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Contribution from the Department of Chemistry, University of California, Riverside, California 92502

Mechanisms of Substitution of Ligand-Bridged Diiron Hexacarbonyl Complexes. $(OC)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_3$. Promotion of an SN1 Mechanism by a Bulky Bridging Ligand

J. N. Gerlach,[1a] S. L. McMullin, and P. C. Ellgen*[1b]

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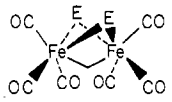
Phosphines and phosphites have been found to displace carbon monoxide from bis(μ-diphenylphosphido)-bis(tricarbonyliron), $(OC)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_3$, at about 150 °C. The kinetics of these reactions are reported. These results contribute to an integrated understanding of the substitution mechanism in a variety of diiron hexacarbonyl complexes containing different bridging groups. Previous papers in this series have described the kinetics and mechanisms of carbonyl displacement reactions of Lewis bases with mercapto-,[2] benzo[*c*]cinnoline-,[3] and ureylene-bridged[3] diiron hexacarbonyl complexes.

All of these complexes[4–8] have the same general structure I: two approximately octahedrally coordinated iron atoms



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share an octahedral face; the vertices of the shared face are occupied by the two bridging atoms and an iron–iron bond. A variety of mechanistically interesting isomerization[8] and carbonyl-substitution[9] reactions have been observed for these complexes.

Substitution reactions of the organosulfur-[2] and organonitrogen-bridged[3] diiron hexacarbonyl complexes obey second-order rate laws, which are first order in the concentrations of both reactants and independent of the carbon monoxide concentration. The second-order rate constants are sensitive to both the electronic and the steric characteristics of the attacking nucleophiles. For these systems, the kinetic data imply a bimolecular substitution mechanism (SN2 or I_a).

The rate law and the thermal substitution mechanism of the organophosphorus-bridged complex are markedly different from those of the organosulfur- and organonitrogen-bridged systems.

Experimental Section

Materials. Ligands were obtained commercially. Diphenylphosphine was distilled and iron pentacarbonyl was filtered before use. Solvents were refluxed over calcium hydride or phosphorus pentoxide (dichloromethane) and then distilled in a nitrogen atmosphere. Carbon monoxide was passed through a trap at −78 °C before use.

Physical Measurements. Reaction rates were determined by monitoring the disappearance of the highest frequency, carbonyl-stretching absorption of the iron carbonyl substrate. Rate experiments were initiated by injection of a 1-ml aliquot of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ stock solution into a previously thermostated solution of the desired ligand, which had been thoroughly purged with carbon monoxide. Pseudo-first-order conditions were ensured by use of a large excess of ligand. Reaction solutions were protected from light. At appropriate intervals, aliquots were transferred from the reaction mixture to a 1-mm path length infrared cell. A matched reference cell contained a solution of ligand at the same concentration as in the reaction mixture. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer and were calibrated against spectra of polystyrene and indene.[10]

Table I. First-Order Rate Constants for Carbonyl-Substitution Reactions of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$[a]

Ligand	[Ligand], M	10^4k_{obsd},[b] s^{-1}	T, °C
$P(C_6H_5)_3$	0.502	1.92 (16)	160
	0.167	1.80 (9)	160
	0.0488	2.01 (12)	160
	0.502	0.63 (4)	150
	0.167	0.59 (5)	150
	0.0488	0.64 (4)	150
	0.502	0.213 (14)	140
	0.167	0.215 (3)	140
	0.0488	0.200 (9)	140
$P(OC_6H_5)_3$	0.956	0.67 (6)	150
	0.0568	0.52 (2)	150
$P(n\text{-}C_4H_9)_3$	0.977	0.63 (1)	150
	0.0867	0.70 (5)	150

[a] In decalin solution; substrate concentration (2–3) × 10^{-3} M. [b] Values in parentheses are the estimated standard deviation in the least significant digit.

Iron Carbonyl Complexes. Diiron nonacarbonyl was prepared from iron pentacarbonyl.[11] Reaction of $HP(C_6H_5)_2$ (11 g, 59 mmol) and $Fe_2(CO)_9$ (25 g, 69 mmol), followed by ultraviolet irradiation,[12] yielded 4.1 g of bis(μ-diphenylphosphido)-bis(tricarbonyliron) (6.3 mmol, 21% of theoretical yield), mp 179 °C (lit.[13] mp 178–179 °C). Infrared spectrum (cm^{-1}), ν_{CO}: 2055 (m), 2019 (vs), 1994 (m), 1968 (s).

