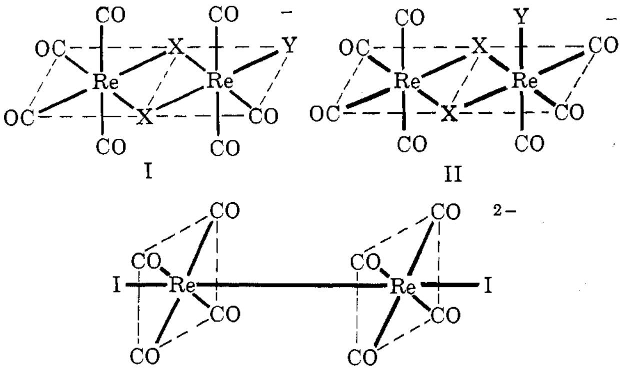

Figure 1.

have C_s symmetry, and in each case seven ($5A' + 2A''$) infrared-active stretching modes are expected. The low solubility of these salts, however, prevents the measurement of satisfactory solution spectra, and only four clear maxima could be distinguished in dilute solutions in chloroform.

The reaction of iodide ions with decacarbonyldirhenium produced a compound with a remarkably simple spectrum containing two bands in the C–O stretching region (Table I). This compound presumably contains the ion $Re_2(CO)_8I_2^{2-}$, with structure III, and is completely analogous to the product of the reaction of decacarbonyldimanganese.[2] Yields of this material were exceedingly small, and only moderately satisfactory analyses could be obtained. The ion does not appear to be stable in most solvents, and, on standing, many extra bands appear in the infrared spectra, presumably owing to decomposition or isomerization.

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Chelate and Bridge Complexes of Metal Carbonyl Compounds with a Ditertiary Phosphine: A Study of Their Formation and Interconversion

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The reactions of the compounds $Co(NO)(CO)_3$ and $Fe(NO_2)(CO)_2$ with a severalfold excess of the diphosphine 1,2-bis(diphenylphosphino)ethane (diphos, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) are shown to yield, in toluene or tetrahydrofuran solution, fairly long-lived intermediates $Co(NO)(CO)_2$(diphos) and $Fe(NO)_2(CO)$(diphos) in which the diphosphine is only attached to the metal by one phosphorus atom. These intermediates are slowly converted to the chelate complexes $Co(NO)(CO)$(diphos) and $Fe(NO)_2$(diphos) at rates which are *independent* of the free diphosphine concentration. Similar results have been obtained for $CH_3Mn(CO)_5$ which is converted, *via* an intermediate believed to be $CH_3COMn(CO)_4$(diphos), to the chelate complex $CH_3COMn(CO)_3$(diphos). Use of metal:diphosphine molar ratios of 2:1 yields complexes of the type $[Co(NO)(CO)_2]_2$(diphos), in which the diphosphine acts as a bridge between two metal atoms. These complexes can also be converted to the corresponding chelate complexes by reaction with excess diphosphine, but at a rate which is *dependent* on the free diphosphine concentration. The unsymmetrical bridge complex, $Fe(NO)_2(CO)$(diphos)$Co(NO)(CO)_2$, has been isolated and characterized.

Introduction

The diphosphine, 1,2-bis(diphenylphosphino)ethane (diphos, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), has been found[1,2] to form a wide variety of complexes with transition metals in which one or more molecules of the diphosphine are attached to the metal by both phosphorus atoms (*i.e.*, chelate complexes).

In the formation of metal complexes with polydentate chelating ligands it is usually impossible to observe the presence of intermediates in which one or more donor atoms are not attached to the metal. It would appear that the rate-determining step for these reactions is the attack on the metal atom by the first donor atom and that subsequent attack by the remaining donor atom or atoms is too fast to allow the observation of an intermediate.

While studying the reactions of various metal carbonyl compounds with uni- and bidentate nucleophiles, it was observed that the reactions of some of these compounds with the diphosphine mentioned above did not follow the pattern of a single rate-determining step followed by a fast second step. This prompted further investigations of these reactions, which are described in this paper.

During the course of this work several new complexes of the diphosphine were prepared, in some of which the diphosphine was chelated to a single metal atom (chelate complexes), while in others the diphosphine acted as a bridge between two metal atoms (bridge complexes). It was even possible to prepare a hetero-metal bridge compound.

Experimental Section

Preparation of Starting Materials.—The diphosphine, 1,2-bis(diphenylphosphino)ethane, was prepared by the method described by Chatt and Hart.[1] The preparation of $CH_3Mn(CO)_5$ from $Mn_2(CO)_{10}$ (a gift from the Ethyl Corporation) was carried

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(1) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).
(2) A. G. Osborne and M. H. B. Stiddard, *ibid.*, 4715 (1962).

out as described in the literature,[3] except that the reaction of $NaMn(CO)_5$ with dimethyl sulfate was carried out at −70°, which improved the yield. The compounds $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ were prepared by methods described in the literature.[4,5]

Preparation of Complexes.—All complexes were prepared under an atmosphere of nitrogen. Yields of the complexes described in sections (a) and (b) ranged from 70 to 90%. In section (c) the yields of pure products after chromatographic separation were 10 to 20%.

(a) **Symmetrical Bridge Complexes. $[Co(NO)(CO)_2]_2$(diphos).**—The diphosphine (0.40 g., 1 mmole) was allowed to react with $Co(NO)(CO)_3$ (0.69 g., 4 mmoles) in toluene (5 ml.) at 25° for several hours. The solvent and excess $Co(NO)(CO)_3$ were removed under reduced pressure. The residue was chromatographed on silica, using dichloromethane–hexane mixtures as eluents, and recrystallized from dichloromethane–hexane. Orange crystals were obtained, m.p. 146°. *Anal.* Calcd. for $[Co[NO][CO)_2P(C_6H_5)_2CH_2]_2$: C, 52.35; H, 3.52; N, 4.07; mol. wt., 688. Found: C, 52.61; H, 3.73; N, 4.37; mol. wt., 656.

