	C	1.133 (7)
Fe	P2	2.222 (2)	C1	C2	1.39 (1)
Fe	C	1.758 (7)	C1	C5	1.402 (9)
Fe	C1	2.106 (6)	C2	C3	1.42 (1)
Fe	C2	2.067 (7)	C3	C4	1.39 (1)
Fe	C3	2.103 (7)	C4	C5	1.41 (1)
Fe	C4	2.094 (7)	C16	C17	1.350 (8)
Fe	C5	2.108 (7)	C18	C19	1.341 (8)
			C27	C28	1.324 (8)
			C29	C30	1.337 (9)

Table IV. Selected Bond Angles (deg) for 7

atom	atom	atom	angle
P1	Fe	P2	94.20 (7)
P1	Fe	C	92.9 (2)
P2	Fe	C	88.5 (2)
C16	P1	C19	91.4 (3)
C27	P2	C30	90.7 (3)
Fe	C	O	177.6 (6)

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(15) (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.

(16) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *227*, 53.

(17) Coville, N. J.; Darling, E. A. *J. Organomet. Chem.* **1984**, *227*, 105.

(18) Coville, N. J.; Loonat, M. S.; White, D.; Carlton, L. *Organometallics* **1992**, *11*, 1082.

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

Table V. Atom Coordinates for 8a

atom	x	y	z
I	0.50572 (7)	0.2060 (1)	0
Fe	0.0568 (1)	0.0767 (2)	0.6823 (2)
P(1)	0.0284 (2)	0.2123 (5)	0.5790 (3)
P(2)	0.1148 (2)	0.2532 (4)	0.7268 (3)
O	0.1875 (8)	−0.046 (1)	0.620 (1)
C(1)	0.194 (1)	0.236 (2)	0.792 (1)
C(2)	0.186 (1)	0.267 (2)	0.871 (1)
C(3)	0.246 (1)	0.246 (2)	0.924 (1)
C(4)	0.311 (1)	0.197 (3)	0.894 (2)
C(5)	0.321 (1)	0.167 (2)	0.814 (2)
C(6)	0.261 (1)	0.186 (2)	0.760 (1)
C(7)	0.0755 (8)	0.199 (2)	0.483 (1)
C(8)	0.108 (1)	0.082 (2)	0.458 (1)
C(9)	0.145 (1)	0.077 (2)	0.383 (1)
C(10)	0.145 (1)	0.188 (3)	0.333 (1)
C(11)	0.114 (1)	0.306 (2)	0.357 (1)
C(12)	0.079 (1)	0.313 (2)	0.433 (1)
C(13)	−0.069 (1)	0.219 (2)	0.545 (1)
C(14)	−0.093 (1)	0.105 (2)	0.512 (1)
C(15)	−0.167 (1)	0.102 (2)	0.483 (1)
C(16)	−0.2089 (9)	0.209 (2)	0.492 (2)
C(17)	−0.182 (1)	0.327 (2)	0.523 (1)
C(18)	−0.112 (1)	0.332 (2)	0.553 (1)
C(19)	0.0495 (9)	0.382 (2)	0.615 (1)
C(20)	0.133 (1)	0.375 (2)	0.645 (1)
C(21)	0.1557 (8)	0.500 (1)	0.687 (1)
C(22)	0.118 (1)	0.512 (2)	0.755 (1)
C(23)	0.0645 (9)	0.398 (2)	0.764 (1)
C(24)	0.0097 (9)	0.415 (1)	0.696 (1)
C(25)	0.209 (1)	0.598 (2)	0.653 (1)
C(26)	0.121 (1)	0.618 (2)	0.818 (1)
C(27)	0.133 (1)	0.008 (2)	0.642 (1)
C(28)	−0.002 (1)	0.063 (3)	0.790 (1)
C(29)	0.042 (1)	−0.050 (2)	0.782 (1)
C(30)	0.022 (1)	−0.120 (2)	0.714 (1)
C(31)	−0.034 (1)	−0.049 (2)	0.680 (1)
C(32)	−0.051 (1)	0.060 (3)	0.726 (1)

