

Journal of Organometallic Chemistry, 423 (1992) 51–64
 Elsevier Sequoia S.A., Lausanne
 JOM 22229

Site selectivity studies on homonuclear metal dimer complexes: substitution reactions of $\text{Re}_2(\text{CO})_9\text{L}$

Wayne L. Ingham and Neil J. Coville

*Centre for Applied Chemistry and Chemical Technology, Department of Chemistry,
 University of the Witwatersrand, P.O. WITS, 2050, Johannesburg (Republic of South Africa)*

(Received July 16, 1991)

Abstract

The reaction of $\text{Re}_2(\text{CO})_9\text{L}$ ($\text{L} = {}^t\text{BuNC}$, $\text{P}(\text{O}-o\text{-tol})_3$, $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$, $\text{R}'\text{CN}$, $\text{R}' = \text{Me}$, Et , Pr , Ph) with L' ($\text{L}' = {}^t\text{BuNC}$, $\text{R}'\text{CN}$) in the presence of PdO or Me_3NO yields the 2,3-, 2,6- or 1,6-isomers of $\text{Re}_2(\text{CO})_8\text{LL}'$. The PdO reactions give only the 2,6-isomer while the Me_3NO induced reactions give statistical mixtures of the 2,6- and 2,3-isomers when $\text{L} = \text{L}' = \text{R}'\text{CN}$. When $\text{L} = {}^t\text{BuNC}$ and $\text{L}' = \text{R}'\text{CN}$ higher ratios ($\sim 5:1$) of 2,6- and 2,3-isomers are observed. The product isomer ratios from the reaction of $\text{Re}_2(\text{CO})_9\text{L}$ and L' were found to be different from those from the reaction of the mixtures of $\text{Re}_2(\text{CO})_5\text{I}/\text{Re}(\text{CO})_4\text{LI}$ with L' . The substitution chemistry of the $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4\text{L}$ dimer is thus not predictable from the chemistry of the monomer fragments. All the new dimer products have been characterised by IR and NMR (${}^1\text{H}$, ${}^{13}\text{C}$, ${}^{31}\text{P}$) spectroscopy.

Introduction

The influence of one metal complex on the reactivity of a second provides an entry into unexpected chemistry, as is shown, for instance, by the use of metal catalysts in the CO substitution chemistry of metal carbonyl complexes [1]. This approach also provides the motivation for the exploration of metal dimer chemistry in which the metals are either bonded to [2], or in close proximity to [3], each other.

Although much work has been reported on the influence of one metal centre on another in mixed metal complexes [4], the same approach can be applied to homometallic dimer complexes in which the two halves of the dimer contain different ligands. Thus, in complexes of the type $\text{ML}_x\text{-ML}'_y$, it can be expected that the electronic and steric properties associated with one half of the molecule will influence the chemistry of the other half. Of particular interest is whether these influences can be predicted from a knowledge of the chemistry of the ML_x and ML'_y fragments.

We report below the results of a study of the CO substitution chemistry of $\text{Re}_2(\text{CO})_9\text{L}$ ($\text{L} = \text{CH}_3\text{CN}$, ${}^t\text{BuNC}$, etc.), in which the chemistry of $\text{Re}(\text{CO})_5$ is contrasted with that of a $\text{Re}(\text{CO})_4\text{L}$ fragment. The di-rhenium complex was chosen

