Catalysed and Non-catalysed Reaction Between [Fe(CO)$_5$] and Isonitriles

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The reaction between [Fe(CO)$_5$] and isonitrile, RNC, is catalysed by CoCl$_2$·H$_2$O and readily yields the complexes [Fe(CO)$_{5-n}$(CNR)$_n$] (n = 1—3, R = Me, C$_6$H$_{11}$, Bu^t, PhCH$_2$, Ph, 2,6-Me$_2$C$_6$H$_3$, or 2,4,6-Me$_3$C$_6$H$_2$; n = 4, R = Bu^t; n = 4 or 5, R = Ph, 2,6-Me$_2$C$_6$H$_3$, or 2,4,6-Me$_3$C$_6$H$_2$). The high-yield synthesis of [Fe(CO)$_4$(CNR)] from [Fe(CO)$_5$] and RNC in the absence of catalyst is also reported. Trimethylamine *N*-oxide has been used to synthesize [Fe(CO)$_3$(CNR)$_2$] from [Fe(CO)$_4$(CNR)] and RNC and results are compared with the CoCl$_2$ catalysed reaction. All products were characterized by i.r. and n.m.r. spectroscopy. The higher substituted derivatives were further characterized by reaction with I$_2$ and tetracyanoethylene (tcne) and gave [Fe(CO)$_{4-n}$(CNR)$_n$(tcne)] (n = 2, R = Bu^t, PhCH$_2$, or 2,6-Me$_2$C$_6$H$_3$; n = 3, R = Bu^t or 2,6-Me$_2$C$_6$H$_3$; n = 4, R = 2,6-Me$_2$C$_6$H$_3$) and *cis*- and *trans*-[Fe(CNC$_6$H$_3$Me$_2$-2,6)$_4$I$_2$] from appropriate starting materials. Mechanistic data suggest that the reaction occurs *via* attack of catalyst at a co-ordinated CO ligand. Subsequent attack by unco-ordinated RNC in an intermolecular, non-bridging mechanism leads to the required isonitrile derivatives.

AN extensive chemistry of transition-metal–isonitrile complexes has been developed and the synthesis of this class of compounds has been well reviewed.[1-4] Synthetic methods are varied and include the substitution of metal carbonyl complexes by isonitriles (RNC) Although a viable and attractive route, direct multiple replacement of CO groups by RNC has in general failed as high temperatures, *i.e.* those which also induce product or reactant decomposition, are required to bring about the CO substitution reaction.

This is exemplified by the reaction between [Fe(CO)$_5$] and RNC. Attempts to prepare [Fe(CO)$_{5-n}$(CNR)$_n$] (n = 1—5) by heating the reactants in the absence of solvent have resulted in the synthesis of only mono- ($n = 1$) or di-substituted ($n = 2$) products.[5,6] Alternative procedures starting from [Fe$_2$(CO)$_9$],[7] [Fe$_3$(CO)$_{12}$],[8] or the photochemical reaction[9] between [Fe(CO)$_5$] and RNC have only led to complexes with $n \leqslant 2$. Similar results were obtained when [Fe(CO)$_5$] was reacted with isonitrile precursors such as isocyanates,[10] phosphine-imines,[11] isocyanide dichlorides,[12,13] and metal bis(trimethylsilyl)amides.[14] Indeed, the only iron(0) complex known with $n > 2$ is the complex [Fe(CNR)$_5$], prepared either *via* metal-atom techniques or by reducing FeBr$_2$ in the presence of RNC.[15]

In this publication we wish to report on our successful attempts to synthesize [Fe(CO)$_{5-n}$(CNR)$_n$] (n = 1—5) from [Fe(CO)$_5$] and RNC in the presence of transition-metal catalysts under mild reaction conditions. We have concentrated our efforts on the use of CoCl$_2$·2H$_2$O as catalyst because of its low cost, ready availability, and the facility with which it catalyses multiple CO substitution reactions. A preliminary report of this work has been published.[16]

For comparison we have also included our data on the thermal reaction between [Fe(CO)$_5$] and RNC in benzene and the ' reagent induced ' reaction between [Fe(CO)$_4$(CNR)] and RNC in the presence of trimethylamine *N*-oxide.[17]

EXPERIMENTAL

Pentacarbonyliron was purchased from Strem Chemicals. The isonitriles were either purchased from Fluka A.G. (Bu^{t}NC, C$_6$H$_{11}$NC, and 2,6-Me$_2$C$_6$H$_3$NC), Aldrich (PhCH$_2$NC), or prepared by the literature methods[18,19] (2,4,6-Me$_3$C$_6$H$_2$NC, PhNC, and MeNC). The catalyst CoCl$_2$·2H$_2$O was obtained by heating CoCl$_2$·6H$_2$O (Riedel-de-Haen A.G.) *in vacuo* at *ca.* 50 °C for 5 h. All reactions were routinely carried out under an argon atmosphere with dry, degassed solvents. Merck Kieselgel 60 (60—200 μm) silica gel and 150 × 2 cm columns were used throughout.

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP 300 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a Bruker WP 80 FTNMR spectrometer, and mass spectra were recorded on a Varian CH5 spectrometer (operating at 70 eV).† Microanalyses were performed by the Microanalytical Laboratories, C.S.I.R. Magnetic susceptibility measurements were determined using a variable-temperature Gouy Balance System (Newport Instruments) fitted with a 10 cm electromagnet and a Stanton model S.M. 12 precision balance.

Preparation of [Fe(CO)$_4$(CNR)] (R = Me, C$_6$H$_{11}$, Bu^t, PhCH$_2$, Ph, 2,6-Me$_2$C$_6$H$_3$, *or* 2,4,6-Me$_3$C$_6$H$_2$) (1a)—(1g).—*Method* (*A*) (*thermal reaction*). [Fe(CO)$_5$] (7.84 g, 40 mmol) and isonitrile (20 mmol) were refluxed for 0.5 h in benzene (60 cm^3). The end of the reaction was evidenced by cessation of CO evolution and a rapid darkening of the reaction solution. The cold solution was passed down a short silica column (*ca.* 50 g) and eluted with benzene. Excess [Fe(CO)$_5$] and solvent were removed on a rotary evaporator to give the products as indicated (Table 1).

Method (*B*) (CoCl$_2$ *catalysed reaction*). [Fe(CO)$_5$] (3.92 g, 20 mmol), isonitrile (20 mmol), and CoCl$_2$·2H$_2$O (0.050 g, 0.3 mmol) were combined with benzene (100 cm^3) in a 250 cm^3 round-bottomed flask, and refluxed for the appropriate time (Table 1). The green reaction solution was allowed to cool, then treated as in Method (A) above, to give the products in the recorded yields (Tables 1 and 2).

Preparation of [Fe(CO)$_3$(CNR)$_2$] (R = Me, C$_6$H$_{11}$, Bu^t,

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† Throughout this paper: 1 eV ≈ 1.602 × 10^{-19} J.

$PhCH_2$, Ph, 2,6-$Me_2C_6H_3$, *or* 2,4,6-$Me_3C_6H_2$) (2a)—(2g).—*Method* (*A*) (*$CoCl_2$ catalysed reaction*). $[Fe(CO)_4(CNR)]$ (3 mmol), $CoCl_2·2H_2O$ (0.017 g, 0.1 mmol), and benzene (20 cm^3) were combined in a reaction flask. Isonitrile (3 mmol) was added to give a green solution, which was then refluxed for the appropriate time (Table 3). The reaction solution was allowed to cool, then passed down a silica column (*ca.* 20 g) and eluted with benzene. The solvent was removed on a rotary evaporator, to give the yellow products (Tables 3 and 4).

TABLE 1

Experimental details for the thermal and $CoCl_2$ catalysed reactions[a] $[Fe(CO)_5] + RNC \longrightarrow [Fe(CO)_4(CNR)] + CO$

		Thermal reaction		$CoCl_2$ catalysed reaction	
	Product	Reaction time[b] (min)	Yield (%)	Reaction time[b] (min)	Yield (%)
(1a)	$[Fe(CO)_4(CNMe)]$	30	79	10	65
(1b)	$[Fe(CO)_4(CNC_6H_{11})]$	30	91	5	89
(1c)	$[Fe(CO)_4(CNBu^t)]$	30	96	5	85
(1d)	$[Fe(CO)_4(CNCH_2Ph)]$	30	87	5	88
(1e)	$[Fe(CO)_4(CNPh)]$	30	95	10	80
(1f)	$[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$	30	95	5	88
(1g)	$[Fe(CO)_4(CNC_6H_2Me_3\text{-}2,4,6)]$	30	95	5	88

[a] See Experimental section. [b] As determined by i.r. spectroscopy.

