Metal Dimers as Catalysts. Part 6.† The Use of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ as a Catalyst in the Metal Carbonyl Substitution Reaction

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The reaction between $[Fe(CO)_2(\eta^5\text{-}C_5H_4R')X]$ and RNC in benzene to give $[Fe(CO)_{2-n}(\eta^5\text{-}C_5H_4R')(CNR)_nX]$ (n = 1 or 2; R′ = H, R = Bu^t, $PhCH_2$, or $2,6\text{-}Me_2C_6H_3$, X = I or Br; R′ = Me, R = Bu^t, X = I) is catalysed by $[\{Fe(CO)_2(\eta^5\text{-}C_5H_4R')\}_2]$. Mechanistic studies (42 °C) reveal that no transfer of ligands takes place between catalyst and substrate and that the reaction is light dependent. These results have been interpreted in terms of an electron-transfer process between the catalyst and the substrate. At higher temperatures (80 °C), a competing radical-chain process is also occurring, as detected by crossover experiments between catalyst and substrate. Predictions that the catalyst $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ should activate metal carbonyl substrates in general and that ligand substitution of ligands other than CO should occur have been verified. Thus, (*a*) the high-yield synthesis of $[Fe(\eta^5\text{-}C_5H_5)(CNR)_3]I$ from $[Fe(\eta^5\text{-}C_5H_5)(CNR)_2I]$ and RNC (R = Bu^t or $2,6\text{-}Me_2C_6H_3$), (*b*) the reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ and Bu^tNC to give $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ in quantitative yield (benzene, 42 °C), and (*c*) mechanistic studies on the reaction $[Fe(CO)_4(CNBu^t)] + Bu^tNC \longrightarrow [Fe(CO)_3(CNBu^t)_2] + CO$, all in the presence of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, are consistent with the mechanistic scheme proposed.

The synthesis of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (1) was first reported by Cotton and Wilkinson [1] in 1954. This synthesis was soon followed by a crystal structure determination of (1) which indicated that the molecule consisted of two $Fe(CO)(\eta^5\text{-}C_5H_5)$ units bridged by two CO groups (Figure).[2] More recently, *X*-ray crystal structure [3] and neutron diffraction data [4] have unambiguously shown that the molecule exists in both *cis* [Figure (*a*)] and *trans* [Figure (*b*)] configurations. The interconversion of these isomers has been elegantly demonstrated and conforms to the Cotton–Adams rules.[5]

The facile synthesis of (1) from relatively cheap starting materials $\{[Fe(CO)_5]$ and $C_{10}H_{12}\}$ [6] and the moderate thermal and air stability of the dimer have allowed it to be used as a precursor for a wide range of complexes employing the $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ unit as template,[7] and consequently the chemistry of (1) is now well established. In this paper we wish to investigate yet another aspect of the chemistry of (1), its use as a catalyst in synthetic organometallic chemistry.

The use of (1) as a catalyst in organometallic chemistry was first reported by Fabian and Labinger.[8] They observed that the reaction between $[Fe(CO)_2(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)]$ and L $[P(OPh)_3$, $P(OMe)_3$ or $PMePh_2]$ was complex and that the reaction was catalysed by (1) when the reaction solution was irradiated with low-intensity light from a u.v. lamp ($\lambda_{max.}$ *ca.* 3 600 Å). This technique, photochemical induced catalysis by (1), has since been exploited by Rosenblum and Waterman [9] in the synthesis of $[Fe(CO)(\eta^5\text{-}C_5H_5)(\sigma\text{-allyl})L]$ [L = $P(OPh)_3$, $P(OMe)_3$, or $P(OCH_2)_3CCH_3$] from $[Fe(CO)_2(\eta^5\text{-}C_5H_5)(\sigma\text{-allyl})]$ and L. A radical chain mechanism, similar to that proposed by Brown and co-workers,[10] was shown to be consistent with the experimental data.

Our own investigations in this area arose from an extension of studies on the use of $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ as a catalyst for the CO substitution reaction (i).[11] It was anticipated that the complications that had been experienced using $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ as catalyst, namely competitive salt formation of the catalyst,[12] could be overcome using (1) as catalyst in related systems. We chose to study the catalytic effects of (1) on the model reaction (ii). This reaction was chosen for a number of reasons. Firstly, we initially anticipated that (1) would function as a radical chain catalyst, as found previously,[9] and thus our substrate molecule should of necessity contain the $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ moiety. Secondly, the reaction between $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$ and RNC has been reported to proceed with difficulty to yield $[Fe(CO)_{2-n}(\eta^5\text{-}C_5H_5)(CNR)_nI]$ (n = 1 or 2).[13,14] Reaction (ii) would thus provide an opportunity to establish the effectiveness of the catalyst and at the same time lead to a facile synthetic route to the multiply substituted isonitrile derivatives.[15] {We have also investigated the reaction between $[Fe(CO)_2(\eta^5\text{-}C_5H_5)Br]$ and an alkyl and an aryl isonitrile for comparative purposes.[16]} Thirdly, synthetic routes to modified catalysts (*e.g.* *via* modification of the $\eta^5\text{-}C_5H_5$ ring) are well documented and the reaction is thus amenable to a detailed investigation.

