

# Reactions of iron carbonyls with various ligands in the presence of chloroform. A new method for the preparation of iron halide complexes

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Iron halide complexes of the type FeCl<sub>2</sub>.2L (L = CH<sub>3</sub>CONH<sub>2</sub>, HCONH<sub>2</sub>, HCONHCH<sub>3</sub>) and FeCl<sub>3</sub>.L (L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CONH<sub>2</sub>) have been prepared by the reaction of iron carbonyls with various ligands in chloroform as solvent. The mechanism of the reaction and the effect of other solvents have also been studied. The magnetic susceptibility measurements and infrared spectral study (4000–200 cm<sup>-1</sup>) suggest that these complexes have tetrahedral configuration. The possible site of bonding in ligands and infrared assignments for Fe-O, Fe-Cl, Fe-N, Fe-P, Fe-As bands have been given. The relative Fe-O bond strengths in various amide complexes have been determined on the basis of metal-oxygen stretching frequency and of shifts in carbonyl stretching frequency.

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#### Introduction

Halogenated hydrocarbons have been found to be involved in reactions with metal carbonyls either as oxidizing agents (1-7) or entering as addition molecules (8-10) besides producing substitution products (5, 11). Webb and Borcherdt (12) produced coupling of allyl radicals by treating allyl halides with nickel carbonyl.

Coffey (1) has allowed many metal carbonyls to react with *gem*-dihalides and has found that these reactions lead to the formation of metal chlorides and ethylenic compounds with evolution of carbon monoxide as shown in the following equation.

 $2Fe(CO)_5 + 2(C_6H_5)_2CCl_2 = 2FeCl_2 + 10CO + (C_6H_5)_2C=C(C_6H_5)_2$ 

He has observed that only *gem*-dihalides can undergo such reactions and chloroform was found to be inert in a similar reaction.

Since halogenated hydrocarbons have been found to react with metal carbonyls in a variety of ways, it was thought to be of interest to carry out a systematic study of this system. This paper describes the reactions of various organic ligands with metal carbonyls in the presence of chloroform and other halogenated hydrocarbons. The structure of the complexes obtained by this method has been elucidated with the help of infrared studies in the range 4000–200 cm<sup>-1</sup> and magnetic susceptibility measurements.

#### Experimental

#### Materials and Manipulations

All the solvents were of reagent grade and were purified and dried before use. Reagent grade iron pentacarbonyl was obtained from K and K Laboratories and was used after distillation over molecular sieves. Diiron nonacarbonyl and triiron dodecacarbonyl were obtained from Alfa Inorganics and were used after drying in vacuum. Other metal carbonyls were used without further purification.

Formamide (FA), N-methylformamide (MFA), and aniline (AN) were purified by distilling under reduced pressure over molecular sieves. Acetamide (AM) and benzamide (BM) were crystallized from chloroform. Triphenylphosphine (TPP) and triphenylarsine (TPA) were used from fresh bottles without further purifications. Reactions were carried out, where essential, in a dry-box flushed with nitrogen.

Infrared spectra of the complexes and ligands were recorded either in Nujol mulls or in solutions on a Perkin-Elmer Model-621 recording spectrophotometer using sodium chloride optics. For far-infrared measurements cesium iodide optics were used.

The magnetic susceptibility measurements were made by the Gouy method, using mercury(II) tetrathiocyanatocobalt(II) as standard. The diamagnetic corrections were estimated by methods outlined by Figgis and Lewis (25).

## Preparation of the Complexes

FeCl<sub>3</sub>.AN, FeCl<sub>3</sub>.BM, FeCl<sub>2</sub>.2AM, FeCl<sub>2</sub>.2FA, and FeCl<sub>2</sub>.2MFA were prepared by refluxing Fe<sub>3</sub>(CO)<sub>12</sub> (2 g) with AN (1.2 g), BM (1.5 g), AM (1.5 g), FA (1.1 g), or MFA (1.5 g) in chloroform (100 ml) till the color of the solution changed from green to light yellow. In each case a white or light-yellow flocculent precipitate separated which was filtered, washed with the solvent, and dried in vacuum. Instead of the trimer, the dimer could be conveniently used. With the monomer Fe(CO)<sub>5</sub> the complex was obtained only when the refluxing was continued for about 48 h.

