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Pd-catalysed carbonyl ligand substitution reactions of $[Mn(CO)_5Br]$ and $[Re(CO)_5Br]$ by isocyanides

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Abstract

The Pd-catalysed carbonyl ligand displacement reactions of $[M(CO)_5Br]$, (M = Mn, Re) with isocyanides to yield the substituted derivatives $[M(CO)_{5-x}(CNR)_xBr]$, (x = 1-5, R = Me, i-Pr, t-Bu, $C_6H_5CH_2$, C_6H_{11}, $C_6H_3Me_2$-2,6), and $[M(CO)_{6-x}(CNR)_x]Br$, (x = 5, 6, R = t-Bu, $C_6H_3Me_2$-2,6), are reported. In general the reactions proceed rapidly in moderate to excellent yields. The substitution proceeds more rapidly with aryl isocyanides than with alkyl isocyanides, and more readily with the Re complex than the Mn complex. Isomerisation reactions as well as substitution pathways leading to the respective substituted products formed were examined. An X-ray crystallographic examination of *trans*-$[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$, (space group: $P4nc$, $Z = 2$, $a = b = 13.663(3)$ Å, $c = 9.384(3)$ Å), revealed that the isocyanide ligands are all in equatorial positions substituted in the complex.

Introduction

An investigation of the substitution reactions of a range of a mixed metal dimer complexes has indicated preferential substitution at one of the metal centres [1–9]. However, the unequivocal determination of the site of substitution remains non-trivial for e.g., dimers such as $[MnRe(CO)_{10}]$ [6,10]. Consequently, a variety of chemical and physical techniques are required in order to establish the site of substitution. One procedure for obtaining the desired information is to prepare the dimer from presubstituted monomeric fragments via a condensation reaction such as:

$$[M(CO)_n(L)_mX] + Na[M'(CO)_x(L')_y] \rightarrow [M(CO)_n(L)_m\text{–}M'(CO)_x(L')_y] + NaX$$

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(No mechanistic implications are implied in the above equation) [11]. This approach requires the ready availability of the substituted monomeric species, $[M(CO)_n(L)_mX]$ and $[M'(CO)_x(L')_y]^-$.

In recent years we have developed catalytic routes to the substitution reactions of a wide range of metal carbonyl complexes of the type, $[M(CO)_n(L)_mX]$ [7,12–14]. Herein we report an extension of this approach, namely the use of Pd catalysts for the substitution reactions of $[M(CO)_5Br]$, (M = Mn, Re), by isocyanides, RNC, to give the complexes $[M(CO)_{x-n}(CNR)_xBr]$. In a future publication we will report on the use of the substituted complexes $[M(CO)_x(CNR)_yBr]$ in the synthesis of the substituted mixed metal dimers $[MnRe(CO)_x(CNR)_y]$, and the use of the products in assisting with the site selectivity problem associated with the metal dimer.

An examination of the literature reveals that several routes to isocyanide substituted Mn and Re carbonyl monomeric fragments have been developed and that numerous derivatives having different degrees of substitution are known [15–17]. For example, preparation of $[M(CO)_4(CNR)Br]$ and $[M(CO)_3(CNR)_2Br]$ complexes has previously been achieved via thermal and photolytic routes [15,18–28]. More highly substituted derivatives have also been synthesised by these procedures. Alternate routes starting from high oxidation state metal precursors and involving the formation of cationic salt complexes also exist, but have mainly been limited to the $[M(CNR)_6]^+$ species. Our catalysed procedure is compared with these alternative procedures. The X-ray crystal structure determination of *trans*-$[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$ is also reported.

Experimental

$[Mn(CO)_5Br]$ and $[Re(CO)_5Br]$ were prepared by cleavage of $[M_2(CO)_{10}]$, M = Mn, Re (purchased from Strem Chemicals) with Br_2 by published procedures [29]. The PdO was purchased from Johnson–Matthey Chemicals and the supported Pd catalysts from Merck Ltd. All the reactions were carried out in distilled solvents. Column chromatography was performed on silica gel, (Merck 60F, 70–230 mesh), under nitrogen.

Infrared spectra were recorded on a Perkin–Elmer 580B IR spectrometer and NMR spectra on a Bruker AC200 NMR spectrometer. Microanalyses were performed by the Microanalytical Laboratories, CSIR, Pretoria.

Preparation of $[M(CO)_4(CNR)Br]$, (M = Mn, Re; R = Me, i-Pr, t-Bu, C_6H_{11}, $CH_2C_6H_5$ and 2,6-$Me_2C_6H_3$)

$[M(CO)_5Br]$ (0.5 mmol) was taken up in benzene or $CHCl_3$(Re) or in THF (Mn) (10 ml) at room temperature. The isocyanide was added (1.0 equiv), followed by PdO catalyst (6–10 mg). Rapid effervescence occurred during the reaction which was monitored by IR spectroscopy. Upon completion the solution was filtered through cellulose and pumped to dryness. The crude reaction product was purified by column chromatography (silica; eluent, benzene) to yield the yellow (Mn) or white (Re) crystalline products. The characterisation of the products is given in Tables 1, 2 (Mn) and 3, 4 (Re).

Preparation of $[M(CO)_3(CNR)_2Br]$, (M = Mn, Re; R = Me, i-Pr, t-Bu, C_6H_{11}, $CH_2C_6H_5$ and 2,6-$Me_2C_6H_3$)

$[M(CO)_5Br]$ (0.5 mmol) was added to benzene (10 ml) or $CHCl_3$ (see Results). The benzene solution was heated to 50 °C and then the isocyanide (2.0 equiv) and

Table 1

Analytical data for the $[Mn(CO)_5Br]$ isonitrile derivatives

Complex	M.p. [a] (°C)	Analysis [b] (%)		
		C	H	N
$[Mn(CO)_4(CNCH_3)Br]$	144–146 [c]	25.99	0.99	4.75
		(25.03)	(1.05)	(4.86)
$[Mn(CO)_4(CNPr\text{-}i)Br]$	59– 60	29.85	2.46	4.89
		(30.41)	(2.23)	(4.43)
$[Mn(CO)_4(CNBu\text{-}t)Br]$	89– 90	33.19	2.81	4.38
		(32.76)	(2.75)	(4.24)
$[Mn(CO)_4(CNCH_2C_6H_5)Br]$	83– 85 [d]	39.87	1.90	3.88
		(39.48)	(2.21)	(3.84)
$[Mn(CO)_4(CNC_6H_{11})Br]$	90– 91	37.52	3.02	3.91
		(37.11)	(3.11)	(3.93)
$[Mn(CO)_4(CNC_6H_3Me_2\text{-}2,6)Br]$	159–161 [e]	41.86	2.53	3.73
		(41.30)	(2.40)	(3.70)
$[Mn(CO)_3(CNPr\text{-}i)_2Br]$	56– 58	36.63	3.81	7.85
		(37.00)	(3.95)	(7.85)
$[Mn(CO)_3(CNBu\text{-}t)_2Br]$	95– 98	41.22	4.86	6.99
		(40.54)	(4.71)	(7.27)
$[Mn(CO)_3(CNCH_2C_6H_5)_2Br]$	126–128	50.31	2.77	6.20
		(50.36)	(3.11)	(6.18)
$[Mn(CO)_3(CNC_6H_{11})_2Br]$	72– 73	46.70	5.29	6.02
		(47.73)	(5.07)	(6.41)
fac-$[Mn(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2Br]$	155–156	50.30	3.52	5.56
		(52.41)	(3.77)	(5.82)
mer, trans-$[Mn(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2Br]$	87– 89	51.74	3.48	5.76
		(52.41)	(3.77)	(5.82)
$[Mn(CO)_2(CNBu\text{-}t)_3Br]$	107–110	45.16	6.27	9.56
		(46.38)	(6.18)	(9.54)
$[Mn(CO)(CNBu\text{-}t)_4Br]$	164–166	52.48	10.90	7.15
		(50.92)	(11.31)	(7.32)
$[Mn(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$	153–155	64.87	5.20	8.10
		(64.64)	(5.28)	(8.15)
$[Mn(CNC_6H_3Me_2\text{-}2,6)_5Br]$	146–156	67.78	5.64	8.88
		(68.35)	(5.74)	(8.86)
$[Mn(CO)(CNC_6H_3Me_2\text{-}2,6)_5]Br$	–	50.66	11.37	7.61
		(53.98)	(12.11)	(7.84)
$[Mn(CNC_6H_3Me_2\text{-}2,6)_6]PF_6$	–	66.93	5.04	8.58
		(65.72)	(5.51)	(8.52)

