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Isomers of $Re(CO)_3(CN^tBu)LX$: synthetic strategies starting from $MnRe(CO)_8(CN^tBu)L$ and $Re(CO)_4LX$ (X = halogen; L = Group 15 donor ligand)

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Abstract

Reaction of $Re(CO)_4LX$ (L = $PMePh_2$, PMe_2Ph, PPh_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(O\text{-}o\text{-}tol)_3$; X = Br, I) with ^tBuNC in the presence of PdO catalyst gave the new complexes $Re(CO)_3(CN^tBu)LX$ in high yield (> 60%). The new complexes were shown by spectroscopic techniques (IR, ^1H and ^{31}P NMR) to comprise a mixture of *mer* and *fac* isomers. The *mer/fac* ratio decreased with reaction temperatures (*e.g.* L = $P(OMe)_3$; 10°C, ratio = 3; 45°C, ratio = 0.25). At high temperatures (90°C) isomerization of the *mer* to the *fac* isomers (L = PMe_2Ph, $P(OMe)_3$) occurred, suggesting that the *mer* isomer was the kinetic product of the catalyzed reaction. Reactions induced by Me_3NO gave similar effects. Halogen cleavage of $MnRe(CO)_8(CN^tBu)L$, prepared from $MnRe(CO)_9(CN^tBu)$ and L in the presence of Me_3NO, yielded either one or two isomers of $Re(CO)_3(CN^tBu)(L)X$ (X = I, Br; 40% yield). For large L (*e.g.* PPh_3) a new *mer* isomer with L *trans* to X was synthesized, and characterized by IR and NMR spectroscopy. For small L (*e.g.* $P(OMe)_3$) a mixture of the two different *mer* products was obtained. The product isomer ratio was determined predominantly by the position of L in the starting dimer.

Key words: Rhenium; Carbonyl; Catalysis; Heterobimetallics; Substitution

1. Introduction

The substitution chemistry of monometallic metal carbonyl complexes is well established and factors (electronic/steric) governing the isomer composition are well known [1,2]. Related studies on the distribution of isomer obtained from substitutions of transition metal dimer complexes have also been reported [3]. These studies have revealed the important role of steric effects, induced by the large metal fragments, on the final distribution of isomer products [3]. Reports on the substitution chemistry of metal carbonyl trimer cluster complexes also support these findings [4]. From the above studies it has become apparent that upon variation of the incoming ligand, L, as well as of the metal fragment, isomer compositions can be predicted. Thus on electronic grounds ligands such as CO, RNC, PR_3 and $P(OR)_3$ prefer to occupy sites *cis* to a metal fragment [5]. However steric effects, due to interaction of L with the metal fragment, can result in preferential formation of *trans* product.

In a recent publication [6] we described an attempt to exploit the above observations to produce monometallic complexes not accessible by classical synthetic strategies. For instance, reaction of $Re_2(CO)_{10}$ with bulky ligands L (L = Group 15 donor ligand) gives *diax*-$Re_2(CO)_8L_2$, and cleavage with halogen, X_2, has been shown to lead to the formation of up to 50% *trans*-$Re(CO)_4LX$. Attempts to make CO-substituted complexes starting from *trans*-$Re(CO)_4LX$ *i.e.*, in which L remains *trans* to X, have however, met with limited success [6]. This is because the isomerization to *cis*-$Re(CO)_4LX$ is more rapid than the CO-substitution. Strategies to overcome this difficulty are thus needed. One possible method to solve this problem, starting from $MnRe(CO)_{10}$, is described below.

Substitution reactions of $MnRe(CO)_{10}$ with L (L = Group 15 donor ligand) leads to a mixture of axial (ax)

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and equatorial (eq) $-MnRe(CO)_9L$ derivatives in which L is predominantly bonded to rhenium. A second substitution could also lead to predominant disubstitution at rhenium. We have thus exploited the use of Me_3NO [7] and catalysts [8] to induce the CO-substitution reaction of $MnRe(CO)_{10}$, and this has permitted the synthesis of a range of doubly rhenium substituted $MnRe(CO)_8LL'$ complexes (L = Group 15 donor ligand; $L' = {}^tBuNC$). Thus, subsequent cleavage with halogen could in principle yield the required complex $Re(CO)_3LL'X$ with a non-CO ligand *trans* to X.

The synthesis, characterization and cleavage reactions of these new $MnRe(CO)_8LL'$ complexes, as well as the spectral properties of the $Re(CO)_3LL'X$ isomers formed in the halogen cleavage reactions, are reported. The synthesis of $Re(CO)_3(CN^tBu)LX$ (L = Group 15 donor ligand; X = Br, I) from *cis*-$Re(CO)_4LX$ is also reported, and the isomers obtained from this reaction are compared with those obtained from the metal dimer cleavage reactions.

TABLE 1. Analytical data for *mer*-1-$Re(CO)_3(CN^tBu)LI$ and $MnRe(CO)_8(CN^tBu)L$

Complex	Analysis [a] (%)		
	C	H	N
$Re(CO)_3(CN^tBu)(PMe_2Ph)I$	30.86 (29.66)	2.93 (3.48)	2.25 (2.31)
$Re(CO)_3(CN^tBu)(PMePh_2)I$	37.19 (37.07)	3.15 (3.26)	2.06 (2.06)
$Re(CO)_3(CN^tBu)(PPh_3)I$	42.42 (42.06)	3.32 (3.25)	1.83 (1.89)
$Re(CO)_3(CN^tBu)(PPh_3)I$ [b]	41.78 (42.06)	2.91 (3.25)	2.08 (1.89)
$Re(CO)_3(CN^tBu)[P(OMe)_3]I$	21.90 (21.86)	2.84 (2.99)	2.32 (2.32)
$Re(CO)_3(CN^tBu)[P(O^iPr)_3]I$	30.05 (29.66)	4.32 (4.39)	2.01 (2.04)
$Re(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]I$	41.87 (41.83)	3.58 (3.63)	1.68 (1.68)
$(CO)_5MnRe(CO)_3(CN^tBu)(PPh_3)$ [c]	44.98 (45.93)	3.63 (2.98)	1.86 (1.73)
$(CO)_5MnRe(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]$ [d]	45.26 (45.34)	3.20 (3.35)	1.60 (1.56)
$(CO)_5MnRe(CO)_3(CN^tBu)[P(O^iPr)_3]$ [e]	35.04 (34.92)	3.98 (3.99)	1.94 (1.85)

[a] Calculated values in parentheses.

