ISOCYANIDE METAL COMPLEXES

I. REACTIONS OF HALOCARBONYLS WITH PHENYLISOCYANIDE

K. K. JOSHI, P. L. PAUSON AND W. H. STUBBS
Chemistry Department, The Royal College of Science and Technology, Glasgow (Great Britain)

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Extensive studies of the reactions of halo-manganese and -rhenium pentacarbonyls (I) with a variety of ligands have been carried out, chiefly by Hieber and his co-workers[1–5]. The results may be represented by the general expression:

$$\underset{\text{(I)}}{\text{XM(CO)}_5} + \text{L} \longrightarrow \underset{\text{(II)}}{\text{XM(CO)}_4\text{L}} \longrightarrow \underset{\text{(III)}}{\text{XM(CO)}_3\text{L}_2}$$

$$\text{a: M=Mn;} \quad \text{b: M=Re}$$

For a given ligand (L), reaction appeared to stop at either stage (II) or (III). Similar reactions[6] of the neutral carbonyls $Fe(CO)_5$ and $M(CO)_6$ (where M = Cr, Mo or W) have likewise been reported to stop after partial replacement of carbon monoxide. With monodentate ligands (L) at least three carbonyl groups were always left attached to the metal atom. This apparent behaviour pattern has never been explained although it is recognised that replacement of CO by a ligand (L) which is less well able to accept back-donation of electrons will lead to a strengthening of the remaining metal–CO bonds. Nevertheless it seemed probable that more extensive replacement of carbon monoxide should be possible, especially with ligands which are known to form stable complexes with these metals in low oxidation states.

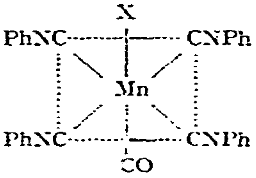
We have therefore examined in detail the reaction of bromomanganese pentacarbonyl with phenyl isocyanide. Among the possible ligands, isocyanides may be considered to be most like carbon monoxide in structure and mode of bonding to a transition metal. They were known to form stable derivatives of manganese in the +1 oxidation state[7]: $[Mn(CNPh)_6]^+$ containing no other groups. But only mono-[1a] (IIa; X = Br; L = CNEt) and bis-isocyanide[1b] derivatives (IIIa; X = Br; L = p-CNC_6H_4OMe) had been reported to be formed from the corresponding carbonyl (Ia; X = Br). We have confirmed that the disubstituted compound (IIIa; X = Br; L = CNPh) is the only product with phenyl isocyanide under Hieber's conditions[1b], using ethanol as solvent. However, in diglyme at 100° the reaction proceeded to the next stage yielding bromodicarbonyltris(phenyl isocyanide)manganese (IV, X = Br). This solvent is known to assist replacement of three carbonyl groups from molybdenum hexacarbonyl by forming an intermediate complex in which it acts as a tridentate ligand[8]. The present result can probably be ascribed to the formation of a similar intermediate and not merely to the higher temperature employed in this case.

In support of this view we have shown that three molecules of carbon monoxide are evolved when bromomanganese pentacarbonyl is heated with diglyme alone.

Still more striking was the effect of using the strongly basic ether tetrahydrofuran as solvent. Its ability to act as a ligand forming stable transition metal complexes is well known. In the present work it was found that bromomanganese pentacarbonyl (Ia; X = Br) loses four molecules of carbon monoxide on refluxing in this medium with the formation of a stable complex[9]. Accordingly reaction with phenyl isocyanide in tetrahydrofuran gave bromocarbonyltetrakis(phenyl isocyanide) manganese (V; X = Br) as the main product accompanied by bromopentakis(phenyl isocyanide)manganese (VI). The former complex (V; X = Br) was also obtained by the action of four molar equivalents of isocyanide on bromotricarbonylbis(triphenylphosphine)manganese (IIIa; X = Br; L = PPh_3) in the same solvent. The carbonyl group in trans position to the halogen would be expected to be the least readily replaceable[10] and we therefore believe (V) to be the correct stereochemical formulation for our product. The precise stereochemistry of the tris-isocyanide complex (IV) is at present unknown, but the bis-isocyanide complex (III; X = Br; M = Mn; L = CNPh) may be assigned the cis configuration on the basis of the work of Angelici, Basolo and Poe[11] and the close resemblance of its infrared spectrum in the carbonyl region to that of the phosphite analogue (III; M = Mn; X = Br; L = $P(OPh)_3$). To complete the series (I–VI) by preparing the mono-isocyanide