$[Fe(NO)_2(CO)]_2$(diphos).—The diphosphine (0.39 g., 1 mmole) was allowed to react with $Fe(NO)_2(CO)_2$ (0.43 g., 2.5 mmoles) in tetrahydrofuran (5 ml.) for 30 min. at 25°. The product was isolated and purified in the same way as the cobalt complex. Deep red crystals were obtained, m.p. 140°. *Anal.* Calcd. for $[Fe(NO)_2(CO)P(C_6H_5)_2CH_2]_2$: C, 49.00; H, 3.52; N, 8.17; mol. wt., 686. Found: C, 48.66; H, 3.54; N, 8.30; mol. wt., 666.

$[CH_3COMn(CO)_4]_2$(diphos).—The diphosphine (0.4 g., 1 mmole) and $CH_3Mn(CO)_5$ (0.525 g., 2.5 mmoles) in ether (50 ml.) were allowed to react at 25° for 2 hr., the phosphine dissolving slowly in the ether as the reaction proceeded. The product was isolated and purified in the same way as the cobalt complex, except that dichloromethane–ether mixtures were used as eluents in the chromatographic purification. Yellow crystals were obtained, m.p. 152°. *Anal.* Calcd. for $[CH_3COMn(CO)_4P(C_6H_5)_2CH_2]_2$: C, 55.75; H, 3.69; mol. wt., 818. Found: C, 55.90; H, 3.71; mol. wt., 780.

$[Ni(CO)_3]_2$(diphos).—This was obtained in the form of colorless crystals as one product of the reaction of $CH_3Mn(CO)_5$, $Ni(CO)_4$, and the diphosphine (see section (c) on unsymmetrical bridge complexes). *Anal.* Calcd. for $[Ni(CO)_3P(C_6H_5)_2CH_2]_2$: C, 56.18; H, 3.54; mol. wt., 684. Found: C, 55.80; H, 3.62; mol. wt., 656.

(b) **Chelate Complexes. Co(NO)(CO)(diphos). Method I.**—The diphosphine (1.0 g., 2.5 mmoles) was allowed to react with $Co(NO)(CO)_3$ (0.35 g., 2 mmoles) in toluene (20 ml.) under nitrogen for 1 day at room temperature, then for 3 days at 70°. (Warming at the start of the reaction caused some decomposition of the $Co(NO)(CO)_3$.) The product was isolated and purified in the same way as the cobalt bridge complex, giving orange crystals, m.p. 166°. *Anal.* Calcd. for $Co(NO)(CO)[P(C_6H_5)_2CH_2]_2$: C, 62.92; H, 4.69; N, 2.72; mol. wt., 515. Found: C, 62.52; H, 4.75; N, 2.79; mol. wt., 499.

Method II.—The diphosphine (0.4 g., 1 mmole) and $[Co(NO)(CO)_2]_2$(diphos) (0.69 g., 1 mmole) were refluxed in toluene for 1 hr. The purification procedure was that used in method I. The resulting orange crystals melted at 166°; mixture melting point with the sample from method I, 166°; mol. wt., 516.

$Fe(NO)_2$(diphos).—This complex had previously been prepared from $Fe(NO)_2(CO)_2$ and the diphosphine by McBride, *et al.*[6]

We were also able to prepare this compound from the bridge complex, $[Fe(NO)_2(CO)]_2$(diphos) (0.34 g., 0.5 mmole), and the diphosphine (0.20 g., 0.5 mmole) by warming in tetrahydrofuran (10 ml.) at 40° for 3 days. The product was isolated and purified in the same way as the bridge complex, except that alumina was used in place of silica. The red-brown crystals obtained melted at 169°, in contrast to the figure given by McBride[6] (147–150°). However, analysis, molecular weight determination, and infrared spectrum leave no doubt as to the identity of the compound. *Anal.* Calcd. for $Fe(NO)_2[P(C_6H_5)_2CH_2]_2$: C, 60.71; H, 4.70; N, 5.44; mol. wt., 514. Found: C, 60.10; H, 4.98; N, 5.20; mol. wt., 521.

$CH_3COMn(CO)_3$(diphos).—The diphosphine (0.6 g., 1.5 mmoles) and $CH_3Mn(CO)_5$ (0.21 g., 1 mmole) were allowed to react in tetrahydrofuran (10 ml.) under nitrogen. After 4 days at 25° solvent was removed and the product purified in the same way as the manganese bridge complex. Yellow needles were obtained, m.p. 162°. *Anal.* Calcd. for $CH_3COMn(CO)_3[P(C_6H_5)_2CH_2]_2$: C, 64.13; H, 4.67; P, 10.68; mol. wt., 580. Found: C, 64.31; H, 4.95; P, 10.47; mol. wt., 572.

$C_6H_5CH_2Mn(CO)_3$(diphos).—A solution of $C_6H_5CH_2MgCl$ was prepared from Mg (0.24 g., 10 mmoles) and $C_6H_5CH_2Cl$ (1.27 g., 10 mmoles) in ether (25 ml.). An approximate 10-fold excess (6.5 mmoles) of the Grignard solution was added dropwise to $Mn(CO)_3$(diphos)Br[2] (0.4 g., 0.65 mmole) in ether (25 ml.). When the addition was complete, the mixture was boiled for 1 hr., during which time a light yellow solid was formed. This was transferred to a filter and purified in the same way as the cobalt complexes. Pale yellow needles, decomposing at 185–187°, were obtained. *Anal.* Calcd. for $C_6H_5CH_2Mn(CO)_3[P(C_6H_5)_2CH_2]_2$: C, 68.79; H, 4.97; P, 9.86. Found: C, 68.15; H, 5.01; P, 9.73.