Carbonyl-substituted derivatives of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ were prepared by treating the substrate with a slight excess of the desired ligand in decalin solution at 150 °C. The reaction mixture was loaded onto a silica gel chromatography column and eluted with hexane to bring off decalin and unreacted starting materials. The derivative was then eluted with successively more benzene-rich hexane–benzene solutions. In each case, the orange derivative was recrystallized from dichloromethane–hexane.

Carbonyl-region infrared spectra were obtained in dichloromethane solutions and were very similar to those previously reported[14] for substitution at one or both of the positions trans to the iron–iron bond. Infrared spectra (cm^{-1}), ν_{CO}: for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(C_6H_5)_3$ (mp 205 °C dec), 2026 (s), 1966 (vs), 1908 (w); for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(OC_6H_5)_3$, 2028 (s), 1970 (vs), 1936 (vw), 1910 (w); for $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(n\text{-}C_4H_9)_3$, 2025 (s), 1957 (s), 1930 (vw), 1900 (w); for $Fe_2(CO)_4(\mu\text{-}P(C_6H_5)_2)_2(P(n\text{-}C_4H_9)_3)_2$, 1995 (s), 1956 (s), 1920 (s), 1900 (sh).

Results and Discussion

The photochemically initiated displacement of carbon monoxide from bis(μ-dimethylphosphido)-bis(tricarbonyliron), $(CO)_3Fe(\mu\text{-}P(CH_3)_2)_2Fe(CO)_3$, by phosphines has been shown[14] to give derivatives similar to those reported here. The infrared spectra of phosphine derivatives of phosphido-bridged complexes are closely similar whether the substitution is effected photochemically or thermally. These spectra are also very similar to those of derivatives in nitrogen-,[3] sulfur-,[2] and carbon-bridged[15] diiron hexacarbonyl systems. It appears that the carbonyl ligands trans to the iron–iron bond are the most readily displaced in all cases.[15–17]

Bis(μ-diphenylphosphido)-bis(tricarbonyliron) undergoes carbonyl substitution reactions much less readily than the organosulfur- and organonitrogen-bridged systems. Whereas the latter complexes react smoothly below 70 °C, the diphenylphosphido-bridged complex undergoes thermal substitution at a similar rate only above 140 °C. First-order rate

Table II. Activation Parameters for Reactions of Ligand-Bridged Diiron Carbonyl Complexes with $P(C_6H_5)_3$

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ [a,b]	37 (2)	+10 (4)
$Fe_2(CO)_6(\mu\text{-}N_2C_{12}H_8)$ [c,d]	10.2 (5)	−34 (2)
$Fe_2(CO)_6(\mu\text{-}OC(NC_6H_4OCH_3)_2)$ [c,d]	15.0 (5)	−20 (2)
$Fe_2(CO)_6(\mu\text{-}OC(NC_6H_5)_2)$ [c,d]	12.7 (5)	−26 (2)
$Fe_2(CO)_6(\mu\text{-}S_2C_6H_3CH_3)$ [c,e]	12.5 (5)	−31 (2)
$Fe_2(CO)_6(\mu\text{-}SC_6H_5)_2$ [c,f]	21.6 (5)	−4 (2)
$Fe_2(CO)_5(\mu\text{-}SC_6H_5)_2P(C_6H_5)_3$ [b,f]	35.5 (7)	+16 (2)

[a] This work. Values in parentheses are estimated standard deviations in the least significant digits. [b] First-order pathway. [c] Second-order pathway. [d] Reference 3; toluene solution. [e] Reference 2; toluene solution. [f] Reference 20; decalin solution.

constants are given in Table I for the reactions of $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ with triphenylphosphine, triphenyl phosphite, and tri-*n*-butylphosphine to give the corresponding monosubstituted products, $(CO)_3Fe(\mu\text{-}P(C_6H_5)_2)_2Fe(CO)_2L$. These rate constants are independent of the nature and concentration of the attacking nucleophile. This result contrasts markedly with those for the organosulfur- and organonitrogen-bridged systems.