[a] Uncorrected. [b] Found, calculated values in parentheses. [c] Darken at 99–103°C. [d] Darken at 70–72°C. [e] Darken at 84–86°C.

either $Pd/CaCO_3$ (20 mg), (Mn) or PdO (6–10 mg), (Re) was added. After an initial induction period of a few minutes, a rapid reaction took place. The reaction was monitored by IR spectroscopy and found to be complete within 30 min. The solution was filtered through cellulose, concentrated, and subjected to column chromatography (silica; eluent, CH_2Cl_2). After removal of the solvent, the dark yellow (Mn) or white (Re) materials were characterised as shown in Tables 1 to 4.

Table 2

Spectroscopic data for the [$Mn(CO)_5Br$] derivatives

Complex	IR [a,b]					NMR [c,d]	
	ν (NC)		ν (CO)			CH_3	Other
[$Mn(CO)_4(CNCH_3)Br$]		2229m	2108m	2030vs	1977s	1.65	–
[$Mn(CO)_4(CNPr$-i)Br]		2209m	2106m	2033vs	1974s	0.57 (d)	C*H* 2.86 (m)
[$Mn(CO)_4(CNBu$-t)Br]		2196m	2103m	2027vs	1974s	0.77	–
[$Mn(CO)_4(CNCH_2C_6H_5)Br$]		2215m	2106m	2034vs	1978s	3.60	C_6H_5 6.9 (m)
[$Mn(CO)_4(CNC_6H_{11})Br$]		2206m	2103m	2029vs	1974s	1.0 (b.m)	–
[$Mn(CO)_4(CNC_6H_3Me_2$-2,6)Br]		2180m	2102m	2032vs	1979s	1.98	C_6H_3 6.5 (m)
[$Mn(CO)_3(CNPr$-i$)_2Br$]	2192m	2172m	2032vs	1986s	1941m	0.66 (t)	C*H* 2.96 (m)
[$Mn(CO)_3(CNBu$-t$)_2Br$]	2187m	2165m	2032vs	1985s	1944m	0.91	–
[$Mn(CO)_3(CNCH_2C_6H_5)_2Br$]	2200m	2182m	2057vs	1991s	1946m	3.62	C_6H_5 6.9 (m)
[$Mn(CO)_3(CNC_6H_{11})_2Br$]	2192m	2175m	2037vs	1986s	1941m	0.9–1.5(m)	
fac-[$Mn(CO)_3(CNC_6H_3Me_2$-2,6$)_2Br$]	2145m	2123m	2040vs	2000m	1953m	2.15	C_6H_3 6.6 (m)
mer, trans-[$Mn(CO)_3(CNC_6H_3Me_2$-2,6$)_2Br$]	–	2127s	2037m	1999vs	1952m	2.17	C_6H_3 6.6 (m)
[$Mn(CO)_2(CNBu$-t$)_3Br$]	2147sh	2127s	1980s	1906s		1.03, 1.08 (2:1)	–
[$Mn(CO)_2(CNC_6H_3Me_2$-2,6$)_3Br$]	2122sh	2100s	1944s	1924s		2.31, 2.32 (2:1)	C_6H_3 6.6 (m)
[$Mn(CO)(CNBu$-t$)_4Br$]	2097s	2065sh	1874m			1.20	–
[$Mn(CO)(CNC_6H_3Me_2$-2,6$)_4Br$]	2080s		1904m			2.45	C_6H_3 6.7 (m)
[$Mn(CNC_6H_3Me_2$-2,6$)_5Br$]	2052s	1999w				2.41, 2.51 (1:4)	C_6H_3 6.7 (m)
[$Mn(CO)(CNBu$-t$)_5$]Br	2142sh	2116s	2062sh	1955m		1.49	–
[$Mn(CNC_6H_3Me_2$-2,6$)_6$]PF_6	2075s	1996vw				2.44	C_6H_3 7.1 (m)

[a] Run in CH_2Cl_2. [b] vs = very strong, s = strong, sh = shoulder, m = medium, w = weak, vw = very weak. [c] Run in C_6D_6 or $CDCl_3$ (salts) relative to TMS. [d] d = doublet, t = triplet, m = multiplet, b = broad.

Table 3

Analytical data for the [Re(CO)$_5$Br] isonitrile derivatives

Complex	M.p. [a] (°C)	Analysis [b] (%)		
		C	H	N
[Re(CO)$_4$(CNCH$_3$)Br]	142–143 [c]	17.1 (17.2)	0.79 (0.72)	3.35 (3.34)
[Re(CO)$_4$(CNPr-i)Br]	91– 93	21.4 (21.5)	1.34 (1.58)	3.16 (3.13)
[Re(CO)$_4$(CNBu-t)Br]	109–112	23.5 (23.4)	1.68 (1.97)	3.10 (3.03)
[Re(CO)$_4$(CNCH$_2$C$_6$H$_5$)Br]	111–112	28.8 (29.1)	1.01 (1.42)	2.90 (2.83)
[Re(CO)$_4$(CNC$_6$H$_{11}$)Br]	112–114	26.4 (27.1)	1.92 (2.27)	2.73 (2.88)
[Re(CO)$_4$(CNC$_6$H$_3$Me$_2$-2,6)Br]	135–138	30.5 (30.5)	1.50 (1.78)	2.78 (2.74)
[Re(CO)$_3$(CNPr-i)$_2$Br]	103–105	26.8 (27.1)	2.81 (2.89)	5.67 (5.74)
[Re(CO)$_3$(CNBu-t)$_2$Br]	163–164	30.6 (30.2)	3.52 (3.51)	5.55 (5.42)
[Re(CO)$_3$(CNBu-t)$_2$I]	138–139	27.8 (27.7)	3.23 (3.20)	4.85 (4.97)
[Re(CO)$_3$(CNCH$_2$C$_6$H$_5$)$_2$Br]	156–158	39.7 (39.1)	2.40 (2.41)	4.85 (4.79)
[Re(CO)$_3$(CNC$_6$H$_{11}$)$_2$Br]	100–103			
[Re(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br]	145–147	41.4 (41.2)	2.86 (2.96)	4.61 (4.60)
[Re(CO)$_2$(CNBu-t)$_3$Br]	170–174	36.5 (35.7)	5.50 (4.76)	8.28 (7.35)
[Re(CO)(CNBu-t)$_4$Br]	> 180 [d]	39.8 (40.3)	5.61 (5.79)	8.70 (8.94)
[Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_4$Br]	250–252	54.2 (64.3)	4.20 (4.43)	6.89 (6.84)
[Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_5$]PF$_6$	198–201	52.5 (54.4)	4.25 (4.47)	6.91 (6.90)
[Re(CNC$_6$H$_3$Me$_2$-2,6)$_6$]PF$_6$	248–252	57.1 (58.0)	4.86 (4.87)	7.51 (7.52)

[a] Uncorrected. [b] Found, calculated values in parentheses. [c] Literature value [33]. [d] Decomposition.