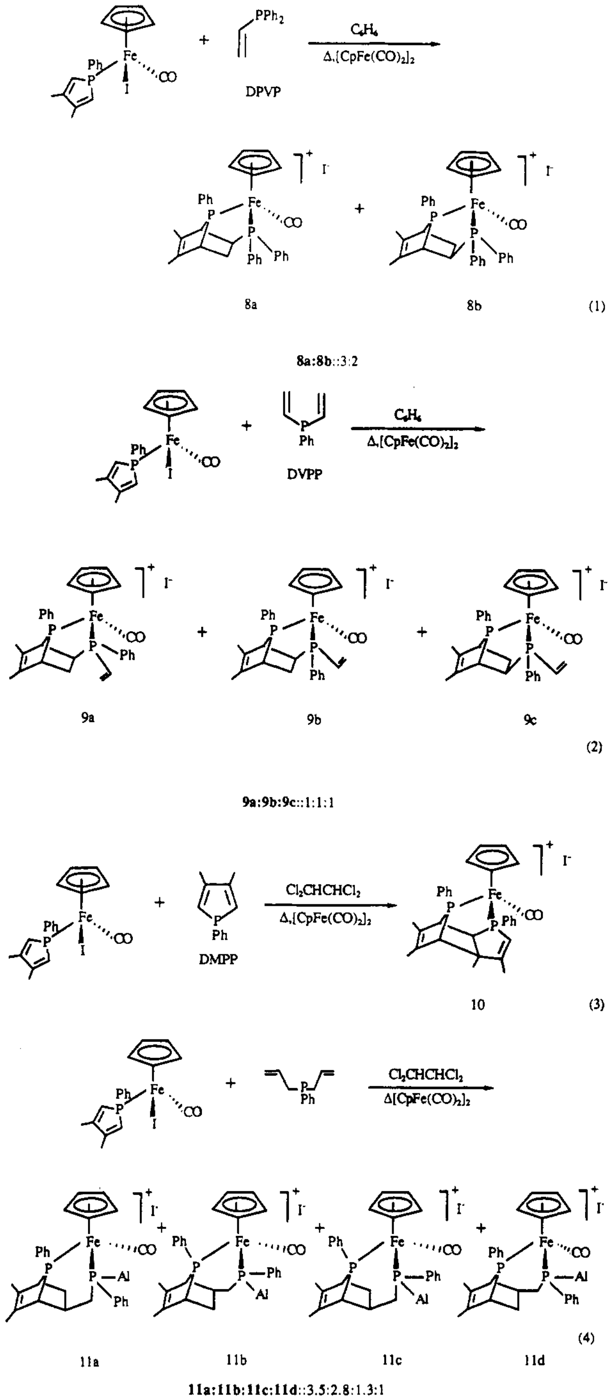
The crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)_2]I$ (7, Figure 1) consists of isolated cations and anions with no short contacts. Selected bond distances and angles are listed in Tables III and IV, respectively. The cation has distorted-octahedral geometry, has no symmetry, and contains a linear carbonyl ligand (Fe–C = 1.758(7) Å; Fe–C–O = 177.6 (6)°; C–O = 1.133 (7) Å), and two phosphines that are not equidistant from iron ($Fe–P_1$ = 2.198 (2) Å; $Fe–P_2$ = 2.222 (2) Å. The structure of complex 7 is similar to that of $[(\eta^5\text{-}C_5H_5)Ru(CO)(DPVP)_2]PF_6$.[20]

Complex 1 reacts with dienophilic phosphines (R_3P) to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)(DMPP)(R_3P)]I$ complexes that undergo spontaneous intramolecular Diels–Alder cycloadditions as illustrated in reactions 1–4 (Scheme I).

