Stepwise Metal Chelate Formation. Isolation of the Intermediates $(\pi\text{-}C_5H_5)Fe(CO)_2[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]^+$ (n = 1, 2, 3) and Their Reactions as Ligands[1]

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Abstract: From reactions between $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ and the di(tertiary phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3; Ph is phenyl) we have isolated the 1:1 complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$, in which a donor site on the di(tertiary phosphine) is not bound. The 1:1 complexes can react as ligands and we have used this reactivity to prepare symmetric, *i.e.*, $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)](PF_6)_2$ or $\text{-}(ClO_4)_2$ (n = 1, 2, 3), and mixed-metal, *i.e.*, $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2\}(PF_6)_2$ or $\text{-}(ClO_4)_2$ (n = 2, 3), complexes in which metal ions are linked by bridging ligands. 2,5-Dithiahexane and pyrazine have also been used as bridging ligands in the complexes $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_3SCH_2CH_2SCH_3)\}(ClO_4)_2$ and $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(NC_4H_4N)\}(ClO_4)_2$. An efficient light-catalyzed path for the conversion of the 1:1 complexes into chelated complexes has been found: $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ (+ h\nu) \rightarrow (\pi\text{-}C_5H_5)Fe(CO)(Ph_2P(CH_2)_nPPh_2)^+ + CO$ (n = 1 or 2).

We have described the preparation of $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ by the reaction[3]

$$2Fe^{3+} + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2(CH_3)_2CO \longrightarrow 2Fe^{2+} + 2(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$$

The bound acetone molecule in $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ is easily displaced by a variety of neutral and anionic ligands to give $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ (L = neutral ligand) and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = anionic ligand).[3] Using mild conditions only the coordinated acetone molecule is labile. The property of having a single labile coordination site introduces an element of synthetic control into the stepwise reactions between $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ and potentially chelating ligands, *e.g.*

$$(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+ + Ph_2PCH_2CH_2PPh_2 \xrightarrow{\text{fast}} (\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)^+ + CH_3)_2CO \quad (1)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)^+ \xrightarrow{\text{slow}} (\pi\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2PPh_2)^+ + CO \quad (2)$$

(Ph is phenyl)

The initial step, displacement of coordinated acetone (reaction 1), is rapid while the closing of the chelate ring in the second step involves displacement of coordinated CO (reaction 2), and it is slow. This pattern in the relative rates of reactions 1 and 2 is opposite that normally observed for stepwise metal chelate formation, where chelate ring closure is the rapid step.[4] As reported here, the relative slowness of reaction 2 using mild reaction conditions allows the isolation of complexes like $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)^+$ in which one of the donor sites on a coordinated ligand is not bound. The subsequent chelation step is much slower although an efficient light-catalyzed path for chelation does exist. The complexes $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$ (n = 1, 2, 3; reaction 1) can themselves react as ligands by using the uncoordinated donor site on the bound di(tertiary phosphines). Part of this work has appeared in a preliminary communication.[5]

Results and Discussion

The reactions which have been carried out using the di(tertiary phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3) are summarized in Scheme I. Some of the complexes which appear in the scheme, or closely related complexes, have been reported previously as products of a variety of reactions.[6-9] Synthetically the scheme has the advantage of offering a common synthetic route to a variety of products using a common intermediate, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$, and it allows synthetic control at each step. Ligands other than the di(tertiary phosphines) can be used; complexes having either 2,5-dithiahexane, $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_3SCH_2CH_2SCH_3)\}(ClO_4)_2$, or pyrazine, $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(NC_4H_4N)\}(ClO_4)_2$, as the bridging ligand have also been prepared. The syntheses outlined in Scheme I are dependent on the fact that the starting complex, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$, has a single, labile coordination site. A pattern of reactions like Scheme I should exist for other metal complexes with similar lability properties.[10,11] Spectral data for the complexes reported here are given in Table I. In cases where pmr spectra are reported, the ratios of $\pi\text{-}C_5H_5$ to ligand protons were determined by integration, and the values so obtained compared satisfactorily with calculated values. In two cases the $\pi\text{-}C_5H_5$ resonances were split, ap-

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[2] National Science Foundation Undergraduate Research Participant, summer, 1970.