Isomerisation of fac-[Mn(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br]

The equilibrium mixture of *fac*- and *mer, trans*-[Mn(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br] obtained above was taken up in a minimum of CH$_2$Cl$_2$ containing a drop of CF$_3$COOH (ca. 10^{-3} *M*). Hexane was added to the solution which was left to crystallise at −20 °C. A first crop of dark yellow crystals was isolated and identified as *mer, trans*-[Mn(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br] which was characterised as shown in Tables 1 and 2. Heating of an equilibrium mixture of [Mn(CO)$_3$-(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br] in CH$_2$Cl$_2$ containing CF$_3$COOH resulted in complete isomerisation to the *mer, trans*-isomer, as identified by the ^{1}H NMR spectrum (C$_6$D$_6$) of the residue following solvent removal.

Preparation of [M(CO)$_2$(CNR)$_3$Br] (M = Mn, Re; R = t-Bu and 2,6-Me$_2$C$_6$H$_3$)

[M(CO)$_5$Br] (0.5 mmol) was taken up in refluxing benzene (10 ml). The respective isocyanide (3.3 equiv) and catalyst were added (PdO, 10 mg for M = Re and Pd/CaCO$_3$, 25 mg for M = Mn). The reaction was monitored by IR spectroscopy and found to be complete after 2.5 h. The solution was cooled, filtered through cellulose to remove the catalyst and the salt products, and the solvent was removed in vacuo. The t-BuNC derivatives were subsequently purified by fractional crystallisation from CH$_2$Cl$_2$/hexane. The Mn-containing 2,6-Me$_2$C$_6$H$_3$NC derivative was purified by column chromatography (silica; eluent CH$_2$Cl$_2$), and the Re derivative by crystallisation. The salt products isolated were purified by recrystallisation from CH$_2$Cl$_2$/hexane. The identification and characterisation of the various complexes and the other products formed are described in the Results Section and are given in Tables 1 to 4.

Table 4

Spectroscopic data for the [Re(CO)$_5$Br] derivatives

Complex	IR [a,b]					NMR [c,d,e]	
	ν (NC)		ν (CO)			CH$_3$	Other
[Re(CO)$_4$(CNCH$_3$)Br]		2228m	2107m	2010vs	1956s	1.62	–
[Re(CO)$_4$(CNPr-i)Br]		2210m	2110m	2020vs	1957s	0.51 (d)	C*H* 2.81 (m)
[Re(CO)$_4$(CNBu-t)Br]		2206m	2110m	2020vs	1959s	0.71	–
[Re(CO)$_4$(CNBu-t)I]		2203m	2106m	2018vs	1959s	0.72	–
[Re(CO)$_4$(CNCH$_2$C$_6$H$_5$)Br]		2215m	2109m	2015vs	1957s	3.56	C_6H_5 6.9 (m)
[Re(CO)$_4$(CNC$_6$H$_{11}$)Br]		2206m	2106m	2016vs	1958s	0.8–1.3(m)	
[Re(CO)$_4$(CNC$_6$H$_3$Me$_2$-2,6)Br]		2180m	2105m	2015vs	1959m, b	1.94	C_6H_3 6.6 (m)
[Re(CO)$_3$(CNPr-i)$_2$Br]	2210m	2190m	2041s	1980s	1923s	0.63(6.4)	C*H* 2.98 (m: 6.5)
[Re(CO)$_3$(CNBu-t)$_2$Br]	2205m	2180m	2036s	1975s	1925s	0.86	–
[Re(CO)$_3$(CNBu-t)$_2$I]	2200m	2175m	2036s	1973s	1924s	0.87	–
[Re(CO)$_3$(CNCH$_2$C$_6$H$_5$)$_2$Br]	2214m	2186m	2036s	1981s	1925s	3.62	C_6H_5 6.9 (m)
[Re(CO)$_3$(CNC$_6$H$_{11}$)$_2$Br]	2210m	2190m	2032s	1985s	1926s	0.8–1.3(m)	
[Re(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br]	2180m	2148m	2036s	1991s	1942s	2.09	C_6H_3 6.6 (m)
[Re(CO)$_2$(CNBu-t)$_3$Br]	2160sh	2130s	1968s	1885s		1.00	–
[Re(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_3$Br]	2130sh	2106s	1983s	1905s		2.25	C_6H_3 6.6 (m)
[Re(CO)(CNBu-t)$_4$Br]	2112s	2064sh	1851m			1.15	–
[Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_4$Br]	2084s		1882m			2.39	C_6H_3 6.7 (m)
[Re(CNC$_6$H$_3$Me$_2$-2,6)$_5$Br]	2080s					2.46, 2.52(4:1)	C_6H_3 6.8 (m)
[Re(CO)(CNBu-t)$_5$]PF$_6$	2150sh	2120s	2070sh	1944m		1.51	–
[Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_5$]PF$_6$	2100sh	2080s		1974m		2.46	C_6H_3 7.2 (m)
[Re(CNC$_6$H$_3$Me$_2$-2,6)$_6$]PF$_6$	2072s	2004vw				2.45	C_6H_3 7.2 (m)

[a] Run in CH$_2$Cl$_2$. [b] s = strong, sh = shoulder, m = medium, w = weak, vw = very weak, b = broad. [c] Run in C$_6$D$_6$ or CDCl$_3$ (salts) relative to TMS. [d] d = doublet, t = triplet, m = multiplet, b = broad. [e] 80 mHz.

Preparation of [M(CO)(CNR)$_4$Br] (M = Mn, Re; R = t-Bu, 2,6-Me$_2$C$_6$H$_3$)

Isocyanide (4 equiv) was added to a solution of [M(CO)$_5$Br] (1.0 mmol) in benzene (20 ml), either refluxing (t-BuNC) or at 40–50 °C (2,6-Me$_2$C$_6$H$_3$NC), followed by either PdO (Re) or Pd/CaCO$_3$ (Mn). The reaction was monitored by IR spectroscopy and found to be complete within 3 h. During the reaction a white precipitate formed, and was readily removed by filtration of the solution through a cellulose column. Elution with acetone gave the product free from the Pd catalyst. The various products were purified by crystallisation from CH$_2$Cl$_2$/hexane. The yields of the various components formed could be altered by variation of the reaction conditions (see Results).

Product analysis indicated that the following products were formed in varying yields:

(a) Using t-BuNC: [M(CO)$_2$(CNBu-t)$_3$Br], [M(CO)(CNBu-t)$_4$Br], [M(CO)(CNBu-t)$_5$]Br and [M(CNBu-t)$_5$Br] (Re only).

(b) Using 2,6-Me$_2$C$_6$H$_3$NC: [M(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_3$Br], [M(CO)(CNC$_6$H$_3$-Me$_2$-2,6)$_4$Br], [M(CNC$_6$H$_3$Me$_2$-2,6)$_5$Br] and [M(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_5$]Br.

The products were characterised as shown in Tables 1 to 4.

Preparation of [M(CNR)$_5$Br] (M = Mn, Re; R = t-Bu, 2,6-Me$_2$C$_6$H$_3$)

Isocyanide (6 equiv) and either Pd/CaCO$_3$ (25 mg) or PdO (10 mg) were added to a solution of [Mn(CO)$_5$Br] or [Re(CO)$_5$Br] (0.5 mmol) in benzene (15 ml, reflux). The reaction was monitored by IR spectroscopy and found to be complete within 6 h. A salt product separated out. The solution was cooled to room temperature and filtered through cellulose to give the benzene-soluble material. Subsequent elution of the cellulose column with acetone resulted in isolation of the salts formed. Product analysis of the reaction mixture indicated that the reaction involving t-BuNC yielded mainly [M(CO)(CNBu-t)$_4$Br] and [M(CO)(CNBu-t)$_5$]Br rather than the desired product (see Results). The yield of the salt product formed was higher than that obtained above. In the case of 2,6-Me$_2$C$_6$H$_3$NC, a mixture of products consisting mainly of [M(CNC$_6$H$_3$Me$_2$-2,6)$_5$Br] and [M(CNC$_6$H$_3$Me$_2$-2,6)$_6$]Br was obtained (see Results). These materials were characterised as indicated in Tables 1 to 4.