Similar reactions of complex 1 with $Me_2NC(O)CH{=}CH_2$, $EtOC(O)CH{=}CH_2$, 2-vinylpyridine, $PhS\text{-}CH{=}CH_2$, $PhS(O)CH{=}CH_2$, and $PhS(O)_2CH{=}CH_2$ all produced approximately 40% yields of 7 by ligand redistribution reactions. In the presence of $AgBF_4$ to aid in the removal of iodide[21] from complex 1, $PhS(O)CH{=}CH_2$, $PhSCH{=}CH_2$, and 2-vinylpyridine underwent intramolecular [4 + 2] Diels–Alder cycloadditions in modest yields as illustrated in reactions 5–7 (Scheme II).

Reactions of complex 7 with DPVP and DVPP under a carbon monoxide atmosphere gave complexes 8a and 8b and 9c and 9b, respectively, in approximately the same overall yields as in reactions 1 and 2 but with much higher diastereoselectivities. Thus, under these conditions the ratio 8a:8b was 7:1 and the ratio 9c:9b was 11:1. Compounds 8a and 8b and 9a, 9b, and 9c were also prepared by reacting compounds 2 and 3, respectively with DMPP in refluxing benzene. The overall yields were essentially the same as in reactions 1 and 2 as were the diastereomeric ratios. Complexes 1, 2, and 8a, 8b could also be synthesized by reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with the appropriate phosphines followed by addition of I_2. Complexes 1 and 2 were obtained in 96 and 99% yields and 8a and 8b in a 2:1 ratio in 95% yield. These observations suggest that the diastereomeric ratios of the products are kinetically controlled.

Scheme I



These reactions provide ready syntheses of chiral complexes containing a variety of conformationally rigid chiral bidentate ligands with diastereoselectivities that are a function of the magnitudes of interligand steric effects and also the rate of coordination of the dienophilic ligand. An increase in the diastereoselectivity in the presence of carbon monoxide is likely the result of a decrease in the

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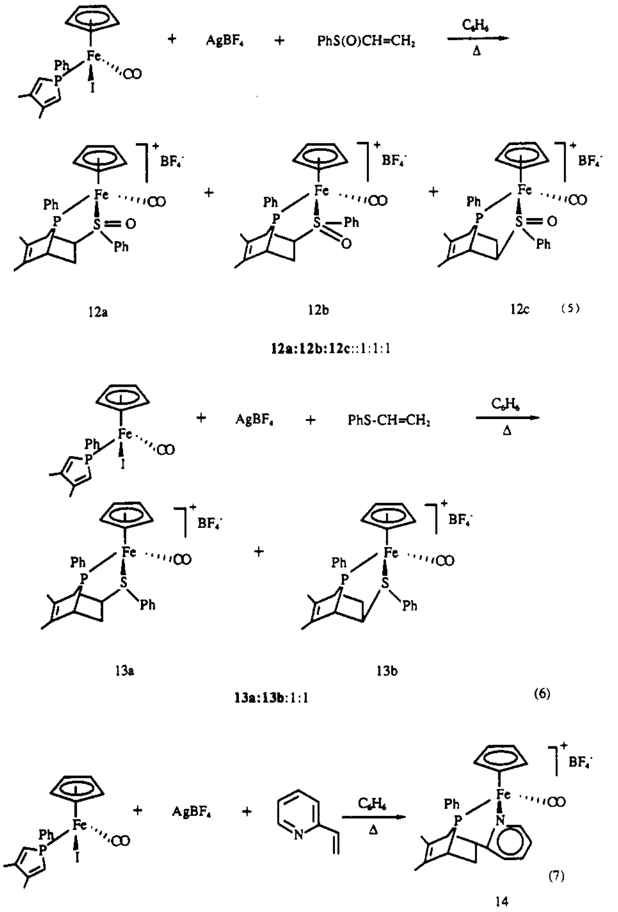
[20] Ji, H. L.; Nelson, J. H.; DeCian, A.; Fischer, J.; Solujic' L.; Milosavljevic', E. B. *Organometallics* **1992**, *11*, 401.

[21] Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

Scheme II



rate of coordination of the dienophilic ligand to iron. New compounds were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Assignments were made by previously described techniques[2-9] and are given in the Experimental Section with atom numbering schemes similar to those used previously. These spectra are characteristic of the assigned structures.