$$[Mo(CO)_3(\eta^5\text{-}C_5H_5)I] + RNC \xrightarrow{\text{catalyst}} [Mo(CO)_{3-n}(\eta^5\text{-}C_5H_5)(CNR)_nI] + nCO \ (n = 1\text{—}3) \quad \text{(i)}$$

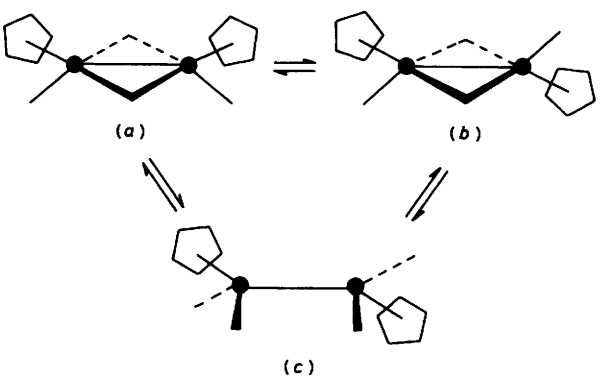

Figure. Bridged and non-bridged structures of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] + RNC \longrightarrow [Fe(CO)_{2-n}(\eta^5\text{-}C_5H_5)(CNR)_nI] + nCO \ (n = 1 \text{ or } 2) \quad \text{(ii)}$$

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† Part 5 is ref. 21.

Table 1. Analytical data for the new isonitrile complexes

			Analysis (%) [a]			
		M.p. (°C)	C	H	N	X
(3a)	$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)Br]$	128—129	43.3 (42.4)	4.65 (4.50)	4.30 (4.50)	25.1 (25.6)
(3b)	$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)Br]$	125—127	49.3 (50.0)	3.60 (3.90)	3.75 (3.90)	23.0 (22.2)
(3c)	$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$	148—150	37.1 (36.8)	3.80 (3.85)	4.00 (3.90)	35.2 (35.4)
(3d)	$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNCH_2Ph)I]$	81—82	43.3 (42.8)	3.05 (3.10)	3.45 (3.55)	32.3 (29.7)
(3e)	$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)I]$	151	44.7 (44.3)	3.35 (3.45)	3.30 (3.45)	
(3f)	$[Fe(CO)(\eta^5\text{-}C_5H_4Me)(CNBu^t)I]$	32—34	38.6 (38.6)	4.35 (4.30)	3.85 (3.75)	
(4a)	$[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_2Br]$	91—94	49.6 (49.1)	6.55 (6.30)	7.80 (7.65)	
(4b)	$[Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_2Br]$	129—131	53.2 (52.6)	4.45 (4.60)	5.40 (5.10)	
(4c)	$[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_2I]$	84—86	44.3 (43.5)	5.60 (5.60)	6.75 (6.75)	30.1 (30.6)
(4d)	$[Fe(\eta^5\text{-}C_5H_5)(CNCH_2Ph)_2I]$	88—89	52.6 (52.3)	3.90 (3.95)	5.75 (5.80)	24.9 (26.3)
(4e)	$[Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_2I]$	163—165	54.6 (54.2)	4.50 (4.55)	5.50 (5.50)	24.3 (24.9)
(4f)	$[Fe(\eta^5\text{-}C_5H_4Me)(CNBu^t)_2I]$	—	44.6 (44.9)	5.90 (5.90)	6.10 (6.55)	
(5a)	$[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_3]Br$	197—199	53.1 (53.4)	7.05 (7.15)	9.10 (9.35)	
(5b)	$[Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_3]Br$ [b]	—	64.3 (64.7)	5.30 (5.45)	6.65 (7.05)	13.4 (13.4)
(5c)	$[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_3]I$	156—158	48.5 (48.3)	6.50 (6.50)	8.25 (8.45)	24.9 (25.5)
(5d)	$[Fe(\eta^5\text{-}C_5H_5)(CNC_6H_3Me_2\text{-}2,6)_3]I$	168—170	59.0 (59.9)	5.05 (5.05)	6.10 (6.55)	

[a] Calculated values are in parentheses. [b] Analysed as CH_2Cl_2 solvate.

As will be apparent from our results, we have also extended the use of (1) as a catalyst to substrates that do not possess the $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ moiety, *e.g.* $[Fe(CO)_5]$, $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$, *etc.* and these results are also discussed in this paper. A preliminary account of this work has appeared.[17]

Experimental

The compounds $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ and $[Fe(CO)_5]$ were purchased from Strem Chemicals. $[\{Fe(CO)_2(\eta^5\text{-}C_5H_4Me)\}_2]$,[6] $[\{Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}_2]$,[6] $[Fe(CO)_2(\eta^5\text{-}C_5H_5)Br]$,[18] $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$,[6] $[Fe(CO)_4(CNBu^t)]$,[19] and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$[6] were all prepared by published procedures or modifications of them. The isonitriles were purchased from Fluka A.G. (Bu^tNC and $2,6\text{-}Me_2C_6H_3NC$) or Aldrich ($PhCH_2NC$).