X-Ray crystal structure analysis of [Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_4$Br]

A single crystal of [Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_4$Br], grown from CH$_2$Cl$_2$/hexane at −20 °C under nitrogen, was mounted on a glass fibre. Lattice constants were measured and refined from 25 reflections in the range $7 \leq \theta \leq 18°$ on an automatic Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation. The crystal data and crystallographic details appear in Table 5. Intensity data were collected in the range $3 \leq \theta \leq 30°$ and standard reflections were measured every hour of exposure time. The data was corrected for Lorentz polarisation effects and an empirical absorption correction was applied [30].

The structure was solved by Patterson methods and subsequent Fourier synthesis revealed the remaining non-hydrogen atoms. Refinement was carried out by means of full-matrix least-squares calculations in which the H atoms were included at calculated positions and all non-hydrogen atoms were assigned anisotropic temperature factors.

Table 5

Crystal data and details of the structure analysis for [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br]

Complex	[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br]
M_r	$C_{37}H_{36}N_4OBrRe$
Colour, shape	yellow cubes
Space group	$P4nc$
a (Å)	13.663(3)
b (Å)	13.663(3)
c (Å)	9.384(3)
$\alpha = \beta = \gamma$ (°)	90
U (Å^3)	1751.89
Z	2
D (calc) (g cm^{-3})	1.55
F(000)	808
μ (cm^{-1})	44.56
λ (Mo-K_α) (Å)	0.7107
Scan mode	$\omega/2\theta$
Range (°)	$3 \geq \theta \geq 30$
Scan width (°)	$0.6 + 0.35 \tan\theta$
Variable scan speed (° min^{-1})	0.97–5.49
Range of hkl	$0 \leq h \leq 19$
	$0 \leq k \leq 19$
	$0 \leq l \leq 13$
Measd intensities	2892
Unique reflectns	1242
Omitted reflectns	405
Cutoff criterion	$F < 4\sigma(F)$
R index [a]	0.0213
R_w index	0.0174
Weighting scheme	$\omega = K\sigma^2(F)$
No. of variables	103
Max shift/esd (non H)	0.07
Max peak in diff. map (eÅ^{-3})	0.94

[a] The conventional R is defined by $R = \Sigma \| F_o \| - \| F_c \| / \Sigma \| F_o \|$ where F_o and F_c are the observed and calculated structure factors respectively.

Table 6

Fractional coordinates (×10^4) and equivalent isotropic temperature factors (Å^2, ×10^3, ×10^4 for Re, Br) for non-hydrogen atoms of [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br]

Atom	x/a	y/b	z/c	U_{eq}
Re	0	0	0	416(1)
Br	0	0	−2845(2)	615(1)
N(1)	2026(4)	1124(4)	−289(8)	57(4)
C(1)	1299(4)	719(4)	−144(12)	47(3)
C(2)	2911(4)	1582(5)	−641(7)	48(4)
C(3)	3119(5)	2503(5)	−64(13)	52(3)
C(4)	3980(6)	2953(5)	−474(8)	74(5)
C(5)	4586(6)	2518(6)	−1439(13)	86(6)
C(6)	4379(5)	1592(7)	−2004(9)	77(6)
C(7)	3525(5)	1114(5)	−1604(9)	60(5)
C(8)	3261(7)	124(5)	−2193(9)	96(7)
C(9)	2422(6)	2989(5)	951(9)	80(6)
C(10)	0	0	2141(1)	50(6)
O(1)	0	0	3313(2)	125(11)

Table 7

Bond lengths and angles observed in [Re(CO)$(CNC_6H_3Me_2$-2,6$)_4$Br]

Re–Br	2.670(2)	Re–C(1)	2.033(5)
C(1)–N(1)	1.146(6)	N(1)–C(2)	1.400(7)
C(2)–C(3)	1.400(8)	C(3)–C(4)	1.382(8)
C(4)–C(5)	1.364(12)	C(5)–C(6)	1.401(11)
C(6)–C(7)	1.389(8)	C(7)–C(2)	1.388(8)
C(7)–C(8)	1.506(8)	C(3)–C(9)	1.502(11)
Re–C(10)	2.009(1)	C(10)–O(1)	1.100(1)
Br–Re–C(10)	180.0(1)	C(1)–Re–Br	86.2(3)
C(1)–Re–C(10)	93.8(3)	Re–C(10)–O(1)	180.0(1)
N(1)–C(1)–Re	176.9(1)	C(2)–N(1)–C(1)	173.0(9)
C(3)–C(2)–N(1)	119.0(6)	C(7)–C(2)–N(1)	118.0(6)
C(7)–C(2)–C(3)	122.9(7)	C(4)–C(3)–C(2)	117.7(8)
C(9)–C(3)–C(2)	121.0(7)	C(9)–C(3)–C(4)	121.3(7)
C(5)–C(4)–C(3)	120.5(8)	C(6)–C(5)–C(4)	121.5(4)
C(7)–C(6)–C(5)	119.4(8)	C(6)–C(7)–C(2)	117.9(7)
C(8)–C(7)–C(2)	120.5(7)	C(8)–C(7)–C(6)	121.6(8)

During refinement rotational disorder was observed in the carbonyl group resulting from motion around the unit cell axis. As a consequence the Re–C and the $C\equiv O$ bond lengths were constrained at 2.009 and 1.100 Å respectively; further refinement was continued until all parameter shifts were less than 0.5σ. The final R and R_w values were 0.0213 and 0.0176 respectively using a weighting scheme $\omega = K\sigma^2(F)$. All calculations were performed on a Cyber-750 computer using the SHELX-76 set of programs [31].

The molecular geometry of [Re(CO)$(CNC_6H_3Me_2$-2,6$)_4$Br] with the atomic numbering scheme used is shown in Fig. 1. Atomic parameters are given in Table 6 and bond lengths and angles in Table 7. Listings of anisotropic thermal parameters and calculated structure factors are available from the authors.

Results and discussion

Substitution reactions of [Mn(CO)$_5$Br]

Choice of catalyst

A variety of Pd-based materials were screened for their ability to bring about the following substitution:

$$[Mn(CO)_5Br] + 2\ t\text{-}BuNC \rightarrow [Mn(CO)_3(CNBu\text{-}t)_2Br] + 2\ CO$$

This reaction was selected because use of less active catalysts may result in formation only of the monosubstituted derivative $[Mn(CO)_4(CNBu\text{-}t)Br]$ while use of very active catalysts may lead to formation of the trisubstituted product, $[Mn(CO)_2(CNBu\text{-}t)_3Br]$. The relative activities of the catalysts tested was assessed by analysing the reaction mixture after 1 h reaction time. The results are shown in Table 8, which indicates the major and minor products formed.