Method (*B*) (*trimethylamine* N-*oxide promoted reaction*). $[Fe(CO)_4(CNR)]$ (3 mmol), trimethylamine *N*-oxide (0.50 g, 4.5 mmol), and isonitrile (3 mmol) were added to 20 cm^3 of benzene. The reaction solution was refluxed for the indicated time and purification, as in Method (A) above, gave the required products (Tables 3 and 4).

TABLE 2

Analytical and spectroscopic data for the complexes $[Fe(CO)_4(CNR)]$ (1a)—(1g)

			Analysis (%)[b]			I.r.[c] (cm^{-1})		^1H N.m.r.[d] (τ)			
	Colour	M.p.[a] (°C)	C	H	N	ν(NC)	ν(CO)	CH_3	CH_2	Aromatic	Mass spectrum[b,e]
(1a)[f]	Pale yellow	34—35	34.4 (34.5)	1.45 (1.45)	6.65 (6.7)	2 199	2 060, 1 993, 1 970	8.18			209 (208.94)
(1b)[g]	Yellow	oil	48.0 (47.65)	4.0 (3.95)	5.45 (5.05)	2 183	2 063, 1 994, 1 967			8.3	277 (277.06)
(1c)[h]	Yellow	50—52	42.3 (43.05)	3.45 (3.6)	5.5 (5.6)	2 167	2 051, 1 992, 1 968	9.22			251 (251.02)
(1d)	Yellow	14—16	51.0 (50.55)	2.5 (2.45)	5.2 (4.95)	2 190	2 065, 1 998, 1 970		6.46	3.25	285 (285.04)
(1e)[i]	Yellow	56—57	49.05 (48.7)	1.9 (1.85)	5.25 (5.15)	2 150	2 050, 1 995, 1 975			3.42	271 (271.01)
(1f)[j]	Yellow	82—83	52.45 (52.2)	3.15 (3.05)	4.7 (4.7)	2 151	2 051, 1 999, 1 975	8.07		3.32	299 (279.09)
(1g)	Yellow	38—39	53.55 (53.65)	3.65 (3.5)	4.5 (4.45)	2 185	2 060, 2 000, 1 872	*k*		3.75	313 (313.09)

[a] Uncorrected. [b] Calculated values in parentheses. [c] Recorded in hexane. [d] Recorded in C_6D_6 relative to $SiMe_4$. [e] Molecular ion. [f] Ref. 5. [g] Refs. 9 and 20. [h] Ref. 25. [i] Refs. 5 and 10. [j] Y. Yamamoto and N. Yamazaki, *J. Org. Chem.*, 1977, **42**, 4138. [k] 8.13 and 8.11, ratio 2 : 1.

Preparation of $[Fe(CO)_2(CNR)_3]$ (R = Me, C_6H_{11}, Bu^t, $PhCH_2$, Ph, 2,6-$Me_2C_6H_3$, *or* 2,4,6-$Me_3C_6H_2$) (3a)—(3g).—$[Fe(CO)_4(CNR)]$ (2 mmol), $CoCl_2·2H_2O$ (0.017 g, 0.1 mmol), and benzene (20 cm^3) were combined in a reaction flask and the solution brought to reflux. Addition of isonitrile (4 mmol) gave a green solution which eventually turned orange after continued reaction in refluxing benzene. The solution was allowed to cool and then filtered under nitrogen. The residue was washed with 10 cm^3 portions of dry, degassed benzene. Solvent was then removed under vacuum and the pure complex recrystallised from toluene–pentane at −78 °C to yield an air-sensitive yellow powder (yield 50—60%) (Table 5).

Preparation of $[Fe(CO)(CNR)_4]$ (R = Bu^t, Ph, 2,6-$Me_2C_6H_3$, *or* 2,4,6-$Me_3C_6H_2$) (4a)—(4d).—$[Fe(CO)_4(CNR)]$ (2 mmol), $CoCl_2·2H_2O$ (0.017 g, 0.1 mmol), and benzene (20 cm^3) were combined in the reaction flask. At reflux, isonitrile (6 mmol) was added and the green solution refluxed for the indicated time (Table 5). The cold reaction solution was treated as above to yield the required air-sensitive products.

Preparation of $[Fe(CNR)_5]$ (R = Ph, 2,6-$Me_2C_6H_3$, *or*

TABLE 3

Experimental details for the $CoCl_2$ catalysed and trimethylamine *N*-oxide promoted reactions[a] $[Fe(CO)_4(CNR)] + RNC \longrightarrow [Fe(CO)_3(CNR)_2] + CO$

		$CoCl_2$ catalysed reaction		Trimethylamine *N*-oxide promoted reaction	
	Product	Reaction time[b] (min)	Yield (%)	Reaction time[b] (min)	Yield (%)
(2a)	$[Fe(CO)_3(CNMe)_2]$	30	88	15	88
(2b)	$[Fe(CO)_3(CNC_6H_{11})_2]$	10	92	20	93
(2c)	$[Fe(CO)_3(CNBu^t)_2]$	10	89	12	87
(2d)	$[Fe(CO)_3(CNCH_2Ph)_2]$	10	90	12	83
(2e)	$[Fe(CO)_3(CNPh)_2]$	10	95	15	95
(2f)	$[Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2]$	10	87	15	94
(2g)	$[Fe(CO)_3(CNC_6H_2Me_3\text{-}2,4,6)_2]$	10	85	15	76

[a] See Experimental section. [b] As determined by i.r. spectroscopy.

TABLE 4

Analytical and spectroscopic data for the complexes $[Fe(CO)_3(CNR)_2]$

	Colour	M.p.[a] (°C)	Analysis[b] (%)			I.r.[c] (cm^{-1})		^{1}H N.m.r.[d] (τ)			Mass spectrum[b,e]
			C	H	N	ν(NC)	ν(CO)	CH_3	CH_2	Aromatic	
(2a)[f]	Yellow	141—144[g]	37.65 (37.85)	2.65 (2.7)	12.3 (12.6)	2 160	2 000, 1 922	7.97			222 (221.99)
(2b)	Yellow	oil	52.45 (53.4)	6.0 (6.0)	7.1 (7.3)	2 130	1 995, 1 922		8.52		358 (358.22)
(2c)[h]	Yellow	98—99	50.2 (51.0)	5.9 (5.95)	9.1 (9.15)	2 130	1 998, 1 922	9.08			306 (306.15)
(2d)	Yellow	72—73	61.15 (60.95)	4.05 (3.75)	7.75 (7.5)	2 140	1 998, 1 928		6.27	3.22	374 (374.18)
(2e)	Yellow	72—73	59.15 (58.95)	2.9 (2.9)	8.2 (8.1)	2 103	1 996, 1 943			3.28	346 (346.13)
(2f)	Yellow	132—134[g]	62.3 (62.7)	4.6 (4.5)	6.95 (6.95)	2 108	2 000, 1 938	7.92		3.35	402 (402.23)
(2g)	Yellow	134—135[g]	63.15 (63.9)	5.05 (5.1)	6.3 (6.5)	2 105	1 995, 1 935	[i]		3.53	430 (430.29)

[a] Uncorrected. [b] Calculated values in parentheses. [c] Recorded in $CHCl_3$. [d] Recorded in C_6D_6 relative to $SiMe_4$. [e] Molecular ion. [f] M.p. 100—130 °C, from ref. 5. [g] With decomposition. [h] Ref. 25. [i] 7.86 and 8.08, intensity ratio 2 : 1

$2,4,6-Me_3C_6H_2$) (5a)—(5c).—$[Fe(CO)_4(CNR)]$ (2 mmol), $CoCl_2{\cdot}2H_2O$ (0.017 g, 0.1 mmol), and benzene (20 cm^3) were added to the reaction flask. Isonitrile (8 mmol) was added, and the solution refluxed for the appropriate time (Table 5). The cold reaction solution was purified as above.

Preparation of $[Fe(CO)_{4-n}(CNR)_n(tcne)]$ (n = 2—4; R = Bu^t, $PhCH_2$, *or* $2,6-Me_2C_6H_3$) (6a)—(6f).—The appropriate $[Fe(CO)_{5-n}(CNR)_n]$ (n = 2—4) complex (2 mmol) was prepared *in situ* as described above. To this warm reaction solution (*ca.* 40 °C) was added tetracyanoethylene (tcne) (2.2 mmol) and stirring was continued until CO evolution had ceased. The reaction solution was filtered and the solvent removed on a rotary evaporator. The crude product was purified by column chromatography (silica gel or neutral alumina, eluant CH_2Cl_2 or $CHCl_3$) or by crystallisation (n = 2, benzene; n = 3 or 4, CH_2Cl_2–hexane mixtures) to give the required products in typically 40—60% yield (Tables 6 and 7).