[b] *mer*-2-$Re(CO)_3(CN^tBu)(PPh_3)I$ from halogen cleavage of $MnRe(CO)_8(CN^tBu)(PPh_3)$.

[c] Melting point: 170–171°C.

[d] Melting point: 124–125°C.

[e] Melting point: 90–92°C.

2. Results and discussion

The synthesis and characterization of the monomeric rhenium complexes are considered first, since the information gained was used in the elucidation of the chemistry of the heteronuclear dimer system.

2.1. Synthesis and characterization of $Re(CO)_3LL'X$ from $Re(CO)_4LX$ and L'(L = Group 15 donor ligand; $L' = {}^tBuNC$; X = Br, I)

The PdO-catalyzed reaction of $Re(CO)_5X$ (X = Br, I) with phosphines and phosphites gave *cis*-$Re(CO)_4LX$ in excellent yield (> 80%) [9]. Treatment of a solution of $Re(CO)_4LX$ (L = $PMePh_2$, PMe_2Ph, PPh_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(O\text{-}o\text{-}Tol)_3$; X = Br, I) in benzene (40–45°C) with a slight excess of ^tBuNC under the influence of the PdO catalyst readily afforded the required $Re(CO)_3(CN^tBu)LX$ products. It should be noted, however, that the analogous reaction between $Re(CO)_4(CN^tBu)X$ and phosphines and phosphites did not occur under our reaction conditions or in the presence of Me_3NO (43°C).

The reaction was monitored by TLC and IR spectroscopy using overlay techniques. TLC showed the presence of two spots corresponding to two new products which were successfully separated by column chromatography. The two products were characterized by IR and NMR (^{31}P and ^1H) spectroscopy and elemental analysis (Tables 1–3). Potentially, CO substitution of *cis*-$Re(CO)_4LX$ with ^tBuNC can give the four isomers shown in Fig. 1; the three *mer* isomers are denoted by *mer*-1-, *mer*-2- and *mer*-3- respectively (see Fig. 1). On electronic grounds isomer 1a is that predicted in the reaction [2,10], while on steric grounds isomer 1b is expected.

The IR spectra of the two new complexes were distinctly different and permitted their characterization as the predicted *fac*- and *mer*-1-isomers of $Re(CO)_3LL'X$ [10,11]. X-ray crystal structure determinations have confirmed these assignments for *fac*-$Re(CO)_3(CN^tBu)(PMe_2Ph)I$ and *mer*-1-$Re(CO)_3(CN^tBu)[P(OMe)_3]I$. The third possible isomer (1c) was not observed in any of these reactions, while isomer 1d, the least likely product of reaction from *cis* labilization arguments [5], was also not detected.

From information given in Tables 2 and 3, the trends in the IR and NMR spectra allow for easy characterization of *mer*-1-/*fac*-$Re(CO)_3(CN^tBu)LX$. All complexes of the *mer*-1- type show a lower ν(NC) absorption in the IR spectrum and a downfield shift in the ^1H and ^{31}P NMR spectra (±0.12 and ±4 ppm, respectively). The *fac*-$Re(CO)_3(CN^tBu)LX$ assignments are further supported by the ^1H NMR spectra for L = PMe_2Ph and $P(O^iPr)_3$, which show the expected two sets of doublets for the non-equivalent CH_3 resonances. The percentages of *fac*-isomer isolated from the reaction sequence are given in Table 4. NMR studies were also performed on the reaction of $Re(CO)_4LI$ (L = PMe_2Ph, $P(OMe)_3$, PPh_3) with

^{t}BuNC at various temperatures and the data are shown in Table 5.

The isomer composition is influenced by both steric [12] and electronic (phosphine *versus* phosphite) effects associated with the ligand already present in the starting complex [13]. Thus, the phosphite ligands give a higher precentage of the *mer*-1 isomer than the phosphines for the ligands studied. However, for the phosphites the amount of *mer*-1 isomer decreases as the ligand sizes increases, while the amount of *mer*-1 isomer increases with the size of the phosphine. Five significant features are to be noted from the above synthetic and NMR data:

(i) substantial amounts of *mer*-1-isomer were obtained from the reactions of $Re(CO)_4LX$ with ^{t}BuNC;
(ii) the amounts of *mer*-1-isomer obtained varied with the ligand, L;
(iii) the amount of *mer*-1-isomer obtained decreased with an increase in temperature;
(iv) the amount of *mer*-1-isomer obtained increased when Me_3NO was used instead of PdO and
(v) change in the halide (I *vs*. Br) had little effect on the isomer ratio (see Table 4).

The third point is significant and suggests that the *mer*-1-isomer is a kinetic product of the reaction. Generally, reactions of octahedral $M(CO)_5L$ or $M(CO)_4LX$ with L (or L′) yields the *cis* or *fac* isomer as the kinetic product [14,15]. This has been readily rationalized in terms of the greater ease of displacement of a CO *trans* to another CO group than of a CO *trans* to a poorer π-acceptor ligand, L. Steric effects can subsequently intervene, and if the two non-CO ligands are bulky, the *mer*-1-isomer will form. Both the PdO and Me_3NO thus influence the course of the CO-substitution reaction in an unexpected manner. This occurs through interaction of the PdO or Me_3NO with $Re(CO)_4LBr$ in such a way that the *trans* CO becomes more labile than the *cis* CO. This is an unexpected result. However, recent photochemical studies by Vanquickenborne and co-workers have shown that the *trans* CO in $Mn(CO)_5X$ can be lost in preference to *cis* CO groups under appropriate conditions [10].

That the isomer ratio is determined in the transition state is revealed by quantitative changes in the isomer ratios on heating $Re(CO)_4(CN^tBu)LX$ at 90°C. When the *mer*-1-isomer is heated it is converted to the *fac* isomer. At room temperature no isomerization occurs.