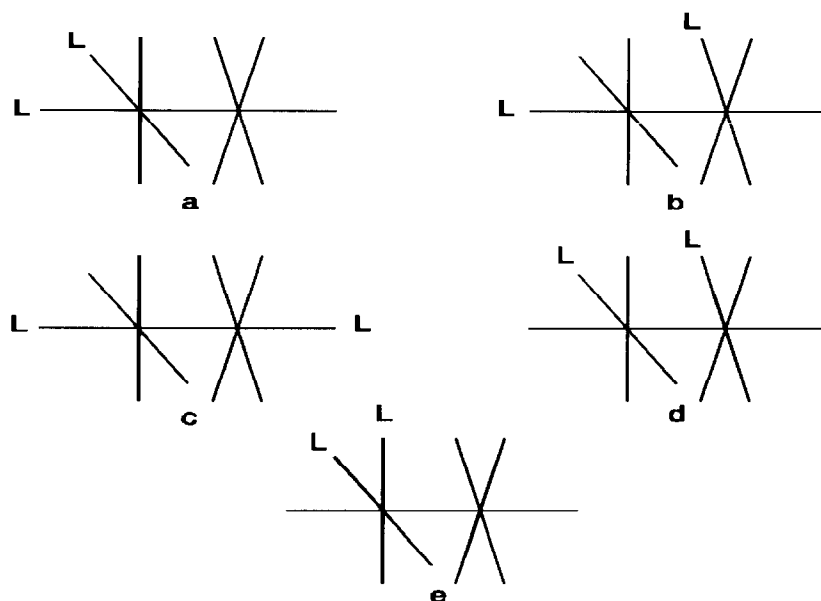


Fig. 1. The possible isomers of $\text{Re}_2(\text{CO})_8(\text{L})_2$.

for study as Re–Re bond cleavage is a high energy process and radical formation should not be a competitive reaction [5]. Even though the Re–CO bonds are not readily susceptible to thermal cleavage in the dimer, alternative procedures using Me_3NO [6,7] or catalysts [1,8] can be employed to facilitate the substitution reaction under mild temperature conditions. In this study we have synthesised a series of $\text{Re}_2(\text{CO})_8\text{LL}'$ complexes from $\text{Re}_2(\text{CO})_9\text{L}$ and L' ($\text{L}' = \text{CH}_3\text{CN}$, $^t\text{BuNC}$, etc.) using Me_3NO induced and PdO catalysed routes. Since numerous disubstituted dimer products are possible (see Fig. 1) we wished to establish some of the factors that would favour the formation of one isomer over another.

Experimental

General

$\text{Re}_2(\text{CO})_{10}$ was purchased from Strem Chemicals. Me_3NO was purchased from Aldrich and dried by azeotrope in toluene. Nitriles were purchased (Saarchem, Fluka, or Eastman) and were distilled prior to use. Ligands were purchased (Fluka, Strem, or Merck) and used without further purification. $\text{Re}_2(\text{CO})_9\text{L}$ were prepared by published procedures ($\text{L} = ^t\text{BuNC}$ [9], $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$, $\text{P}(\text{O}-o\text{-tol})_3$ [10]). $(\text{CH}_3\text{CH}_2)_3\text{NO}$ was prepared by the Cope method [11]. Solvents were distilled from appropriate drying agents and degassed prior to use. Elemental analyses were performed by the Division of Energy and Technology Laboratories, CSIR, Pretoria, Republic of South Africa. NMR spectra were recorded on a Bruker 200 MHz spectrometer and IR spectra on a Perkin Elmer 580 B spectrometer.

Reaction of $\text{Re}_2(\text{CO})_{10}$ and 1.1 equiv. Me_3NO in RCN

(i) $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 . $\text{Re}_2(\text{CO})_{10}$ (0.33 mmol) was dissolved in RCN (30 ml) to give a pale yellow solution and solid Me_3NO (0.36 mmol) was added. All the

Table 1

Infrared spectroscopic data for the complexes $\text{Re}_2(\text{CO})_{10-x}\text{L}_x$ ($x = 1, 2$)