TABLE 5

Reaction times and spectroscopic data for the complexes $[Fe(CO)_{5-n}(CNR)_n]$ (n = 3—5)

	Complex	Reaction time[a] (min)	I.r.[b] (cm^{-1})		^{1}H N.m.r.[c] (τ)
			ν(NC)[d]	ν(CO)	CH_3 or CH_2
(3a)	$[Fe(CO)_2(CNMe)_3]$	180	2 128, 2 098 (sh)	1 923, 1 885	7.62
(3b)	$[Fe(CO)_2(CNC_6H_{11})_3]$	35	2 108, 2 090 (sh)	1 926, 1 884	8.72
(3c)	$[Fe(CO)_2(CNBu^t)_3]$	35	2 092, 2 061 (sh)	1 922, 1 883	8.83
(3d)	$[Fe(CO)_2(CNCH_2Ph)_3]$	25	2 134 (sh), 2 109	1 934, 1 892	6.06
(3e)	$[Fe(CO)_2(CNPh)_3]$	5	2 083, 2 053 (sh)	1 947, 1 917	
(3f)	$[Fe(CO)_2(CNC_6H_3Me_2-2,6)_3]$	5	2 065, 2 045 (sh)	1 940, 1 906	7.83
(3g)	$[Fe(CO)_2(CNC_6H_2Me_3-2,4,6)_3]$	5	2 075, 2 050 (sh)	1 940, 1 905	7.73, 8.04[e]
(4a)	$[Fe(CO)(CNBu^t)_4]$	400	2 086, 2 041	1 881	8.88
(4b)	$[Fe(CO)(CNPh)_4]$	5	2 055	1 910	
(4c)	$[Fe(CO)(CNC_6H_3Me_2-2,6)_4]$	5	2 045, 1 990 (sh)	1 903	7.69
(4d)	$[Fe(CO)(CNC_6H_2Me_3-2,4,6)_4]$	5	2 040, 2 000	1 899	7.61, 8.01[e]
(5a)	$[Fe(CNPh)_5]$	10	2 041, 1 990, 1 917 (sh)		
(5b)	$[Fe(CNC_6H_3Me_2-2,6)_5]$	10	2 028, 1 960, 1 920 (sh)		7.61
(5c)	$[Fe(CNC_6H_2Me_3-2,4,6)_5]$	10	2 014, 1 989, 1 900 (sh)		7.53, 7.99[e]

[a] Estimated by i.r. spectroscopy. [b] Recorded in C_6H_6. [c] Recorded in C_6D_6 relative to $SiMe_4$. [d] sh = Shoulder. [e] Intensity ratio 2 : 1.

Preparation of cis- *and* trans-$[Fe(CNC_6H_3Me_2-2,6)_4I_2]$ (6g) *and* (6h).—Iodine (2.0 mmol), in benzene (5 cm^3), was added dropwise to a warm reaction solution containing $[Fe(CO)(CNC_6H_3Me_2-2,6)_4]$ (2 mmol). On completion of I_2 addition the solvent was then removed on a rotary evaporator. The solid residue was then chromatographed on silica gel (eluant benzene, followed by CH_2Cl_2) and yielded green *trans*-$[Fe(CNC_6H_3Me_2-2,6)_4I_2]$ and finally brown *cis*-$[Fe(CNC_6H_3Me_2-2,6)_4I_2]$. Both materials were recrystallised from CH_2Cl_2–hexane (combined yield, 80%) (Tables 6 and 7).

Preparation of β-$[CoX_2(CNC_6H_3Me_2-2,6)_4]$ (X = Cl, Br, *or* I).—$CoX_2{\cdot}6H_2O$ (X = Cl, Br, or I; 2.0 mmol) was dissolved in acetone (40 cm^3), with heating to boiling if necessary. $2,6-Me_2C_6H_3NC$ (8.5 mmol) was added, and the mixture stirred for 15 min. The green (or brown, X = I) precipitate was filtered off and washed with several 10 cm^3 portions of cold diethyl ether. Recrystallisation was achieved from hot methanol solutions to give the required product in >70% yield (Table 8).

RESULTS AND DISCUSSION

$[Fe(CO)_4(CNR)]$ (1a)—(1g) can be prepared either by refluxing a two-fold excess of $[Fe(CO)_5]$ with RNC in benzene or *via* a transition-metal catalysed reaction between equimolar quantities of $[Fe(CO)_5]$ and RNC, also in refluxing benzene. In both instances reaction times are short, product purification trivial, and yields good to excellent. Surprisingly, only one previous attempt has been made to synthesize $[Fe(CO)_4(CNR)]$ derivatives thermally in solution (heptane).[20] The derivatives are pale yellow to yellow crystalline solids [except (1b), a yellow oil] and all are mildly oxygen and light sensitive. When pure, the compounds can be stored in the dark and under an inert atmosphere for several months with only minimal decomposition.

The catalysed and non-catalysed reactions are both trivial; however, purification of the product from the non-catalysed reaction is more simple (see below). Thus, for the studies involving the use of $[Fe(CO)_4$-

(CNR)] reported herein, we have preferred to synthesize the monosubstituted derivative in the absence of a catalyst. Care, however, must be exercised in the use of the non-catalysed reactions. The end of the reaction is very often evidenced by the rapid darkening of the reaction solution (*i.e.* from yellow or orange to green or brown). Although this effect does not appear adversely to affect the product yield, an undesirable colour is imparted to the product and purification to remove the discolouration has proved difficult. The reason for this darkening has not been thoroughly investigated, but is almost certainly due to reaction of the excess [Fe(CO)$_5$] with the product, [Fe(CO)$_4$(CNR)]. Thus, reaction of [Fe(CO)$_4$(CNC$_6$H$_3$Me$_2$-2,6)] with [Fe(CO)$_5$] under the reaction conditions produces an identical darkening of the reaction solution.

TABLE 6

Analytical data for the complexes [Fe(CO)$_{4-n}$(CNR)$_n$(XY)] (n = 2—4; XY = tcne or I$_2$)

	Complex	Colour	M.p. (°C)	Analysis [a] (%) C	H	N	halogen
(6a)	[Fe(CO)$_2$(CNBu^t)$_2$(tcne)]	Yellow	>200 [b]	53.65 (53.2)	4.65 (4.45)	20.8 (20.7)	
(6b)	[Fe(CO)$_2$(CNCH$_2$C$_6$H$_5$)$_2$(tcne)]	Yellow	[b]	61.55 (60.75)	3.15 (2.95)	17.7 (17.7)	
(6c)	[Fe(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_2$(tcne)]	Yellow	197—198 [b]	66.2 (66.2)	4.7 (4.15)	15.25 (14.5)	
(6d)	[Fe(CO)(CNBu^t)$_3$(tcne)]	Yellow	>200	56.9 (57.25)	5.8 (5.85)	21.35 (21.25)	
(6e)	[Fe(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_3$(tcne)]	Yellow	198—200 [b]	66.25 (67.45)	4.3 (4.45)	16.1 (16.2)	
(6f)	[Fe(CNC$_6$H$_3$Me$_2$-2,6)$_4$(tcne)]·0.5CHCl$_3$	Yellow	>200	66.6 (66.4)	4.6 (4.7)	14.65 (14.6)	6.35 (6.95)
(6g)	*cis*-[Fe(CNC$_6$H$_3$Me$_2$-2,6)$_4$I$_2$]	Brown	195—200 [b]	51.25 (51.3)	4.35 (4.35)	6.65 (6.7)	31.3 (30.45)
(6h)	*trans*-[Fe(CNC$_6$H$_3$Me$_2$-2,6)$_4$I$_2$]	Green	198—200 [b]				

[a] Calculated values in parentheses. [b] Decomposes without melting.