(c) **Unsymmetrical Bridge Complexes. $Co(NO)(CO)_2$(diphos)$Fe(NO)_2(CO)$.**—A mixture of $Co(NO)(CO)_3$ (0.26 g., 1.5 mmoles) in toluene (2.5 ml.) and $Fe(NO)_2(CO)_2$ (0.26 g., 1.5 mmoles) in toluene (5 ml.) was treated with a solution of the diphosphine (0.5 g., 1.25 mmoles) in toluene (10 ml.). The mixture was allowed to stand at 25° for 2.5 hr., and the solvent then was removed under reduced pressure. By chromatography on a 7-ft. column of silica, using as eluent a 3:1 mixture of hexane and dichloroethane, the mixture was almost completely separated into three components. Further purification of the second component by recrystallization from a dichloromethane–hexane mixture gave the desired unsymmetrical bridge complex as red needles, m.p. 144°. *Anal.* Calcd. for $Co(NO)(CO)_2P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2Fe(NO)_2(CO)$: C, 50.68; H, 3.52; N, 6.12. Found: C, 50.80; H, 3.60; N, 6.27. (The first and third components were the symmetrical cobalt and iron bridge complexes, respectively.)

Attempt to Prepare $CH_3COMn(CO)_4$(diphos)$Ni(CO)_3$.—The diphosphine (0.8 g., 2 mmoles) and $CH_3Mn(CO)_5$ (0.42 g., 2 mmoles) were allowed to react in tetrahydrofuran until no $CH_3Mn(CO)_5$ remained. The solution was then added to excess $Ni(CO)_4$ and allowed to stand for a few minutes, after which the solvent and excess $Ni(CO)_4$ were removed under reduced pressure. Chromatography of the residue on silica using mixtures of hexane, dichloromethane, and ether yielded (i) the symmetrical bridge complex $[Ni(CO)_3]_2$(diphos) (see section (a) on symmetrical bridge complexes) and (ii) the symmetrical bridge complex $[CH_3COMn(CO)_4]_2$(diphos), shown by infrared spectrum and mixture melting point to be identical with that prepared from $CH_3Mn(CO)_5$ and the diphosphine.

Analyses.—These were performed by Microtech Laboratories, Skokie, Ill.

Molecular Weight Determinations.—These were carried out by Miss H. Beck of this department. They were performed in approximately 5 × 10^{-2} *M* benzene solutions, using a Mechrolab Inc. Model 302 osmometer.

Kinetic Data.—Reactions were carried out in foil-wrapped, nitrogen-filled flasks kept in constant-temperature baths. Aliquots were withdrawn from the flasks through a serum cap, transferred to 0.2-mm. KBr cells, and their infrared spectra measured against that of a reference solution containing no metal complex. Measurements were performed on a Perkin-Elmer 337 spectrophotometer. In most cases, rates were determined from the disappearance of the highest energy carbonyl band of the start-

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[3] T. H. Coffield, R. D. Closson, and J. Kozikowski, *J. Org. Chem.*, **22**, 598 (1957).

[4] F. Seel, *Z. anorg. allgem. Chem.*, **269**, 40 (1952).

[5] W. Hieber and H. Beutner, *ibid.*, **320**, 101 (1963).

[6] D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962).

TABLE I

C–O AND N–O STRETCHING FREQUENCIES FOR COMPLEXES OF THE DIPHOSPHINE AND RELATED TRIPHENYLPHOSPHINE COMPLEXES

Complex	Solvent	νC–O, cm.$^{-1}$	νN–O, cm.$^{-1}$	Ref.
$[Co(NO)(CO)_2]_2$(diphos)	Benzene	2037, 1979	1759	*a*
$Co(NO)(CO)_2P(C_6H_5)_3$	Cyclohexane	2035, 1981	1761	7
Co(NO)(CO)(diphos)	Benzene	1965	1712	*a*
$Co(NO)(CO)[P(C_6H_5)_3]_2$	Cyclohexane	1957	1717	7
$[Fe(NO)_2(CO)]_2$(diphos)	Dichloromethane	2013	1760, 1713	*a*
$Fe(NO)_2(CO)P(C_6H_5)_3$	Tetrachloroethylene	2009	1764, 1722	6
$Fe(NO)_2$(diphos)	Tetrachloroethylene	. . .	1726, 1679	6
$[CH_3COMn(CO)_4]_2$(diphos)	Dichloromethane	2075, 2000, 1965, 1612^c	. . .	*a*
trans-$CH_3COMn(CO)_4P(C_6H_5)_3$	Hexane	2066, 1995, 1959, 1631^c	. . .	8
$CH_3COMn(CO)_3$(diphos)	Dichloromethane	1996, 1914, 1600	. . .	*a*
$[Ni(CO)_3]_2$(diphos)	Dichloromethane	2070, 1990	. . .	*a*
$Ni(CO)_3P(C_6H_5)_3$	Cyclohexane	2070, 2000	. . .	*b*
$Fe(NO)_2(CO)$(diphos)$Co(NO)(CO)_2$	Dichloromethane	2040, 2013, 1979	1761, 1716	*a*

[a] This work. [b] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959). [c] Acetyl C–O stretching frequency.

ing material. Metal complex concentrations used were *ca.* 5×10^{-3} *M*, as compared with diphosphine concentrations ranging from 5×10^{-2} to 5×10^{-1} *M*.