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Scheme I

$$(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+ + Ph_2P(CH_2)_nPPh_2 \longrightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ + (CH_3)_2CO$$

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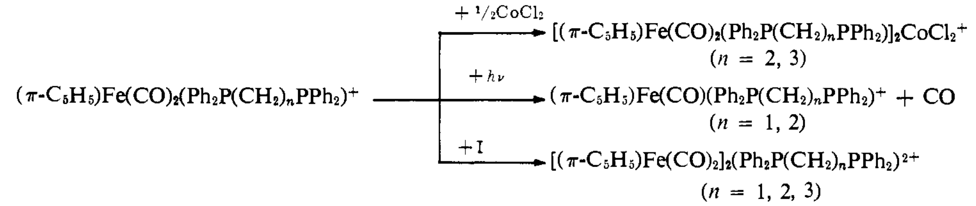


$$(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ \xrightarrow{+\,^1/_2CoCl_2} [(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2^+ \quad (n = 2, 3)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ \xrightarrow{+h\nu} (\pi\text{-}C_5H_5)Fe(CO)(Ph_2P(CH_2)_nPPh_2)^+ + CO \quad (n = 1, 2)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ \xrightarrow{+I} [(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2P(CH_2)_nPPh_2)^{2+} \quad (n = 1, 2, 3)$$

Table I. Spectral Properties of the Compounds

Compound	ν_{CO}, cm^{-1}	λ_{max}, nm[a]	$\tau(\pi\text{-}C_5H_5)$	$\tau(C_6H_5)$
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)]ClO_4$	2054, 2012[a]	350 sh	4.48, 4.49[b]	2.48, 2.68
$[(\pi\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2PPh_2)]ClO_4$	1982[a]		4.75[b]	2.70
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)](BPh_4)_2$	2055, 2015[a]		4.99[d]	2.45,[e] 2.93, 3.07
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]ClO_4$	2057, 2014[a]	350 sh	4.50[b]	2.50, 2.71
$[(\pi\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2PPh_2)]ClO_4$	1980[a]		4.90[b]	2.45
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$	2050, 1998[c]		4.88[d]	2.56
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)]ClO_4$	2059, 2014[a]	350 sh	4.47[b]	2.30, 2.38
$[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$	2050, 2009[a]		4.85, 4.87[d]	2.43
$[(\pi\text{-}C_5H_5)Fe(CO)_2(CH_3SCH_2CH_2CH_3)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$	2071, 2033[c]		4.52[d]	
$[(\pi\text{-}C_5H_5)Fe(CO)_2(NC_4H_4N)Fe(CO)_2(\pi\text{-}C_5H_5)](ClO_4)_2$	2067, 2031[c]		4.11[d]	
$\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]_2CoCl_2\}(PF_6)_2$	2061, 2011[a]	340 sh, 595, 640 sh, 650, 715		
$\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)]_2CoCl_2\}(PF_6)_2$	2056, 2011[a]	340 sh, 597, 640 sh, 660, 690		

[a] In dichloromethane. [b] In acetone-d_6 relative to acetone-d_5 at τ 7.93. [c] In Nujol mulls. [d] In acetonitrile-d_3 relative to acetonitrile-d_2 at τ 8.00. [e] Multiplet.

parently by ^{31}P splitting. We have been unable to prepare an analytically pure sample of the complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2(CH_2)_3PPh_2)]^+$ as either its perchlorate or hexafluorophosphate salts.