L	Iso- mer ^a	$\nu(\text{CO})$ (cm^{-1}) ^a						
<i>x = 1</i>								
CH_3CN		2104w 2046m	1994vst	1988sh	1960m	1928m		
$\text{C}_2\text{H}_5\text{CN}$		2103w 2045m	1993vst	–	1960m	1927m		
$\text{C}_3\text{H}_7\text{CN}$		2104w 2046m	1994vst	1987sh	1960m	1928m		
$\text{C}_6\text{H}_5\text{CN}$		2103w 2047m	1993vst	1987sh	1960m	1931m		
¹ BuNC ^b		2099w 2045m	1996vst	1988sh	–	1940m		
$\text{P}(\text{O}-o\text{-tol})_3$		2112w 2046m	2001vst	–	1960m	1942sh		
$\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$		2106w 2032w	1995vst	–	1960w	1934st		
<i>x = 2</i>								
CH_3CN	2,6	2072w	–	2016st	1969vst	1933m	1906st	–
	2,3	2077w	–	2002st	1962vst	–	1906sh	1892m
$\text{C}_2\text{H}_5\text{CN}$	2,6	2070w	2037w	2016st	1969vst	1933m	1906st	–
	2,3	2077w	2037vw	2002st	1961vst	–	1906sh	1894m
$\text{C}_3\text{H}_7\text{CN}$	2,6	2070w	–	2016st	1970vst	1933m	1904m	–
	2,3	2077w	2035w	2002m	1961st	–	1908sh	1894m
$\text{C}_6\text{H}_5\text{CN}$	2,6	2070w	–	2018st	1964vst	1927m	1908m	–
	2,3	2076w	2037m	2002st	1962vst	–	1913m	1900m

^a Recorded in CH_2Cl_2 . ^b Ref. 9. ^c 2,3- or 2,6- $\text{Re}_2(\text{CO})_8\text{L}_2$ isomer.

starting material had reacted within 10 min as shown by the disappearance of the characteristic $\text{Re}_2(\text{CO})_{10}$ IR absorption band at 2074 cm^{-1} and the deepening of the yellow colour of the solution. The solution was stirred for a further 30 min and the solvent removed under vacuum. The product mixture was purified by column chromatography on Al_2O_3 (hexane/ C_6H_6 mixtures as eluent) and isolated in > 80% yield. Spectroscopic data for the dimers are given in Tables 1 and 2. Analytical data are given in Table 3.

(ii) $\text{R} = \text{C}_6\text{H}_5$. $\text{Re}_2(\text{CO})_{10}$ was treated with Me_3NO in $\text{C}_6\text{H}_5\text{CN}$ as described above. After all the starting material had reacted the solvent was removed by short arm distillation under vacuum at 80°C . The residual brown oil was purified by column chromatography on silica (hexane/ C_6H_6 mixtures as eluent) and isolated in 45% yield. Yellow crystals were obtained after solvent removal and storage under vacuum for 24 h. Spectroscopic data for the dimer are given in Tables 1 and 2.

Reaction of $\text{Re}_2(\text{CO})_{10}$ and 2.1 equiv. Me_3NO in RCN

(i) $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$. $\text{Re}_2(\text{CO})_{10}$ (0.5 mmol) was dissolved in RCN (50 ml) to give a pale yellow solution. Solid Me_3NO (1.05 mmol) was added and the disappearance of starting material was monitored by IR spectroscopy. The formation of two new products was detected by TLC (hexane/ethyl acetate 4:1 as eluent). After solvent removal under vacuum the crude material was purified by column chromatography on silica (hexane/ CH_2Cl_2 mixtures as eluent) to give both a yellow and an almost colourless pale yellow product. $\text{Re}_2(\text{CO})_{10}$ in CH_3CN was also treated with $\text{R}'_3\text{NO}$ ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$) by the slow addition of a CH_3CN solution (5 ml) containing the amine oxide (2.1 equiv.). Identical products to those obtained by the addition of the amine-oxide as a solid were obtained. Spectro-

Table 2a

¹H NMR spectroscopic data for the complexes Re₂(CO)_{10-x}L₂ (x = 1,2)