Results

(A) Cobalt.—The reaction of cobalt nitrosyl tricarbonyl, $Co(NO)(CO)_3$, with an excess of diphosphine in toluene at 25° was followed by observing the changes in the infrared spectrum of the solution. The bands due to C–O and N–O stretching frequencies of the starting material were replaced by bands at 2038 and 1982 cm.$^{-1}$ in the C–O stretching region and at 1762 cm.$^{-1}$ in the N–O stretching region. This initial reaction was followed by a second, much slower, reaction, which could conveniently be studied by raising the temperature to 40°. The final product, which exhibited one band in the C–O stretching region at 1965 cm.$^{-1}$ and one in the N–O region at 1712 cm.$^{-1}$, was found (by repeating the reaction on a preparative scale and isolating and characterizing the product) to be the chelate complex, Co(NO)(CO)(diphos). The infrared spectrum of this complex is closely related, as expected, to that of $Co(NO)(CO)[P(C_6H_5)_3]_2$[7] (see Table I).

There appeared to be three possible structures for the intermediate formed during this reaction: (a) a five-coordinate chelate complex $Co(NO)(CO)_2$(diphos); (b) a bridge complex, $[Co(NO)(CO)_2]_2$(diphos), in which the diphosphine bridges two cobalt atoms; (c) a monodentate diphosphine complex that is a compound $Co(NO)(CO)_2$(diphos) in which the diphosphine is acting as a monodentate ligand, with one phosphorus atom not coordinated to the metal.

Possibility (a) appeared to be ruled out by the extreme similarity, in position and in relative intensity, of the bands due to C–O and N–O stretching vibrations for the intermediate and for the four-coordinate complex $Co(NO)(CO)_2P(C_6H_5)_3$[7] (see Table I). Such a close similarity would hardly be expected for two compounds with different coordination numbers and symmetries, but *would* be expected if the intermediate were of type (b) or (c). In order to decide between these two alternatives it was necessary to isolate and study the bridge compound, $[Co(NO)(CO)_2]_2$(diphos). This was obtained from the reaction of $Co(NO)(CO)_3$ with the diphosphine in toluene at 25°, using a molar ratio of rather more than 2:1. As anticipated, the positions and relative intensities of the bands due to C–O (2037, 1979 cm.$^{-1}$) and N–O (1759 cm.$^{-1}$) stretching vibrations in the infrared spectrum of the complex in benzene solution were extremely similar to those for the intermediate and for $Co(NO)(CO)_2P(C_6H_5)_3$.

TABLE II

RATE CONSTANTS FOR THE REACTIONS OF COBALT COMPOUNDS WITH THE DIPHOSPHINE

Solvent	Diphosphine concn., *M*	Obsd. rate const., sec.$^{-1}$	Order in diphosphine	Rate constant
(a) $Co(NO)(CO)_3 \xrightarrow{25°}$ intermediate (monodentate complex)				
Toluene	0.042	2.4×10^{-4}	First	5.7×10^{-3} M^{-1} sec.$^{-1}$
	0.084	4.8×10^{-4}		
	0.097	5.7×10^{-4}		
	0.124	7.1×10^{-4}		
Tetrahydrofuran	0.071	5.4×10^{-4}	First	7.8×10^{-3} M^{-1} sec.$^{-1}$
	0.111	8.7×10^{-4}		
	0.143	1.1×10^{-3}		
(b) intermediate (monodentate complex) $\xrightarrow{40°}$ chelate complex				
Toluene	0.084	2.9×10^{-4}	Zero	2.9×10^{-4} sec.$^{-1}$
	0.124	2.9×10^{-4}		
	0.169	2.8×10^{-4}		
Tetrahydrofuran	0.071	3.5×10^{-4}	Zero	3.6×10^{-4} sec.$^{-1}$
	0.111	3.7×10^{-4}		
	0.143	3.6×10^{-4}		
(c) bridge complex $\xrightarrow{40°}$ chelate complex				
Toluene	0.053	6.4×10^{-6}	First	1.2×10^{-4} *M*$^{-1}$ sec.$^{-1}$
	0.108	1.3×10^{-5}		
	0.142	1.7×10^{-5}		
Tetrahydrofuran	0.065	4.9×10^{-6}	First	7.6×10^{-5} *M*$^{-1}$ sec.$^{-1}$
	0.101	7.6×10^{-6}		
	0.225	1.7×10^{-5}		

A study was then made of the rates and diphosphine dependence of the various reactions involved. Diphosphine concentrations were kept at least ten times greater than the concentrations of the metal complexes, to ensure pseudo-first-order conditions. The bridge complex $[Co(NO)(CO)_2]_2$(diphos) was found to react with the diphosphine at 40° in tetrahydrofuran or toluene to form the chelate complex Co(NO)(CO)(diphos) at a rate which was linearly dependent on the free diphosphine concentration, the reaction being first order

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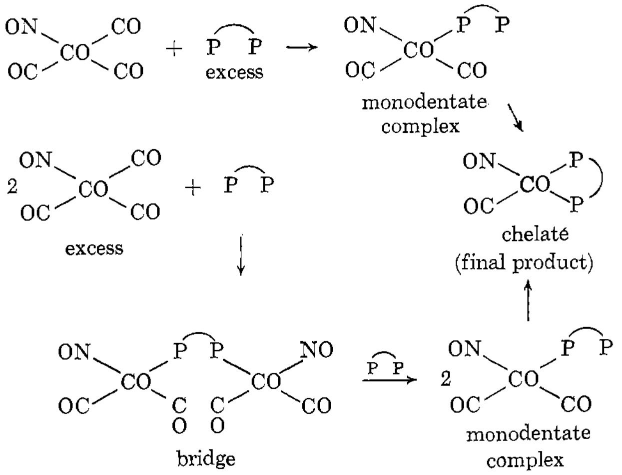
(7) W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

with respect to both bridge complex and diphosphine. By contrast, under the same conditions of solvent and temperature, the intermediate formed in the reaction of $Co(NO)(CO)_3$ with excess diphosphine was converted to Co(NO)(CO)(diphos) at a rate which was *independent* of the free diphosphine concentration, the reaction being first order with respect to the intermediate and zero order with respect to diphosphine. The rate constants for these reactions and for the formation of the intermediate from $Co(NO)(CO)_3$ are listed in Table II.