These results indicate that PdO and Pd/Al_2O_3 are very effective catalysts for this substitution reaction, whereas Pd/C displays little catalytc activity. The choice of

Table 8

Screening of Pd catalysts for their efficiency to effect the t-BuNC substitution reaction of [$Mn(CO)_5Br$]

Catalyst [a]	Major reaction product	Minor reaction product	Relative ratio of trisubstituted product [b]
Pd/Al_2O_3	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_2(CNR)_3Br$	6
$Pd/BaCO_3$	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_4(CNR)Br/$ $Mn(CO)_2(CNR)_3Br$	2
$Pd/BaSO_4$	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_4(CNR)Br/$ $Mn(CO)_2(CNR)_3Br$	2
Pd/C	$Mn(CO)_5Br$	$Mn(CO)_4(CNR)Br$	trace
$Pd/CaCO_3$	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_2(CNR)_3Br$	4
Pd	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_4(CNR)Br$	1
PdO	$Mn(CO)_3(CNR)_2Br$	$Mn(CO)_2(CNR)_3Br$	6

[a] Loadings on the support are 10%. [b] This only describes the relative amount of trisubstituted product formed for the different catalysts examined and does not describe the ratio of disubstituted to trisubstituted product formed for the respective materials. Thus in the PdO catalysed reaction six times as much trisubstituted product is formed as in the Pd catalysed reaction.

catalyst used in the substitution reactions was dictated by the activity of the material and the product distribution obtained. Thus PdO and $Pd/CaCO_3$ were selected as the catalysts for the study.

Synthesis of [$Mn(CO)_4(CNR)Br$]

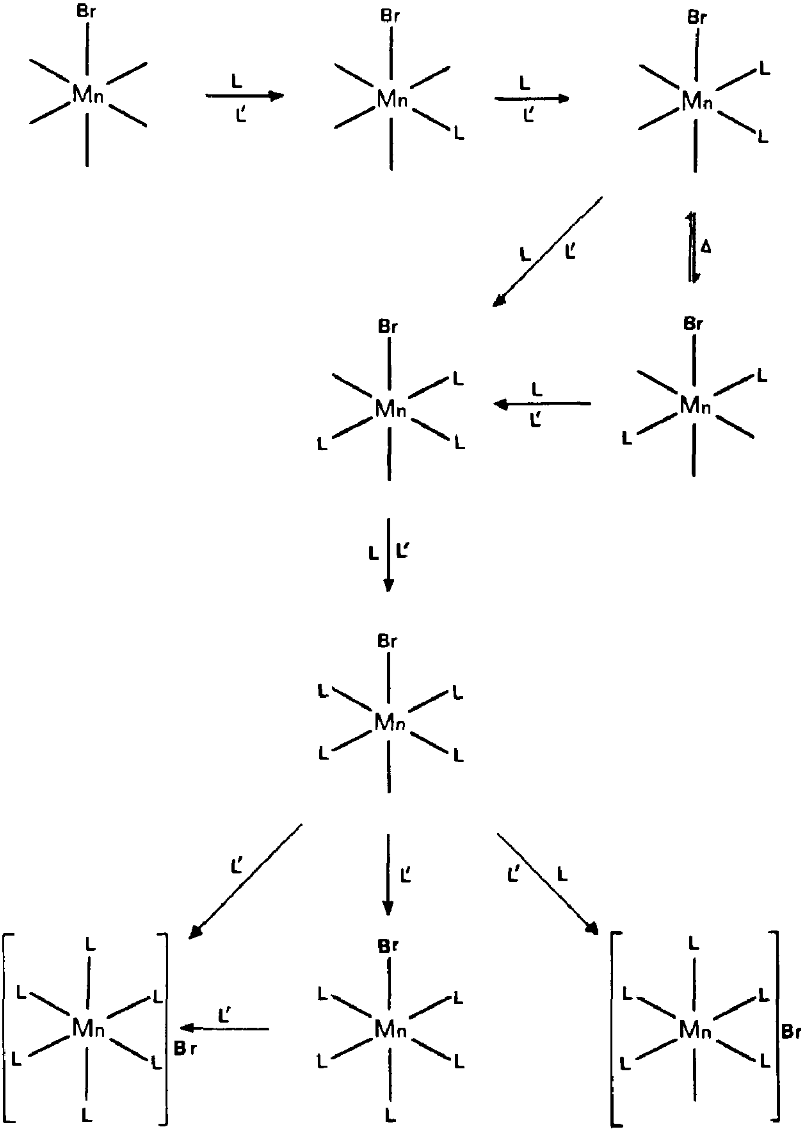
The reaction of [$Mn(CO)_5Br$] with one equivalent of isocyanide in the presence of PdO catalyst was found to proceed rapidly to give the monosubstituted derivative in 50 to 65% yield (after purification); the remainder of the starting material being still present or converted into the disubstituted complex. The reaction times varied from 20 min (t-BuNC, 2,6-$Me_2C_6H_3NC$, i-PrNC) to 60 min (MeNC). Numerous attempts to increase the yield were made by varying the reaction solvent (benzene, CH_2Cl_2, THF), temperature, and method of isocyanide addition. The best solvent was found to be THF, since the material is readily soluble in this medium and no catalyst deactivation was observed. Variation of the reaction temperature (0 to 50 °C) significantly altered the rate of reaction (2,6-$Me_2C_6H_3NC$; < 5 min, 50 °C; 60 min, 0 °C) but with only minor variation in the composition of the product mixture or overall yield. Corresponding blank reactions revealed little if any occurrence of reaction in the same reaction times.

Use of the optimum method found (1.0 equiv of RNC in THF at room temp) gave a range of [$Mn(CO)_4(CNR)Br$] derivatives (see Experimental), which were fully characterised (Tables 1 and 2). Spectral characterisation indicated that the site of substitution was *cis* to the Br atom.

Synthesis of [$Mn(CO)_3(CNR)_2Br$]

In the presence of $Pd/CaCO_3$ the disubstituted product was formed rapidly (< 30 min) in benzene at 50 °C. After column chromatography, purified products were obtained in $70 \pm 5\%$ yield; small amounts of the mono and trisubstituted products were also formed. The characterisation data for the disubstituted isocyanide complexes are given in Tables 1 and 2. These yields and reaction conditions compare very favourably with those of earlier workers (e.g. for the MeNC derivative [21]).

The IR spectra of the purified reaction products are consistent with *cis* substitution to give the *fac*-[Mn(CO)$_3$(CNR)$_2$Br] isomer. However slight shoulders on the ν(NC) absorptions in the IR spectra were noted, and suggested that a minor amount of an isomer, the *mer*, *trans* species, was present. This was confirmed for the product, [Mn(CO)$_3$(CNC$_6$H$_3$Me$_2$-2,6)$_2$Br], which upon recrystallisation from CH$_2$Cl$_2$/hexane in the presence of a trace amount of CF$_3$COOH, [32], crystallised preferentially to give the pure *mer, trans* isomer (Tables 1 and 2). Significantly the ν(CO) and ν(NC) absorptions of this complex corresponded exactly with the shoulder observed in the IR spectrum of the *fac* complex obtained from the catalysed reaction.



Scheme 1. Scheme showing the systematic isocyanide substitution pathway for [Mn(CO)$_5$Br] (L = t-BuNC, L′ = 2,6-Me$_2$C$_6$H$_3$NC).

Heating of the *fac*-isomer in CH_2Cl_2 (reflux) also resulted in rapid isomerisation to the *mer, trans*-isomer. (Scheme 1).

Synthesis of [Mn(CO)$_2$(CNR)$_3$Br]

The preparation of the trisubstituted derivatives was only examined for t-BuNC and 2,6-$Me_2C_6H_3NC$ as representative alkyl and aryl isocyanides.

The catalysed reaction involving t-BuNC as the ligand and Pd/$CaCO_3$ as the catalyst proceeded readily in refluxing benzene and was complete in 2.5 h. The desired product was obtained in 80 ± 5% yield. Spectral data were consistent with the expected equatorial substitution (Tables 1, 2 and Scheme 1).

Use of similar conditions for the reaction between [$Mn(CO)_5Br$] and 2,6-$Me_2C_6H_3NC$ did not result in exclusive formation of the trisubstituted derivative, but instead gave a mixture of the tri- and tetra-substituted complexes. This trisubstituted complex was, however, isolated by column chromatography.