Discussion

We have previously shown that [4 + 2] cycloadditions of vinylphosphines with DMPP within the coordination spheres of transition-metal complexes[2-9] occur readily. Except for some of the platinum reactions,[5] the mixed-ligand phosphole–vinylphosphine intermediates were not observed in these reactions. Likewise, with the iron complexes, Diels–Alder products were formed immediately upon ligand substitution.

Table VI. Selected Bond Distances (Å) for 8a

atom 1	atom 2	dist	atom 1	atom 2	dist
Fe1	C28	2.09 (2)	P2	C20	1.84 (2)
Fe1	C29	2.09 (2)	P2	C23	1.81 (2)
Fe1	C30	2.11 (2)	C19	C20	1.61 (2)
Fe1	C31	2.08 (2)	C20	C21	1.47 (2)
Fe1	C32	2.10 (2)	C21	C22	1.33 (2)
Fe1	C27	1.69 (2)	C21	C25	1.48 (2)
C27	O	1.18 (2)	C22	C23	1.50 (2)
Fe1	P1	2.232 (5)	C22	C26	1.48 (3)
Fe1	P2	2.173 (5)	C23	C24	1.52 (2)
P1	C19	1.82 (2)	C24	C19	1.56 (2)

Table VII. Selected Bond Angles (deg) for 8a

atom 1	atom 2	atom 3	angle
P1	Fe1	P2	83.6 (2)
P1	Fe1	C27	97.5 (6)
P2	Fe1	C27	93.1 (7)
Fe1	C27	O	174 (2)
Fe1	P1	C19	104.9 (2)
P1	C19	C20	105 (1)
C19	C20	C21	112 (1)
C19	C20	P2	94 (1)
P2	C20	C21	105 (1)
C20	C21	C22	109 (2)
C21	C22	C23	111 (2)
C22	C23	C24	106 (1)
C22	C23	P2	103 (1)
P2	C23	C24	100 (1)
C23	C24	C19	108 (1)
C24	C19	P1	112 (1)
C20	P2	C23	80.0 (7)

Table VIII. Atom Coordinates for 9c[a]

atom	x	y	z	B(eq), Å^2
I	0.29283 (5)	0.13539 (6)	0.65701 (3)	5.07 (3)
Fe	0.08770 (8)	0.16209 (8)	0.36820 (5)	2.20 (4)
P(1)	0.2290 (2)	0.2836 (1)	0.3982 (1)	2.30 (7)
P(2)	0.0062 (2)	0.2988 (2)	0.4145 (1)	2.35 (7)
O	0.0022 (5)	0.2391 (4)	0.2206 (3)	4.5 (3)
C(1A)	0.3701 (5)	0.2305 (5)	0.4185 (4)	2.5 (3)
C(1B)	0.4303 (7)	0.1983 (6)	0.4881 (4)	3.1 (3)
C(1C)	0.5351 (7)	0.1481 (7)	0.5020 (5)	4.3 (4)
C(1D)	0.5770 (8)	0.1260 (8)	0.4458 (6)	5.0 (4)
C(1E)	0.5188 (8)	0.1574 (8)	0.3771 (6)	5.0 (5)
C(1F)	0.4147 (7)	0.2107 (7)	0.3619 (5)	3.8 (4)
C(2H)	−0.0977 (9)	0.2611 (7)	0.5197 (5)	4.2 (4)
C(2G)	−0.0047 (7)	0.2666 (6)	0.5041 (4)	3.1 (3)
C(2A)	−0.1313 (6)	0.3501 (6)	0.3602 (3)	2.8 (3)
C(2B)	−0.2100 (7)	0.2744 (8)	0.3210 (5)	4.1 (4)
C(2C)	−0.3159 (8)	0.311 (1)	0.2778 (5)	5.0 (4)
C(2D)	−0.3411 (8)	0.428 (1)	0.2751 (5)	4.6 (4)
C(2E)	−0.2633 (8)	0.5059 (9)	0.3142 (5)	4.4 (4)
C(2F)	−0.1586 (7)	0.4688 (7)	0.3574 (4)	3.8 (4)
C(3)	0.3043 (6)	0.4786 (6)	0.4680 (4)	2.8 (3)
C(3A)	0.3694 (9)	0.5399 (9)	0.5374 (5)	4.2 (4)
C(4)	0.3038 (6)	0.4962 (6)	0.4002 (4)	2.8 (3)
C(4A)	0.362 (1)	0.588 (1)	0.3707 (6)	5.0 (5)
C(5)	0.2154 (6)	0.4211 (6)	0.3472 (4)	2.8 (3)
C(6)	0.1019 (6)	0.4664 (6)	0.3525 (4)	2.7 (3)
C(7)	0.0991 (6)	0.4257 (6)	0.4283 (4)	2.4 (3)
C(8)	0.2206 (6)	0.3851 (6)	0.4072 (4)	2.4 (3)
C(9)	0.1151 (7)	−0.0067 (6)	0.3371 (5)	3.3 (3)
C(10)	0.0081 (7)	−0.0012 (6)	0.3448 (4)	3.1 (3)
C(11)	0.0197 (8)	0.0324 (6)	0.4165 (4)	3.4 (3)
C(12)	0.1350 (7)	0.0438 (6)	0.4535 (4)	3.5 (3)
C(13)	0.1924 (8)	0.0190 (6)	0.4036 (5)	3.7 (4)
C(14)	0.0359 (6)	0.2127 (6)	0.2776 (4)	2.9 (3)