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TABLE I Melting points and elemental analyses of complexes

	Malting	Fe	(%)	Cl (	%)	С(	%)	Н (	%)	N (	%)	Р (	%)
	point (°C)* Colo	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
FeCl <sub>2</sub> .2AM FeCl <sub>2</sub> .2FA FeCl <sub>2</sub> .2MFA FeCl <sub>2</sub> .4FA FeCl <sub>3</sub> .AN FeCl <sub>3</sub> .TPP FeCl <sub>3</sub> .TPA $(C_6H_5)_2C=(C_6H_5)_2$ FeCl <sub>3</sub> .BM	116 White 200d Yellowis 140 White 156 Yellowis — Yellow 118 Light yel 130 Dark yel 222 White 158 Brown	22.95 1 25.81 22.95 1 18.24 21.96 ow 13.19 ow 11.99 19.78	22.52 25.24 22.64 18.16 21.53 12.83 12.62 19.42	28.70 32.72 28.70 23.12 42.54 25.08 22.48 37.63	28.26 32.31 28.52 23.73 41.97 25.60 22.50 36.99	19.79 11.05 19.79 15.64 28.24 50.88 46.15 93.97 29.68	19.62 11.71 19.25 15.04 27.82 50.23 44.99 93.66 28.94	4.10 2.76 4.10 3.90 2.69 3.57 3.51 6.05 2.47	4.12 2.92 3.81 4.23 3.41 3.51 3.49 5.41 2.79	11.06 12.90 11.06	11.39 13.55 12.01 4.57	-	

### SINGH AND RIVEST: REACTIONS OF IRON CARBONYLS WITH VARIOUS LIGANDS

FeCl<sub>3</sub>.TPP and FeCl<sub>3</sub>.TPA were prepared by refluxing Fe<sub>3</sub>(CO)<sub>12</sub> (2 g) and TPP (3.2 g) or TPA (5.6 g) in chloroform (100 ml) for 12 h; the solution was then filtered. The residue was rejected and the filtrate concentrated by vacuum evaporation. To the concentrate *n*-hexane was added and the mixture was vigorously shaken until a dark-yellow viscous mass separated. The supernatant liquid was rejected and the residue treated with small quantities of absolute alcohol. A yellow solid was thus obtained which was washed with *n*-hexane and dried in vacuum. It was recrystallized from absolute alcohol. The complex could also be prepared by refluxing Fe(CO)<sub>4</sub>.TPP with chloroform, and completing the process as described above.

 $MoCl_3$ .TPP was also similarly prepared from Mo-(CO)<sub>6</sub> (2 g) and TPP (2 g) but the refluxing time was 5 days.

#### Isolation of $(C_6H_5)_2C = C(C_6H_5)_2$

Fe(CO)<sub>4</sub>.TPA (5.3 g) was mixed with 4 ml of diphenyldichloromethane and refluxed in 150 ml of benzene with stirring for 15 h. A viscous layer appeared which was separated from the supernatant liquid. The supernatant liquid was concentrated by vacuum evaporation when a white compound crystallized out; it was filtered, washed several times with acetone, and dried in vacuum. It was recrystallized from an acetone-water mixture and identified as tetraphenylethylene by its melting point, elemental analysis, and infrared spectrum.

## Analysis of the Compounds

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Iron and chlorine were estimated as oxide and silver halide respectively. Carbon, hydrogen, and nitrogen were analyzed by microtechniques from Galbraith Laboratories Incorporated. The results obtained are given in Table I.

#### Results

All the three iron carbonyls (monomer, dimer, and trimer) react with various organic ligands in the presence of chloroform and form halide adducts of the type FeCl<sub>2</sub>.2L and FeCl<sub>3</sub>.L. Molybdenum carbonyl also reacts similarly with TPP and forms MoCl<sub>3</sub>.L. Chromium and tungsten carbonyls under similar conditions do not form any complex. The substituted carbonyl complex Fe(CO)<sub>4</sub>.L also forms halide complexes (FeCl<sub>3</sub>.L) when refluxed with chloroform. The solvents other than chloroform which have been found to lead to similar oxidation reactions are carbon tetrachloride, tetrachloroethane, and benzyl chloride. Dichloroethane and methylene dichloride have been found to lead to some sort of decomposition giving rise to impure compounds.