Synthesis of higher substituted Mn derivatives

Reaction of [$Mn(CO)_5Br$] with four equivalents of t-BuNC in refluxing benzene gave a yellow benzene soluble material, [Mn(CO)(CNBu-t)$_4$Br], as well as a white salt, [Mn(CO)(CNBu-t)$_5$]Br. The products were identified from their IR spectra and by analogy with previous literature reports on similar complexes [20,21]. This route to the tetra-substituted complex does not give the complex in high yield, and the product is always contaminated with small amounts of the tri-substituted product.

Attempts to prepare [Mn(CNBu-t)$_5$Br] and [Mn(CNBu-t)$_6$]Br via the PdO catalysed reaction were unsuccessful. Possible reasons for this are discussed below.

Reaction of [$Mn(CO)_5Br$] with four equivalents of 2,6-$Me_2C_6H_3NC$ in refluxing benzene readily gave the tetra-substituted species [Mn(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] (1 h). Spectroscopic analysis of the crude reaction product indicated the presence of minor quantities of the penta-substituted complex [Mn($CNC_6H_3Me_2$-2,6)$_5$Br] and the salt [Mn(CO)($CNC_6H_3Me_2$-2,6)$_5$]Br [21]. No attempt to isolate and characterise the salt was made.

Use of an even larger molar ratio of 2,6-$Me_2C_6H_3NC$ to [$Mn(CO)_5Br$] enabled the preparation and isolation of the penta-substituted complex [Mn($CNC_6H_3Me_2$-2,6)$_5$Br] together with the salt [Mn($CNC_6H_3Me_2$-2,6)$_6$]PF_6 (made by counter-ion exchange). The characterisation data for these derivatives are listed in Tables 1 and 2.

It is apparent that the complete range of substituted complexes [$Mn(CO)_{5-x}$$(RNC)_x$Br] ($x = 1$–5) can be synthesized by use of the Pd-catalysed reaction under relatively mild conditions. This represents another example of the use of catalysts to achieve systematic substitution of carbonyl complexes, as previously observed in other synthetic studies [12–14].

Substitution reactions of [Re(CO)$_5$Br]

General comments

The substitution reactions of [$Re(CO)_5Br$] with isocyanides generally followed a similar course to those observed with [$Mn(CO)_5Br$]. The mono- and di-substituted isocyanide derivatives were prepared analogously for a series of isocyanides (MeNC, i-PrNC, t-BuNC, $CH_2C_6H_5NC$, $C_6H_{11}NC$ and 2,6-$Me_2C_6H_3NC$), and further substitution was attempted only in the case of t-BuNC and 2,6-$Me_2C_6H_3NC$. The results obtained in the synthesis of the lower-substituted derivatives provided a guideline to the synthesis of the higher substituted derivatives. The characterisation of the new derivatives prepared in this section are given in Tables 3 and 4.

Synthesis of [Re(CO)$_4$(CNR)Br]

The reaction of [Re(CO)$_5$Br] and t-BuNC in the presence of catalytic amounts of PdO was performed in benzene at room temperature. The solution was initially turbid owing to the low solubility of [Re(CO)$_5$Br] in this medium, but became clear within 10–20 min after addition of the isocyanide and the PdO catalyst. The progress of the reaction was monitored by IR spectroscopy and indicated that the reaction proceeded readily to completion. The crude product mixture always contained some of the disubstituted product, but the yield of the desired product was ± 80%. Attempts were made to increase the yield of this product by varying the temperature and the solvent, and hence the reagent solubility. A reaction in toluene at 0 °C was examined, and although a slower reaction occurred ($\approx$ 80 min), a mixture of products was again obtained. When $CHCl_3$, in which [Re(CO)$_5$Br] is completely soluble, was used, a very rapid reaction occurred (20 min, t-BuNC; 5 min, 2,6-$Me_2C_6H_3NC$) to give the required product in > 95% yield.

The reaction of [Re(CO)$_5$I) with t-BuNC in the presence of PdO gave the desired product in 90% yield (40 min).

Synthesis of [Re(CO)$_3$(CNR)$_2$Br]

The disubstituted derivatives were prepared by a procedure similar to that used for the [Re(CO)$_4$(CNR)Br] complexes. A 1/2 ratio of [Re(CO)$_5$Br] and isocyanide was stirred in benzene at 50 °C in the presence of PdO and this rapidly gave the desired disubstituted product (e.g. < 15 min for t-BuNC). The reaction is vigorous and CO can be seen to bubble out of the solution. In the presence of 2,6-$Me_2C_6H_3NC$ a mixture of soluble products was obtained, and these were identified as the complexes [Re(CO)$_{5-x}$(L)$_x$Br] ($x = 1, 2$); there was also a white precipitate, identified as [Re(CO)(CNC$_6$H$_3$Me$_2$-2,6)$_5$]Br (see below). In $CHCl_3$ the desired disubstituted product was formed cleanly at room temperature (< 20 min).

Thus the disubstituted derivatives can be readily synthesized in high yield in the presence of PdO using; (1) Benzene/50 °C, (except for 2,6-$Me_2C_6H_3NC$) or (2) $CHCl_3$ at room temperature (for 2,6-$Me_2C_6H_3NC$).

Synthesis of [Re(CO)$_2$(CNR)$_3$Br]

Addition of three equivalents of t-BuNC to [Re(CO)$_5$Br] in either refluxing benzene or toluene in the presence of PdO resulted in rapid formation of [Re(CO)$_2$(CNBu-t)$_3$Br] as indicated by IR spectroscopy. However the reaction was not clean; [Re(CO)(CNBu-t)$_4$Br] and [Re(CO)(CNBu-t)$_5$]Br also being formed in minor amounts. The salts could be readily removed by elution through a Celite column, and the non salt products could be purified by fractional crystallisation. The products were characterised by elemental analysis and IR and ^{1}H NMR spectroscopy (see Tables 3 and 4).

The reaction between [Re(CO)$_5$Br] and 2,6-$Me_2C_6H_3NC$ to form [Re(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_3$Br] was best carried out by adding two equivalents of 2,6-$Me_2C_6H_3NC$ to [Re(CO)$_5$Br] and PdO at room temperature, followed by dropwise addition of 2,6-$Me_2C_6H_3NC$ in benzene to the refluxing mixture. The addition was continued until the required product was at a maximum, as indicated by IR spectroscopy. A white precipitate formed during the reaction, and after isolation was identified as *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] (see below). The yellow benzene soluble material was purified by crystallisation and characterized as [Re(CO)$_2$($CNC_6H_3Me_2$-2,6)$_3$Br], (IR and NMR spectroscopy and elemental analysis).

From the above it is evident that use of PdO does not enable preparation of the desired trisubstituted products in high yield, but the method still compares favourably with the available alternative methods [33].

Synthesis of higher-substituted Re derivatives

The preparation of the substituted derivatives [Re(CO)$_{5-x}$(CNR)$_x$Br] ($x = 4$–6) was not straightforward, since a number of competing substitution and isomerisation reactions of the complexes are possible.