$Mn(CNPh)_3(CO)_2X$

(IV)



(V)

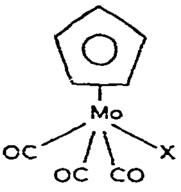
$Mn(CNPh)_5Br$

(VI)

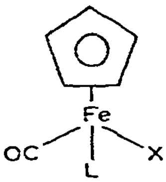
complex (IIa; X = Br; L = CNPh), we have utilized the dimeric halocarbonyl[3a], $Mn_2(CO)_8Br_2$. As expected the isocyanide caused cleavage of the halogen bridges in this molecule under conditions too mild to result in replacement of carbon monoxide.

Further differences in reactivity may be expected to result from variation of the halogen atoms in the halopentacarbonyls (I). These differences have recently been investigated quantitatively by Basolo and coworkers, who find that both for carbon monoxide exchange[4b] and for reaction with a variety of other ligands[4a], the rates fall in the order Cl > Br > I. Both these results and the differences in the infrared spectra[3a] can be correlated with the decreasing electronegativity of these halogens, which will lead to more effective back-donation to CO in the iodide, i.e. to stronger metal–carbon bonding. Our own results, though qualitative, reveal equally striking differences. Thus, under conditions where the bromide (Ia; X = Br) was partly converted to the pentakis-isocyanide derivative (VI), the iodide (Ia; X = I) gave only the tetrakis derivative (V; X = I), but the chloride gave ionic hexakis(phenyl isocyanide) manganese(I) chloride, $[Mn(CNPh)_6]^+Cl^-$.

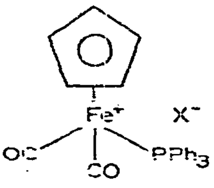
Similar results have been obtained with carbonyl halides of molybdenum and iron: Phenyl isocyanide displaced three molecules of carbon monoxide from chlorotricarbonylcyclopentadienylmolybdenum (VII; X = Cl) and gave tris(phenyl isocyanide)cyclopentadienylmolybdenum chloride, $C_5H_5Mo(CNPh)_3Cl$. It reacted with the corresponding iodide (VII; X = I) by replacement of only one carbonyl group. The analogous iron compounds (VIII; L = CO) were treated with the isocyanide in benzene. The iodide (VIII; X = I; L = CO) afforded a mixture of mono- (VIII; X = I; L = XNPh) and bis(phenyl isocyanide) derivatives. The bromide gave only the latter type, and the chloride underwent addition and substitution to give the ionic tris(phenyl isocyanide)cyclopentadienyliron chloride. These iron compounds



(VII)



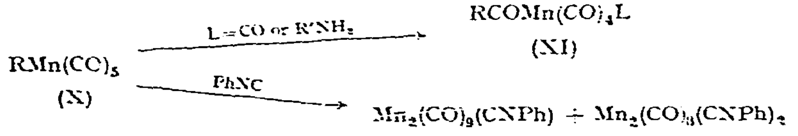
(VIII)



(IX)

show similar differences in their reactions with triphenylphosphine. The chloride (VIII; X = Cl; L = CO) has been shown[12] to give mainly the ionic addition product (IX; X = Cl) whereas the iodide (VIII; X = I; L = CO) gives a mixture of the addition (IX; X = I) and substitution (VIII; X = I; L = PPh_3) products[9]. The latter compound was found to react with phenyl isocyanide in the same manner as the corresponding dicarbonyl (VIII; X = I; L = CO), but attempts to bring about the reverse process, replacement of isocyanide (or CO) from complex (VIII; X = I; L = CNPh) by triphenylphosphine failed. Together with the abovementioned behaviour of bromotricarbonylbis(triphenylphosphine)manganese, these experiments show that replacement of the phosphine is easier than replacement of either carbon monoxide or isocyanide from such mixed complexes.