Solvents were routinely dried and distilled before use, and all reactions were routinely carried out under argon or nitrogen. Galvinoxyl [2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy] and hydroquinone were used as purchased. Merck ' Kieselgel 60 ' 60—200-μm silica gel was used for column chromatography (2 cm × 150 cm columns) unless otherwise stated. No attempt was made rigorously to exclude stray light (laboratory light) from the reactions but all reactions were carried out under identical lighting conditions, unless otherwise stated. Consequently, reproducible results (within *ca.* 10%) have been obtained for all the qualitative rate data obtained from i.r. spectroscopic measurements. It should also be noted that $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ was used consistently from one batch (Strem Chemicals) throughout this study.

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP300 spectrophotometer and ^1H n.m.r. spectra were recorded on a WP80 FTNMR spectrometer. Microanalyses were performed by the Microanalytical Laboratories, C.S.I.R.

Preparation of $[Fe(CO)(\eta^5\text{-}C_5H_4R')(CNR)X]$ ($R' = H$, $R = Bu^t$, $PhCH_2$, *or* $2,6\text{-}Me_2C_6H_3$, $X = I$; $R' = H$, $R = Bu^t$ *or* $2,6\text{-}Me_2C_6H_3$, $X = Br$; $R' = Me$, $R = Bu^t$, $X = I$) (3a)—(3f).—$[Fe(CO)_2(\eta^5\text{-}C_5H_4R')X]$ (1 mmol) and $[\{Fe(CO)_2(\eta^5\text{-}C_5H_4R')\}_2]$ (0.05 mmol) were added to benzene (10 cm^3) and the solution brought to reflux. RNC (1.1 mmol) was then added and the reaction monitored by i.r. spectroscopy. The i.r. spectra typically indicated that the reaction was complete in *ca.* 5 min. The reaction solution was then cooled and the solvent volume reduced to *ca.* 3 cm^3. This solution was then eluted through a silica-gel column with benzene as eluant. The major fraction eluted from the column was recrystallized from benzene–hexane to yield the required product in 60—80% yield (Table 1). Small amounts of $[Fe(CO)_2(\eta^5\text{-}C_5H_4R')X]$ and $[Fe(\eta^5\text{-}C_5H_4R')(CNR)_2X]$ were also isolated from the reaction mixture.

Preparation of $[Fe(\eta^5\text{-}C_5H_4R')(CNR)_2X]$ ($R' = H$, $R = Bu^t$, $PhCH_2$, *or* $2,6\text{-}Me_2C_6H_3$, $X = I$; $R' = H$, $R = Bu^t$ or $2,6\text{-}Me_2C_6H_3$, $X = Br$; $R' = Me$, $R = Bu^t$, $X = I$) (4a)—(4f).—$[Fe(CO)_2(\eta^5\text{-}C_5H_4R')X]$ (1.0 mmol) and $[\{Fe(CO)_2(\eta^5\text{-}C_5H_4R')\}_2]$ (0.05 mmol) were added to benzene (10 cm^3) and the solution brought to reflux. RNC (2.1 mmol) was then added and the reaction monitored by i.r. spectroscopy. The i.r. spectra typically indicated that the reaction had reached completion within 5 min. Solid material deposited during the reaction. This was filtered off and identified as $[Fe(\eta^5\text{-}C_5H_4R')(CNR)_3]^+X^-$ (see below). The required product (Table 1) was purified by column chromatography (as above) and recrystallized from benzene–hexane (60% yield). A small amount of $[Fe(CO)(\eta^5\text{-}C_5H_4R')(CNR)X]$ was also isolated from the reaction mixture by column chromatography.

The required compounds can alternatively be prepared from (3a)—(3f) (1 mmol), RNC (1.1 mmol), and catalyst (0.05 mmol) in benzene (10 cm^3).

Preparation of $[Fe(\eta^5\text{-}C_5H_5)(CNR)_3]^+X^-$ ($R = Bu^t$ *or* $2,6\text{-}Me_2C_6H_3$, $X = Br$ *or* I) (5a)—(5d).—$[Fe(CO)_2(\eta^5\text{-}C_5H_5)X]$ (1 mmol), $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (0.05 mmol) and RNC (4 mmol) were refluxed in benzene (10 cm^3). The reaction solution eventually turned pale yellow (*ca.* 45 min) and a copious precipitate formed. The precipitate was filtered off and recrystallization from acetone–hexane afforded the required complex (Table 1).