TABLE 2. Melting point and spectroscopic data for $Re(CO)_3(CN^tBu)LX$ derivatives, X = Br, I

Compound	M.p [a] (°C)	IR [b]	
		ν(NC)	ν(CO)
mer-1-$Re(CO)_3(CN^tBu)(PMe_2Ph)I$	74– 75	2168m	2056m 1968vs 1914m
fac-$Re(CO)_3(CN^tBu)(PMe_2Ph)I$	104–105	2180m	2031vs 1963s 1917s
mer-1-$Re(CO)_3(CN^tBu)(PMePh_2)I$	88– 89	2164m	2037m 1968s 1923m
fac-$Re(CO)_3(CN^tBu)(PMePh_2)I$	119–121	2166m	2033vs 1967s 1920s
mer-1-$Re(CO)_3(CN^tBu)(PPh_3)I$	121–123	2174m	2039s 1971vs 1923s
fac-$Re(CO)_3(CN^tBu)(PPh_3)I$	134–135	2179m	2034s 1964m 1922m
mer-2-$Re(CO)_3(CN^tBu)(PPh_3)I$	141–142	2180w	2058w 1968vs
mer-1-$Re(CO)_3(CN^tBu)[P(OMe)_3]I$	119–120	2179m	2068w 1979vs 1929m
fac-$Re(CO)_3(CN^tBu)[P(OMe)_3]I$	102–103	2185m	2043vs 1977s 1927s
mer-1-$Re(CO)_3(CN^tBu)[P(O^iPr)_3]I$	70– 71	2178m	2036w 1974vs 1926m
fac-$Re(CO)_3(CN^tBu)[P(O^iPr)_3]I$	51– 52	2183m	2037vs 1969s 1927s
mer-1-$Re(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]I$	101–102	2181m	2039m 1989vs 1934m
fac-$Re(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]I$	oil	2187m	2048s 1989m 1935m
mer-1-$Re(CO)_3(CN^tBu)(PMe_2Ph)Br$	67– 68	2174m	2034w 1968s 1909s
fac-$Re(CO)_3(CN^tBu)(PMe_2Ph)Br$	95– 96	2186m	2036vs 1964m 1913m
mer-1-$Re(CO)_3(CN^tBu)(PMePh_2)Br$	114–115	2170w	2038w 1969s 1909s
fac-$Re(CO)_3(CN^tBu)(PMePh_2)Br$	oil	2184m	2036vs 1969m 1911m
fac-$Re(CO)_3(CN^tBu)(PPh_3)Br$	159–160	2181w	2035s 1969m 1917m
mer-1-$Re(CO)_3(CN^tBu)[P(OMe)_3]Br$	106–107	2178m	2043w 1975vs 1925m
fac-$Re(CO)_3(CN^tBu)[P(OMe)_3]Br$	oil	2185w	2043s 1976m 1923m
mer-1-$Re(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]Br$	oil	2184m	2052w 1969s 1931m
fac-$Re(CO)_3(CN^tBu)[P(O\text{-}o\text{-}Tol)_3]Br$	oil	2186m	2060s 1992m 1993m
mer-1-$Re(CO)_3(CN^tBu)[P(O^iPr)_3]Br$	80– 81	2178m	2050w 1975vs 1923m
fac-$Re(CO)_3(CN^tBu)[P(O^iPr)_3]Br$	71– 72	2188m	2042s 1970m 1923m

[a] Uncorrected.

[b] Recorded in CH_2Cl_2.

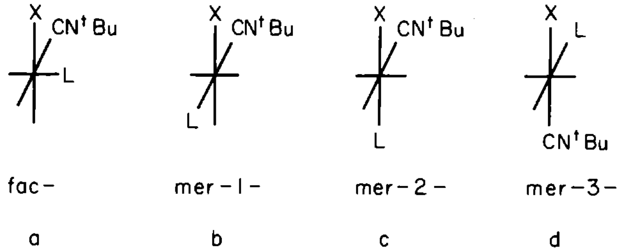


Fig. 1. Isomers of Re(CO)$_3$(CN^{t}Bu)LX (L = PR$_3$/P(OR)$_3$; X = Br, I)

TABLE 4. Yield (%) of *fac*-Re(CO)$_3$(CN^{t}Bu)LX isolated [a] from the PdO-catalyzed reaction of Re(CO)$_4$LX with ^{t}BuNC (L = Group 15 donor ligand, X = Br, I)

L	% *Fac* Isomer	
	Br	I
P(OMe)$_3$	9	10
PMe$_2$Ph	55	66
P(O^{i}Pr)$_3$	15	16
PMePh$_2$	59	47
P(O-*o*-Tol)$_3$	29	28
PPh$_3$	35	37

[a] Method of isolation: column chromatography (see Experimental section).

This is to be contrasted with the reaction of Re(CO)$_4$LX with ^{t}BuNC, in which increase in temperature (10–40°C) causes an increase in the *fac* product!

It is also noteworthy that CO-substitution reactions of [Mn(CO)$_4$(L-L)]$^+$ [13] (L-L = bidentate ligand) with various donor ligands have led to unusual substitution patterns in the presence of Me$_3$NO. The relationship between these studies and our results is not yet apparent, but reveals the advantages of carrying out substitution reactions at low temperatures in the presence of Me$_3$NO or other reagents or catalysts.