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

On the basis of previous studies,[2-9,22] four diastereomers (two enantiomeric pairs) are possible for the products of reaction 1. This is because the syn–exo geometry of the bidentate disphosphine is fixed by the intramolecular nature of these cycloadditions,[7] leaving the ring conjunction carbon and the iron atom as the only two stereogenic atoms of variable absolute configuration. Two products were observed in a 3:2 ratio for reaction 1. Complex 4 reacted with DPVP to produce the same two products in a 7:1 ratio when the reaction was conducted under a CO atmosphere. Each of the two products is a racemic mixture of two enantiomeric diastereomers. These two diastereomeric pairs were separated by fractional crystallization and the major diastereomer (8a) was characterized by X-ray crystallography (Figure 2). The structure consists of isolated cations and anions with no short contacts. Selected bond distances and angles are listed in Tables VI and VII, respectively. As can be seen in Figure 2, the major

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[22] Brunner, H.; Mokhlesur Rahman, A. F. M. *J. Organomet. Chem.* 1981, *214*, 373.

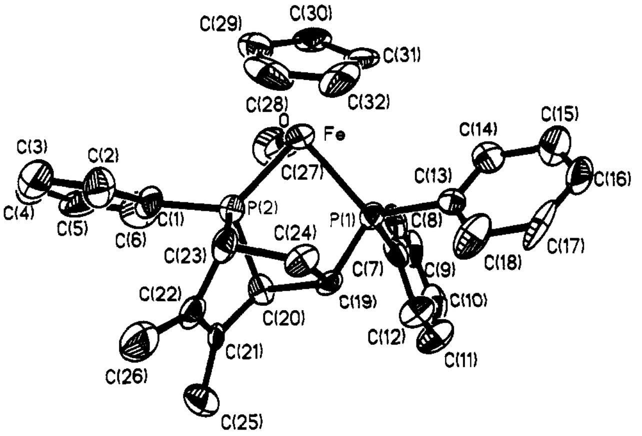
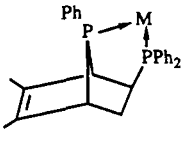


Figure 2. ORTEP drawing of the cation of **8a** showing that arom numbering scheme. (50% probability ellipsoids). Hydrogen atoms are omitted.