Preparation of $[\{Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)\}_2]$.[20]—$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (1 mmol) and Bu^tNC (2.5 mmol) were added to toluene (10 cm) at reflux and the reaction was monitored by i.r. spectroscopy. After 120 min the reaction was *ca.* 85% complete. The reaction mixture was then cooled

Table 2. Spectral data for the new isonitrile complexes

	I.r.[a] (cm^{-1})		^1H N.m.r.[b] (δ/p.p.m.)		
Complex	ν(NC)	ν(CO)	C_5H_5	CH_3	Aromatic
(3a)	2 160	1 990	4.25	0.97	—
(3b)	2 135	1 990	4.31	2.18	6.7
(3c)	2 150	1 985	4.24	0.96	—
(3d)	2 160	1 985	4.23	[c]	7.03
(3e)	2 130	1 990	4.30	2.18	6.7
(3f)	2 140	1 975	[d]	0.99	—
(4a)	2 130, 2 100, 2 060		4.40	1.18	—
(4b)	2 130, 2 080		4.54	2.34	6.75
(4c)	2 130, 2 105, 2 075 (sh)		4.39	1.16	—
(4d)	2 150, 2 110, 2 080 (sh)		4.41	[e]	7.1
(4e)	2 120, 2 075		4.53	2.34	6.7
(4f)	2 115, 2 090 (sh), 2 062		[f]	1.18	—
(5a)	2 175, 2 135		4.77	1.53	—
(5b)	2 160, 2 120		5.34	2.44	7.35, 7.16
(5c)	2 170, 2 130		4.77	1.53	—
(5d)	2 185, 2 145		5.35	2.45	7.36, 7.16

[a] Recorded in $CHCl_3$. [b] Recorded in C_6D_6 relative to $SiMe_4$. [c] CH_2 (s, 3.98). [d] C_5H_4Me (m, 4.26 and 4.13); $C_5H_4CH_3$ (s, 1.76). [e] CH_2 (s, 4.24). [f] C_5H_4Me (m, 4.39 and 4.16); $C_5H_4CH_3$ (s, 1.94).

and the product purified by column chromatography (alumina). Recrystallization (as reported previously)[20] afforded the product as green crystals in >60% yield.

Reaction Between $[Mo(CO)_3(\eta^5-C_5H_5)I]$ *and* Bu^tNC.[11]—$[Mo(CO)_3(\eta^5-C_5H_5)I]$ (0.3 mmol) and $[\{Fe(CO)_2(\eta^5-C_5H_5)\}_2]$ (0.3 mmol) were added to benzene (10 cm^3) at 45 °C. Bu^tNC (0.3 mmol) was then added and the reaction monitored by i.r. spectroscopy and t.l.c. (silica gel plates). On completion of the reaction (250 min) the product, $[Mo(CO)_2(\eta^5-C_5H_5)(CNBu^t)I]$, was purified as reported previously.[11]

Catalysed Reaction Between $[Fe(CO)_4(CNBu^t)]$ *and* Bu^tNC.[19]—The reaction between $[Fe(CO)_4(CNBu^t)]$ (1 mmol) and Bu^tNC (1 mmol) in the presence of $[\{Fe(CO)_2(\eta^5-C_5H_5)\}_2]$ (0.1 mmol) as catalyst was carried out in benzene (10 cm^3, 80 °C). The reaction was monitored by i.r. spectroscopy and the product, $[Fe(CO)_3(CNBu^t)_2]$, purified and characterized as previously.[19]

Attempted Use of $[\{Fe(CO)_2(\eta^5-C_5H_5)\}_2]$ *as a Catalyst for the Substitution of Metal Carbonyl Substrates by Isonitriles.*—Reactions were carried out with reactants (1 mmol), catalyst (0.05 mmol), and benzene (10 cm^3, reflux) unless otherwise stated.

Mechanistic Studies.—Reactions were typically carried out in a two-necked round-bottom flask under nitrogen in a fume hood and were monitored by i.r. spectroscopy and t.l.c. (silica gel plates). Two sets of reaction conditions were generally employed, depending on the reaction temperature. At 80 °C, 1 mmol of reactants and 0.05 mmol of catalyst (1) were heated together in benzene (10 cm^3) while at 42 °C, 0.5 mmol of (1) and 1 mmol of reactants were used.

Results and Discussion

Addition of RNC (1.1 mmol) to a refluxing benzene solution (10 cm^3) of $[Fe(CO)_2(\eta^5-C_5H_4R')X]$ (2) (1 mmol) in the presence of (1) (0.05 mmol) as catalyst results in the rapid synthesis (<5 min) of $[Fe(CO)(\eta^5-C_5H_4R')(CNR)X]$ (3a)—(3f), Table 1. In the absence of catalyst, reactions occur slowly to give mixtures of mono- and di-substituted products.[13,14] The reaction can be readily monitored by i.r. spectroscopy and was terminated when the ν(CO) vibration at 2 043 cm^{-1} due to (2) either disappeared or remained constant with time. Elution of the crude reaction material through a silica gel column with benzene yielded (3a)—(3f) as the major product (typically 60—80% yield) and small amounts of unreacted (2) and $[Fe(\eta^5-C_5H_4R')(CNR)_2I]$.