It is therefore clear that the intermediate formed in the reaction of $Co(NO)(CO)_3$ with excess diphosphine is not a bridge complex, but a monodentate diphosphine complex which can form the chelate complex Co(NO)(CO)(diphos) by an intramolecular process which does not involve a molecule of free diphosphine. A suggested mechanism for the various interconversions is shown below.



Here the rate-determining step in the reaction of the bridge complex to form the chelate is envisaged as being the attack by a molecule of diphosphine on one of the two cobalt atoms of the bridge complex, resulting in the breaking of the bridge and the formation of two molecules of the monodentate diphosphine complex. Over the range of diphosphine concentrations which can conveniently be used, this step is considerably slower than the subsequent chelation of the monodentate complex and hence is completely rate determining.

(B) **Iron.**—Iron dinitrosyl dicarbonyl, $Fe(NO)_2(CO)_2$, reacted with excess diphosphine in toluene at 25° to form a species whose infrared spectrum showed one band at 2012 cm.$^{-1}$ due to a C–O stretching vibration and two, at 1759 and 1716 cm.$^{-1}$, due to N–O stretching vibrations. This intermediate was then converted, very slowly at 25° but more rapidly at 40°, to the previously described[6] chelate compound $Fe(NO)_2$(diphos). Similar results were obtained when tetrahydrofuran was used as the solvent. The similarity of the spectrum of the intermediate to that of $Fe(NO)_2(CO)P(C_6H_5)_3$[6] (see Table I) suggested that it was either a bridge complex, $[Fe(NO)_2(CO)]_2$(diphos), or a monodentate diphosphine complex, $Fe(NO)_2(CO)$(diphos), with one phosphorus atom not attached to the metal.

Table III

Rate Constants for the Reactions of Iron Compounds with the Diphosphine

Solvent	Diphosphine concn., M	Obsd. rate const., sec.$^{-1}$	Order in diphosphine	Rate constant
(a) $Fe(NO)_2(CO)_2 \xrightarrow{25°}$ intermediate (monodentate complex)				
Toluene	0.064	3.6×10^{-4}	First	5.1×10^{-3} M^{-1} sec.$^{-1}$
	0.086	4.4×10^{-4}		
	0.127	6.4×10^{-4}		
Tetrahydrofuran	0.066	1.7×10^{-3}	Nonzero[a]	...
	0.198	2.9×10^{-3}		
	0.296	3.9×10^{-3}		
(b) intermediate (monodentate complex) $\xrightarrow{40°}$ chelate complex				
Toluene	0.064	5.8×10^{-5}	Zero	5.8×10^{-5} sec.$^{-1}$
	0.086	5.8×10^{-5}		
	0.127	5.9×10^{-5}		
Tetrahydrofuran	0.064	6.8×10^{-5}	Zero	6.8×10^{-5} sec.$^{-1}$
	0.132	6.7×10^{-5}		
	0.198	6.9×10^{-5}		
(c) bridge complex $\xrightarrow{40°}$ chelate complex				
Toluene	0.065	9.3×10^{-7}	First	1.5×10^{-5} M^{-1} sec.$^{-1}$
	0.098	1.5×10^{-6}		
	0.150	2.4×10^{-6}		
Tetrahydrofuran	0.066	3.1×10^{-6}	Nonzero[a]	...
	0.098	3.6×10^{-6}		
	0.203	4.3×10^{-6}		
	0.505	5.5×10^{-6}		

[a] The kinetics of these reactions are more complicated, probably owing to solvent participation in the reaction. It is hoped to discuss these reactions more fully in a later publication.

It was found that the bridge complex could be isolated from the reaction of $Fe(NO)_2(CO)_2$ with the diphosphine, in a molar ratio of rather more than 2:1, at 25° in tetrahydrofuran. The infrared spectrum of the bridge complex in dichloromethane showed a band at 2014 cm.$^{-1}$ (C–O stretching vibration) and bands at 1760 and 1713 cm.$^{-1}$ (N–O stretching vibrations). As in the cobalt case, there was a strong resemblance between this spectrum and those of the intermediate and of $Fe(NO)_2(CO)P(C_6H_5)_3$.

Kinetic studies of the reaction between the diphosphine and $Fe(NO)_2(CO)_2$ using (as in the case of $Co(NO)(CO)_3$) a molar ratio of 10:1 or greater to ensure pseudo-first-order conditions showed that the rate of conversion of the intermediate to the chelate compound, $Fe(NO)_2$(diphos), at 40° was independent of the free diphosphine concentration in both toluene and tetrahydrofuran. By contrast the bridge complex, $[Fe(NO)_2(CO)_2]$(diphos), reacted with the diphosphine to form the chelate compound at a rate which *was* dependent on diphosphine concentration. These results, which are listed in Table III, showed that under the conditions used the bridge complex could not be the intermediate formed in the reaction of $Fe(NO)_2(CO)_2$ with the diphosphine. As in the cobalt case, the intermediate appears to be a monodentate diphosphine complex.