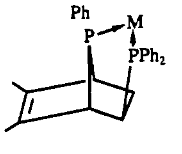
Table IX. Selected Bond Lengths (Å) for 9c

atom	atom	dist	atom	atom	dist
Fe	P1	2.187 (2)	C2H	C2G	1.29 (1)
Fe	P2	2.210 (2)	P2	C2G	1.820 (8)
Fe	C9	2.091 (7)	P2	C7	1.833 (7)
Fe	C10	2.107 (7)	O	C14	1.094 (8)
Fe	C11	2.078 (7)	C3	C4	1.327 (9)
Fe	C12	2.076 (7)	C3	C8	1.512 (9)
Fe	C13	2.081 (8)	C4	C5	1.521 (9)
Fe	C14	1.767 (8)	C5	C6	1.55 (1)
P1	C5	1.842 (7)	C6	C7	1.550 (9)
P1	C8	1.844 (7)	C7	C8	1.557 (9)

diastereomer contains the ligand with ring conjunction A rather than B:



A



B

Structure A is favored over structure B by the smaller magnitude of interligand steric interactions within the coordination sphere of the metal. The two Fe–P distances are quite different with Fe–P$_1$ (2.258 (3) Å) being longer than Fe–P$_2$ (2.165 (3) Å). This is also the case for all other complexes of this ligand that have been structurally characterized.[2-9] The cation has distorted octahedral geometry with no symmetry. It contains a slightly bent carbonyl ligand (Fe–C$_{27}$ = 1.69 (2) Å; Fe–C$_{27}$–O = 174 (2)°; C$_{27}$–O = 1.18 (2) Å). Compared to the structure of **7** the Fe–P distances are longer and shorter in **8a** than in **7**; the Fe–C distance is shorter, and the C–O distance is longer in **8a**. The P$_2$–C$_{20}$ (1.84 (2) Å) and P$_2$–C$_{23}$ (1.81 (2) Å) distances are only slightly different and the C$_{20}$–P$_2$–C$_{23}$ angle is small (80.0 (7)°) as is normally the case for the 7-phosphanorbornene structure.[2-9]

There are eight possible diastereomeric products (four enantiomeric pairs) for reaction 2 as now the ring conjunction carbon, the iron atom, and the exocyclic phosphorus atom are stereogenic centers with variable absolute configuration. Three Diels–Alder products (**9a–c**) were formed in a 1:1:1 ratio. In marked contrast, **4** reacted with DVPP under a CO atmosphere to form only two products (**9c,b**) in a 11:1 ratio. In both cases **9c** could be separated by fractional crystallization, and it was characterized by X-ray crystallography (Figure 3). The structure consists of isolated cations and anions with no short contacts. Selected bond distances and angles are listed in Tables IX and X respectively. As can be seen in Figure 3, **9c** contains the ligand with the structure B which is unusual for these type reactions. Moreover, within the Ni[2], Pd[4], Pt[4], and Ru[6,7,9] coordination spheres the exocyclic phosphorus absolute configuration illustrated in structure C is highly favored over that illustrated in structure D:

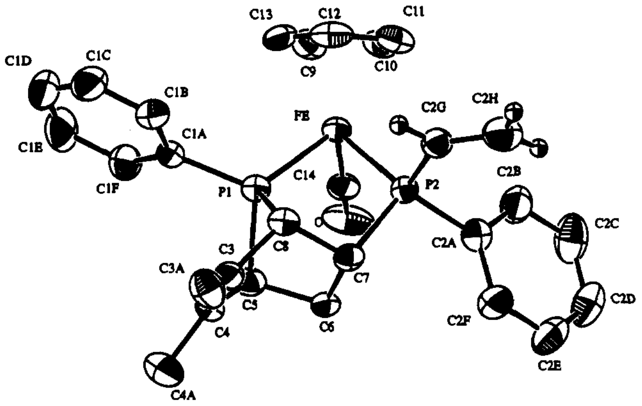
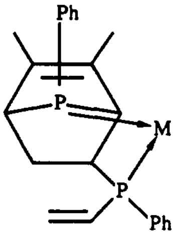


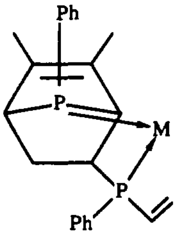
Figure 3. ORTEP drawing of the cation of **9c** showing the atom numbering scheme. (50% probability ellipsoids). Hydrogen atoms are omitted.