The organic ligands which have been found to form complexes of the type  $\text{FeCl}_2.2\text{L}$  are formamide, monomethylformamide, and acetamide, whereas those which form the  $\text{FeCl}_3.\text{L}$ type are aniline, benzamide, triphenylphosphine, and triphenylarsine. It has been noticed that all the ligands which have a phenyl group give rise to an iron complex of higher oxidation state.

Acetonitrile, dimethylformamide, and triphenylstibine do not form pure complexes, probably due to the formation of excess FeCl<sub>2</sub> during the course of the reaction. Triphenylamine and triphenylbismuthine do not react at all.

This method of preparing halide complexes is an improvement over the direct synthesis from the halides as the latter involves difficulty in dissolution of the halide in nonpolar organic solvents and in its handling. Out of the three forms of iron carbonyls, the dimer and the trimer are best suited for this purpose and can safely be handled even in open air.

# Mechanism of the Reaction

The formation of complexes of the type FeCl<sub>2</sub>.2L or FeCl<sub>3</sub>.L by the reaction of iron carbonyl with various ligands in the presence of halogenated hydrocarbons suggests two possible reaction mechanisms. On the lines of the Coffey (1) mechanism it can be suggested that the halogenated hydrocarbon first reacts with the carbonyl and forms ferrous chloride which further reacts with the ligand and forms the complex. The possibility of this mechanism is ruled out because iron pentacarbonyl does not react with chloroform in the absence of the ligand, and the formation of ferric chloride has never been observed in any kind of reaction in which iron carbonyl reacts with any halogenated hydrocarbon. The second possible mechanism is through the formation of a substituted carbonyl complex of the type Fe(CO)<sub>4</sub>.L, which reacts with halogenated hydrocarbons to give rise to a halide complex. To verify this, Fe(CO)<sub>4</sub>.L was allowed to react with chloroform, and the halide complex was obtained. In order to establish the reaction mechanism we tried to isolate the product formed from chloroform after its involvement in the oxidation reaction but failed to identify or isolate any such compound. We therefore replaced the chloroform with diphenyldichloromethane and allowed this to react with Fe(CO)<sub>4</sub>.TPA. We could thus isolate tetraphenylethylene besides the halide complex. A possible mechanism of the reaction therefore can be suggested as

 $Fe(CO)_{5} + 2L = Fe(CO)_{3}L_{2} + 2CO$ 2Fe(CO)\_{3}L\_{2}+2(C\_{6}H\_{5})\_{2}CCl\_{2} = 2FeCl\_{2}L\_{2} + (C\_{6}H\_{5})\_{2}C=(C\_{6}H\_{5})\_{2} + 6CO.

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TABLE II Assignments of infrared bands of ligands and complexes

	FeCl <sub>2</sub> .2FA		FeCl <sub>2</sub> .2AM		FeCl <sub>2</sub> .2MFA		FeCl <sub>3</sub> .BM	
Assignments	Ligand (CHCl <sub>3</sub> soln.)	Complex (Nujol)	Ligand (CHCl <sub>3</sub> soln.)	Complex (Nujol)	Ligand (CHCl <sub>3</sub> soln.)	Complex (Nujol)	Ligand (CHCl <sub>3</sub> soln.)	Complex (Nujol)
N—H stretch (asym.)	3550 (s)	3400 (s)	3560 (s)	3400 (s)			3555 (s)	3440 (s)
N-H stretch (sym.)	3425 (s)	3280 (s)	3440 (s)	3280 (s)	3483 (s)	3340 (s)	3440 (s)	3340 (s)
Amide I	1710 (s)	1690 (s)	1710 (s) 1685 (s)	1670 (s)	1690 (s)	1635 (s)	1675 (s)	1652 (s)
Amide II	1590 (m)	1570 (s)	1605 (s)	1580 (s)			1590 (s)	1560 (s)
C-N stretch	1300 (s)	1335 (m)	1380 (s)	1410 (m)	1410 (s)	1445 (s)	1070 (0)	
Fe-Cl stretch	(0)	373 (wb) 330 (mb)		350 (wb)		380 (sb) 360 (s)		375 (mb) 288 (mb)
Fe—O stretch		400 (vw)		420 (vw)		475 (vw)		475 (s)
Fe—O stretch $+ \delta NCO$		585 (sh)		560 (s)		540 (m)		538 (s)