Experiments were also carried out in an attempt to isolate this intermediate. By allowing $Fe(NO)_2(CO)_2$ to react with excess diphosphine in tetrahydrofuran at 25° until no $Fe(NO)_2(CO)_2$ remained, and then removing the solvent, the crude product could be chromatographed on silica, using mixtures of dichloromethane and hexane as eluents. When diphosphine: $Fe(NO)_2(CO)_2$ molar ratios of greater than about 2:1 were used, only two products were isolated. One was excess diphosphine, and the other was a red-brown oil whose infrared spectrum in dichloromethane solution matched that of the intermediate, but which could not be persuaded to crystallize. It seemed very probable that this oil was the monodentate diphosphine complex $Fe(NO)_2(CO)$(diphos). At molar ratios lower than 2:1 increasing amounts of the bridge complex $[Fe(NO)_2(CO)]_2$(diphos) were isolated as well as the monodentate complex and free diphosphine. This was presumably the result of a competition for $Fe(NO)_2(CO)_2$ between the unattached phosphorus atom on the monodentate complex and free diphosphine. At high diphosphine: $Fe(NO)_2(CO)_2$ molar ratios this competition was evidently negligible, but at a 1:1 ratio it led to the formation of a considerable proportion of bridge complex.

(C) **Manganese.**—On allowing methyl manganese pentacarbonyl, $CH_3Mn(CO)_5$, to react with excess diphosphine in tetrahydrofuran at 25°, the bands in the infrared spectrum of the solution due to $CH_3Mn(CO)_5$ were replaced by bands at 2065, 1990, and 1955 cm.$^{-1}$ in the terminal C–O stretching region and at 1620 cm.$^{-1}$ in the acetyl C–O stretching region. The positions and relative intensities of these bands were very similar to those for *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$[8] (see Table I), and, by analogy with the results obtained with $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$, we assume this compound to be the monodentate diphosphine complex *trans*-$CH_3COMn(CO)_4$(diphos), with one phosphorus atom not attached to the metal.

Over a period of 4 days at 25°, this intermediate was converted to the chelate compound, $CH_3COMn(CO)_3$(diphos), which was isolated and fully characterized. The infrared spectrum of the chelate compound in dichloromethane solution showed bands due to terminal C–O stretching frequencies at 1996 and 1914 cm.$^{-1}$ and an acetyl C–O stretching frequency at 1600 cm.$^{-1}$. The appearance of only two terminal C–O stretching frequencies is in marked contrast to the spectra of the complexes[2] $Mn(CO)_3$(diphos)X, where X is halogen, and the new complex $C_6H_5CH_2Mn(CO)_3$(diphos), whose preparation is described in the Experimental Section of this paper, all of which exhibit three terminal C–O stretching frequencies of roughly equal intensity. This latter arrangement appears to be typical of compounds containing the two donor atoms (both phosphorus in these cases) *cis* to the halogen or alkyl group.[9] It therefore seems plausible that in the compound $CH_3COMn(CO)_3$(diphos) the appearance of only two bands in the terminal C–O stretching region signifies that one phosphorus atom is *cis* to the acetyl group and the other *trans*.

As in the cases of $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$, the reaction of $CH_3Mn(CO)_5$ with the diphosphine in tetrahydrofuran at 25°, using a molar ratio of about 2.5:1, led to the formation of a bridge complex, $[CH_3COMn(CO)_4]_2$(diphos). The infrared spectrum of this complex in dichloromethane solution (terminal C–O stretching bands at 2075, 2000, and 1965 cm.$^{-1}$, acetyl C–O stretching band at 1612 cm.$^{-1}$) is so closely related to that of *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$[8] that we assume it to have the structure *trans,trans*-$[CH_3COMn(CO)_4]_2$(diphos).

The results obtained with $CH_3Mn(CO)_5$ led us to investigate the reaction of manganese pentacarbonyl bromide, $Mn(CO)_5Br$, with excess diphosphine in toluene at 25°. Although the infrared spectrum of the solution showed signs of the presence of an intermediate with a spectrum similar to that of $Mn(CO)_4P(C_6H_5)_3Br$, the conversion of this intermediate to the final chelated product $Mn(CO)_3$(diphos)Br took place at a rate comparable to its rate of formation from $Mn(CO)_5Br$, thus allowing no clear-cut division of the reaction into steps which could be studied separately.

(D) **Nickel.**—The bridge complex, $[Ni(CO)_3]_2$(diphos), was isolated as a product of the reaction between $CH_3Mn(CO)_5$, the diphosphine, and $Ni(CO)_4$ (see section (E) for further details).

(E) **Unsymmetrical Bridge Complexes.**—In an attempt to prepare a complex in which the diphosphine bridged two different metal atoms, equimolar amounts of $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ in toluene solution were treated with slightly less than an equimolar amount of the diphosphine. Qualitative tests using thin layer chromatography showed that maximum separation of the three products of this reaction was obtained on silica, using as eluent a 1:3 mixture of 1,2-dichloroethane and hexane. The reaction mixture was therefore chromatographed on a 7-ft. column of silica, using this solvent mixture as eluent. Although complete separation of the three bands was not achieved, a plot of the intensity ratio of the C–O stretching band at 2013 cm.$^{-1}$ (characteristic of the grouping $Fe(NO)_2(CO)P$, where P is one of the two phosphorus atoms of the diphosphine) and the C–O stretching band at 1979 cm.$^{-1}$ (characteristic of the grouping $Co(NO)(CO)_2P$ for each 50-ml. fraction of eluent (Figure 1) is proof that there are three distinct compounds present, the first containing only cobalt, the second containing both cobalt and iron, and the third only iron.