2.2. Synthesis of Re(CO)$_4$(L)(CN^{t}Bu)X from MnRe(CO)$_8$(CN^{t}Bu)L (L = Group 15 donor ligand) and X$_2$ (X = I, Br)

The Re-substituted MnRe(CO)$_9$(CN^{t}Bu) starting material, in which ^{t}BuNC is *cis* to the Mn–Re bond,

TABLE 3. NMR spectroscopic data for Re(CO)$_3$(CN^{t}Bu)LX derivatives, X = Br, I

Compound	NMR [a,b]		
	^{1}H	Ph	^{31}P
mer-1-Re(CO)$_3$(CN^{t}Bu)(PMe$_2$Ph)I	0.84s, 1.78[d,CH$_3$,*J*(PH)8]	6.96–7.11, 7.29–7.39	−39.19
fac-Re(CO)$_3$(CN^{t}Bu)(PMe$_2$Ph)I	0.72s, 1.74[dd,CH$_3$,*J*(PH)8]	6.95–7.07, 7.31–7.40	−46.30
mer-1-Re(CO)$_3$(CN^{t}Bu)(PMePh$_2$)I	0.86s, 2.29[d,CH$_3$,*J*(PH)8]	6.94–7.04, 7.50–7.65	−19.30
fac-Re(CO)$_3$(CN^{t}Bu)(PMePh$_2$)I	0.68s, 2.23[d,CH$_3$,*J*(PH)8]	6.98–7.05, 7.50–7.59	−22.60
mer-1-Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)I	0.88s	6.94–7.00, 7.09–7.88	−2.51
fac-Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)I	0.71s	6.95–7.08, 7.76–7.86	−7.63
mer-2-Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)I	0.75s	6.94–6.98, 7.48–7.52	17.31
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(CH$_2$Ph)$_3$]I [c]	0.84s, 3.59[d,CH$_2$,*J*(PH)8]	–	−16.80
fac-Re(CO)$_3$(CN^{t}Bu)[P(CH$_2$Ph)$_3$]I [c]	0.77s, 3.58[d,CH$_2$,*J*(PH)8]	–	−22.50
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(OMe)$_3$]I	0.84s, 3.41[d,CH$_3$,*J*(PH)11]	–	112.61
fac-Re(CO)$_3$(CN^{t}Bu)[P(OMe)$_3$]I	0.81s, 3.39[d,CH$_3$,*J*(PH)11]	–	108.61
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(O^{i}Pr)$_3$]I	0.89s, 1.35[d,CH$_3$,*J*(PH)6]	4.96–5.11 [d]	102.78
fac-Re(CO)$_3$(CN^{t}Bu)[P(O^{i}Pr)$_3$]I	0.85s, 1.27[dd,CH$_3$,*J*(PH)3]	4.87–4.97 [d]	98.94
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(O-*o*-Tol)$_3$]I	0.76s, 2.43s	6.84–6.94	98.69
fac-Re(CO)$_3$(CN^{t}Bu)[P(O-*o*-Tol)$_3$]I	0.75s, 2.32s	6.82–6.94, 7.61–7.71	91.16
mer-1-Re(CO)$_3$(CN^{t}Bu)(PMe$_2$Ph)Br	0.84s, 1.71[d,CH$_3$,*J*(PH)8]	6.95–7.11, 7.35–7.41	−34.61
fac-Re(CO)$_3$(CN^{t}Bu)(PMe$_2$Ph)Br	0.73s, 1.64[dd,CH$_3$,*J*(PH)8)]	7.04–7.13, 7.37–7.48	−38.67
mer-1-Re(CO)$_3$(CN^{t}Bu)(PMePh$_2$)Br	0.86s, 2.18[d,CH$_3$,*J*(PH)8]	6.99–7.06, 7.56–7.62	−12.61
fac-Re(CO)$_3$(CN^{t}Bu)(PMePh$_2$)Br	0.68s, 2.13[d,CH$_3$,*J*(PH)8]	6.99–7.06, 7.53–7.64	−15.71
fac-Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)Br	0.68s	6.95–7.09	1.75
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(OMe)$_3$]Br	0.98s, 3.63[d,CH$_3$,*J*(PH)11]	–	117.40
fac-Re(CO)$_3$(CN^{t}Bu)[P(OMe)$_3$]Br	0.83s, 3.43[d,CH$_3$,*J*(PH)11]	–	113.68
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(O-*o*-Tol)$_3$]Br	0.81s, 2.44s	6.83–6.89, 7.42–7.62	100.32
fac-Re(CO)$_3$(CN^{t}Bu)P[(O-*o*-Tol)$_3$]Br	0.76s, 2.41s	6.83–6.96, 7.17–7.75	93.61
mer-1-Re(CO)$_3$(CN^{t}Bu)[P(O^{i}Pr)$_3$]Br	0.87s, 1.27[d,CH$_3$,*J*(PH)6]	4.82–4.98 [d]	107.62
fac-Re(CO)$_3$(CN^{t}Bu)[P(O^{i}Pr)$_3$]Br	0.83s, 1.24[dd,CH$_3$,*J*(PH)6]	4.87–5.03 [d]	104.53

[a] Recorded in C$_6$D$_6$ relative to TMS (^{1}H) or H$_3$PO$_4$ (^{31}P).
[b] s = singlet, d = doublet, dd = doublet of doublets, q = quartet.
[c] Ref. 6.
[d] Multiplet.

TABLE 5. Percentage *mer*-1-/*fac*-Re(CO)$_3$(CN^{t}Bu)LI (L = P(OMe)$_3$, PMe$_2$Ph, PPh$_3$) products formed when Re(CO)$_4$LI is treated with ^{t}BuNC [a]

L	Conditions	θ [b]	T (°C)	% Isomer *mer*-1-	% Isomer *fac*-
P(OMe)$_3$	–	107	80	–	90 [c]
	Me$_3$NO	107	43	50	50
	PdO	107	10	72	28
	PdO	107	43	20	80
PMe$_2$Ph	PdO	122	23	20	80
	PdO	122	43	17	83
PPh$_3$	PdO	145	23	50	50
	PdO	145	43	33	67
	PdO	145	80	11	89

[a] As detected by NMR spectroscopy.
[b] Tolman cone angle (degrees), see ref. 12.
[c] 10% unreacted Re(CO)$_4$(CN^{t}Bu)I evidenced by NMR spectroscopy.

was synthesized from MnRe(CO)$_{10}$ and ^{t}BuNC using PdO [16]. Spectroscopic data for the complex were found to be in agreement with those of compounds prepared in earlier studies, confirming that equatorial substitution of CO had taken place [16]. Yields of isolated products are in the region of 60–65%.