Amide I	1710 (s)	1690 (s)	1710 (s)	1670 (s)	1690 (s)	1635 (s)	1675 (s)	1652 (s)
Amide II C—N stretch Fe—Cl stretch	1590 (m) 1300 (s)	1570 (s) 1335 (m) 373 (wb) 330 (mb)	1605 (s) 1605 (s) 1380 (s)	1580 (s) 1410 (m) 350 (wb)	1410 (s)	1445 (s) 380 (sb) 360 (s)	1590 (s)	1560 (s) 375 (mb) 288 (mb)
Fe—O stretch Fe—O stretch $+ \delta NCO$		400 (vw) 585 (sh)		420 (vw) 560 (s)		475 (vw) 540 (m)		475 (s) 538 (s)
s = strong, m = medium, w =	weak, v = very, b =	broad.						
			TAB	LE III				
		Assignments	of infrared bar	nds of ligands an	d complexes			
	FeCl <sub>3</sub> .	AN	FeCl	3.TPP	FeCl	3.TPA	MoC	l <sub>3</sub> .TPP
Assignment	FeCl <sub>3</sub> . Ligand (CHCl <sub>3</sub> soln.)	AN Complex (Nujol)	FeCl Ligand (Nujol)	3.TPP Complex (Nujol)	FeCl Ligand (Nujol)	3.TPA Complex (Nujol)	MoC Ligand (Nujol)	l <sub>3</sub> .TPP Complex (Nujol)
Assignment N—H stretch (asym.)	FeCl <sub>3</sub> . Ligand (CHCl <sub>3</sub> soln.) 3478 (s) 2400 (c)	AN Complex (Nujol) 3360 (sb)	FeCl Ligand (Nujol)	3.TPP Complex (Nujol)	FeCl Ligand (Nujol)	a.TPA Complex (Nujol)	MoC Ligand (Nujol)	l <sub>3</sub> .TPP Complex (Nujol)
Assignment N—H stretch (asym.) N—H stretch (sym.) NH <sub>2</sub> bending	FeCl <sub>3</sub> . Ligand (CHCl <sub>3</sub> soln.) 3478 (s) 2400 (s) 1620 (s)	AN Complex (Nujol) 3360 (sb) 1640 (s)	FeCl Ligand (Nujol)	3.TPP Complex (Nujol)	FeCl Ligand (Nujol)	3.TPA Complex (Nujol)	MoC Ligand (Nujol)	l <sub>3</sub> .TPP Complex (Nujol)
Assignment N—H stretch (asym.) N—H stretch (sym.) NH <sub>2</sub> bending Fe—N stretch M—Cl stretch	FeCl <sub>3</sub> . Ligand (CHCl <sub>3</sub> soln.) 3478 (s) 2400 (s) 1620 (s)	AN Complex (Nujol) 3360 (sb) 1640 (s) 462 (s) 375 (m) 290 (w)	FeCl Ligand (Nujol)	3.TPP Complex (Nujol) 370 (s) 320 (w)	FeCI Ligand (Nujol)	3.TPA Complex (Nujol) 360 (s) 330 (m)	MoC Ligand (Nujol)	330 (s) 335 (sh)
Assignment N—H stretch (asym.) N—H stretch (sym.) NH <sub>2</sub> bending Fe—N stretch M—Cl stretch Phenyl—P M—P	FeCl <sub>3</sub> . Ligand (CHCl <sub>3</sub> soln.) 3478 (s) 2400 (s) 1620 (s)	AN Complex (Nujol) 3360 (sb) 1640 (s) 462 (s) 375 (m) 290 (w)	FeCl Ligand (Nujol) 1095 (s)	3.TPP Complex (Nujol) 370 (s) 320 (w) 1105 (s) 525 (s)	FeCI Ligand (Nujol)	3.TPA Complex (Nujol) 360 (s) 330 (m)	MoC Ligand (Nujol)	I3.TPP           Complex (Nujol)           330 (s)           335 (sh)           522 (s)

s = strong, m = medium, w = weak, b = broad, sh = shoulder, M = Fe, Mo.