Chelation. The 1:1 complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$ (n = 1, 2, 3), are stable in dichloromethane solution for days. Chelation does not occur even if the dichloromethane solutions are refluxed for periods as long as 5 hr in the absence of light. It is not surprising that the chelation reactions are slow since they involve the displacement of CO. Substitution for CO by other ligands in complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ is known to be slow.[7,12]

For the complexes with n = 1 or 2 an efficient light-catalyzed path exists

$$(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Fe(CO)(Ph_2P(CH_2)_nPPh_2)^+ + CO \quad (n = 1 \text{ or } 2)$$

Using a 275 W GE sun lamp in contact with the reaction flask, a solution *ca.* 2 × 10^{-3} M in $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)^+$ in dichloromethane was completely converted into the chelated complex after 3 min of photolysis. The progress of the photolytic reactions in acetone-d_6 was monitored by pmr and in dichloromethane by infrared spectra. No attempt was made to isolate the chelated complexes. Both complexes (n = 1, 2) have been prepared by other synthetic routes[7,8] and they were characterized by their spectral properties as summarized in Table I. The initial light induced chelation step is followed by a slower photodecomposition reaction in which CO is lost from the chelated complexes. This reaction was not studied in detail.

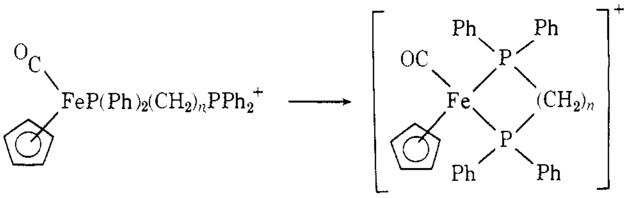
The light-catalyzed path for chelate ring closure is an efficient photoreaction from our qualitative observations. The mechanism for these reactions may be the same in general detail as that found for the light-catalyzed displacement of CO in the simple binary metal carbonyls[13] and specifically for the complex $(\pi\text{-}C_5H_5)Mn(CO)_2PPh_3$,[14] which is essentially isoelectronic with the iron 1:1 complexes. In this mechanism, the initial absorption of light is followed by ejection of a CO group giving a lower coordinated (or weakly solvated) intermediate

$$(\pi\text{-}C_5H_5)Mn(CO)_2PPh_3 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mn(CO)PPh_3 + CO$$

which reacts rapidly with the free ligand

$$(\pi\text{-}C_5H_5)Mn(CO)PPh_3 + PPh_3 \longrightarrow (\pi\text{-}C_5H_5)Mn(CO)(PPh_3)_2$$

The interesting feature of this chemistry for the iron 1:1 complexes is that capture of the lower coordinated intermediates, if formed, occurs by an internal reaction (chelate ring formation) rather than by an external bimolecular reaction.



All attempts to prepare the chelated complex $(\pi\text{-}C_5H_5)Fe(CO)(Ph_2P(CH_2)_3PPh_2)^+$ were unsuccessful. Our

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(12) A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, **83**, 525 (1961).

(13) W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 370 (1964).

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inability to prepare this complex may reflect a lesser stability for the six-membered chelate ring system,[15] although it may be that chelate ring closure for the longer ligand is not competitive with recapture by CO.

Ligand Bridged Complexes. At room temperature the 1:1 complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$ (n = 2 or 3) react rapidly with $CoCl_2 \cdot 6H_2O$ (or with anhydrous cobalt(II) chloride) in acetone–ethanol mixtures, *viz.*

$$2(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+ + Co(II) + 2Cl^- \longrightarrow [(\pi\text{-}C_5H_5)(CO)_2Fe(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2{}^{2+} \quad (n = 2, 3)$$

The bridged metal complexes can be isolated as perchlorate or hexafluorophosphate salts. We have been unable to isolate the analogous complex with n = 1, probably because of increased steric repulsions imposed by the shorter bridging ligand. We have obtained spectral evidence that a relatively slow reaction does occur when both $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)^+$ and anhydrous cobalt(II) chloride are present in ethanol–acetone solution. The complexes are easily decomposed in solution. If a few drops of water are added to acetone solutions of $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2{}^{2+}$, an immediate reaction occurs giving cobalt(II) and $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$. The pmr spectra of the cobalt complexes show extensive paramagnetic shifts as expected.[16,17] Unfortunately, we have been unable to assign these spectra with any certainty.