We have also examined the reactions of phenyl isocyanide with methyl- and phenylpentacarbonylmanganese (X; R = Me or Ph). By analogy with their behaviour



with carbon monoxide[6] and with amines[13], we expected addition to occur with the formation of acyl derivatives of the type (XI; L = CNPh). Instead, the only products isolated, albeit in low yield, were mono- (XII) and disubstitution products (XIII) of dimanganese decacarbonyl. The fate of the methyl and phenyl groups in these reactions has not been determined.

EXPERIMENTAL

All reactions were conducted under nitrogen.

Starting materials were prepared by the literature methods indicated: $BrMn(CO)_5$[3a]; PhNC[14]; $Mn(CNPh)_6^+I^-$[7]; $C_5H_5Mo(CO)_3X$[15]; $C_5H_5Fe(CO)_2X$[16]; Me- and $PhMn(CO)_5$[17]; $Br_2Mn_2(CO)_8$[3a]; $BrMn(CO)_3(PPh_3)_2$[1a]; $C_5H_5Fe(CO)(PPh_3)I$[9].

[Text continued p. 57]

TABLE I

Reactant with quantity (g and mmole)			Quantity of Phenyl isocyanide (g and mmole)		Solvent* Quantity in ml		Reaction temp.†	Time (h)	Structure	Product g	% yield or recovery
$Br_2Mn_2(CO)_8$	0.43	0.87	0.8	8	T	50	r.t.	4	$BrMn(CO_4)CNPh$	0.14	45
$BrMn(CO)_5$	2.75	10	2.06	20	A	60	60°	3	$BrMn(CO)_3(CNPh)_2$	3.05	70
$BrMn(CO)_5$	1.37	5	1.54	15	D	50	100°	3	$BrMn(CO)_2(CNPh)_3$	1.6	65
$IMn(CO)_5$	0.5	1.5	1.0	10	T	30	R	3	$IMn(CO)(CNPh)_4$	0.47	51
$BrMn(CO)_3(PPh_3)_2$	1.83	2.5	1.03	10	T	50	R	3	$BrMn(CO)(CNPh)_4$	0.63	44
$BrMn(CO)_5$	2.75	10	5.15	50	T	100	R	6	$BrMn(CO)(CNPh)_4$**	2.3	40
									$BrMn(CNPh)_5$**	0.4	6.1
$ClMn(CO)_5$	2.3	10	5.15	50	T	50	R	4	$Cl[Mn(CNPh)_6]$	2.3	32
$C_5H_5Mo(CO)_3I$	1.8	5	4.12	40	T	50	R	3.5	$C_5H_5Mo(CO)_2(CNPh)I$	0.42	19
$C_5H_5Mo(CO)_3Cl$	1.4	5	1.5	15	T	50	R	4	$C_5H_5Mo(CNPh)_3Cl$	1.2	45
$C_5H_5Fe(CO)_2I$	18.2	60	9.0	870	B	150	R	6	$C_{10}H_{10}Fe$***	0.1	1
									$C_5H_5Fe(CO)_2I$***	9.7	53
									$C_5H_5(CO)(CNPh)I$***	8.5	35
									$C_5H_5Fe(CNPh)_2I$***	2.3	8
$C_5H_5Fe(CO)_2Br$	1.28	5	1.01	10	B	60	R	3	$C_5H_5Fe(CNPh)_2Br$	0.75	37
$C_5H_5Fe(CO)_2Cl$	4.24	20	6.18	60	B	50	R	1.5	$Cl[C_5H_5Fe(CNPh)_3]$	6.3	68
$C_5H_5Fe(CO)(CNPh)I$	1.23	3.3	0.87	3.3††	B	60	R	3	$C_5H_5Fe(CO)(CNPh)I$	1.1	89
$C_5H_5Fe(CO)(PPh_3)I$	1.08	2	0.2	2	B	60	R	3	$C_5H_5Fe(CO)(CNPh)I$***	0.048	6
									$C_5H_5Fe(CO)(PPh_3)I$***	0.1	9
									$C_5H_5Fe(CNPh)_2I$***	0.38	42
$CH_3Mn(CO)_5$	2.1	10	1.8	18	T	40	R	3	$Mn_2(CO)_{10}$***	0.015	
									$Mn_2(CO)_9CNPh$***	0.132	5.6
									$Mn_2(CO)_8(CNPh)_2$***	0.112	4
$C_6H_5Mn(CO)_5$	2.7	10	1.0	10	T	60	R	2	$C_6H_5Mn(CO)_5$***	—	—
									$Mn_2(CO)_9CNPh$***	0.14	5
									$Mn_2(CO)_8(CNPh)_2$***	0.095	3