The disubstituted product was synthesized in an analogous manner. Thus, addition of RNC (2.1 mmol) to $[Fe(CO)_2(\eta^5-C_5H_4R')X]$ (1 mmol), or alternatively, addition of RNC (1.1 mmol) to $[Fe(CO)(\eta^5-C_5H_4R')(CNR)X]$ (1 mmol) in the presence of (1) (0.05 mmol) rapidly yielded $[Fe(\eta^5-C_5H_4R')(CNR)_2X]$ (4a)—(4f) (Table 1). Small quantities of an insoluble material, identified as the salt $[Fe(\eta^5-C_5H_5)(CNR)_3]^+X^-$ (see below), were precipitated from solution during the reaction. The reaction material was purified by passage through a silica column to give (4a)—(4f) (>60% yield) and small amounts of monosubstituted complex (3).

The new isonitrile complexes (3a)—(3f) and (4a)—(4f) were completely characterized by i.r. and n.m.r. spectroscopy (Table 2) and elemental analyses (Table 1). The i.r. data for (3) reveal one CO and one NC stretching vibration (as expected) while the i.r. data for (4) generally indicate three NC stretching vibrations although only two NC vibrations are expected. This phenomenon has been commented on previously for these[16] and related complexes.[21]

The n.m.r. spectra show no anomalous behaviour either in terms of chemical shifts or resonance intensities. Although the monosubstituted derivatives (3) are chiral, we have not observed resolution of the diastereotopic protons on the methylene group in $[Fe(CO)(\eta^5-C_5H_5)(CNCH_2Ph)I]$. This could arise from either a fluxional process in which the protons are made equivalent[22] or from a non-detectable chemical shift difference between the two different protons.

Further studies were undertaken to establish the mechanism of the reaction. Some of these pertinent reactions are given below.

(*a*) Reaction (iii) [1 mmol reactants, toluene (10 cm^3,

$$[Fe(CO)_2(\eta^5-C_5H_5)I] + PPh_3 \longrightarrow [Fe(CO)(\eta^5-C_5H_5)(PPh_3)I] + CO \qquad (iii)$$

reflux)] is catalysed by (1) (0.05 mmol) and gives the product slowly but in high yield (>65%, 100 min).[23] The catalysed reaction is hence not dependent on the presence of the RNC ligand.

(*b*) The reaction between (1) and Bu^tNC (1 mmol reactants) in benzene (10 cm^3, reflux) gives $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ (<10 min, quantitative), in agreement with previous studies.[24]

(*c*) Crossover experiments were performed [reactions (iv)—(vi): 0.5 mmol reactants, benzene (10 cm^3, reflux)] and monitored by i.r. spectroscopy. The products of reaction (v) were analysed by n.m.r. spectroscopy; those of reaction (vi) were identified by t.l.c. and i.r. spectroscopy.

The above experiments are consistent with the formation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet$ radicals under the reaction conditions (benzene, reflux).[25] A radical chain mechanism, similar to that proposed by Brown [8-10] can account for the data (Scheme 1).

$$[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)] + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \longrightarrow [\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + [Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]\ (>80\%,\ 60\ \text{min}) \qquad \text{(iv)}$$

$$[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)] + [Fe(CO)_2(\eta^5\text{-}C_5H_4Me)I] \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I] + \text{other products} \qquad \text{(v)}$$

$$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + [Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_2I] \longrightarrow [Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)] + [Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]\ (1\ \text{h} > 40\%) \qquad \text{(vi)}$$

$$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] \overset{\text{heat, } h\nu}{\rightleftharpoons} 2\ Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet \qquad \text{(vii)}$$

$$Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet + RNC \longrightarrow Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)^\bullet + CO \qquad \text{(viii)}$$

$$Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)^\bullet + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \longrightarrow Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet + [Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] \qquad \text{(ix)}$$

Scheme 1.

Reaction (viii) was confirmed by the reaction between tropylium tetrafluoroborate, $C_7H_7{}^+BF_4{}^-$, and $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$. In the absence of RNC, compound (1) was exclusively formed [26] but in the presence of RNC (R = Bu^t or $2,6\text{-}Me_2C_6H_3$ [27]) either $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNR)]$ or $[\{Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)\}_2]$ were synthesized. It is to be noted that when the reaction was carried out in the presence of PPh_3, $PMePh_2$, or $PhC{\equiv}CH$, only (1) was detected, suggesting that CO loss from the radical $Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet$ occurs *via* an associative process.[28,29]

In order to obtain information on the fate of the catalyst in the catalytic reaction it was necessary to increase the concentration of (1) in reaction (ii). To monitor the reaction (i.r. spectroscopy and t.l.c.) it was thus necessary to perform the reaction at a lower temperature.

A convenient temperature for the reaction between $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$ (0.5 mmol) and Bu^tNC (0.55 mmol) in the presence of (1) (0.25 mmol) in benzene (10 cm^3) was found to be 42 ± 2 °C. Under these conditions >90% $[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ was formed in 45 min. In the absence of (1) <5% of the reaction product was detected in 2 h. It was also found that the reaction between $[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ (1) and Bu^tNC requires *ca.* 70 min at 42 °C to give $[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_2I]$ (>80% yield) and (1) as the final products. This indicates the activation barriers to the mono- and di-substituted products must be similar, but more significantly that Bu^tNC substitution of $[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ occurs in preference to substitution of (1).