L	Isomer ^a	δ (ppm) ^{b,c}		
<i>x</i> = 1				
CH ₃ CN		0.45 [s, CH ₃]		
C ₂ H ₅ CN		0.13 [t, CH ₃ (7.6)]	1.00 [q, CH ₂ (7.6)]	
C ₃ H ₇ CN		0.28 [t, CH ₃ (7.7)]	0.62 [q, CH ₂ (7.5)]	1.08 [t, CH ₂ (7.1)]
C ₆ H ₅ CN		6.42–7.11 [m, C ₆ H ₅]		
¹ BuNC		0.75 [s, CH ₃]		
P(O- <i>o</i> -tol) ₃		2.22 [s, CH ₃]	6.83–6.97 [m, C ₆ H ₄ ^d]	7.29 [d, C ₆ H ₄ ^e (8.1)]
P(CH ₂ C ₆ H ₅) ₃		3.17 [d, CH ₂ (9.0)]	6.96–7.09 [m, C ₆ H ₅]	
<i>x</i> = 2				
CH ₃ CN	2,6	0.57 [s, CH ₃]		
	2,3	0.69 [s, CH ₃]		
C ₂ H ₅ CN	2,6	0.31 [t, CH ₃ (10.0)]	1.18 [q, CH ₂ (7.6)]	
	2,3	0.41 [t, CH ₃ (7.5)]	1.38 [q, CH ₂ (7.6)]	
C ₃ H ₇ CN	2,6	0.38 [t, CH ₃ (7.3)]	0.77 [q, CH ₂ (7.3)]	1.25 [t, CH ₂ (7.2)]
	2,3	0.46 [t, CH ₃ (7.1)]	0.84 [q, CH ₂ (7.4)]	1.44 [t, CH ₂ (7.1)]
C ₆ H ₅ CN	2,6	6.45–7.20 [m, C ₆ H ₅]		
	2,3	6.50–7.20 [m, C ₆ H ₅]		
¹ BuNC	2,6	0.85 [s, CH ₃]		
	2,3	0.89 [s, CH ₃]		

^a 2,3- or 2,6-Re₂(CO)₈L₂ isomer. ^b In C₆D₆ relative to TMS. ^c Coupling constant (Hz) in parentheses.^d *Meta* and *para* C₆H₅ protons. ^e *Ortho* C₆H₅ protons.

spectroscopic data for the new complexes are given in Tables 1 and 2. Product yields and isomer ratios for the reactions are given in Table 4a. Analytical data for the complexes are given in Table 3.

(ii) R = C₆H₅. Re₂(CO)₁₀ and Me₃NO were reacted as above in C₆H₅CN to give a similar reaction mixture. The solvent was removed by short arm distillation

Table 2b

¹³C NMR spectroscopic data for the complexes Re₂(CO)_{10-x}L₂ (x = 1,2)

L	Iso-mer ^b	δ (ppm) ^a							
		RNC		CN	CO				
<i>x</i> = 1									
CH ₃ CN		0.85		126.0	185.8	193.1	196.2br	200.9	
C ₂ H ₅ CN		8.9	11.2	130.1	185.9	193.5	196.4br	200.9	
C ₃ H ₇ CN		12.8	18.4	19.0	129.4	185.9	193.1	196.5br	200.9
<i>x</i> = 2									
CH ₃ CN	2,6	1.2		126.3	189.4	197.7	208.0		
	2,3	1.3		126.4	188.3	199.9	201.6		
C ₂ H ₅ CN	2,6	9.1	11.5	130.4	189.5	197.8	208.0		
	2,3	9.2	11.6	130.4	–	200.1	201.7		
C ₃ H ₇ CN	2,6	12.9	18.6	19.4	129.7	189.7	197.7	208.1	
	2,3	11.6	17.2	18.5	128.2	196.0	198.6	200.3	

^a Recorded in C₆D₆ relative to TMS. ^b 2,3- or 2,6-Re₂(CO)₈L₂ isomer.