TABLE 7

Spectroscopic data for the complexes [Fe(CO)$_{4-n}$(CNR)$_n$(XY)] (n = 2—4; XY = tcne or I$_2$)

	I.r.[a,b] (cm^{-1})			^{1}H N.m.r.[c,d] (τ)		
	ν(CN)	ν(NC)	ν(CO)	CH$_3$	CH$_2$	Aromatic
(6a)	2 230 (sh)	2 206, 2 186 (sh)	2 070, 2 026, 2 012	8.48		
(6b)	2 231 (sh)	2 216	2 081, 2 034		4 97	2.50
(6c)	2 236w	2 201 (sh), 2 176, 2 156 (sh)	2 070, 2 026	7.48		2.75
(6d)	2 225 (sh)	2 210 (sh), 2 185	1 979	8.41, 8.51 [e]		
(6e)	2 230w	2 189m, 2 155	2 014	7.47, 7.53 [e]		2.80, 2.90 [e]
(6f)	2 224w	2 176m, 2 131, 2 106 (sh)		7.45, 7.54 [f]		2.80, 2.92 [f]
(6g)		2 180w, 2 142, 2 134 (sh), 2 112		7.29, 7.49 [f]		2.80, 2.82 [f]
(6h)		2 134		7.34		2.77

[a] All bands strong unless otherwise stated; w = weak, m = medium, sh = shoulder. [b] KBr matrix. [c] Recorded in CDCl$_3$ relative to SiMe$_4$. [d] Methyl and methylene resonances, singlets. [e] Relative intensity 1 : 2. [f] Relative intensity 1 : 1.

The catalysed synthesis of (1a)—(1g) has been achieved using a variety of transition-metal and other catalysts (see below) but only the use of CoCl$_2$·2H$_2$O as catalyst has been systematically investigated in detail. The addition of catalytic amounts (*ca.* 1.5 mol %) of CoCl$_2$ to [Fe(CO)$_5$] and RNC results in vigorous CO evolution from the green reaction solution. The reaction was monitored by i.r. spectroscopy and indicated at most, small amounts of [Fe(CO)$_3$(CNR)$_2$] as impurity in the reactions. No darkening of the reaction solution on completion of the reaction was evidenced in these catalysed reactions.

Purification of the reaction mixture from the catalysed reaction requires elution through a silica gel column to remove catalyst (and possibly other impurities) followed by crystallisation. By contrast the products from the non-catalysed reaction can be purified by crystallisation alone, although in general columns were used. The only difficulties that occur with the purification of the non-catalysed reaction product relate to the use of C$_6$H$_{11}$NC and PhNC. Trace amounts of the unreacted RNC made purification of the products difficult and necessitated the use of columns to obtain [Fe(CO)$_4$(CNR)] free from RNC.

The disubstituted derivatives, [Fe(CO)$_3$(CNR)$_2$] (2a)—(2g), have been synthesized by two routes; one involving the reagent trimethylamine *N*-oxide and the other route involving the use of CoCl$_2$ as catalyst.

The reaction between [Fe(CO)$_4$(CNR)] and RNC (refluxing benzene) in the presence of CoCl$_2$ as catalyst

TABLE 8

Analytical and spectroscopic data for the complexes β-[CoX$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_4$] (X = Cl, Br, or I)

	I.r. (cm^{-1})		Analysis [c] (%)				
Complex	ν(NC) [a]	ν(NC) [b]	C	H	N	halogen	$\mu_{eff.}$[d]/B.M.
β-[CoCl$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_4$]·MeOH	2 180	2 184	63.65 (64.7)	5.7 (5.85)	8.35 (8.15)	10.5 (10.35)	2.06
β-[CoBr$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_4$]	2 180	2 182	56.7 (58.15)	5.05 (4.85)	7.3 (7.55)	22.15 (21.55)	2.00
β-[CoI$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_4$]	2 170	2 170	50.75 (51.6)	6.25 (6.7)	6.45 (6.7)	30.7 (30.35)	1.82

[a] Recorded in CHCl$_3$. [b] KBr matrix. [c] Calculated values in parentheses. [d] Gouy method (293 K).

results in the rapid, facile synthesis of (2a)—(2g) in high yield (Table 3). In the absence of a catalyst the above reaction proceeds with difficulty (R = Me, C_6H_{11}, Bu^t, or $PhCH_2$) or not at all (R = Ph, 2,6-$Me_2C_6H_3$, or 2,4,6-$Me_3C_6H_2$).

The products are generally free of contamination by either starting material or higher substituted derivatives. Purification by silica-gel column chromatography (in the absence of light) is necessary to remove the catalyst which otherwise discolours the final product.

The use of trimethylamine *N*-oxide in organometallic synthesis has yielded a range of products not readily prepared by conventional means. Thus the CO substitution of $[Os_3(CO)_{12}]$,[21] $[Mn_2(CO)_{10}]$,[22] $[Fe(CO)_5]$,[23] *etc.* by ligands such as PR_3 and CH_3CN is readily achieved under mild conditions. We have thus carried out an investigation of the reaction $[Fe(CO)_4(CNR)] + RNC \longrightarrow [Fe(CO)_3(CNR)_2]$ in the presence of trimethylamine *N*-oxide to compare the results with the $CoCl_2$ catalysed reaction. Results are reported in Table 1 and it can be seen that the amine oxide route also gives the required product, rapidly, and in high yield. However, the reaction only proceeds to completion in the presence of excess of both amine oxide and RNC. Consequently excess amine oxide, isonitrile, and $[Fe(CO)_2(CNR)_3]$ are found mixed with the required product. We have also observed that the final reaction solutions are often coloured a bright yellow and this colouration is difficult to remove from the product, even by column chromatography.

Disubstituted derivatives containing two different RNC groups [6] can also be prepared by the $CoCl_2$ catalysed route. Thus, the reaction of $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$ with Bu^tNC readily produces $[Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)(CNBu^t)]$. In general, however, the preparation of the mixed derivatives is complicated by RNC exchange (see below) and separation of the disubstituted products has proven difficult.

The catalytic synthesis of $[Fe(CO)_3(CNR)_2]$ complexes can also be achieved by addition of two equivalents of RNC (either stepwise or by simultaneous addition) to $[Fe(CO)_5]$. The products prepared in this manner contain a larger percentage of $[Fe(CO)_2(CNR)_3]$ than that obtained from the $[Fe(CO)_4(CNR)]$–RNC reaction.

The complexes (2a)—(2g) are yellow crystalline solids, oxygen and light sensitive, particularly in the presence of impurities. They are generally difficult to store for extended periods of time but, if necessary, can be stored in the dark, under nitrogen, below 0 °C.

The $[Fe(CO)_2(CNR)_3]$ derivatives (3a)—(3g) have been synthesized by the $CoCl_2$ catalysed reaction between $[Fe(CO)_4(CNR)]$ and RNC in refluxing benzene (Table 5). In the absence of a catalyst no reaction between $[Fe(CO)_3(CNR)_2]$ and RNC has been detected (or reported in the literature). The only evidence we have obtained for a non-catalytic synthesis of $[Fe(CO)_2(CNR)_3]$ is *via* the reaction between $[Fe_3(CO)_{12}]$ and Bu^tNC (benzene, 80 °C). Infrared spectra recorded on the reaction mixture indicated the presence of $[Fe(CO)_2(CNBu^t)_3]$ (*ca.* 30%).

Whereas the synthesis of $[Fe(CO)_4(CNR)]$ (1a)—(1g) and $[Fe(CO)_3(CNR)_2]$ (2a)—(2g) all required reaction times of less than 10 min, a marked difference in the reactivity of alkyl and aryl isonitriles is apparent in the synthesis of $[Fe(CO)_2(CNR)_3]$ (3a)—(3g). Thus complete synthesis of (3a)—(3d) requires 25—35 min whereas those for the aryl derivatives (3e)—(3g) are all complete in $\leqslant$5 min.

The synthesis of (3a)—(3g) can also be achieved by the stepwise addition of two or three equivalents of RNC to either $[Fe(CO)_4(CNR)]$ or $[Fe(CO)_5]$ and the final product is obtained in good yield and purity.

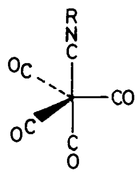
Compounds (3a)—(3g) are all yellow solids which are oxygen and light sensitive. The complexes rapidly darken and decompose even under an inert atmosphere. Stability has been found to decrease from aryl- to alkyl-isonitrile complexes. Due to their oxygen sensitivity the $[Fe(CO)_2(CNR)_3]$ complexes must be handled under an inert atmosphere and in dry, degassed solvents at all times. Purification was achieved by precipitation from the reaction mixture followed by recrystallisation. The alkyl derivatives (*e.g.* RNC = MeNC or Bu^tNC) react with solvents such as $CHCl_3$ and CH_2Cl_2, presumably *via* an oxidation mechanism.

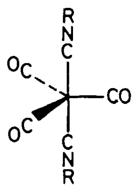
Addition of three equivalents of RNC to $[Fe(CO)_4(CNR)]$ in the presence of $CoCl_2$ in refluxing benzene yields the new complexes $[Fe(CO)(CNR)_4]$ (4a)—(4d). Simultaneous or stepwise addition of the equivalents of RNC leads to the same product. Attempts to prepare $[Fe(CO)(CNR)_4]$ (R = Me, C_6H_{11}, or $PhCH_2$), even with extended reaction times (*ca.* 24 h) were unsuccessful and the prolonged reaction time only resulted in reactant decomposition. $[Fe(CO)(CNBu^t)_4]$ was obtained only with difficulty (*ca.* 50% yield after 7 h) and the use of other solvents, *e.g.* tetrahydrofuran (thf) or toluene, did not give this product in higher yield.