## Infrared Study

# Amide Complexes

Amides can coordinate either through the nitrogen of the NH<sub>2</sub> group or the oxygen of the C=O group. A reference to Table II shows that there is a negative shift of the carbonyl stretching frequency and a positive shift of the C-N stretching on complex formation, suggesting coordination through the carbonyl oxygen of the amides. A negative shift in NH<sub>2</sub> bending or amide II band on coordination also indirectly supports coordination through oxygen, as coordination through nitrogen would cause a positive shift in this band (20). However, a marked negative shift in the N-H stretching frequency of the amide is also observed. The reason for such a negative shift in N-H stretching frequency is hydrogen bonding between the NH<sub>2</sub> of the amide and chlorine of the metal halide. Such hydrogen bonding has been observed by Chatt et al. (13) in a series of amine complexes of platinous chloride. There is also ample evidence (14, 15) for the presence of hydrogen bonding between the hydrogen of amine complexes and anions such as halides. It is worth mentioning that the magnitude of the shift due to hydrogen bonding is even greater than the shift due to coordination, and can be of the order of 200 cm<sup>-1</sup>. If one makes a molecular model of the complexes one finds quite a good possibility of such a hydrogen bonding. As such, the negative shift in N-H stretching frequency is not due to coordination through nitrogen, but due to hydrogen bonding.

Previous workers on amide and urea complexes (16) have not noticed such a marked shift in N-H stretching frequency when coordination took place through oxygen. Since our observation is the first of its kind it is interesting to explain it in detail. Intermolecular hydrogen bonding between oxygen of the carbonyl group and hydrogen of  $NH_2$  is well known (17) in amides and has a marked effect on the positions of N-H and C-O stretching vibrations. It is therefore essential to record the spectrum of the ligand in very dilute solution so that hydrogen bonding is completely eliminated. We have therefore compared the spectrum of the complexes with that of a very dilute solution of the ligand and have deduced the magnitude of the shift. However, if the spectrum of the complex is compared with that of the ligand in solid phase or in concentrated solution, where hydrogen bonding is not eliminated, no negative shift will be observed, as in ref. 16.

Since the spectrum in the far infrared region provides direct evidence of bonding, we recorded the spectrum in this region also and the assignments are given in Table II. The weak band in the region 400–475  $\text{cm}^{-1}$  (for which there are no corresponding ligand bands) is assigned to pure Fe-O stretching vibration. Nakamoto et al. (18, 19) also observed a weak band for M-O stretching frequency and gave the assignment for this band in the region  $430-490 \text{ cm}^{-1}$ . The band in the region 538-585 cm<sup>-1</sup> has been assigned as a combination band of metaloxygen stretching frequency and C-C bending vibration (18, 19), or O-C-O bending (34), or N-C-O bending (16). Since the N-C-O bending vibration is present in all the amide complexes, we assign the band in this region to Fe-O stretching vibration plus N-C-O bending vibration.

On the basis of inductive effects, one can fairly well establish that the three amides will have the order of donor ability MFA > AM > FA, because in MFA the methyl group will tend to repel the electrons towards the carbonyl, this effect being absent in FA. Acetamide is intermediate, due to the methyl group on carbon. If coordination takes place through the carbonyl group we should then observe an increase in  $\Delta v$ (C==O) from FeCl<sub>2</sub>.2FA to FeCl<sub>2</sub>.2MFA and also an increase in the Fe-O stretching in the same order indicating an increase in bond order. Table IV gives results which confirm these assumptions. A similar relationship has also been elucidated by Nakamoto in acetylacetonate and oxalato complexes (18, 19).