The cobalt–iron mixed-metal complexes have properties characteristic of the isolated metal ions. We have found no evidence that there is a significant electronic interaction between the metal centers. For the CO groups bound to iron, the ν(CO) values are only slightly shifted from the values found for the uncomplexed ions $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$ (n = 2, 3) (Table I). For the mixed-metal complexes the pattern of electronic bands in the visible region of the spectrum (Table I) is essentially the same as that found for $Co(PPh_3)_2Cl_2$[18] (λ_{max} at 675, 645 (sh), and 594 nm in dichloromethane) which indicates that the ligand geometry at cobalt is tetrahedral.[19] The bands which appear at 350 nm (shoulder) for the iron 1:1 complexes are nearly unaffected by complexation to cobalt. We have found no bands in the region 2000–220 nm which can be attributed to electron transfer between the metal centers. The available spectral evidence indicates that in the cobalt–iron complexes, the saturated bridging ligands effectively shield the metal centers from any significant interaction.

In summary, the complexes $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)^+$ (n = 1, 2, 3) can function as ligands because of the unbound donor site on the coordinated di(tertiary phosphine). As ligands, in either symmetrical, $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)]^{2+}$ (n = 1, 2, 3), or mixed-metal, $[(\pi\text{-}C_5H_5)(CO)_2Fe(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2{}^{2+}$ (n = 2, 3), complexes, they appear to behave as typical alkyl–aryl phosphines, and their most interesting property is that they link metal centers. In the bridged complexes the metal centers are apparently isolated electronically. However, the reactions summarized in Scheme I are flexible synthetically and by varying the bridging ligand and added metal ion materials may be isolated which have, to some extent, the combined properties of both metal centers in either ground or excited states. We are currently exploring this possibility.

Experimental Section[20]

Bis(π-cyclopentadienyldicarbonyliron) (Alfa Inorganics) and 1,2-bis(diphenylphosphino)ethane (Arapahoe Chemicals) were used without further purification. The di(tertiary phosphine) ligands, bis(diphenylphosphino)methane and 1,3-bis(diphenylphosphino)propane, were prepared as described in the literature.[21]

Infrared spectra were recorded on Perkin-Elmer 421 or Perkin-Elmer 257 spectrophotometers. Pmr spectra were obtained using a JEOL C6OHL spectrometer. Ultraviolet–visible spectra were recorded on either Cary 14, Cary 17, or Unicam spectrophotometers. Elemental analyses were performed by either Galbraith Laboratories, Knoxville, Tenn., or Meade Microanalytical Laboratory, Amherst, Mass. Iron analyses were carried out as described previously,[22] and cobalt(II) was determined spectrophotometrically in the presence of thiocyanate ions.[23]

Preparations. Warning! Several of the following preparations call for the use of solutions containing perchlorate ions and labile organometallic complexes, followed by the isolation of organometallic perchlorate salts. The solutions and/or the salts may be explosive, and due care should be taken in working with them.

All preparations in which the acetone complex, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$, is used were carried out under an atmosphere of nitrogen.

(1) The Acetone Intermediate $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$. In a typical experiment $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0.525 g, 1.51 mmol) and anhydrous ferric perchlorate (1.766 g, 4.9 mmol) were dissolved together in deaerated acetone (20 ml). After 20 min the solution was reduced in volume to *ca.* 1 ml using a stream of nitrogen. The residue was extracted with dichloromethane (3 × 15 ml) and the dichloromethane washings were chromatographed twice on Florisil (60–100 mesh, 3 × 1 cm). The chromatographed solution was evaporated to *ca.* 5 ml. At this point solutions contain between 30 and 70% of the acetone complex, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$, based on the amount of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ used initially, and they are free of iron(II) and iron(III). In later preparations in which the acetone complex is used, solutions were prepared as described above, and the amount of the acetone complex present was estimated from the amount of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ used initially.