Table 3

Selected analytical data

	m.p. (°C)	C	H	N
Re ₂ (CO) ₉ (CH ₃ CN)	110–112	19.81(19.85)	0.43(0.46)	2.01(2.10)
Re ₂ (CO) ₉ (C ₃ H ₇ CN)	41– 42	22.46(22.51)	0.96(1.01)	2.00(2.02)
Re ₂ (CO) ₉ (C ₆ H ₅ CN)	87– 91	26.21(26.41)	0.63(0.69)	1.82(1.93)
2,6-Re ₂ (CO) ₈ (CH ₃ CN) ₂	136–138	21.32(21.24)	0.86(0.89)	4.00(4.13)
2,3-Re ₂ (CO) ₈ (CH ₃ CN) ₂	122–124	20.84(21.24)	0.85(0.89)	4.12(4.13)
2,6-Re ₂ (CO) ₈ (C ₂ H ₅ CN) ₂	87– 91	27.59(27.79)	1.30(1.43)	3.74(3.97)
2,6-Re ₂ (CO) ₈ (C ₃ H ₇ CN) ₂	75– 76	25.91(26.16)	1.85(1.92)	3.67(3.81)
2,6-Re ₂ (CO) ₈ (CH ₃ CN)(¹ BuNC)	103–106	24.95(25.01)	1.66(1.67)	3.86(3.89)
2,6-Re ₂ (CO) ₈ (C ₂ H ₅ CN)(¹ BuNC)	77– 79	26.14(26.16)	1.78(1.92)	3.78(3.81)
2,6-Re ₂ (CO) ₈ (C ₃ H ₇ CN)(¹ BuNC)	56– 58	26.96(27.27)	2.01(2.15)	3.70(3.74)
2,6-Re ₂ (CO) ₈ (C ₆ H ₅ CN)(¹ BuNC)	115–117	30.63(30.96)	1.69(1.80)	3.58(3.58)
2,6-Re ₂ (CO) ₈ (CH ₃ CN)(P(O- <i>o</i> -tol) ₃)	124–126	37.66(37.61)	2.44(2.44)	1.71(1.42)

Table 4a

Yields and isomer ratios obtained from the reaction of Re₂(CO)₉L with L' in the presence of Me₃NO

L	L'	Yield (%)	Isomer ratio ^a
¹ BuNC	CH ₃ CN	62	2:1
¹ BuNC	C ₂ H ₅ CN	96	6:1
¹ BuNC	C ₃ H ₇ CN	93	6:1
¹ BuNC	C ₆ H ₅ CN	59	5:1
CH ₃ CN	CH ₃ CN	84	2:1
C ₂ H ₅ CN	CH ₃ CN	75	2:1
C ₃ H ₇ CN	CH ₃ CN	> 60	2:1
C ₆ H ₅ CN	CH ₃ CN	^b	3.5:1
CO	CH ₃ CN ^c	69	2:1
CO	C ₂ H ₅ CN ^c	70	2:1
CO	C ₃ H ₇ CN ^c	70	3:1
CO	C ₆ H ₅ CN ^c	≤ 10 ^d	1:1
P(CH ₂ C ₆ H ₅) ₃	CH ₃ CN	41	1:0 ^e
P(O- <i>o</i> -tol) ₃	CH ₃ CN	60	1:0 ^e

^a 2,6:2,3-Re₂(CO)₈L₂ isomer ratio. ^b NMR experiment; no yield available. ^c Two equivalents of ligand added to form Re₂(CO)₈(L')₂. ^d Low yield due to work-up conditions. ^e 1,6:1,3-Re₂(CO)₈L₂ isomer ratio.