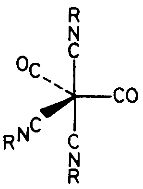
Complex (4a) was found to precipitate from the hot reaction solution as a yellow crystalline material. Filtration under nitrogen followed by recrystallisation from toluene–pentane at −78 °C gave the pure product. Complexes (4b)—(4d) were completely soluble in the reaction solution and were purified by crystallisation from toluene–pentane at −78 °C; (4a)—(4d) are all yellow or orange, oxygen and light sensitive materials.

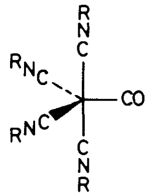
The simultaneous or stepwise addition of four equivalents of RNC to $[Fe(CO)_4(CNR)]$ in refluxing benzene and in the presence of $CoCl_2$ leads to the $[Fe(CNR)_5]$ derivatives (5a)—(5c). Attempts to prepare $[Fe(CNBu^t)_5]$ [15,24] *via* this route have been unsuccessful. The complexes (5a)—(5c) are red, oxygen and light sensitive materials, susceptible to oxidation by O_2 and solvents such as $CHCl_3$ and CH_2Cl_2.

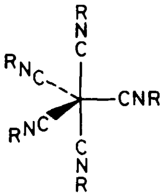
Product Characterization.—All the complexes have been characterized by i.r. and n.m.r. spectroscopy (Tables 2, 4, and 5). Where possible, the complexes have also been characterized by mass spectrometry and elemental analyses. Possible structures for the complexes $[Fe(CO)_{5-n}(CNR)_n]$ (n = 1—5), assuming idealized trigonal-bipyramidal structures, are shown below.











The $[Fe(CO)_4(CNR)]$ derivatives (1a)—(1g) all contain one ν(NC) and three ν(CO) stretching frequencies consistent with axial substitution of the trigonal bipyramid by RNC, as reported previously.[25]. The ν(NC) stretching frequencies are all higher than ν(NC) for the free ligand, consistent with the higher π-acceptor ability of CO relative to RNC.[1-4] The ^1H n.m.r. spectra all show the expected singlet for the CH_2 or CH_3 resonance (where applicable) and in every case the resonance is moved downfield relative to the free isonitrile. No long-range ^1H–^{14}N coupling, as detected for $[Cr(CO)_5(CNR)]$,[26] was observed. The $[Fe(CO)_4(CNR)]$ complexes were further characterized by mass spectrometry. In every case the spectra indicated the presence of the parent ion, M^+, as well as fragments corresponding to the stepwise loss of CO groups. In addition, fragments corresponding to breakdown of the RNC ligand were also observed on occasion. The mass spectral data (fragments, intensity data) for a typical example, $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$, are given in Table 9.

TABLE 9

Mass spectral data for the complexes $[Fe(CO)_{5-n}(CNC_6H_3Me_2\text{-}2,6)_n]$ (n = 1—5) [a]

	$n = 1$ [b]	$n = 2$ [c]	$n = 3$ [d]	$n = 4$	$n = 5$
FeL_5^+					5
$Fe(CO)L_4^+$			<1	<1	<5
FeL_4^+			1	<1	12
$Fe(CO)_2L_3^+$			3		
$Fe(CO)L_3^+$			5		
FeL_3^+			23	5	22
$Fe(CO)_3L_2^+$		16	9		
$Fe(CO)_2L_3^+$		24	16		
$Fe(CO)L_2^+$		20	13		
FeL_2^+		100	100	100	74
$Fe(CO)_4L^+$	7				
$Fe(CO)_3L^+$	12				
$Fe(CO)_2L^+$	14				
$Fe(CO)L^+$	30				
FeL^+	100	92	91	74	40
L^+	49	50	91	78	100
Fe^+	63	57	39	72	51

[a] Only m/z values >100 reported (except Fe^+); spectra recorded at 25—200 °C. [b] $m^* = 162.5$ $[Fe(CO)L^+ \longrightarrow FeL^+]$; doubly charged ions, $Fe(CO)_{3-n}L^{2+}$ (n = 0—3) and L^{2+}, observed at m/z = 135.5, 121.5, 107.5, 93.5, and 64.5 respectively (intensity <1%). [c] $m^* = 292$ $[Fe(CO)L_2^+ \longrightarrow FeL_2^+]$. [d] $m^* = 292$ $[Fe(CO)L_2^+ \longrightarrow FeL_2^+]$; doubly charged ions FeL_3^{2+} (m/z = 224.5) $Fe(CO)L_2^{2+}$ (173), FeL_2^{2+} (159), and FeL^{2+} (93.5) were observed.

The i.r. data for the $[Fe(CO)_3(CNR)_2]$ derivatives are consistent with the data reported previously, *i.e.* diaxial substitution of the trigonal bipyramid.[25] The unexpected observation of two ν(CO) bands has already received attention and is most probably a result of a deviation from the idealised D_{3h} symmetry obtained by the bending of the CNC unit of the isonitrile ligand. A crystal structure determination is presently underway to confirm this prediction. The frequency of ν(NC) in (2a)—(2g) is lowered with respect to ν(NC) in (1a)—(1g) and this is interpreted in terms of an increase in electron density on the Fe atom due to the greater σ-donor ability of the RNC ligand, relative to CO.

The ^1H n.m.r. spectra show the expected singlets for the CH_3 and CH_2 resonances where applicable. The mass spectra of (2a)—(2g) all show fragments corresponding to M^+, loss of CO, and breakdown of the RNC ligand. Mass spectral data for $[Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2]$ are shown in Table 9.

Trisubstitution of $[Fe(CO)_5]$ leads to $[Fe(CO)_2(CNR)_3]$ and the overall geometry is expected to consist of a trigonal-bipyramidal structure containing two CO ligands in the equatorial plane. An analysis of this structure (C_{2v} symmetry) leads to the expectation of two ν(CO) and three ν(NC) absorptions in the i.r. spectrum. The i.r. spectra are all found to contain two ν(CO) and one broad ν(NC) band centred at 2 060—2 110 cm^{-1} which are reasonably consistent with the analysis. However, a structure containing one axial and one equatorial CO group (C_s symmetry) on analysis would also be consistent with the data, *i.e.* two ν(CO) and one ν(NC) band. The ^1H n.m.r. data all show singlets for the methyl or methylene resonances, where appropriate. The n.m.r. data thus indicate that the structure is fluxional at ambient temperature and hence do not differentiate between the C_s and C_{2v} structures. The mass spectrum of $[Fe(CO)_2(CNC_6H_3Me_2\text{-}2,6)_3]$ is in agreement with the structure formulation and the data are recorded in Table 9. A feature of these data is the appearance of fragments corresponding to $Fe(CO)_3L_2^+$ and $Fe(CO)L_4^+$. This suggests that a reaction such as $2[Fe(CO)_2L_3] \longrightarrow [Fe(CO)_3L_2] + [Fe(CO)L_4]$ is occurring in the mass spectrometer, as has been observed for the isonitrile derivatives of Group 6 metal hexacarbonyls.[26] Two independently synthesized and purified samples of $[Fe(CO)_2(CNC_6H_3Me_2\text{-}2,6)_3]$ gave mass spectra with identical intensity data ratios (180 °C) and this implies that the above results are not attributable to the presence of $[Fe(CO)_3L_2]$ and $[Fe(CO)L_4]$ impurities.

The $[Fe(CO)(CNR)_4]$ complexes can have either of two possible geometries, a structure with the CO axial (C_{3v}) or equatorial (C_{2v}) with respect to a trigonal-bipyramidal structure. An analysis of both structures indicates that either one ν(CO) and three ν(NC) (C_{3v}) or one ν(CO) and four ν(NC) (C_{2v}) absorption bands are expected. The i.r. data indicate a single ν(CO) band at 1 880—1 910 cm^{-1} and one or two broad bands [ν(NC)], between 1 990 and 2 100 cm^{-1}. Band overlap thus makes it impossible to decide on the structure geometry on i.r. evidence alone, although the C_{2v} structure is expected on electronic grounds.[27] The ^1H n.m.r. spectra all show single methyl resonances for (4a), (4c), and (4d), and again fluxional behaviour is observed. The mass spectrum of one of the derivatives, $[Fe(CO)(CNC_6H_3Me_2\text{-}2,6)_4]$ (Table 9), confirms the identity of the tetrasubstituted complexes.