Under the above reaction conditions (benzene, 42 °C) reactions (x) and (xi) proceed to <5% completion in 2 h. It thus seems unlikely that reactions (viii) and (ix) (Scheme 1) contribute to the catalytic cycle observed at 42 °C. It is further to be noted that under the reaction conditions neither $[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ nor $[Fe(\eta^5\text{-}C_5H_5)(CNBu^t)_2I]$ react with (1) to yield $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ (120 min).

Crossover experiments using labelled cyclopentadienyl rings [reactions (xii) and (xiii)] yielded the products indicated (>80%, 60 min).

From the above data it can thus be deduced that a mechanism different to the radical chain mechanism (Scheme 1) must be operating at 42 °C and must also of necessity be occurring at 80 °C in competition with the chain mechanism.

Further support for an alternative mechanism has been obtained from our studies using radical inhibitors and the effect of visible light on the reaction. Addition of hydroquinone (14 mol %) or galvinoxyl (4 mol %) to $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$ (1 mmol), Bu^tNC (1 mmol), and (1) (0.5 mmol) at 42 °C results in reaction times of 180 and 90 min respectively for conversion of reactants to $[Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ (>95% product formed, as detected by i.r. spectroscopy). Under our standard reaction conditions (see Experimental section), the corresponding reaction time is 45 min. Irradiation of the above reaction mixture with a 500-W light bulb gives a dramatic effect and the reaction is complete in *ca.* 1 min. It is also apparent that even under our standard reaction conditions that stray laboratory light affects the reaction. If the reaction flask is wrapped in aluminium foil to exclude all visible light, then the reaction time increases to 180 min.

The irradiation of solutions of Bu^tNC and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$ in the *absence* of (1) results in the slow formation of product mixtures containing $[Fe(CO)_{2-n}(\eta^5\text{-}C_5H_5)(CNBu^t)_nI]$ (n = 1 or 2) (80% reaction, 45 min). Rupture of the Fe–CO bond on irradiation is expected.[30] The results indicate, however, that this substitution pathway is a slow process relative to a pathway which involves (1).

We have similarly observed that light increases the rates of

$$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + Bu^tNC \longrightarrow [Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)] \qquad \text{(x)}$$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] + [Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)] \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I] \qquad \text{(xi)}$$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] + [\{Fe(CO)_2(\eta^5\text{-}C_5H_4Me)\}_2] + Bu^tNC \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)I] \qquad \text{(xii)}$$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_4Me)I] + [\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + Bu^tNC \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_4Me)(CNBu^t)I] \qquad \text{(xiii)}$$

reactions (x) and (xi) (*ca.* 80% Bu^{t}NC transfer, 15 min) but that the reactions are slow compared to the catalytic reaction. A possible mechanism consistent with the experimental data is given in Scheme 2.

$$[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2] \overset{h\nu,\,\Delta}{\rightleftharpoons} (A) \qquad \text{(xiv)}$$

$$(A) + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \rightleftharpoons (A)\text{–}[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \qquad \text{(xv)}$$

$$(A)\text{–}[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] + RNC \rightleftharpoons (A)\text{–}[Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] + CO \qquad \text{(xvi)}$$

$$(A)\text{–}[Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] \rightleftharpoons (A) + [Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] \qquad \text{(xvii)}$$

Scheme 2.

The significant feature of Scheme 2 is the suggestion that (A) [derived by excitation of (1), see below] interacts with the substrate [Fe(CO)$_2$(η^5-C$_5$H$_5$)I], to induce ligand activation [reaction (xv)] and subsequently product formation [reaction (xvii)]. Scheme 2 requires no transfer of ligands between the catalyst and substrate. The mechanism suggests two important consequences: (*a*) the activation process should apply to substrates that *do not* contain the Fe(CO)$_2$(η^5-C$_5$H$_5$) unit and (*b*) the interaction should lead to general ligand activation of the substrate.

The first statement is supported by our finding that (1) catalyses the reaction between [Fe(CO)$_5$] and PR$_3$ to give [Fe(CO)$_4$(PR$_3$)] (PR$_3$ = PPh$_3$ or PMePh$_2$).[31] This and other examples are discussed more fully below.

Support for the second statement is given by the reaction between [Fe(η^5-C$_5$H$_5$)(CNR)$_2$I] and RNC. In refluxing benzene, and in the absence of (1), no reaction occurs (60 min). However, in the presence of catalytic amounts of (1), salt formation is observed and near-quantitative yields of [Fe(η^5-C$_5$H$_5$)(CNR)$_3$]$^+$I$^-$ are formed (45 min), *i.e.* I$^-$ is being catalytically displaced by RNC. (These new complexes have been completely characterized for R = Bu^t and 2,6-Me$_2$C$_6$H$_3$; see Table 1.) We have also observed a similar displacement of I$^-$ by phosphines in the synthesis of [Fe(CO)(η^5-C$_5$H$_5$)(PR$_3$)$_2$]$^+$I$^-$ from [Fe(CO)$_2$(η^5-C$_5$H$_5$)I] and PR$_3$ (PR$_3$ = PPh$_3$ or PMePh$_2$).[32] This reaction also indicates that the catalysed reaction is not dependent on an incoming ligand having the propensity to have bridging properties.