TABLE IV Infrared spectra assignments

Complex	Position of $v(C=0)$ (cm <sup>-1</sup> )	$\Delta v(C=0)$	= v(M_O) (cm <sup>-1</sup> )
FeCl <sub>2</sub> .2FA	1690	20	400
FeCl <sub>2</sub> .2AM	1665	40	420
FeCl <sub>2</sub> .2MFA	1635	55	475

Note. The benzamide complex has not been included in this sequence as the metal is in a different oxidation state.

# Analine, Triphenylphosphine, and Triphenylarsine Complexes

Since these ligands have only one center of

coordination, the discussion of the infrared spectrum in the regular region is hardly of any interest. We have therefore confined our discussion to the far infrared region, and the assignments are given in Tables II and III.

In the case of the aniline complex there is a strong band at 462 cm<sup>-1</sup> corresponding to which there is no ligand band. This band therefore can reasonably be assigned to the Fe-N stretching vibration. Previous workers (21-24) have given M---N assignments in the same region.

In triphenylphosphine complexes of iron and molybdenum there appear bands at 525  $cm^{-1}$ and 522 cm<sup>-1</sup> respectively, whereas in the triphenylarsine complex a band appears at 450 cm<sup>-1</sup>. There are no ligand bands corresponding to these bands which can be assigned to Fe-P, Mo-P. and Fe-As stretching vibrations respectively. Assignment for M-P stretching vibration has been given in the same region by Rivest et al. (27) and Westland and Westland (35). Coates and Parkins (26) have observed that the Pd—P stretching frequency is higher than the Pd—As stretching frequency in palladium dichloride complexes. A similar observation has been made by Rivest et al. (27) in the case of stannic halide complexes of triphenylphosphine and triphenylarsine. Our assignments have a similar relation.

#### Fe—Cl Bands

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The assignments of Fe---Cl vibrations are given in Tables II and III. We find that there are bands at about 375  $cm^{-1}$  in all the iron halide complexes corresponding to which there are no ligand bands. The presence of these bands in all the complexes strongly suggests that they are due to Fe-Cl stretching vibrations. This assignment is in good agreement with the assignments given by Woodward and Taylor (28) and Adams (29) for M—Cl bands.

# Magnetic Susceptibility and Structural Studies

It is well known that  $Cl^{-}$  (30) has a weak and TPP a strong ligand field (31). To evaluate the ligand field strength of amides, FeCl<sub>2</sub>.4FA was prepared and its magnetic susceptibility measured, which was found to correspond to four unpaired electrons, showing that the ligand field due to amides is weak. A diamagnetic complex  $(d_{\epsilon}^{6}d_{\gamma}^{0})$  was expected from a strong field.

The number of unpaired electrons in FeCl<sub>2</sub>.2L

and FeCl<sub>3</sub>.L complexes are four and five respectively. These values favor a tetrahedral structure for the complexes. Chatt and Shaw (32) have also observed that in a weak field only a tetrahedral structure is possible and that the field required for a square planar complex must be very high.

The number of bands in the far infrared region also supports the tetrahedral configuration for these complexes. The complexes of the type FeCl<sub>2</sub>.2L have a  $C_2 v$  symmetry and those of FeCl<sub>3</sub>.L type have  $C_3 v$  symmetry, if treated as tetrahedral (33). The number of stretching vibrations expected for FeCl<sub>2</sub>.2L is four (two for Fe-L and two for Fe-Cl) and for FeCl<sub>3</sub>.L is three (one for Fe-L and two for Fe-Cl). The bending vibrations have not been taken into account as they will appear below 200  $\text{cm}^{-1}$ . We observed the expected number of bands (Tables II and III) in the far infrared region of the complexes which is in conformity with the tetrahedral configuration for these complexes.

The molecular weight determinations could not be made because the complexes dissociate in solution; however, the fact that these complexes have a low melting point and are easily soluble with dissociation is indirect evidence of their monomeric nature. If one accepts the hypothesis that they are monomeric, the other data support the tetrahedral configuration for these complexes.

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