The reaction between (CO)$_5$MnRe(CO)$_4$(CN^{t}Bu) and L (L = PMePh$_2$, PMe$_2$Ph, PPh$_3$, P(OMe)$_3$, P(O^{i}Pr)$_3$ and P(O-*o*-Tol)$_3$) was carried out in the presence of Me$_3$NO as the decarbonylating agent. The reactions were monitored by TLC and IR spectroscopy. The disappearance of the starting material absorption band at ±2002 cm^{-1} was used to monitor progress of the reaction. Similar experiments performed under thermal conditions (90°C, 24 h) or in the presence of a PdO-catalyst at ambient or elevated temperatures (90°C, 40 min) produced no evidence that any reaction took place.

The crude material was subjected to column chromatography and only one band was isolated from the column. For L = PPh$_3$, P(O-*o*-Tol)$_3$ and P(CH$_2$Ph)$_3$, only one complex was isolated from this band, as detected by IR and NMR spectroscopy (see Tables 6 and 7). The analytical data (Table 1) and the reaction stoichiometry (1:1) are consistent with the formation MnRe(CO)$_8$(CN^{t}Bu)L.

The reaction could occur at either the Mn or the Re atom [17], and the range of possible di-Re substituted reaction products is illustrated in Fig. 2. (Mn substituted products are also possible but are not shown.)

An X-ray crystal structure determination was performed on MnRe(CO)$_8$(CN^{t}Bu)(PPh$_3$) [18]. The data revealed that *cis* ^{t}BuNC and *axial* PPh$_3$ substituents are both present and attached to Re in the new complex (Fig. 2b). Similarly, the large P(O-*o*-Tol)$_3$ ligand is also expected to occupy an *axial* substitution site on Re and the spectral data, when compared with those for the PPh$_3$ complex confirm this suggestion.

For L = PMePh$_2$, PMe$_2$Ph, P(OMe)$_3$ and P(O^{i}Pr)$_3$ the band isolated by column chromatography consisted of two non-separable components as detected by spectroscopy (see below). The two products obtained from the reactions of MnRe(CO)$_9$(CN^{t}Bu) with L (L = P(OMe)$_3$, P(O^{i}Pr)$_3$, PMe$_2$Ph, PMePh$_2$) were identified spectroscopically (Tables 6, 7) and by cleavage reactions (Table 7) as a mixture of the two isomers 2a and 2b (see below). The ratio of these two isomers [ax (2b), eq (2a); identified below] is shown in Table 8. As can be seen, the major isomer formed is 2b. Thus even for small π-accepting ligands such as P(OMe)$_3$ steric effects largely determine the product isomer. No obvious correlation of isomer ratio and electronic parameters associated with L (*e.g.* pK_a [19]) is apparent.

Cleavage of the MnRe(CO)$_8$(CN^{t}Bu)L dimers (in C$_6$D$_6$ in NMR tubes) with halogens provided a facile route to isomers of Re(CO)$_3$(CN^{t}Bu)LX. Br$_2$ or I$_2$ (0.9 eq) was introduced into the NMR tubes via a syringe and ^{31}P spectra were recorded immediately after addition of halogen (Table 8). Halogen cleavage may result in the formation of the isomers shown in Fig. 3.

For L = PPh$_3$, addition of I$_2$ to MnRe(CO)$_8$(CN^{t}Bu)L gave only a single new resonance in the ^{31}P

TABLE 6. IR spectral data for MnRe(CO)$_8$(CN^{t}Bu)L complexes

L	Yield (%)	IR [a] ν(NC)	IR [a] ν(CO)
MnRe(CO)$_8$(CN^{t}Bu)(PMePh$_2$)	30	2160m	2063m 2059sh 2006m 1967vs 1948sh 1918w
MnRe(CO)$_8$(CN^{t}Bu)(PMe$_2$Ph)	66	2164m	2057s 2003s 1965vs 1948s 1906w
MnRe(CO)$_8$(CN^{t}Bu)(PPh$_3$)	32	2163w	2065m 2059sh 2007m 1968vs 1948sh
MnRe(CO)$_8$(CN^{t}Bu)[P(OMe)$_3$]	55	2166w	2068s 2011s 1970vs 1946sh 1910w
MnRe(CO)$_8$(CN^{t}Bu)[P(O^{i}Pr)$_3$]	39	2169w	2065m 2009m 1969vs 1946sh 1905w
MnRe(CO)$_8$(CN^{t}Bu)[P(O-*o*-Tol)$_3$]	19	2166w	2071m 2057sh 2017w 1978vs 1954sh
MnRe(CO)$_8$(CN^{t}Bu)[P(CH$_2$Ph)$_3$]	18	2160w	2064m 2008m 1969vs 1964sh 1951sh

[a] Recorded in CH$_2$Cl$_2$.

TABLE 7. NMR spectral data for MnRe(CO)$_8$(CN^{t}Bu)L complexes

	^{1}H ^{a,b}			^{31}P ^{a}	
	^{t}BuNC	other	Ph	before ^{d}	after ^{d}
MnRe(CO)$_8$(CN^{t}Bu)(PMePh$_2$)	0.75s	1.99[d,CH$_3$,*J*(PH)8]	6.95–7.02, 7.30–7.37	−6.47; −15.28	−15.5 ^{e}
MnRe(CO)$_8$(CN^{t}Bu)(PMe$_2$Ph)	0.72s	1.53[d,CH$_3$,*J*(PH)9], 1.64[d,CH$_3$,*J*(PH)9]	6.98–7.02, 7.24–7.28	−31.9; −41.7	−37.3; −43.2 ^{e}
MnRe(CO)$_8$(CN^{t}Bu)(PPh$_3$)	0.75s	–	6.92–6.99, 7.03–7.57	12.8	17.8 ^{f}
MnRe(CO)$_8$(CN^{t}Bu)[P(OMe)$_3$]	0.87s	3.21[d,CH$_3$,*J*(PH)12], 3.24[d,CH$_3$,*J*(PH)18]	–	124.6; 119.2	121.7; 113.8 ^{e}
MnRe(CO)$_8$(CN^{t}Bu)[P(O^{i}Pr)$_3$]	0.89s	1.16[d,CH$_3$,*J*(HH)18], 4.50–4.70[m,CH]	–	112.4; 109.9	111.2; 104.3 ^{e}
MnRe(CO)$_8$(CN^{t}Bu)[P(O-*o*-Tol)$_3$]	0.86s	2.23[s,CH$_3$]	6.81–6.93	105.6	101.4 ^{f}
MnRe(CO)$_8$(CN^{t}Bu)[P(CH$_2$Ph)$_3$]	0.88s	3.34[d,CH$_2$,*J*(PH)8]	7.01–7.07	−19.19	–

[a] Recorded in C$_6$D$_6$. Values are relative to H$_3$PO$_4$ (^{31}P) and TMS (^{1}H).