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* A = ethanol; B = benzene; D = diethylene glycol dimethyl ether; E = ether; L = ligroin, b.p. 60/80°; M = methylene chloride; P = pentane; T = tetrahydrofuran.

** Separated by extraction of $BrMn(CO)(CNPh)_4$ with benzene, leaving $BrMn(CNPh)_5$ almost undissolved.

*** Separated by chromatography on alumina; products (incl. recovered starting material) are given in order of elution.

† r.t. = room temperature; R = at reflux.

†† Triphenylphosphine.

TABLE 2

Product	*Solvent(s) for crystallisation**	*M.p. (°C)*	*Principal I.R. maxima (cm⁻¹): medium*	*Colour*
$BrMn(CO)_4CNPh$	M/L	86–87	2188(w), 2107(w), 2045(s), 1993(m): CCl_4	Yellow
$BrMn(CO)_3(CNPh)_2$	P	84–86	2198(m), 2174(s), 2053(s), 2004(s), 1954(s): KCl	Pale Yellow
$BrMn(CO)_2(CNPh)_3$	E	129–130	2179(w), 2114(s), 2049(s), 2020(s), 1942(s): KCl	Yellow
$IMn(CO)(CNPh)_4$	E	171	2088(s), 1992(m), 1894(s): KCl	Yellow
$BrMn(CO)(CNPh)_4$	T	180 (dec.)	2101(v.s.), 2012(m), 1919(s): CCl_4	Orange
$BrMn(CNPh)_5$	T	213 (dec.)	2101(v.s.), 2012(m): $C_2H_4Cl_2$	Colourless
$Cl[Mn(CNPh)_6]$	M/L	178	2114(v.s.), 2016(s): KCl	Pale Yellow
$C_5H_5Mo(CO)_2(CNPh)I$	P	75	2141(s), 2070(m), 2004(s), 1942(s): CCl_4	Red
$C_5H_5Mo(CNPh)_3Cl$	M/L	180 (dec.)	2169 (m), 2096 (s): KCl	Red
$C_5H_5Fe(CO)(CNPh)I$	M/L	108	2151(s), 1969(s): KI	Brown
$C_5H_5Fe(CNPh)_2I$	M/L	104–105	2155(s), 2056(s), 2024(w): KI	Red
$C_5H_5Fe(CNPh)_2Br$	M/L	107	2155(s), 2087(s), 2020(w): KI	Purple
$Cl[C_5H_5Fe(CNPh)_3]$	M/L	174	2190(s), 2123(s): KCl	Orange
$Mn_2(CO)_9CNPh$	P	54	2169(s), 2102(s), 2045(s), 2016(s), 1980(s): CCl_4	Yellow
$Mn_2(CO)_8(CNPh)_2$	P	111	2165(w), 2128(m), 2061(m), 2020(m), 1996(s), 1957(m): CCl_4	Yellow

* As in Table 1.