Speculation on the Nature of the Catalyst.—The above information allows us to draw some tentative conclusions pertaining to the nature of the active form of the catalyst [(A), Scheme 2].

Species (A) could be either monometallic or bimetallic. For instance, (A) could correspond to the Fe(CO)$_2$(η^5-C$_5$H$_5$)$^\cdot$ radical which is readily generated from (1). Interaction of Fe(CO)$_2$(η^5-C$_5$H$_5$)$^\cdot$ with the substrate must lead to metal–CO bond weakening in [Fe(CO)$_2$(η^5-C$_5$H$_5$)I] if ligand substitution is to occur and this could be achieved *via* a one-electron transfer process which will involve either oxidation or reduction of the substrate (both processes will lead to metal–CO bond weakening[33]).

Species (A) could also correspond to an activated CO-bridged dimer, similar to that proposed by Tyler and co-workers[34,35] in which the formal M–M bond[36] of (1) is cleaved but the dimer is not disrupted. It is possible that this CO-bridged dimer could interact with the substrate to induce metal–CO bond weakening *via* an electron-transfer process between catalyst and substrate.

As formulated in Scheme 2, the substitution reaction can best be described as occurring *via* a non-chain radical process.[11,17] However, it is possible that a radical chain process, different from that proposed in Scheme 1, could also be occurring. One possibility involving substrate oxidation is indicated in Scheme 3.

$$(A) + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \longrightarrow (A^-) + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I]^+ \qquad \text{(xviii)}$$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]^+ + RNC \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I]^+ \qquad \text{(xix)}$$

$$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I]^+ + (A^-) \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] + (A) \qquad \text{(xx)}$$

$$[Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I]^+ + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I] \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(CNR)I] + [Fe(CO)_2(\eta^5\text{-}C_5H_5)I]^+ \qquad \text{(xxi)}$$

Scheme 3.

The only difference between Scheme 2 and Scheme 3 relates to whether (A) and the substrate remain together during the CO substitution reaction.

Precedent for Scheme 3 has been documented in both organic[37] and organometallic[38] chemistry.

A mechanism similar to Scheme 3 but involving initial substrated reduction is also feasible.[39] Indeed, recent reports on the catalytic use of chemical,[40] electrochemical,[41] or photochemically initiated procedures[42] have suggested a general pathway to the metal–CO substitution reaction occurring *via* 19-electron metal carbonyl radical anions.

At present we favour Scheme 2 over Scheme 3 as it provides a *general* mechanism for explaining our results at both 42 and 80 °C. Thus, (A)–[Fe(CO)$_2$(η^5-C$_5$H$_5$)I] allows for both the *possibility* of atom transfer and/or electron transfer depending on reaction conditions. Most significantly, both Scheme 2 and Scheme 3 suggest that electron-transfer reagents *in general* could act as catalysts for the CO substitution reaction. Indeed, we have discovered from our search for electron-transfer catalysts that a variety of supported metals[43] (*e.g.* Pd) and metal–metal bonded carbonyl complexes[44] (dimers, trimers, and tetramers) also act as catalysts for the CO substitution reaction. This aspect of the catalytic reaction will be discussed more fully in future publications.

We will now extend the use of (1) (and related substituted complexes) as a CO replacement catalyst to a range of metal carbonyl complexes which do not contain the Fe(CO)$_2$(η^5-C$_5$H$_5$) unit.

Catalysed Reaction between $[Fe(CO)_4(CNR)]$ *and* RNC.—We have previously explored the reaction between $[Fe(CO)_4(CNR)]$ and RNC to give $[Fe(CO)_3(CNR)_2]$ using $CoCl_2$ as a catalyst in some detail.[19] These studies suggested that reaction (xxii) could be used to screen potential CO substitution

$$[Fe(CO)_4(CNBu^t)] + Bu^tNC \longrightarrow [Fe(CO)_3(CNBu^t)_2] + CO \quad \text{(xxii)}$$

catalysts for catalytic activity.

Addition of either (1) or $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ (10 mol %) to reaction (xxii) (benzene, 80 °C) did result in moderate catalysis (95% product formation in 75 min; thermal blank 120 min). The corresponding reaction in the presence of $[\{Fe(CO)(\eta^5\text{-}C_5H_5)(CNBu^t)\}_2]$ (10 mol %) gave a complete reaction in <2 min.

The room temperature reaction between $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, $[Fe(CO)_4(CNBu^t)]$, and Bu^tNC (0.1 : 1.0 : 1.2 mol ratio) in benzene carried out in the dark, and in the presence of visible light (500-W bulb) indicates little or no catalysis in the dark (4 h reaction time), but formation of approximately 20—30% of $[Fe(CO)_3(CNBu^t)_2]$ in the presence of light in 4 h. A similar increase in reaction was observed in the presence of light with $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ as catalyst.