[b] s = singlet, d = doublet, m = multiplet.

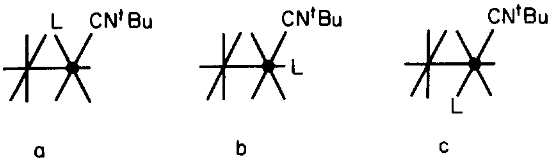
[c] Data for ax/eq mixtures. Ligand in axial position is reported first.

[d] Before/after cleavage of dimer with halogen.

[e] Cleavage with Br$_2$.

[f] Cleavage with I$_2$.

spectrum. Similar results were obtained for L = P(O-*o*-Tol)$_3$ when X = Br$_2$ or I$_2$, were used (see Table 8). The new product formed from the reaction with L = PPh$_3$ was isolated and characterized by elemental analysis (Table 1) as an isomer of Re(CO)$_3$-(CN^{t}Bu)LX. Further, the IR (2200–1800 cm^{-1}) and NMR (^{31}P and ^{1}H) spectra recorded on this complex did not correlate with the spectral data for the independently synthesized *mer*-1- or *fac*-Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)I (see Tables 2 and 3).



a b c

Fig. 2. Isomers of (CO)$_5$MnRe(CO)$_3$(CN^{t}Bu)L where ● = Re and L = PR$_3$/P(OR)$_3$

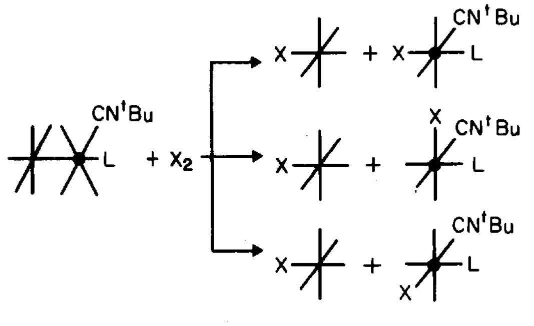


Fig. 3. Halogen cleavage of (CO)$_5$MnRe(CO)$_3$(CN^{t}Bu)L (L = PR$_3$/P(OR)$_3$ and ● = Re)

The product from the cleaved dimer was thus judged to be the third, *mer*-2, isomer of Re(CO)$_3$-(CN^{t}Bu)(PPh$_3$)I (Fig. 1c) in which the halogen and PPh$_3$ are *trans* to each other. This is the isomer predicted provided no ligand rearrangement occurs during the iodination. The new Re(CO)$_3$[P(O-*o*-Tol)$_3$](CN^{t}Bu)X (X = Br, I) products obtained from the cleavage of MnRe(CO)$_8$(CN^{t}Bu)[P(O-*o*-Tol)$_3$] and X$_2$ were similarly identified by comparison of IR/NMR spectral patterns with the *mer*-1-/*fac*-Re(CO)$_3$(CN^t-Bu)LX isomers. The ^{31}P resonances showed a downfield shift when compared with these for the independently synthesized *mer*- and *fac*-isomers, Re(CO)$_4$-[P(O-*o*-Tol)$_3$]X.

The results from the above cleavage reactions were used to provide a basis for the interpretation of the products produced in the cleavage of MnRe(CO)$_8$-(CN^{t}Bu)L (L = PMe$_2$Ph, PMePh$_2$, P(O^{i}Pr)$_3$, P(O-Me)$_3$) complexes. It should be noted that all the starting dimers, MnRe(CO)$_8$(CN^{t}Bu)L, consisted of a mixture with an ax/eq ratio greater than two (Table 8).

TABLE 8. Percentage of ax-MnRe(CO)$_8$(CN^{t}Bu)L obtained from the reaction between MnRe(CO)$_9$L and ^{t}BuNC

L	% ax-Isomer	Cone Angle ^{a}	pK$_a$ ^{b}
P(OMe)$_3$	83	107	2.6
PMe$_2$Ph	67	122	6.5
P(O^{i}Pr)$_3$	86	130	4.08
PMePh$_2$	90	136	4.57
P(O-*o*-Tol)$_3$	100	141	−1.83
PPh$_3$	100	145	2.73

[a] Tolman cone angle (degrees), see Ref. 12.

[b] See Ref. 21.

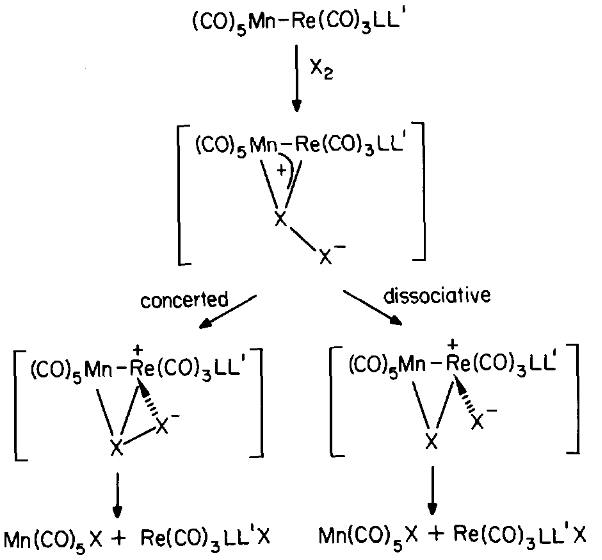


Fig. 4. Cleavage of MnRe(CO)$_8$LL' with X$_2$

With one exception on cleavage of the dimers (Fig. 4) two new complexes were detected, in a *ca.* 2:1 ratio. The exception was for L = PMePh$_2$, where only one complex was detected. Furthermore, heating the cleaved reaction products (L = P(OMe)$_3$, PMePh$_2$, P(O^{i}Pr)$_3$) in an NMR tube to 90°C for up to 3 h caused no change in the product distribution as indicated by ligand proton resonances. One of the products of the cleavage reaction was identified by ^{31}P NMR spectroscopy as *fac*-Re(CO)$_3$(CN^{t}Bu)LX, the other is suggested to be *mer*-2 isomer 1c. (Spectral characteristics of these isomers are consistent with the data for Re(CO)$_3$(CN^{t}Bu)(PPh$_3$)I and are not comparable with those of the *mer*-1-isomers discussed above).