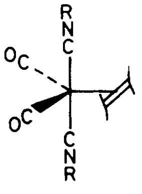
Characterization of the $[Fe(CNR)_5]$ derivatives has also been achieved by a combination of i.r. and n.m.r. spectroscopy. The i.r. spectra all contain a broad complex absorption in the region 1 900—2 050 cm^{-1} and the i.r. spectrum of (5b) is in complete agreement with that reported previously.[15] The ^1H n.m.r. spectra of (5b) and (5c) both show singlets for the methyl resonances. It has been reported that (5b) is fluxional down to low temperatures (−90 °C) and (5a) and (5c) most probably behave similarly at low temperatures. The mass spectrum of $[Fe(CNC_6H_3Me_2\text{-}2,6)_5]$ is shown in Table 9 and further confirms the proposed formulation of the substituted derivatives.

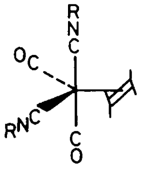
We have further characterized the new complexes $[Fe(CO)_{5-n}(CNR)_n]$ (n = 2—4) by chemical reaction with tcne and iodine. The oxidation reactions lead to stable products of the type $[Fe(CO)_{4-n}(CNR)_nL]$ (n = 2—4 L = tcne or I_2). The tcne derivatives are similar to the $[Fe(CO)_{4-n}(CNR)_n(olefin)]$ (n = 1—3) complexes which we have previously prepared from $[Fe(CO)_4(olefin)]$ and RNC in the presence of $[RhCl(CO)(PPh_3)_2]$ as catalyst.[28]

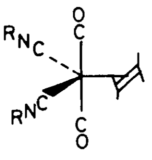
Thus addition of tcne to $[Fe(CO)_{5-n}(CNR)_n]$ (n = 2, R = Bu^t, $PhCH_2$, or $2,6\text{-}Me_2C_6H_3$; n = 3, R = Bu^t or $2,6\text{-}Me_2C_6H_3$; n = 4, R = $2,6\text{-}Me_2C_6H_3$) gives the complexes $[Fe(CO)_{4-n}(CNR)_n(tcne)]$ (6a)—(6f). Similarly, addition of I_2 to $[Fe(CO)(CNC_6H_3Me_2\text{-}2,6)_4]$ gives *cis*- and *trans*-$[Fe(CNC_6H_3Me\text{-}2,6)_4I_2]$ (6g)—(6h).

The reactions are facile and reflect the ease of oxidation of the parent zerovalent isocyanide complexes. Although the displacement of either CO or RNC is possible, on the basis of the products detected, the dominant, if not exclusive reaction, is CO displacement.

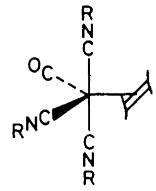
The new complexes (6a)—(6h) have been completely characterized by i.r. and n.m.r. spectroscopy (Table 7) and elemental analyses (Table 6). Complexes (6b) and (6c) each show two bands while (6a) shows three bands attributable to ν(CO) in their respective i.r. spectra (KBr). The latter is probably due to a solid-state effect since in CH_2Cl_2 only two ν(CO) bands are observed (2 063 and 2 009 cm^{-1}) for (6a). The ^1H n.m.r. spectra of (6a)—(6c) show only single peaks for the methyl and methylene resonances. Neither i.r. nor n.m.r. spectroscopy can thus be used to distinguish between the three possible isomeric structures for (6a)—(6c) shown below.

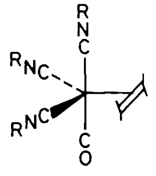




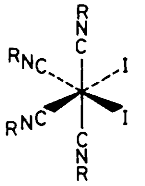


Complexes (6d)—(6e) both show a single ν(CO) band in the i.r. spectrum. This together with the ^1H n.m.r. spectra (2 : 1 ratio for the CH_3 resonance) is consistent with either of the two structures shown below.

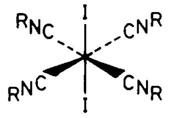




The similarity between the i.r. and n.m.r. data for (6f) and (6g) suggest that (6g) is the *cis* isomer of $[Fe(CNC_6H_3Me_2\text{-}2,6)_4I_2]$. This is also apparent from the n.m.r. and i.r. spectra of (6h) which are consistent with a *trans* configuration (see below). The isomers (6g) and (6h) are readily separated by column chromatography but thermally interconvert in benzene (80 °C).



cis

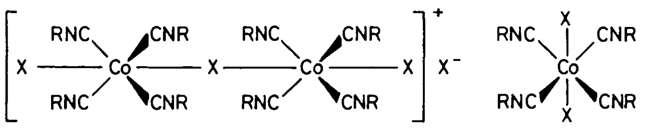


trans

Mechanistic Studies.—Addition of Bu^tNC to $[Fe(CO)_4(CNBu^t)]$ and $CoX_2\cdot nH_2O$ (X = Cl, Br, or I; n = 2, 3, or 4 respectively) under standard reaction conditions (see Experimental section) results in the rapid formation of $[Fe(CO)_3(CNBu^t)_2]$. During this reaction the catalyst changes colour from blue to green, the solution turns green, and vigorous evolution of CO (as detected by I_2O_5) takes place. No CO_2 evolution, as detected by aqueous solutions of $Ba(OH)_2$, is observed. Infrared spectra and elemental analyses of the used catalyst are in accordance with its formulation as $[CoX_2(CNBu^t)_4]$.

This compound can readily be prepared from $CoX_2\cdot nH_2O$ and Bu^tNC in refluxing methanol, benzene, or acetone. Addition of catalytic amounts of $[CoX_2(CNBu^t)_4]$, prepared as above, to $[Fe(CO)_4(CNBu^t)]$ and Bu^tNC results in the same rapid catalysis and colour changes as observed for the addition of the appropriate $CoX_2\cdot nH_2O$ catalyst (see below). Identical results were also observed when $[Fe(CO)_4(CNR)]$ was reacted with RNC (catalysed by $CoCl_2\cdot 2H_2O$) to give $[Fe(CO)_3(CNR)_2]$ (R = Me, C_6H_{11}, $PhCH_2$, Ph, $2,6\text{-}Me_2C_6H_3$, or $2,4,6\text{-}Me_3C_6H_2$) and for the catalytic synthesis of $[Fe(CO)_{5-n}(CNR)_n]$ (n = 1—5) derivatives.

It is thus apparent that the initial step in the reactions under investigation is the formation of $[CoX_2(CNR)_4]$ from CoX_2 and RNC. Complexes of this type are known to exist in two forms, one diamagnetic [α modification, (a)] and the other paramagnetic [β modification, (b)].[29] A magnetic moment determination (Gouy method) on $[CoX_2(CNC_6H_3Me_2\text{-}2,6)_4]$ (X = Cl, Br, or I) has established the paramagnetic nature of these complexes (Table 8). Further, the data are in agreement with previously reported magnetic moment data on related complexes.[29,30]



(a) (b)

Further observations pertaining to the use of the catalysts have been made and are listed below.

(1) Water has no effect on the reaction. Although we have routinely dried the cobalt salts *in vacuo*, use of $CoCl_2{\cdot}6H_2O$ does not detectably influence the course of the reaction. In practice, addition of $CoCl_2{\cdot}6H_2O$ to refluxing benzene prior to reactant addition was found to dehydrate the catalyst, as detected by a colour change of the catalyst from pink to blue.

(2) The use of $Co(PF_6)_2$, $CoSO_4$, $Co(NO_3)_2$, and $Co(O_2CMe)_2$ as catalysts for the substitution reaction rules out the need for halide participation and the use of $Co(PF_6)_2$ rules out the need for a bridging anion in the reaction mechanism (see below).

(3) The catalysed and uncatalysed reaction $[Fe(CO)_4(CNR)] + RNC \longrightarrow [Fe(CO)_3(CNR)_2]$ is unaffected by light, by radical inhibitors (galvinoxyl,[*] hydroquinone), or radical initiators (azobisisobutyronitrile).