The reactions (*a*) $[Fe(CO)_4(CNBu^t)]$ + 2,6-$Me_2C_6H_3NC$ + $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ (1.0 : 0.5 : 0.5 mol ratio, benzene, 80 °C) and (*b*) $[Fe(CO)_4(CNC_6H_3Me_2\text{-}2,6)]$ + Bu^tNC + $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNC_6H_3Me_2\text{-}2,6)]$ (1.0 : 0.5 : 0.5 mol ratio, benzene, 80 °C) were carried out. The progress of each reaction was monitored by i.r. spectroscopy (2 200—1 600 cm^{-1}), and the nature of the final products confirmed by n.m.r. spectroscopy. Both reactions gave $[Fe(CO)_3(CNBu^t)(CNC_6H_3Me_2\text{-}2,6)]$ rapidly [reaction (*a*) 2 min and reaction (*b*) *ca.* 45 min]. The transfer of isonitrile from the catalyst, $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNR)]$, to $[Fe(CO)_4(CNR)]$ occurred only in trace amounts upon extended heating (2 h).

These results suggest that the catalytic substitution of the metal carbonyl substrate by isonitrile occurs *via* a rapid intermolecular attack of isonitrile on the catalyst–substrate intermediate and that if any intramolecular transfer of isonitrile from the catalyst to the substrate is occurring it is *via* a slower secondary step.

The conclusion drawn from the mechanistic studies on reaction (xxii) is that the data are not inconsistent with the mechanism proposed in Schemes 2 or 3.

Reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ *and* RNC.—We have previously reported on the reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ and RNC using $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ as catalyst.[11] Herein we wish only to add pertinent mechanistic data that relate to the use of (1) in reaction (xxiii). Thus,

$$[Mo(CO)_3(\eta^5\text{-}C_5H_5)I] + Bu^tNC \longrightarrow [Mo(CO)_2(\eta^5\text{-}C_5H_5)(CNBu^t)I] + CO \quad \text{(xxiii)}$$

reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ (0.3 mmol), Bu^tNC (0.3 mmol), and (1) (0.3 mmol) in benzene (10 cm^3, 45 °C) results in the synthesis of $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(CNBu^t)I]$ (95% reaction as determined by i.r. spectroscopy; 250 min). In the absence of (1), <5% reaction is observed. Replacement of (1) by $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(Bu^tNC)]$ results in a more rapid reaction (95% reaction; <50 min). Further, the equimolar reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ and $[Fe_2(CO)_3(\eta^5\text{-}C_5H_5)_2(CNBu^t)]$ results in no isonitrile transfer to the Mo complex under reaction conditions similar to those listed above.

The possibility that mixed-metal carbonyl derivatives were prepared during the reaction was investigated. In refluxing benzene, mixtures of (1) and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ did react to give $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$, $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ and $[MoFe(CO)_5(\eta^5\text{-}C_5H_5)_2]$.[45] Similar scrambling occurred when $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)I]$ were heated together. However, at lower temperatures only a very slow scrambling reaction (~5%; 6 h) occurred strongly suggesting that only low concentrations of $Fe(CO)_2(\eta^5\text{-}C_5H_5)^\bullet$ radicals are present in solution at this temperature.

These results on the $[Mo(CO)_3(\eta^5\text{-}C_5H_5)I]$ substitution reaction are thus in agreement with the mechanism proposed in Schemes 2 and 3.

Other Catalysed Reactions.—The use of (1) and related dimers as catalysts has also been extended to reactions of metal carbonyl substrates with Group 5B donor ligands, *e.g.* equations (xxiv)[31] and (xxv).[32]

$$[Fe(CO)_5] + PR_3 \longrightarrow [Fe(CO)_4(PR_3)] + CO \quad \text{(xxiv)}$$

$$[Fe(CO)_2(\eta^5\text{-}C_5H_5)I] + PR_3 \longrightarrow [Fe(CO)(\eta^5\text{-}C_5H_5)(PR_3)I] + [Fe(CO)(\eta^5\text{-}C_5H_5)(PR_3)_2]I \quad \text{(xxv)}$$

The extension of the use of (1) and related dimers to CO substitution reactions of dimers (*e.g.* $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$) and clusters {*e.g.* $[Ru_3(CO)_{12}]$} with isonitriles has been successful but will be reported elsewhere.[32]

The use of (1) as a catalyst is, however, not without its limitations. For instance, no catalysis has been observed for reactions between $[Co_4(CO)_{12}]$ and $C_6H_3Me_3$, $[Mo(CO)_3(\eta^5\text{-}C_5H_5)Me]$, and Bu^tNC, or $[Mo(CO)_6]$ and PPh_3. Further work on the extensions and limitations of the catalytic utility of (1) are in progress.

Conclusions

The use of (1) as a catalyst for the substitution reaction $[M(CO)_n] + L \longrightarrow [M(CO)_{n-1}L] + CO$ has been shown to occur by two different pathways. One of these pathways is a radical chain pathway involving atom transfer and has been well documented by Brown and co-workers.[10] A second pathway involving radicals which requires electron transfer but no atom transfer has been observed to occur at lower temperatures. This second pathway provides a general catalytic route to ligand substitution reactions and should have important consequences in synthetic organometallic chemistry as well as in catalytic systems using metal–metal bonded catalysts.[46]

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