3. Conclusion

The Me$_3$NO-induced substitution of MnRe(CO)$_9$(CN^{t}Bu) by L (L = phosphine/phosphite) occurred to give products in which L occupied both the equatorial and the axial site on the Re-atom (Fig. 2a and 2b). Substitution of CO by L at the equatorial site is expected on electronic grounds. Since the axial site is the least sterically hindered position in the dimer, products with L in this position are observed when L is bulky. For L with $\theta > 136°$, [12] *i.e.*, L = PPh$_3$ and P(O-*o*-Tol)$_3$, indeed (only) the axially substituted complex is detected. For L with $\theta < 136°$, products with L in both the axial and equatorial positions are detected.

When substitution of the dimer by L occurs only in the axial position, then halogen cleavage yields only the *mer*-2-Re(CO)$_3$(CN^{t}Bu)LX isomer (Fig. 1c). When ax/eq substitution occurs in the dimer, cleavage results in the formation of both the *fac*- and *mer*-2-isomers (Fig. 1a, c). It should be noted that the *mer*-1-isomer is not a product of the halogen cleavage of the dimer.

In summary, we have shown that substitution of *cis*-Re(CO)$_4$LX by ^{t}BuNC occurs under the influence of a catalyst (PdO) or in the presence of Me$_3$NO to give only *mer*-1- and *fac*-Re(CO)$_3$(CN^{t}Bu)LX in varying yields depending on the ligand size and reaction conditions. Unexpectedly, the *fac*-isomer is the thermodynamically favoured isomer. Isomerization of *mer*-1- to *fac*-Re(CO)$_3$(CN^{t}Bu)LI (L = PMe$_2$Ph, P(OMe)$_3$) occurs at elevated temperatures (*ca.* 90°C) suggesting that the formation of the *mer*-1 isomer is the kinetic product formed in the presence of Me$_3$NO and PdO. The thermal reaction, by contrast, yields the *fac* isomer directly. Strategies have thus been developed for the synthesis of three isomers of the type Re(CO)$_3$L'LX.

4. Experimental section

4.1. General methods

MnRe(CO)$_{10}$ was synthesized by the published procedure [20]. Iodine and bromine were purchased from BDH and Merck, respectively. Me$_3$NO.2H$_2$O was purchased from Aldrich, and dried by azeotropic distillation in tolene prior to use. Reactions were routinely performed under nitrogen in degassed solvents. Infrared spectra were recorded on a Bruker IFS 85 and NMR (^{1}H, ^{31}P) spectra on a Bruker AC200 spectrometer. Melting points were obtained with a Köffler hot stage apparatus and are uncorrected. Microanalyses were performed by the Division of Energy Technology, CSIR, Pretoria, RSA.

4.2. Preparation of mer-1-/fac-Re(CO)$_3$(CN^{t}Bu)LX (L = PMePh$_2$, PMe$_2$Ph, PPh$_3$, P(OMe)$_3$, P(O^{i}Pr)$_3$, P(O-o-Tol)$_3$; X = I, Br)

A solution of Re(CO)$_4$LX (0.100 g, 0.180 mmol) on C$_6$H$_6$ (20 ml) was heated to 40–45°C and ^{t}BuNC (1.1 eq) was added followed by PdO (5 mg). After an induction period of a few minutes, effervescence was noted. The reaction was monitored by observing changes in the ν(CO) region of the IR spectrum and by TLC (eluent: hexane/benzene), and generally found to be complete within 30 min. The catalyst was removed by filtration of the cooled reaction solution through cellulose. White to pale yellow materials were obtained upon removal of the solvent. These products were dissolved in a minimum amount of benzene and subjected to column chromatography (silica; eluent: hexane/benzene) which allowed separation of the isomers. After removal of the solvent, pale white to yellow *mer*-1- and *fac*-Re(CO)$_3$(CN^{t}Bu)LX complexes were obtained and were characterized by elemental analysis

(Table 1) and by spectroscopic methods (Tables 2 and 3).

4.3. Preparation of $MnRe(CO)_8(CN^tBu)L$ ($L = PMePh_2$, PMe_2Ph, PPh_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(O\text{-}o\text{-}Tol)_3$)

$MnRe(CO)_9(CN^tBu)$ (0.100 g, 0.180 mmol) and L (1.1 eq) were dissolved in C_6H_6 (25 ml). Me_3NO (0.023 g, 0.300 mmol) was added with stirring and the reaction was monitored by IR spectroscopy and TLC (eluent: hexane/benzene). Upon completion of the reaction, solvent was removed from the cooled solution under vacuum and the crude material was chromatographed on a silica column (eluent: hexane/benzene). Removal of solvent from the eluate at room temperature afforded the required yellow product (~ 40% yield), which was characterized by IR and ^{31}P and ^1H NMR spectroscopy and elemental analysis (Tables 1, 5 and 6).

4.4. NMR scale reaction of $Re(CO)_4LI$ with ^tBuNC ($L = PPh_3$, PMe_2Ph, $P(OMe)_3$)

$Re(CO)_4LI$ (0.040 mmol) and PdO (1 mg) were taken up in C_6D_6 (0.35 ml) in an NMR tube and ^tBuNC (0.9 eq) was added from a syringe; bubbling was observed. The reaction was monitored by ^{31}P spectroscopy. Results of the study are given in the Discussion.