(2) 1:1 Complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)]ClO_4$ (n = 1, 2, 3). A solution of the acetone intermediate, prepared as described above, was added to bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (0.9238 g, 2.4 mmol, *ca.* eightfold excess), in benzene (10 ml). The solution was stirred for 3 hr and then added slowly to ether (80 ml) which precipitated $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)](ClO_4)$ as a yellow powder. The product was washed with benzene (5 ml), ether (20 ml), and then dissolved in acetone, filtered, and reprecipitated with ether, giving the yellow product in 37% yield. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2PPh_2)ClO_4$: C, 58.18; H, 4.09; Fe, 8.45. Found: C, 57.46; H, 4.20; Fe, 7.42. The analogous complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)](ClO_4)$ (n = 2, 3) were prepared similarly using 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane in 5–10 molar excesses. Yields of from 30 to 63% based on the amount of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ used initially were obtained. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)ClO_4$: C, 58.73; H, 4.34; P, 9.18; Cl, 5.25. Found: C, 57.86; H, 4.50; P, 8.91; Cl, 4.60. Calcd for $(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)ClO_4$: C, 59.28; H, 4.50; Fe, 8.10. Found: C, 57.60; H, 5.34; Fe, 7.15.

(3) 2:1 Complexes. (a) $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2P(CH_2)_nPPh_2)\}(ClO_4)_2$ (n = 2, 3). To a solution of the acetone intermediate in *ca.* eightfold excess was added 1,3-bis(diphenylphosphino)-

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(20) Ph is used here as an abbreviation for $-C_6H_5$.

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(23) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

propane (0.0495 g, 0.12 mmol) in benzene (4 ml). The solution color changed from red to yellow after stirring for 2 hr, and an oil formed. Acetone (3 ml) was added to dissolve the oil. The solution was then added dropwise to ether giving $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2P(CH_2)_3PPh_2)\}(ClO_4)_2$ as a yellow powder. The complex was collected and washed with benzene (5 ml) and ether (20 ml). It was then dissolved in acetonitrile, filtered, reprecipitated with ether, collected, and air-dried giving the yellow solid in 87% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2PCH_2CH_2CH_2PPh_2)\}(ClO_4)_2$: C, 51.10; H, 3.75; P, 6.43; Cl, 7.32; Fe, 11.56. Found: C, 49.50; H, 3.87; P, 6.47; Cl, 7.19; Fe, 10.72. The 2:1 complex of 1,2-bis(diphenylphosphino)ethane was prepared similarly using *ca.* a fourfold excess of the acetone intermediate. It was obtained in 83% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2PCH_2CH_2PPh_2)\}(ClO_4)$: C, 50.50; H, 3.61; P, 6.51; Cl, 7.45. Found: C, 51.85; H, 3.81; P, 6.56; Cl, 7.49.

(b) $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2PCH_2PPh_2)\}(BPh_4)_2$. To the acetone intermediate in *ca.* ninefold excess was added bis(diphenylphosphino)methane (0.0794 g, 0.206 mmol) in benzene (3 ml). The solution was stirred for 2 hr. The yellow 2:1 complex was precipitated using ether (*ca.* 250 ml), collected, and washed with benzene (10 ml) and then with ether (20 ml). *This perchlorate salt is explosive when dry and should not be isolated!* Rather, before the solid dried it was dissolved in acetonitrile (10 ml), added slowly to 20 ml of an aqueous solution of sodium tetraphenylboron (0.34 g, 1 mmol), and precipitated by the addition of ether (500 ml). The solid which precipitated was dissolved in acetonitrile, filtered, and reprecipitated by adding ether, collected, and air-dried giving the orange solid $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2PCH_2PPh_2)\}(BPh_4)_2$ in 39% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(Ph_2PCH_2PPh_2)\}(BPh_4)_2$: C, 75.92; H, 5.23; P, 4.51; Fe, 8.11. Found: C, 76.35; H, 5.45; P, 4.63; Fe, 8.15.