(4) The reaction is not limited to cobalt(II) catalysts. For instance, $NiX_2{\cdot}nH_2O$ (X = Cl, Br, or I) has been found to catalyse efficiently the reactions $[Fe(CO)_{5-n}(CNR)_n] + RNC \longrightarrow [Fe(CO)_{4-n}(CNR)_{n+1}]$ (n = 0 or 1). Typically, a yield of 80—90% of product has been obtained for the reaction with $n = 1$ and $NiCl_2{\cdot}4H_2O$ as catalyst (R = Me, C_6H_{11}, Bu^tNC, $PhCH_2$, 2,6-$Me_2C_6H_3$, or 2,4,6-$Me_2C_6H_2$). Reaction times are all <10 min (1 mmol reactants, 20 mg catalyst, in benzene at 80 °C). In addition, $NiCl_2{\cdot}4H_2O$ has also been used to synthesize $[Fe(CO)_2(CNC_6H_3Me_2\text{-}2,6)_3]$ but the attempted synthesis of $[Fe(CO)_{5-n}(CNC_6H_3Me_2\text{-}2,6)_n]$ (n = 4 or 5) was unsuccessful. The major disadvantage to the use of nickel(II) halides as catalysts for the above substitution reactions is the competing catalytic polymerization of isonitrile that occurs in the presence of the nickel salts (see below).

(5) The reaction between $[Fe(CO)_5]$ and RNC is not only catalysed by metal(II) salts. To date we have obtained catalysis, with varying degrees of success, with over 50 transition-metal complexes. Our results using some of these catalysts have already been reported: $[RhCl(PPh_3)_3]$,[28,31] $[RuCl_2(PPh_3)_3]$,[31] and $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$.[32] The use of other catalysts such as Pd/C, PtO_2, and $[Mn_2(CO)_{10}]$, $[Os_3(CO)_{12}]$, and $[Ir_4(CO)_{12}]$ will be reported in the near future.[33]

(6) The effect of different solvents on the reaction $[Fe(CO)_4(CNBu^t)] + Bu^tNC \longrightarrow [Fe(CO)_3(CNBu^t)_2] + CO$ has also been investigated (Table 10). No apparent correlation between solvent properties and catalytic activity is apparent from the data. The excellent results for the solvents thf and benzene are, however, to be noted. Since the $CoCl_2$ reaction takes place under both homogeneous (acetone as solvent) and heterogeneous conditions (hexane as solvent) the reaction using $CoCl_2{\cdot}2H_2O$ as catalyst could occur at both the surface of the undissolved $CoCl_2$ as well as *via* interaction with the dissolved $[CoCl_2(CNR)_{4-n}]$ (n = 1—4) species. The data could thus reflect the number of active sites available for catalysis but, to date, we have made no effort to ascertain the real number of active catalyst molecules in the different solvents.

TABLE 10

Effect of solvent on the $CoCl_2$ catalysed reaction[a] $[Fe(CO)_4(CNBu^t)] + Bu^tNC \longrightarrow [Fe(CO)_3(CNBu^t)_2] + CO$

Solvent[b]	Reaction time[c] (min)
Pentane (36.1)	15 (n.r.)[d]
Hexane (68.9)	15 (30%)[e]
Heptane (98.4)	15
Cyclohexane (80.7)	10
Dichloromethane (40.0)	15
Chloroform (61.2)	15
1,2-Dichloroethane (83.4)	4
Tetrahydrofuran (65.4)	3
Benzene (80.1)	2
Acetonitrile (81.6)	4
Acetone (56.2)	5
Methyl ethyl ketone (79.6)	4
Methanol (64.5)	10
Ethanol (78.3)	8

[a] $[Fe(CO)_4(CNBu^t)]$: Bu^tNC : $CoCl_2{\cdot}2H_2O$, 1.0 : 1.4 : 0.1 mmol; solvent (reflux), 10 cm³. [b] Boiling point (°C) in parentheses. [c] As determined by i.r. spectroscopy. [d] n.r. = No reaction. [e] 30% reaction in 15 min.

(7) Transition-metal salts are known to catalyse the polymerization of isonitriles and this competing reaction has been found to cause loss of catalyst activity.[34] Thus, relatively long reaction times {particularly for the synthesis of the higher substituted isonitrile derivatives of $[Fe(CO)_5]$} and reactions carried out in high-boiling solvents have on occasion been found to result in catalyst deactivation. This may be observed by the slow formation of yellow reaction solutions as well as by the appearance of a yellow insoluble material. Thus, a decrease in catalytic activity obtained from qualitative kinetic data on the reaction between $[Fe(CO)_4(CNC_6H_{11})]$ and $C_6H_{11}NC$ in the presence of $CoCl_2{\cdot}2H_2O$ as catalyst (1 : 5 : 0.1 mmol respectively; in benzene at 45 °C) can be associated with a simultaneous gradual change in colour of the reaction solution to yellow. At increased isonitrile concentrations (*e.g.* $C_6H_{11}NC : CoCl_2{\cdot}2H_2O$, 100 : 1) a yellow solid (>95% yield based on isonitrile) is rapidly formed, even at room temperature. This material, insoluble in common organic solvents and water, was shown by i.r. spectroscopy [ν(NC) *ca.* 1 630 cm⁻¹, ν(NH) *ca.* 3 400 cm⁻¹; KBr] to have the same structure as that of a polyisonitrile with a poly(Schiff base) structure[34] of the type shown below. Similar observations have been made for the $CoCl_2$ catalysed substitution reactions of the Group 6 metal hexacarbonyls with isonitriles.[35] In general our observations suggest that alkyl isonitriles

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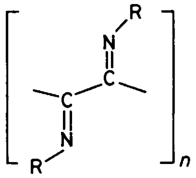
[*] 2,6-Di-t-butyl-α-(3,5-di-t-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*p*-tolyloxy.

are more susceptible to catalytic polymerization than the corresponding aryl derivatives. It is thus apparent from our results that the CO substitution reaction competes favourably with the isonitrile polymerisation reaction but that deviations from the reaction procedures listed can result in poor substitution reactions.[35] Unfortunately, the competing polymerization reaction has thus far had adverse effects on our attempts to obtain quantitative kinetic data for the substitution reaction.



(8) The isonitrile originally attached to the catalyst can readily be transferred to the iron-carbonyl reagent. For instance, reaction of $[Fe(CO)_5]$ with 2,6-$Me_2C_6H_3NC$, in the presence of $[CoCl_2(CNC_6H_3Me_2\text{-}2,6)_4]$ as catalyst $\{[Fe(CO)_5]$: RNC : catalyst, 10 : 2 : 0.3 mmol; in benzene at 80 °C$\}$ yields 2.7 mmol of $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$, *i.e.* 0.7 mmol more than the yield (2 mmol) expected from free isonitrile alone. A similar effect was observed for the reaction between $[Fe(CO)_5]$ and $[CoCl_2(CNBu^t)_4]$ (ratio, 10 : 0.3 mmol) in which $[Fe(CO)_4(CNBu^t)]$ was readily formed. During this reaction the solution changed from blue-green to yellow (*ca.* 5 min). Addition of further amounts of Bu^tNC to the reaction solution resulted in a regeneration of the blue-green colour and a renewal of catalytic activity. Similar observations have been made on the reaction between $[Mo(CO)_6]$ and Bu^tNC.[35] The mechanism of the transfer of the isonitrile to the metal carbonyl substrate could involve either an inter- or intra-molecular process. In an intermolecular process, $[CoCl_2(CNR)_4]$ could produce free isonitrile by the dissociation mechanism shown below. Any one of the cobalt species could thus act as a

$$\begin{aligned}
[CoCl_2(CNR)_4] &\rightleftharpoons [CoCl_2(CNR)_3] + RNC\\
[CoCl_2(CNR)_3] &\rightleftharpoons [CoCl_2(CNR)_2] + RNC\\
[CoCl_2(CNR)_2] &\rightleftharpoons [CoCl_2(CNR)] + RNC\\
[CoCl_2(CNR)] &\rightleftharpoons CoCl_2 + RNC
\end{aligned}$$

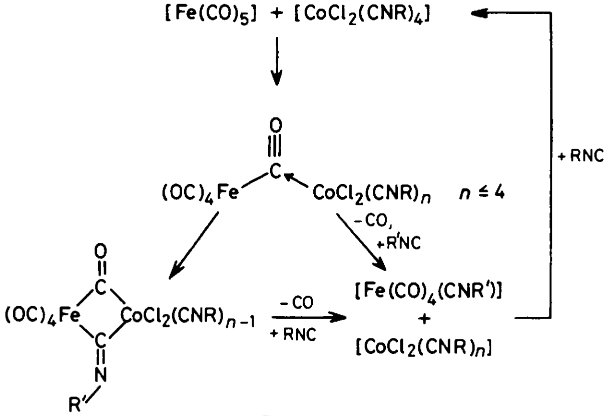
catalyst in the reaction below ($m \leqslant 4$; R'NC = solution isonitrile). Alternatively, a bridging mechanism (intra-

$$[M(CO)_n] + R'NC \xrightarrow{[CoCl_2(CNR)_m]} [M(CO)_{n-1}(CNR')]$$

molecular process) involving direct transfer of isonitrile from cobalt to iron with simultaneous tranfer of CO from iron to colbalt could also explain the data. {This mechanism has been observed, for instance, when $[RhCl(CO)(PPh_3)_2]$ is used as a catalyst.[31]} The two possible mechanisms are shown in the Scheme.