By collecting the product from the fractions in the central flat section of the curve and recrystallizing, sharply melting red needles of the unsymmetrical bridge complex $Fe(NO)_2(CO)$(diphos)$Co(NO)(CO)_2$ were obtained. As Figure 1 illustrates, the infrared spectrum of the unsymmetrical bridge complex (bands due to C–O stretching vibrations at 2040, 2013, and 1979 cm.$^{-1}$, bands due to N–O stretching vibrations at

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[8] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

[9] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

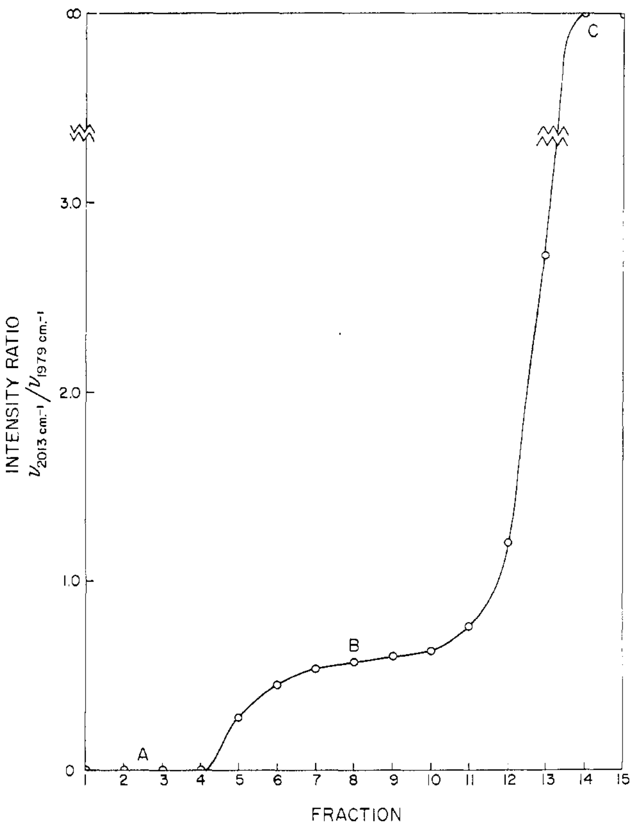

Figure 1.—Separation by column chromatography of A, $[\mathrm{CoNO(CO)_2}]_2$(diphos); B, $\mathrm{CoNO(CO)_2}$(diphos)$\mathrm{Fe(NO)_2CO}$; C, $[\mathrm{Fe(NO)_2CO}]_2$(diphos). Plot of relative intensities of bands at 2013 and 1979 cm.$^{-1}$ for each 50-ml. fraction of eluent.

1761 and 1716 cm.$^{-1}$) is a superposition of the spectra of the two symmetrical bridge compounds (see Table I).

The other two components of the reaction mixture were the symmetrical cobalt and iron bridge complexes.

In an effort to obtain a second complex of this type, equimolar amounts of $\mathrm{CH_3Mn(CO)_5}$ and the diphosphine were allowed to react in tetrahydrofuran at 25°, and the solution was then allowed to react with excess $\mathrm{Ni(CO)_4}$. Purification of the reaction mixture yielded only two products, the symmetrical bridge complexes $[\mathrm{CH_3COMn(CO)_4}]_2$(diphos) and the new complex, $[\mathrm{Ni(CO)_3}]_2$(diphos), which at first sight is most surprising. However, the fact that equimolar amounts of $\mathrm{Fe(NO)_2(CO)_2}$ and the diphosphine were found (see section (B)) to yield a considerable amount of the bridge complex $[\mathrm{Fe(NO)_2(CO)}]_2$(diphos) as well as the monodentate diphosphine complex, $\mathrm{Fe(NO)_2(CO)}$(diphos), suggests that the reaction between $\mathrm{CH_3Mn(CO)_5}$ and the diphosphine may take a similar course, leading to the formation of some $[\mathrm{CH_3COMn(CO)_4}]_2$(diphos) and leaving some unreacted diphosphine. This would then react with the excess of $\mathrm{Ni(CO)_4}$ added, giving $[\mathrm{Ni(CO)_3}]_2$(diphos). This explains the isolation of the two symmetrical bridge complexes but fails to explain the absence of the unsymmetrical bridge complex, which must presumably have decomposed during the purification procedure.

Attempts to prepare unsymmetrical bridge complexes of $\mathrm{Ni(CO)_4}$ with both $\mathrm{Fe(NO)_2(CO)_2}$ and $\mathrm{Co(NO)(CO)_3}$ were unsuccessful. Although infrared spectra of the products suggested that the desired compounds had been formed, it was not found possible to isolate them in the pure state.

Discussion

The diphosphine, 1,2-bis(diphenylphosphino)ethane, had previously been shown to form similar bridge complexes with some metal carbonyl compounds under the influence of ultraviolet light.[10] A few other complexes are known[11,12] in which two metal atoms are bridged by more than one molecule of this and similar diphosphines. The existence in solution, however, in the reaction of carbonyl complexes with the diphosphine, of fairly stable intermediates containing one phosphorus atom coordinated to the metal and the other free had not previously been observed.