Table X. Selected Bond Angles (deg) for 9c

atom	atom	atom	angle
P1	Fe	P2	82.95 (8)
P1	Fe	C14	94.0 (2)
P2	Fe	C14	95.4 (2)
Fe	P1	C5	118.3 (2)
Fe	P1	C8	111.8 (2)
C5	P1	C8	81.1 (3)
Fe	P2	C2G	115.1 (2)
Fe	P2	C7	105.7 (2)
C2G	P2	C7	104.9 (3)
C2A	P2	C7	105.8 (3)
C4	C3	C8	110.3 (6)
Fe	C14	O	176.8 (6)
C3	C4	C5	110.9 (6)
P1	C5	C4	101.5 (5)
P1	C5	C6	100.7 (5)
C4	C5	C6	104.9 (6)
C5	C6	C7	104.8 (6)
P2	C7	C6	107.7 (5)
P2	C7	C8	108.1 (4)
C6	C7	C8	105.9 (6)
P1	C8	C3	103.0 (5)
P1	C8	C7	94.2 (4)
C3	C8	C7	110.4 (5)



C



D

The two Fe–P distances in **9c** (Fe–P$_1$ = 2.187 (2) Å; Fe–P$_2$ = 2.210 (2) Å) do not differ by as much as those in **8a** as the longer distance is shorter and the shorter distance longer than in **8a**. The distance to the 7-phosphaphosphorus atom is however still the shorter of the two distances. Complex **9c** also has a longer Fe–C$_{14}$ (1.767 (8) Å) distance and a shorter C$_{14}$–O (1.094 (8) Å) distance than does **8a** and a linear Fe–C$_{14}$–O (176.8 (6)°) group. The C$_5$–P$_1$–C$_8$ angle (81.1 (3)°) is small and in the normal range for 7-phosphanorbornenes.

Table XI. 121.66-MHz $^{31}P\{^1H\}$ NMR Chemical Shifts for the Complexes and Ligand Structure Assignments[a]

compd	δP_7	δP_2	$\Delta\delta = \delta P_7 - \delta P_2$	ligand struct
8a	173.10	70.47	102.63	A
8b	171.27	88.09	83.18	B
9a	171.19	64.42	106.77	A
9b	174.43	66.66	107.77	A
9c	168.55	83.39	85.16	B
11a	144.57	38.31	106.26	B
11b	144.27	34.43	109.84	A
11c	145.30	38.79	106.51	B
11d	141.57	30.34	111.23	A
12a	174.2			A
12b	169.8			A
12c	165.8			B
13a	170.1			A
13b	166.9			B
14	155.4			A

[a] In ppm; P_7 is the 7-phosphaphosphorus atom and P_2 is the exocyclic 2-phosphinophosphorus atom.

Table XII. Redox Characteristics of the Complexes[a]

		$E_{1/2}$, V (ΔE, mV)	
struct	complex formula	Fe(II)/ Fe(III)	Fe(II)/Fe(I)
1	$[CpFe(CO)(DMPP)I]$	0.19 (65)	
2	$[CpFe(CO)(DPVP)I]$	0.23 (55)	
3	$[CpFe(CO)(DVPP)I]$	0.23 (68)	
7	$[CpFe(CO)(DMPP)_2]PF_6$	0.99[b]	−1.77[c]
8a	$[CpFe(CO)(DMPP)(DPVP)]PF_6$ ([4 + 2]A)	1.06 (80)	−2.05 (109)
8b	$[CpFe(CO)(DMPP)(DPVP)]PF_6$ ([4 + 2])B)	1.06 (80)	−2.05 (109)
9c	$[CpFe(CO)(DMPP)(DVPP)]PF_6$ ([4 + 2])C)	1.10[d]	−2.09 (170)

[a] In CH_2Cl_2 containing 0.1 M TBAP at 25 °C, $V = 200$ mV s^{-1}, volts vs Fc/Fc^+. [b] E_{max} determined by differential pulse voltammetry (due to slight impurities, peak potentials could not be determined by cyclic voltammetry. [c] E_{Pc} only. [d] E_{Pa} only.