(c) $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_3SCH_2CH_2SCH_3)\}(ClO_4)_2$. To the acetone intermediate in *ca.* sixfold excess was added dithiahexane, $CH_3SCH_2CH_2SCH_3$ (0.24 mmol), in a 1:1 volume mixture of benzene–acetone. The dithiahexane solution was added dropwise with stirring over a 10 min interval. After 3 hr benzene (5 ml) was added. The solution was allowed to stand for 12 hr, and the golden precipitate was collected, washed with benzene (5 ml) and ether (20 ml), and air-dried giving an 81% yield of $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_3SCH_2CH_2SCH_3)\}(ClO_4)_2$. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_3SCH_2CH_2SCH_3)\}(ClO_4)_2$: C, 31.92; H, 3.28; Cl, 10.47; S, 9.47. Found: C, 32.19; H, 3.29; Cl, 10.32; S, 9.57.

(d) $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(NC_4H_4N\}(ClO_4)_2$. To the acetone intermediate in *ca.* fourfold excess was added pyrazine, dissolved in a 50–50 mixture of benzene–acetone (5 ml), dropwise with stirring over a 10 min interval. After 12 hr benzene was added (5 ml), and the golden precipitate was collected and washed with dichloromethane (6 × 5 ml) giving $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(NC_4H_4N)\}(ClO_4)_2$ in 38% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(NC_4H_4N)\}(ClO_4)_2$: C, 34.21; H, 2.08; Cl, 11.22; N, 4.43. Found: C, 33.92; H, 2.40; Cl, 11.00; N, 4.32.

(4) Complexes with Cobalt(II), $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPPh_2)]_2CoCl_2\}(ClO_4)_2$ or -$(PF_6)_2$ ($n = 2, 3$). To anhydrous cobalt(II) chloride (0.0247 g, 0.19 mmol) in ethanol (1 ml) was added $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]PF_6$ (0.195 g, 0.266 mmol) in acetone (3 ml) with stirring. After 2 hr, ether (25 ml) was added which precipitated a turquoise solid. The solid was dissolved in dichloromethane, filtered, and reprecipitated with ether. $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]_2CoCl_2\}(PF_6)_2$ was recrystallized from chloroform–ether giving a 53% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]_2CoCl_2\}(ClO_4)_2$: C, 53.58; H, 3.95; Cl, 9.59; Co, 3.98. Found: C, 54.34; H, 4.05; Cl, 10.53; Co, 3.77. The complex $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_3PPh_2)]_2CoCl_2\}(PF_6)_2$ was prepared similarly in 48% yield. *Anal.* Calcd for $\{[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)]_2CoCl_2\}(PF_6)_2$: Fe, 6.98; Co, 3.69. Found: Fe, 6.96; Co, 3.45.

(5) Conversion to Hexafluorophosphate and Tetraphenylborate Salts. The perchlorate salts were dissolved in a minimum of acetone or acetonitrile, and after filtering the solutions they were added to aqueous solutions containing large excesses of ammonium hexafluorophosphate or sodium tetraphenylboron,

(6) Chelated Complexes, $[(\pi\text{-}C_5H_5)Fe(CO)(Ph_2P(CH_2)_nPPh_2)]^+$. Solutions of the 1:1 complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2P(CH_2)_nPh_2)](PF_6)$ or -(ClO_4) (n = 1, 2) in dichloromethane or acetone-d_6 (3×10^{-4}–6×10^{-2} *M*) were irradiated using a GE 275W sunlamp. The irradiations were carried out for varying lengths of time, from a few seconds to as long as 10 min. The progress of the reactions in dichloromethane was followed by infrared spectroscopy in the region from 2200 to 1800 cm^{-1} and in acetone-d_6 by pmr measurements.

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