The difference in rates of the two reactions

$$\mathrm{Fe(NO)_2(CO)_2} + \text{diphos} \longrightarrow \underset{\text{monodentate complex}}{\mathrm{Fe(NO)_2(CO)(diphos)}} + \mathrm{CO}$$

$$\mathrm{Fe(NO)_2(CO)(diphos)} \longrightarrow \underset{\text{chelate complex}}{\mathrm{Fe(NO)_2(diphos)}} + \mathrm{CO}$$

may relate to the increasing difficulty of displacing successive molecules of carbon monoxide from a metal carbonyl complex. The fact that the removal of one molecule of carbon monoxide from a carbonyl complex causes the remaining carbonyl groups to be held more tightly is suggested by the shift of the C–O stretching frequencies to lower energy as more and more carbonyl groups are replaced by other ligands (see Table I). This increase in metal–CO bond strength with decrease in the number of carbonyl groups is believed to be due to the sharing of metal-to-ligand π bonding between fewer and fewer metal–CO bonds and depends on the assumption that there will be little metal-to-ligand π bonding between the metal and the other ligands present. (In the case of $\mathrm{Fe(NO)_2(CO)_2}$ and $\mathrm{Co(NO)(CO)_3}$ the situation is complicated somewhat by the presence of the strongly π-bonding nitrosyl groups, and it is evident from the lowering of N–O stretching frequencies with increasing replacement of CO by phosphines that the metal–NO bonds are also strengthened as CO is replaced.)

Since in the reaction of $\mathrm{Mn(CO)_5Br}$ with the diphosphine, the rates of formation of the intermediate and of its subsequent conversion to the chelate complex, $\mathrm{Mn(CO)_3}$(diphos)Br, are too similar to allow separate observation of the two steps of the reaction, the observation of a fairly long-lived intermediate in the reaction of $\mathrm{CH_3Mn(CO)_5}$ with the diphosphine is presumably caused by the fact that the reaction

$$\mathrm{CH_3Mn(CO)_5} + \text{diphos} \longrightarrow \mathrm{CH_3COMn(CO)_4}\text{diphos}$$

involves a so-called insertion reaction rather than the actual elimination of a molecule of CO. Although an

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(10) J. Lewis, R. S. Nyholm, A. G. Osborne, S. S. Sandhu, and M. H. B. Stiddard, *Chem. Ind.* (London), 1398 (1963).

(11) F. Zingales and F. Canziani, *Gazz. chim. ital.*, **92**, 343 (1962).

(12) J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1005 (1964).

exact comparison is not available, it is evident[13,14] that the activation energy for the insertion reaction is several kcal./mole less than that for a corresponding carbonyl displacement reaction of $Mn(CO)_5Br$.

By contrast the second step, that of the formation of the chelate

$$CH_3COMn(CO)_4(diphos) \longrightarrow CH_3COMn(CO)_3(diphos) + CO$$

is very similar to the corresponding step for $Mn(CO)_5Br$ and will probably have a similar activation energy. This, therefore, gives an added measure of stability to the monodentate phosphine complex $CH_3COMn(CO)_4(diphos)$.

The isolation of bridge complexes from the reactions of metal carbonyl compounds with the diphosphine is a consequence of the stability of the monodentate diphosphine complexes. The slow rate at which these intermediates are converted to chelate complexes allows them to react preferentially with more metal carbonyl complex (if present) to form the bridge complexes. Thus, the criteria for the formation of a good yield of bridge complex are: (a) a monodentate diphosphine complex which is formed from starting material at a rate considerably faster than that at which it is converted to the corresponding chelate complex; (b) an excess of metal carbonyl complex over diphosphine.

The isolation of an unsymmetrical bridge complex, $Fe(NO)_2(CO)(diphos)Co(NO)(CO)_2$, believed to be the first compound of this type to be prepared with the diphosphine, is a natural extension of the isolation of symmetrical bridge complexes.

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Metal Complexes of Cyanocarbons. I. Preparation of Some Platinum Compounds of Tetracyanoethylene

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Reactions of tetracyanoethylene with various platinum complexes have been investigated, and the first examples of this cyanocarbon covalently bonded to a transitional metal ion have been synthesized. These compounds, which are formulated as $Pt(PR_3)_2(C_6N_4)$ where R is C_2H_5 and C_6H_5, were prepared by two methods, the first being the replacement of phenylacetylene from complexes of the type $Pt(PR_3)_2(C_6H_5C{\equiv}CH)$, and the second being the reaction of tetracyanoethylene with some platinum hydrides.

Introduction

Metal complexes containing hydrocarbons bonded to a transitional metal ion have been the subject of much study. Replacement of the hydrogen atoms by fluorine in such compounds has resulted in fluorocarbon derivatives of metal ions, which in many cases are uniquely different from the parent hydrocarbon complexes.[3] One might suppose that cyanocarbons, analogous to hydrocarbons and fluorocarbons, would give rise to interesting metal complexes. Such a hypothesis can now be subjected to scrutiny, because several years ago a series of cyanocarbons was synthesized.[4] We have commenced an investigation of the reactions of such substances with transitional metal compounds and have chosen tetracyanoethylene, C_6N_4, for our initial work. The organic chemistry of this particular cyanocarbon has been extensively studied.[5]

Reactions of tetracyanoethylene with metal complexes have received cursory attention. It was noted that $Ni(CO)_4$ is decarbonylated and oxidized by this cyanocarbon.[6] Another worker[7] found that $Ni(CO)_4$ and C_6N_4 reacted violently. Oxidation of the nickel atom occurred and probably the tetracyanoethylene anion radical was formed as an intermediate, which under the conditions employed led to polymeric materials with nonstoichiometric nickel content. Reaction of copper(I) halides with C_6N_4 did not yield complexes but resulted in oxidation of the copper.[8] The solid-state reaction of ferrocene and tetracyanoethylene was reported to give a salt, ferricinium tetracyanoethylenide.[9] Recent work, however, indicates that the com-

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