Reaction 3 produced compound **10** which could not be isolated in pure form and fully characterized. The structure was assigned on the basis of the low field ^{31}P chemical shift (δ 183.24) and the large magnitude of $^2J(PP) = 52.50$ Hz that are characteristic of [4 + 2] phosphole dimers.[23]

Similarly, the four diastereomeric products of reaction 4 could not be separated and fully characterized. That they are [4 + 2] Diels–Alder products is indicated by their ^{31}P NMR data.[9] The $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_2(DAPP)]PF_6$ system is the only other metal system for which we have observed [4 + 2] cycloadditions between a phosphole and an allyl phosphine.[9]

Reactions 5 and 6 are noteworthy for their lack of diastereoselectivity. By way of comparison, $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_2CH_3CN]PF_6$ reacts with $PhS(O)CH{=}CH_2$, $PhS{-}CH{=}CH_2$, and 2-vinylpyridine to produce single diastereomers in each case.[9] However, the diastereoselectivites of the reactions of the aforementioned ruthenium complex with DPVP and DVPP (two diastereomers, 5:1 and two mono Diels–Alder diastereomers, 3:1, respectively) are lower than for the reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(DMPP)]I$ with these same dienophiles (7:1 and 11:1, respectively).

$^{31}P\{^1H\}$ NMR and Stereochemistry. We have observed that for the 2-phosphino-7-phosphanorbornene ligands coordinated to the $(\eta^5\text{-}C_5H_5)RuL'$ moiety that the ring conjunction position, structure A or B can be deduced from the magnitude of the difference in the ^{31}P chemical shifts (Table XI) of the two phosphorus atoms in the chelate ring. Structure A gives rise to a significantly larger difference in chemical shifts than does structure B. On this basis compound **8a** would be predicted to contain a ligand with structure A and compound **9c** would be predicted to contain a ligand with structure B. Both predictions are confirmed by the X-ray crystal structures of these two complexes. The ligand structures for the remainder of the diphosphine complexes were deduced on this basis and are listed in Table XI. The ligand structures for the monophosphine Diels–Alder adducts are predicted on the basis that the 7-phosphaphosphorus chemical shift for ligand structure A is usually found downfield of that for ligand structure B, but the structures predicted on this basis are less certain and need further structural confirmation. Note that these iron complexes are the first examples where more than one diastereomer of the ligand has been observed for the [4 + 2] Diels–Alder adducts of $PhS(O)CH{=}CH_2$ and $PhSCH{=}CH_2$.

Redox Properties of the Complexes. The electrochemical behavior of some of the complexes prepared in this study was investigated by cyclic voltammetry (Table XII). For most of these complexes the Fe(II)/Fe(III) redox couple is a reversible one-electron process or a process that approaches reversibility. Comparison of the $E_{1/2}$ values for the oxidations of **1**–**3** indicates that the σ-donor ability of the three phosphines decreases in the order DMPP > DPVP > DVPP but their is not much difference. Similar to what was found for similar ruthenium complexes,[9] the bidentate phosphines do not have better donor abilities than two comparable monodentate ligands based upon $E_{1/2}$ values. Compare the $E_{1/2}$ values for **8a**, **8b**, and **9c** with that of **7**. The $[CpFe(CO)(R_3P)_2]PF_6$ complexes also undergo quasi-reversible one-electron reductions. A limited number of electrochemical studies of similar systems have been reported in the literature.[24-27] Though the reference electrodes differ considerably among these studies, the redox potentials and electrochemical behavior of similar complexes are comparable to those reported herein.

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Supplementary Material Available: For the three structures, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (U) (38 pages). Ordering information is given on any current masthead page.

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(23) Nelson, J. H.; Mathey, F. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH publishers: Deerfield Beach, FL, 1987; pp 665–694.

(24) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77.

(25) Rogers, W.; Page, J. A.; Baird, M. C. *J. Organomet. Chem.* **1978**, *156*, C37.

(26) Grant, M. E.; Alexander, J. J. *J. Coord. Chem.* **1979**, *9*, 205.

(27) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.