Both activation parameters for substitution on the phosphido-bridged complex are also distinctly different from those for the corresponding organosulfur- and organonitrogen-bridged systems. Activation parameters for the reactions of triphenylphosphine with the variously bridged diiron hexacarbonyl complexes are given in Table II. For $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, $\Delta H^{\ddagger}$ is more than 15 kcal/mol and $\Delta S^{\ddagger}$ more than 14 eu greater than for the corresponding substitution reactions of the sulfur- and nitrogen-bridged diiron hexacarbonyl complexes.

The rate law, large activation enthalpy, positive activation entropy, and insensitivity to the nature of the entering group imply that the rate-limiting step for the substitution reaction of the phosphido-bridged complex is the dissociative loss of a carbonyl ligand to give $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2$. This reactive intermediate is then rapidly trapped by the entering group (an SN1 or D mechanism). However, a slightly more complex alternative cannot be eliminated: an intramolecular iron–phosphorus bond rupture (bridge opening) could be the rate-limiting step. This would be followed by entering group capture, loss of carbon monoxide, and reclosure of the bridge.

Evidently, the SN2 or I_a mechanism which is found for organosulfur- and organonitrogen-bridged diiron hexacarbonyl complexes is inaccessible to the diphenylphosphido-bridged complex. To some extent, this mechanistic difference may represent an effect of the bridging substituent on the iron–carbon bond strength; however, this is unlikely to be the major factor. Infrared[2,3,16,18] and Mössbauer[19] spectra suggest similar electronic environments for iron and carbon monoxide in the phosphorus-, nitrogen-, and sulfur-bridged complexes.

The substitution rates of sulfur- and nitrogen-bridged diiron hexacarbonyl complexes are sensitive to the steric characteristics of the bridging ligands. Bulky bridging groups which project over the carbonyl ligand trans to the iron–iron bond inhibit the bimolecular substitution reaction. This observation has been interpreted as a reflection of steric destabilization of the seven-coordinate activated complex.[2,3] For $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, molecular models indicate that the phenyl groups effectively block the iron octahedral face defined by the bridging ligands and the apical carbonyl. Accordingly, the kinetic observations reported here can be given a simple interpretation: the bimolecular mechanism observed for other substrates is not observed for $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ because steric destabilization of the seven-coordinate activated complex increases the activation energy of this process to a value greater than that necessary for carbonyl dissociation.

This interpretation is supported by a recent study[20] of the second step in the reaction of triphenylphosphine with $(OC)_3Fe(\mu\text{-}SC_6H_5)_2Fe(CO)_3$. In this complex, both of the carbonyl ligands trans to the iron–iron bond can be displaced by triphenylphosphine. Whereas displacement of the first carbonyl to give $(OC)_3Fe(\mu\text{-}SC_6H_5)_2Fe(CO)_2P(C_6H_5)_3$ follows a second-order rate law and an SN2 mechanism,[2,20] Basato has shown that displacement of the second carbonyl to give $[Fe(\mu\text{-}SC_6H_5)(CO)_2P(C_6H_5)_3]_2$ follows a first-order rate law and an SN1 mechanism. This change of mechanism is attributed to steric inhibition of the second substitution step by the triphenylphosphine ligand.[20] The activation parameters for carbon monoxide dissociation from this substituted, organosulfur-bridged complex and from $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$ are very similar (see Table II).

Registry No. $Fe_2(CO)_6(\mu\text{-}P(C_6H_5)_2)_2$, 19599-68-9; $P(C_6H_5)_3$, 603-35-0; $P(OC_6H_5)_3$, 101-02-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(C_6H_5)_3$, 58409-41-9; $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(OC_6H_5)_3$, 58409-42-0; $Fe_2(CO)_5(\mu\text{-}P(C_6H_5)_2)_2P(n\text{-}C_4H_9)_3$, 58409-43-1; $Fe_2(CO)_4(\mu\text{-}P(C_6H_5)_2)_2(P(n\text{-}C_4H_9)_3)_2$, 58409-44-2.

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Contribution No. 2258 from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Ligand Dissociation and Intramolecular Rearrangement in ML_5 Complexes. Evidence for Closely Related Transition States

A. D. English,* P. Meakin,* and J. P. Jesson*

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There have been many studies of substitution reactions in planar d^8 transition metal complexes.[1-3] However, information about the nature of the transition states and the role of possible intramolecular processes has been difficult to obtain. We have