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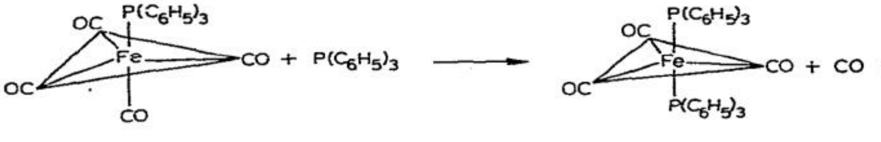
Substitution reactions of trigonal bipyramidal complexes of iron pentacarbonyl

Kinetic investigations of substitution reactions have been carried out on a large variety of octahedral, square planar, and tetrahedral coordination compounds[1]. From these studies it is obvious that the geometry of the metal complex plays a major role in determining the mechanism by which substitution occurs. It was the purpose of the present study to examine the substitution reactions of the trigonal bipyramidal complexes of iron pentacarbonyl[2]. This geometry is of particular interest since in the substitution reactions of many octahedral complexes by S_N1 mechanisms, a trigonal bipyramidal intermediate is frequently postulated to undergo nucleophilic attack by a ligand to form the six-coordinated product[3]. One might therefore suspect that stable complexes of trigonal bipyramidal symmetry would also be likely to undergo substitution by an S_N2 mechanism.

Iron pentacarbonyl has been known for many years to undergo substitution by a wide variety of ligands, L, to form $Fe(CO)_4L$, also of trigonal bipyramidal symmetry[4]. Hieber and Pigenot[5] noted that $Fe(CO)_5$ and aryl isocyanides react in toluene at 60° to form the mono-substituted product. In attempting to determine the kinetics of this reaction we have found that the reaction proceeds at a measurable rate at 60° because of the presence of impurities in the $Fe(CO)_5$. Repeated distillation of the $Fe(CO)_5$ under a nitrogen atmosphere yields purer $Fe(CO)_5$ which, however, reacts very slowly even at 90°. Because $Fe(CO)_5$ undergoes rapid decomposition under these conditions, it was not possible to study the simple rate of carbon monoxide replacement in this system.

Since in the reaction of $Fe(CO)_5$ with phosphines both the mono- and disubstituted products were obtained[4,6], it was assumed that $Fe(CO)_4L$ reacts with more L to form $Fe(CO)_3L_2$. Because of the ease of preparation of $Fe(CO)_4P(C_6H_5)_3$, its reaction with $P(C_6H_5)_3$ to form $Fe(CO)_3[P(C_6H_5)_3]_2$ was studied. The geometries[4] of the complexes are shown in the following equation:



(1)

Experimental

Preparation and purification of materials. $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3$-$[P(C_6H_5)_3]_2$ were prepared by irradiating a cyclohexane solution of $Fe(CO)_5$ (a gift of Antara Chemicals, Inc.) and $P(C_6H_5)_3$ with an ultraviolet lamp[7]. Both were identified from their infrared spectra. $Fe(CO)_4P(C_6H_5)_3$ was sublimed at 185° in vacuum before use in the kinetic studies. The solvent, decalin, was purified by refluxing over sodium and then distilling under an atmosphere of nitrogen.

Determination of rates. The rate of reaction (1) was determined by following the disappearance of the 2045 cm^{-1} C–O stretching absorption of $Fe(CO)_4P(C_6H_5)_3$ as it reacted to form $Fe(CO)_3[P(C_6H_5)_3]_2$ which exhibits only one strong absorption at 1887 cm^{-1}. The reaction was conducted in a tube fitted with a side arm for the introduction of nitrogen gas. Since the reaction proceeded from 10 to 30% faster in the presence of laboratory light, the reaction vessel was always carefully wrapped with aluminum foil. An oil bath was used to maintain the temperature within 0.1°. Prior to a run a decalin solution of $Fe(CO)_4P(C_6H_5)_3$ (1.3×10^{-3} M) was thermostatted at the desired temperature for about 15 min after which $P(C_6H_5)_3$ was added and the solution shaken well. Samples were withdrawn periodically and examined in a Beckman IR-8 infrared spectrophotometer at 2045 cm^{-1}. The slopes of first order plots of $\ln(A-A_\infty)$ *versus* time which were linear to at least 75% completion of the reaction gave first order rate constants, k. In the absence of $P(C_6H_5)_3$, $Fe(CO)_4P(C_6H_5)_3$ decomposed under the kinetic conditions at a rate which was less than 3% of its rate of reaction with $P(C_6H_5)_3$. The enthalpy and entropy of activation were calculated with a least-squares computer program[8] which also determined standard deviations for these quantities.

Results and discussion

$Fe(CO)_4P(C_6H_5)_3$ has been observed to react with $P(C_6H_5)_3$ to yield only $Fe(CO)_3[P(C_6H_5)_3]_2$ as shown in equation (1). The results of the kinetic studies are collected in Table 1 and indicate that within experimental error reaction (1) obeys the following first order rate law:

TABLE 1

RATES[a] OF THE REACTION

$Fe(CO)_4[P(C_6H_5)_3] + P(C_6H_5)_3 \rightarrow Fe(CO)_3[P(C_6H_5)_3]_2 + CO$

IN DECALIN SOLVENT

$[P(C_6H_5)_3]$, *(moles/l)*	*Temp.* (°C)	10^5 k, (sec^{-1})
0.211	159.6	3.08
0.483	170.1	10.7
0.483	174.3	15.6
0.0121	179.0	25.6
0.0407	179.0	26.1
0.967	179.0	28.6

[a] $\Delta H^* = 42.5 \pm 1.2$ kcal/mole and $\Delta S^* = +18.4 \pm 2.8$ e.u. Limits of error are one standard deviation.

$$\text{Rate} = k[Fe(CO)_4P(C_6H_5)_3]$$

The dependence of the rate only on the $Fe(CO)_4P(C_6H_5)_3$ concentration suggests an S_N1 dissociative mechanism:

$$Fe(CO)_4P(C_6H_5)_3 \xrightarrow[\text{slow}]{-CO} Fe(CO)_3P(C_6H_5)_3 \xrightarrow[\text{fast}]{P(C_6H_5)_3} Fe(CO)_3[P(C_6H_5)_3]_2$$

Although the rate determining step is the dissociation of a CO group from $Fe(CO)_4$-$P(C_6H_5)_3$, it is not known whether an equatorial or the axial CO group is actually involved in the dissociation. The high positive entropy of activation (Table 1) also offers strong support for a dissociative mechanism. The very high enthalpy of activation reflects the well-known inertness of this compound. It should be noted, however, that despite the very high free energy of activation of the S_N1 path, the reaction does not provide an S_N2 mechanism of any lower energy. The high electron density present in the metal orbitals which in this d^8 system are directed between the ligands apparently acts as a strong deterrent to nucleophilic attack*.

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* F. Basolo and H. Wawersik find that another 5-coordinated complex, $Mn(NO)(CO)_4$, reacts with $P(C_6H_5)_3$ by an S_N2 mechanism. (Private communication)