4.5. Cleavage reaction of $MnRe(CO)_8(CN^tBu)L$ ($L = PMe_2Ph$, $PMePh_2$, PPh_3, $P(OMe)_3$, $P(O^iPr)_3$, $P(O\text{-}o\text{-}tol)_3$) with halogen

$MnRe(CO)_8(CN^tBu)L$ (0.1 mmol) and C_6D_6 (0.4 ml) were placed in an NMR tube. Halogen (Br_2, I_2; 0.9 eq in C_6D_6) was added to the mixture and the reaction monitored by NMR spectroscopy. For $L = PPh_3$ and $P(O\text{-}o\text{-}tol)_3$ the solvent was removed in vacuum and the crude products recrystallized from C_6D_6.

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References

1 J.D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brookes/Cole Publishing Company, Monterey, CA, USA, 1985.

2 (a) J.D. Atwood and T.L. Brown, *J. Am. Chem. Soc.*, *12* (1975) 3380; (b) J.D. Atwood, and T.L. Brown, *J. Am. Chem. Soc.*, *11* (1976) 3155; (c) J.D. Atwood, *J. Organomet. Chem.*, *383* (1990) 59.

3 W.L. Ingham and N.J. Coville, *Inorg. Chem.*, *31* (1992) 4084.

4 D.J. Darensbourg, in D.F. Shriver, H.D. Kaesz and R.D. Adams, (eds.), *The Chemistry of Metal Cluster Complexes, Ch. 4*, VCH Publishers, New York, 1990.

5 J.D. Atwood and T.L. Brown, *J. Am. Chem. Soc.*, *11* (1976) 3160.

6 W.L. Ingham and N.J. Coville, *Organometallics*, *11* (1992) 2551.

7 F. Basolo, *Polyhedron*, *9* (1990) 1503.

8 N.J. Coville in W.C. Trogler (ed.), *Synthetic Applications of Electron Transfer Catalysis, Ch. 4*, Elsevier, Amsterdam, 1990.

9 (a) A.E. Leins and N.J. Coville, *J. Organomet. Chem.*, *407* (1991) 357; (b) A.E. Leins and N.J. Coville, *Inorg. Synth.*, in press.

10 K. Pierloot, P. Hoet and L.G. Vanquickenborne, *J. Chem. Soc., Dalton Trans.*, (1991), 2363.

11 (a) R.H. Riemann and E. Singleton, *J. Organomet. Chem.*, *59* (1973) 309 and references therein; (b) E. Singleton, J.T. Moelwyn-Hughes and A.W.B. Garner, *J. Organomet. Chem.*, *21* (1970) 449; (c) M. Freni, D. Giusto and P. Romiti, *J. Inorg. Nucl. Chem.*, *29* (1967) 761; (d) J.T. Moelwyn-Hughes, A.W.B. Garner and N. Gordon, *J. Organomet Chem.*, *26* (1971) 373; (e) A.M. Bond, R. Colton and M.E. McDonald, *Inorg. Chem.*, *17* (1978) 2842; (f) L.K. Peterson, I.W. Johnson, J.K. Hoyano, S. Au-Yeung and B. Gour, *J. Inorg. Nucl. Chem.*, *43* (1981) 935; (g) P.W. Jolly and F.G.A. Stone, *J. Chem. Soc.*, (1965) 5259; (h) P.G. Douglas and B.L. Shaw, *J. Chem. Soc. A.*, (1969) 1491; (i) N.J. Coville, P. Johnston, A.E. Leins and A.J. Markwell, *J. Organomet. Chem.*, *378* (1989) 401.

12 C.A. Tolman, *Chem. Rev.*, *77* (1977) 313.

13 (a) F.J. García Alonso, V. Riera, F. Villafane and M.J. Vivanco, *J. Organomet. Chem.*, *276* (1984) 39; (b) F.J. Carriedo and V. Riero, *J. Organomet. Chem.*, *394* (1990) 275; (c) G.A. Carriedo, M.C. Crespo, C. Diaz and V. Riera, *J. Organomet. Chem.*, *397* (1990) 309; (d) F.J. García Alonso, V. Riera and M. Vivanco, *J. Organomet. Chem.*, *398* (1990) 275; (e) F.J. García Alonso, A. Llamazares, V. Riera, M. Vivanco, M.R. Díaz and S. García Granda, *J. Chem. Soc., Chem. Commun.*, (1991) 1059.

14 (a) T.L. Brown, *Inorg. Chem.*, *28* (1989) 3229; (b) W.G. Jackson, *Inorg. Chem.*, *26* (1987) 3004; (c) R.D. Davy and M.B. Hall, *Inorg. Chem.*, *28* (1989) 3524; (d) R.J. Angelici and A.J. Poë, *J. Am. Chem. Soc.*, *85* (1963) 2215; (e) F.J. García Alonso, V. Riera, M.L. Valin, D. Moreiras, M. Vivanco and X. Solans, *J. Organomet. Chem.*, *326* (1987) C71.

15 (a) D.J. Darensbourg and M.A. Murphy, *J. Am Chem. Soc.*, *100* (1978) 463; (b) D.J. Darensbourg, *Inorg. Chem.*, *18* (1979) 14; (c) D.J. Darensbourg and R.L. Gray, *Inorg. Chem.*, *23* (1984) 2993; (d) B.D. Dombeck and R.J. Angelici, *J. Am. Chem. Soc.*, *98* (1976) 4110; (e) D.J. Darensbourg and A.H. Graves, *Inorg. Chem.*, *18* (1979) 1257.

16 D.J. Robinson, E.A. Darling and N.J. Coville, *J. Organomet. Chem.*, *310* (1986) 203.

17 D. Sonnenberger and J.D. Atwood, *J. Am. Chem. Soc.*, *102* (1980) 3484.

18 A.E. Leins, D.G. Billing, D.C. Levendis, J. du Toit and N.J. Coville, *Inorg. Chem.*, *31* (1992) 4756.

19 M.M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, *Organometallics*, *8* (1989) 1.

20 S.P. Schmidt, F. Basolo, C.M. Jensen and W.C. Trogler, *J. Am. Chem. Soc.*, *108* (1986) 1894.