Addition of four or more equivalents of t-BuNC to [Re(CO)$_5$Br] resulted in the formation of a range of higher substituted derivatives. For instance, addition of 4–7 equivalents of t-BuNC to [Re(CO)$_5$Br] or more than two equivalents of t-BuNC to [Re(CO)$_{5-n}$(CNBu-t)$_n$Br], ($n = 2, 3$), gave [Re(CO)(CNBu-t)$_4$Br], [Re(CNBu-t)$_5$Br] and the salt complex [Re(CO)(CNBu-t)$_5$]Br. The ratio of the products could be varied by varying the reaction conditions. Thus addition of five equivalents of t-BuNC to [Re(CO)$_5$Br] in benzene at room temperature gave [Re(CO)(CNBu-t)$_5$]Br, (a white precipitate), rapidly (20 min) in high yield, and only minor amounts of non-salt material. On the other hand, when four equivalents of t-BuNC were added to the [Re(CO)$_5$Br] solution at the reflux temperature for 24 h, [Re(CO)(CNBu-t)$_4$Br], (along with minor amounts of [Re(CO)$_2$(CNBu-t)$_3$Br]) was readily isolated in reasonable yield. A benzene-insoluble white product was also isolated, and was characterized as [Re(CNBu-t)$_5$Br] by IR spectroscopy and elemental analysis.

The possible interconversion of the different reaction products from the above reactions was examined by heating a solution of [Re(CO)(CNBu-t)$_5$]Br in toluene for 24 h in the absence of t-BuNC. This gave a toluene-soluble product, [Re(CO)(CNBu-t)$_4$Br], and a toluene-insoluble product, [Re(CNBu-t)$_5$Br]. Thus in these highly substituted derivatives, thermal displacement of either the CO or the t-BuNC ligand to form the non-salt complex is possible.

Higher substituted [Re(CO)$_5$Br] derivatives containing 2,6-$Me_2C_6H_3NC$ were also obtained by varying the reaction conditions. Remarkably, addition of three or four equivalents of 2,6-$Me_2C_6H_3NC$ to a solution of [Re(CO)$_5$Br] and PdO in benzene at *room temperature* resulted in the rapid formation of predominantly [Re(CO)$_3$($CNC_6H_3Me_2$-2,6)$_2$Br] and [Re(CO)($CNC_6H_3Me_2$-2,6)$_5$]Br, (product ratio $\approx 1/2$). The products were readily separated on a Celite column. An identical procedure at 50 °C (or higher) with four equivalents of isocyanide, however, gave predominantly [Re(CO)$_2$($CNC_6H_3Me_2$-2,6)$_3$Br], (benzene soluble), and *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br], (benzene insoluble), which was readily separated on a Celite column (product ratio $\approx 1/6$). The geometry of the latter complex was confirmed by an X-ray structure determination (see below). In these reactions the product ratio could be altered by varying the reaction temperature and the identity of the isocyanide.

The route to the highly-substituted derivatives was investigated by examining the possible isomerisation of the salt product [Re(CO)($CNC_6H_3Me_2$-2,6)$_5$]Br both in the presence and the absence of isocyanide under a variety of reaction conditions. When a solution of the complex was heated in the presence of 2,6-$Me_2C_6H_3NC$ with or without PdO, no *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] was detected. In the absence of isocyanide a minor amount of [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] was formed. This complex was characterized by IR and NMR spectroscopy. Its solubility characteristics were different from those of *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br], and it is suggested that the complex has the CO and Br groups *cis* to each other. These results indicate that although conversion of the salt to non-salt complexes is possible, it does not represent the route to the tetra-substituted complex, *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br].

Reaction of [Re(CO)$_5$Br] with excess isocyanide ($>$ 6 equiv) yielded the fully substituted salt species [Re($CNC_6H_3Me_2$-2,6)$_6$]Br. This product was isolated as the PF_6 derivative in high yield following anion exchange with NH_4PF_6.

The results obtained clearly indicate that there are significant differences in reactivities of the various aryl and alkyl isocyanides, and these give rise to the various reaction products obtained.

X-Ray crystallographic examination of [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br]

The X-ray structure of the yellow [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] complex shows that the 2,6-$Me_2C_6H_3NC$ groups lie in the equatorial plane, forming *trans*-[Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] (see Fig. 1). Bond length and bond angle data are given in Table 7. The bond lengths observed within the isocyanide ligands are all similar to those observed in related structures [34,35]. Slight bending of the isocyanide group (3.8°) towards the Br atom is observed. The 2,6-$Me_2C_6H_3NC$ groups are interleaved and the mean plane through the xylyl ring lies at an angle of 117.8° to the Re–Br bond. The Re–Br bond length (2.67 Å), is typical for these and related complexes [34,36]. Rotational disorder was observed in the CO group, and thus the Re–C and C≡O bond lengths were constrained during refinement (see Experimental). Variation of these bond lengths from the expected values may result from unresolved disorder.

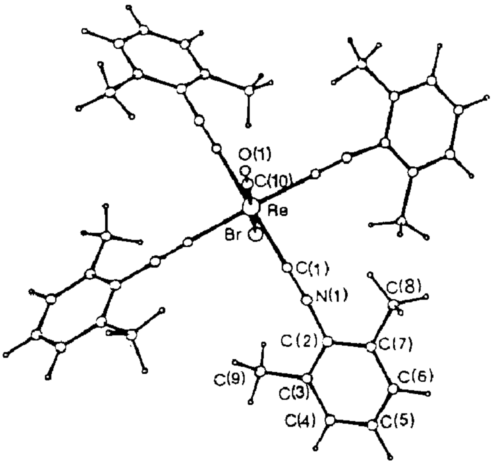


Fig. 1. An ORTEP plot of [Re(CO)($CNC_6H_3Me_2$-2,6)$_4$Br] showing the orientation of the ligands.

Summary of findings

The above results indicate that the Pd-catalysed substitution reactions of $[M(CO)_5Br]$ (M = Mn, Re) proceed rapidly to give, in many cases, the desired products in good yields. It is noteworthy that the preparations of the mono- and disubstituted products need not be performed in dry air-free solvents and furthermore that light has no effect on the outcome of the reaction.

The objectives of this study were to investigate systematically the catalysed isocyanide substitution of $[M(CO)_5Br]$ (M = Mn, Re). Since the compounds are not novel and similar types of complexes have been prepared and described by many other workers, only specific features of their synthesis will be discussed further.

In the catalysed reaction some general features may be noted;

(1) Substitution involving aryl isocyanides proceeds more rapidly than that involving alkyl isocyanides. This is consistent with the results obtained in the thermal reaction [20,21].