On the basis of the results obtained above, attempts have been made to establish the source of the iron-co-ordinated isonitrile. Thus, reactions were carried out in which $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$, $[CoCl_2(CNR)_4]$, and R'NC (1.0 : 1.0 : 1.0 mmol) were heated in benzene (10 cm^3, 80 °C) for short periods of time (3 min). The reaction solutions were then analysed by n.m.r. spectroscopy. The exchange reaction, $[CoCl_2(CNR)_4] + R'NC \longrightarrow [CoCl_2(CNR)_3(CNR')] + RNC$, was also studied under identical reaction conditions (1.0 mmol reagents, in benzene at 80 °C). These results are summarized by reactions (i)—(viii).

It is apparent from the above results that ligand exchange is occurring at the catalyst centre and that the exchange reaction is in complete agreement with the isonitrile distribution eventually obtained on the iron substrate. Thus, the major pathway involves attack of solution isonitrile on the iron-carbonyl substrate. The results further indicate that cobalt has more affinity for alkyl than aryl isonitriles, *i.e.* for σ-donating ligands rather than for π-accepting ligands. By extension, the possibility of replacing an isonitrile by CO (a poor σ-donor, good π-acceptor ligand) seems highly unlikely and further rules out the possibility of an intramolecular mechanism.



SCHEME

It must be noted however that a pathway involving catalytic exchange between isonitrile bound to the iron substrate and free isonitrile may also be significant: $[Fe(CO)_4(CNR)] + R'NC \longrightarrow [Fe(CO)_4(CNR')] + RNC$. We have found no evidence (by n.m.r. spectroscopy) for the exchange reaction in the absence of catalyst, but such exchange in the presence of Co^{II} has been detected. Thus, the reaction between $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$ and Bu^tNC (1.0 : 1.0 mmol, in benzene at 80 °C) carried out in the presence of $CoCl_2$ as catalyst yields $[Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)(CNBu^t)]$ (60%), $[Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2]$ (20%), and $[Fe(CO)_3(CNBu^t)_2]$ (20%), as detected by n.m.r. spectroscopy {similar results have been found for the $[Mo(CO)_6]$–RNC–$CoCl_2$ reaction [35]}.

(9) Further evidence against a bridging intramolecular exchange mechanism is provided by the following results. (*i*) No spectroscopic evidence for the formation of a Co–CO complex has been observed in our reactions. (*ii*) $CoCl_2$ catalyses the substitution of $[Fe(CO)_5]$ by non-bridging ligands such as phosphines and phosphites.[36]

$$[\mathrm{Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)}] + [\mathrm{CoCl_2(CNC_6H_3Me_2\text{-}2,6)_4}] + \mathrm{PhCH_2NC} \longrightarrow [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2}]\ (100\%) \qquad \text{(i)}$$

$$[\mathrm{CoCl_2(CNC_6H_3Me_2\text{-}2,6)_4}] + \mathrm{PhCH_2NC} \longrightarrow [\mathrm{CoCl_2(CNC_6H_3Me_2\text{-}2,6)_3(CNCH_2Ph)}] + \mathrm{2,6\text{-}Me_2C_6H_3NC}\ (100\%) \qquad \text{(ii)}$$

$$[\mathrm{Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)}] + [\mathrm{CoCl_2(CNCH_2Ph)_4}] + \mathrm{2,6\text{-}Me_2C_6H_3NC} \longrightarrow [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)(CNCH_2Ph)}]\,(ca.\ 60\%) + [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2}]\ (ca.\ 40\%) \qquad \text{(iii)}$$

$$[\mathrm{CoCl_2(CNCH_2Ph)_4}] + \mathrm{2,6\text{-}Me_2C_6H_3NC} \longrightarrow \text{partial exchange to leave } \mathrm{PhCH_2NC}\ (ca.\ 55\%) \text{ and } \mathrm{2,6\text{-}Me_2C_6H_3NC}\ (ca.\ 45\%) \text{ in solution} \qquad \text{(iv)}$$

$$[\mathrm{Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)}] + [\mathrm{CoCl_2(CNC_6H_3Me_2\text{-}2,6)_4}] + \mathrm{Bu^tNC} \longrightarrow [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2}]\ (ca.\ 95\%) + [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)(CNBu^t)}]\ (ca.\ 5\%) \qquad \text{(v)}$$

$$[\mathrm{CoCl_2(CNC_6H_3Me_2\text{-}2,6)_4}] + \mathrm{Bu^tNC} \longrightarrow \text{partial exchange to leave } \mathrm{2,6\text{-}Me_2C_6H_3NC}\ (ca.\ 90\%) \text{ and } \mathrm{Bu^tNC}\ (ca.\ 10\%) \text{ in solution} \qquad \text{(vi)}$$

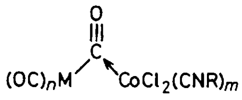
$$[\mathrm{Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)}] + [\mathrm{CoCl_2(CNBu^t)_4}] + \mathrm{2,6\text{-}Me_2C_6H_3NC} \longrightarrow [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)(CNBu^t)}]\ (ca.\ 60\%) \text{ and } [\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2}]\ (ca.\ 40\%)$$

N.B: in the early stages of the reaction (< 10% reaction) and also under milder reaction conditions (45 °C) the reaction product is $[\mathrm{Fe(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2}]$ (vii)

$$[\mathrm{CoCl_2(CNBu^t)_4}] + \mathrm{2,6\text{-}Me_2C_6H_3NC} \longrightarrow \text{partial exchange to leave } \mathrm{Bu^tNC}\ (ca.\ 55\%) \text{ and } \mathrm{2,6\text{-}Me_2C_6H_3NC}\ (ca.\ 45\%) \text{ in solution} \qquad \text{(viii)}$$

In summary, our mechanistic data indicate that the initial interaction between $\mathrm{CoX_2}$ and RNC leads to the complex $[\mathrm{CoX_2(CNR)}_n]$ ($n = 4$). These complexes, with $n = 1$—4, are believed to be the active form of the catalyst. Further, a reaction mechanism involving these species does not require a bridging mechanism between catalyst and substrate which involves either the halide (X) or RNC.

Since the predominant effect of the catalyst must be to destabilize the M–CO bond, this destabilization must occur *via* catalyst interaction with the metal (*e.g.* Fe) or the CO group attached to the metal. Although attack at five-co-ordinate iron by cobalt might be possible, attack at the sterically crowded $[\mathrm{Cr(CO)_6}]$ molecule[35] seems unlikely. Thus, attack of the catalyst presumably occurs at the CO ligand, either at C or O, as shown below.



$$\mathrm{(OC)}_n\mathrm{M{-}C{\equiv}O{:}{\rightarrow}CoCl_2(CNR)}_m$$

Carbonyl attack at O by Lewis acids such as $\mathrm{AlBr_3}$ is known[37] but $\mathrm{AlBr_3}$ has not been found to catalyse the substitution reaction under investigation. In the case of CO attack at C, the carbonyl ligand attacked is not necessarily the CO displaced and *cis*[38] or *trans*[39] effects, resulting from the novel ligand $-\mathrm{C(O)CoCl_2(CNR)}_n$, could be dominant. Further work will be required to determine the exact nature of the CO–catalyst interaction.

An alternative mechanism based on the expected oxidizing ability of $\mathrm{CoCl_2}$ {and presumably $[\mathrm{CoCl_2(CNR)}_n]$} and involving an outer-sphere electron-transfer process can also be envisaged:[39] $[\mathrm{Fe(CO)_5}] + [\mathrm{CoX_2(CNR)}_n] \longrightarrow [\mathrm{Fe(CO)_5}]^+ + [\mathrm{CoX_2(CNR)}_n]^-$. The 17-electron $[\mathrm{Fe(CO)_5}]^+$ species formed could be expected to be involved in a chain[40] or non-chain[32] radical process in which the CO was replaced by isonitrile. Our results on the use of radical inhibitors, initiators, *etc.* (see above) do not favour such a mechanism for the $\mathrm{CoCl_2}$ reactions. However, our results on the use of $[\{\mathrm{Fe(CO)_2(\eta^5\text{-}C_5H_5)}\}_2]$ as catalyst for the above substitution reaction,[32] as well as the recent electrochemical studies on the substitution of CO on $[\mathrm{Fe(CO)_5}]$ by $\mathrm{PPh_3}$,[41] suggest that in *general* a pathway involving radical anions and cations is viable.

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