TABLE 3

Product	*Empirical Formula*	*Found* *C*	*Found* *H*	*Found* *N*	*Found* *Other*	*Calcd.* *C*	*Calcd.* *H*	*Calcd.* *N*	*Calcd.* *Other*
$BrMn(CO)_4CNPh$	$C_{11}H_5BrMnNO_4$	37.4	1.8	4.2		37.7	1.4	4.0	
$BrMn(CO)_3(CNPh)_2$	$C_{17}H_{10}BrMnN_2O_3$	48.7	2.4	7.0		48.0	2.4	6.6	
$BrMn(CO)_2(CNPh)_3$	$C_{23}H_{15}BrMnN_3O_2$	55.4	3.0	8.7		55.2	3.0	8.4	
$IMn(CO)(CNPh)_4$	$C_{29}H_{20}IMnN_4O$	55.6	3.3	9.2		55.9	3.3	9.0	
$BrMn(CO)(CNPh)_4$	$C_{29}H_{20}BrMnN_4O$	61.2	4.0	9.7	Br, 14.0 O, 3.1 mol.wt., 567*	60.6	3.5	9.7	Br, 13.9 O, 2.8 mol.wt., 573
$BrMn(CNPh)_5$	$C_{35}H_{25}BrMnN_5$	64.9	4.3	11.0	Br, 12.5	64.6	3.9	10.8	Br, 12.2
$Cl[Mn(CNPh)_6]$**	$C_{42}H_{30}ClMnN_6$	70.7	4.5	11.8		71.1	4.3	11.8	
$C_5H_5Mo(CO)_2(CNPh)I$	$C_{14}H_{10}IMoNO_2$	37.0	2.4	3.3	O, 7.0	37.6	2.3	3.1	O, 7.2
$C_5H_5Mo(CNPh)_3Cl$	$C_{26}H_{20}ClMoN_3$	63.9	3.6	8.5		64.1	4.0	8.3	
$C_5H_5Fe(CO)(CNPh)I$	$C_{13}H_{10}FeINO$	41.7	2.8	3.8		41.2	2.7	3.7	
$C_5H_5Fe(CNPh)_2I$	$C_{19}H_{15}FeIN_2$	50.0	3.7	5.5		50.2	3.3	6.1	
$C_5H_5Fe(CNPh)_2Br$				7.1				6.9	
$Cl[C_5H_5Fe(CNPh)_3]$	$C_{26}H_{20}ClFeN_3$	67.0	4.5	9.1		67.0	4.3	9.0	
$Mn_2(CO)_9CNPh$	$C_{15}H_5Mn_2NO_9$	41.1	1.5	3.1		41.3	1.1	3.0	
$Mn_2(CO)_8(CNPh)_2$	$C_{22}H_{10}Mn_2N_2O_8$	49.1	2.6	5.2		48.9	1.9	5.2	

* Cryoscopically in benzene.

** Conductivity measured in nitrobenzene at 25°: $\lambda\infty = 28.4\ \Omega^{-1}$ for $[Mn(CNPh)_6]I$, $\lambda\infty = 27\ \Omega^{-1}$.

Reaction conditions are indicated in Table 1; properties of the products in Table 2 and analyses in Table 3.

The mixtures were heated with stirring at the temperatures and for the times indicated. The solvent and excess isocyanide (if any) were then removed by distillation *in vacuo* and the products purified by chromatography and/or by recrystallisation as indicated.

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SUMMARY

The reactions of phenyl isocyanide with various halomanganese carbonyls, methyl- and phenylmanganese pentacarbonyls, halocyclopentadienyl-molybdenum and -iron carbonyls are described. The dependence of the degree of substitution on the nature of the halogen and the solvent is examined. As a result a number of new isocyanide derivatives of these metals have been isolated and characterised.

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