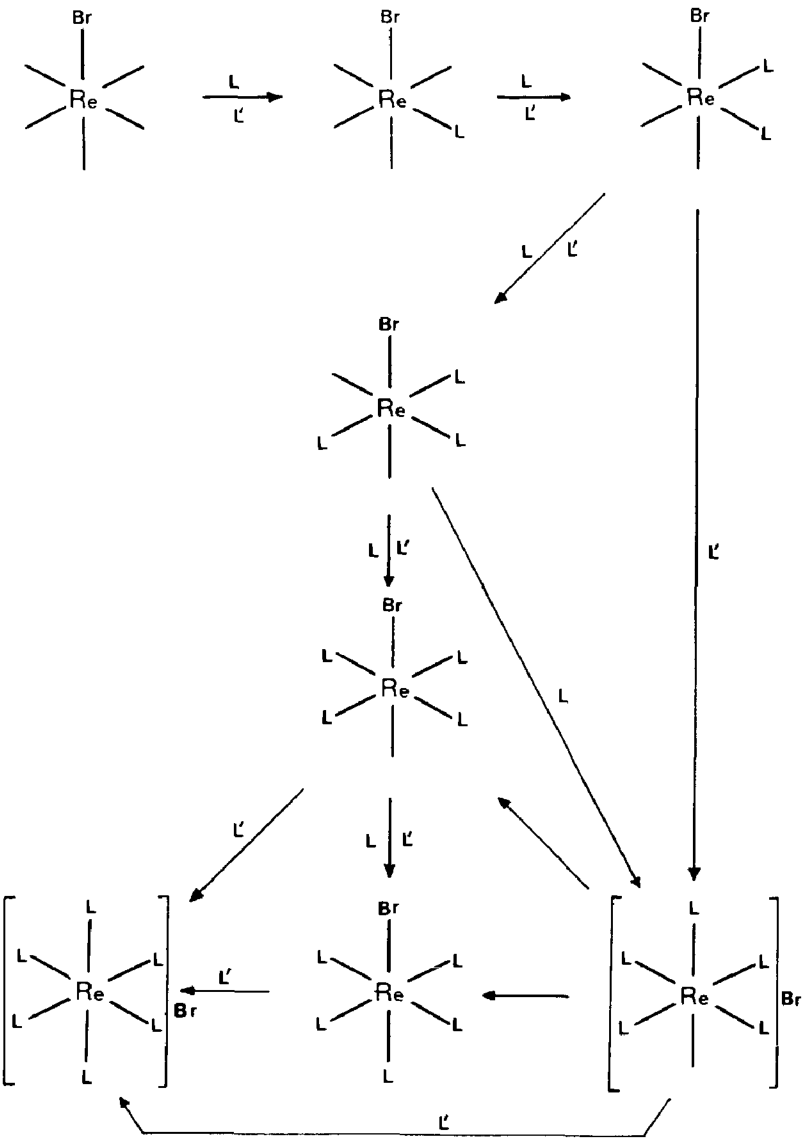
Isocyanides are known to have greater σ-donor but weaker π-acceptor bonding properties than CO ligands [37]. Alkyl isocyanides have been shown to display poorer π-acceptor properties than aryl isocyanides, and thus display significantly different reactivities. The synthesis of the fully substituted non-salt derivative proved difficult in the case of $2,6\text{-}Me_2C_6H_3NC$, and was not achieved with t-BuNC. Since the $[M(CNBu\text{-}t)_6]PF_6$ complexes with M = Mn or Re have been prepared by other routes, the restriction on the degree of substitution does not appear to be due to steric problems arising from placing six RNC groups around the metal atom. Salt formation, i.e. Br^- replacement, relieves the increase of electron density at the metal atom, and loss of either a CO ligand or a Br ligand become competitive as further substitution occurs.

(2) The greater ease of further substitution with the Re complex than with Mn may result from the greater ability of the Re to accommodate this increased electron density and from the relative sizes of the Mn and Re atoms.

(3) A remarkable feature of the reaction sequence is the facile conversion of $[Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2Br]$ into $[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_5]^+$ rapidly at room temperature. At higher temperatures this product is not favoured, and *lower*-substituted neutral complexes are formed. We suggest as a possible rationalization of these observations that at the lower temperature the disubstituted product is formed as *fac*-$[Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2Br]$ and $2,6\text{-}Me_2C_6H_3NC$ can either displace CO or Br from the starting material. If the Br is displaced preferentially at the lower temperature the product will be $[Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_3]^+$. This complex is expected to be more reactive than the starting material, and the substitution should continue readily and rapidly at room temperature on the cation, ultimately to form $[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_5]^+$. This proposal is supported by the electrochemical studies on $[Re(CO)_3(CNMe)_2Br]$ [33].

At higher temperatures isomerisation occurs to give *mer, trans*-$[Re(CO)_3(CNC_6H_3Me_2\text{-}2,6)_2Br]$. (The results obtained for the Mn analogue suggest that this is not an unreasonable suggestion.) This complex now has two mutually labile *cis* CO groups and hence reaction will take place with loss of CO rather than of Br, to give $[Re(CO)_2(CNC_6H_3Me_2\text{-}2,6)_3Br]$. Finally, and more slowly, $[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$ is formed.

(4) As the degree of substitution is increased, the time needed to bring about



Scheme 2. Scheme showing the systematic isocyanide substitution pathway for [Re(CO)$_5$Br] (L = t-BuNC, L′ = 2,6-Me$_2$C$_6$H$_3$NC).

further substitution increases. Substitution usually occurs *cis* to the Br atom when possible, and *cis* to any isocyanide groups present, since the RNC ligand is a weaker π-acceptor ligand than CO; the CO ligand *trans* to an isocyanide is less labile than a CO group *trans* to a CO group [38].

(5) Reaction schemes summarising the sequential CO substitution pathways are illustrated in Schemes 1 and 2 for the various isocyanide derivatives.

(6) Examination of the position of the methyl resonance in the ^{1}H NMR spectrum of the [M(CO)$_{5-n}$(CNR)$_n$Br] complexes (M = Mn, Re; R = t-BuNC, 2,6-Me$_2$C$_6$H$_3$NC), shows that there is a progressive downfield shift with increasing isocyanide substitution. The near linearity of a plot of the chemical shift with degree

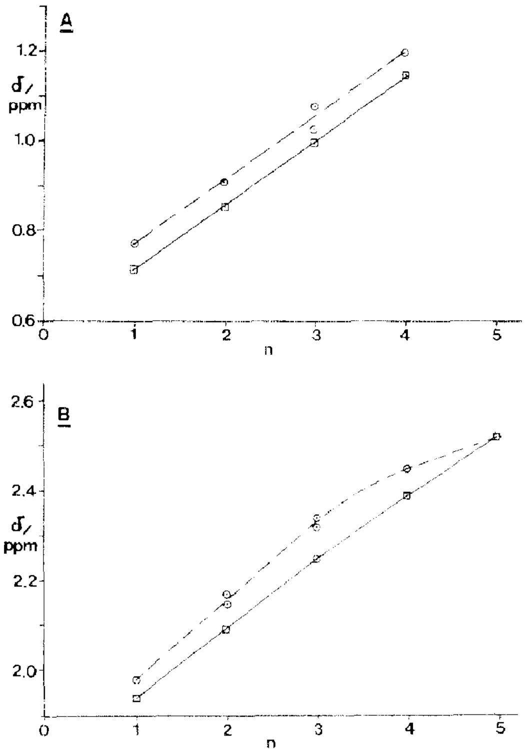


Fig. 2. Variation of the methyl NMR resonances with degree of substitution in $[M(CO)_{5-n}(CNR)_nBr]$ complexes. (A) ⊙ = $[Mn(CO)_{5-n}(CNBu\text{-}t)_nBr]$, ◻ = $[Re(CO)_{5-n}(CNBu\text{-}t)_nBr]$. (B) ⊙ = $[Mn(CO)_{5-n}(CNC_6H_3Me_2\text{-}2,6)_nBr]$, ◻ = $[Re(CO)_{5-n}(CNC_6H_3Me_2\text{-}2,6)_nBr]$.

of substitution (Fig. 2) is consistent with a systematic increase of electron density on the metal atom upon substitution [39].

It is clear that the chemical shift of the ligand resonances provides a very simple and definitive means of determining the degree of substitution and assessing the variation of the electronic nature of the isocyanide substituted carbonyl complexes.
(7) An X-ray crystallographic study of the yellow *trans*-$[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$ confirmed the sites of substitution of the isocyanide groups. An ORTEP plot of the complex showing the orientation of the ligands is shown in Fig. 1.

It is interesting to note that the high degree of symmetry of the complex is also maintained in the crystal structure. The complex crystallised in the tetragonal space group *P*4*nc*. The isocyanide groups are interleaved. Slight bending (3.8°) of the isocyanide groups toward the Br atom is observed.

Conclusion

This study has extended and throws further light on the use of Pd catalysts to facilitate the systematic isocyanide substitution of CO ligands in the monomeric $[M(CO)_5Br]$ complexes (M = Mn, Re). The observations, involving rapid reactions under mild conditions clearly reveal the value of this synthetic route. The scope of these catalysts as well as their limitations, namely the relative difficulty in cleanly synthesizing the multiply-substituted derivatives, is demonstrated. The use of Pd catalysts evidently represents an improvement on the classical routes, both thermal and photolytic, for preparing these derivatives in good yield.

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