Table 4b

Yields and isomer ratios obtained from the reaction of Re₂(CO)₉L with ¹BuNC in the presence of PdO

L	Ratio of 2,6:2,3 substitution products	Yield (%)
CH ₃ CN	1:0	65
C ₂ H ₅ CN	1:0	70
C ₃ H ₇ CN	1:0	60
P(CH ₂ C ₆ H ₅) ₃	1:0 ^a	80
P(O- <i>o</i> -tol) ₃	1:0 ^a	85

^a Ratio of 1,6:1,3-Re₂(CO)₈L₂ isomers.

Table 5
Infrared spectroscopic data for the complexes $\text{Re}_2(\text{CO})_8\text{LL}'$.^a

L	L'	Iso- mer ^b	$\nu(\text{CO})$ (cm^{-1})	2037w	2017st	2002st	1970bst	1932m	1906st	1893m
CH_3CN	$\text{C}_2\text{H}_5\text{CN}$	2,6	2072w	2037w	2017st	2002st	1970bst	1932m	1906st	1893m
CH_3CN	$\text{C}_3\text{H}_5\text{CN}$	2,3	2077w	2037w	2016st	2003w	1961vst	1931m	1906sh	1893m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,6	2070w	2037m	2016m	2003st	1968vst	1931m	1904st	1897sh
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,3	2078w	2016st	2016st	2003st	1968vst	1931m	1904st	1893m
CH_3CN	CH_3CN	2,6	2066w	2020st	2020st	2003m	1972vst	1941sh	1910st	1893m
CH_3CN	CH_3CN	2,3	2076w	2020st	2020st	2002st	1969vst	1927w	1910st	1899m
CH_3CN	$\text{C}_2\text{H}_5\text{CN}$	2,6	2066w	2020st	2020st	2002st	1973vst	1933sh	1912st	1899m
CH_3CN	$\text{C}_3\text{H}_7\text{CN}$	2,3	2077w	2036w	2017m	2002st	1968vst	1929w	1912st	1899m
CH_3CN	$\text{C}_3\text{H}_7\text{CN}$	2,6	2066m	2020st	2020st	2002st	1972vst	1935sh	1912st	1899m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,3	2076w	2035w	2015sh	2002st	1968vst	1929m	1913m	1901m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,6	2076w	2021st	2021st	2003st	1975vst	1938sh	1913m	1901m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,3	2077w	2020sh	2020sh	2003st	1967vst	1928m	1935st	1901m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,6	2060w	2029m	2029m	2003st	1978vst	1945sh	1935st	1901m
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,3	2065m	2032s	2032s	2003st	1987vst	1952m	1935st	1901m
CH_3CN	$\text{P}(\text{O}-o\text{-tol})_3$	1,6	2082m	2026m	2026m	2003st	1982vst	1949st	1921m	1901m
CH_3CN	$\text{P}(\text{CH}_2\text{C}_6\text{H}_4)_3$	1,6	2074w	2026sh	2026sh	2003st	1974vst	1927st	1914m	1901m
CH_3CN	$\text{P}(\text{O}-o\text{-tol})_3$	1,6	2076m	2029m	2029m	2003st	1983vst	1954st	1935sh	1901m
CH_3CN	$\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$	1,6	2066m	2032sh	2032sh	1995st	1978vst	1931st	1924m	1901m

^a IR recorded in hexane. ^b 2,3-, 2,6- or 1,6-isomer.

and the products separated by column chromatography on silica. Spectroscopic data for the complexes are given in Tables 1 and 2.

Reaction of $Re_2(CO)_9(L)$ and 1.1 equiv. Me_3NO in RCN

(i) $L = R'CN$ ($R = R' = CH_3, C_2H_5, C_3H_7, C_6H_5$). $Re_2(CO)_9(L)$ (0.37 mmol) and Me_3NO (0.45 mmol) were reacted in a solution of CH_3CN (30 ml) at room temperature. The disappearance of all the starting material, detected by the total disappearance of the characteristic IR absorption band at $\sim 2105\text{ cm}^{-1}$, was accompanied by a deepening of the yellow colour of the solution. The two new products identified by TLC (hexane/ethyl acetate 4:1 as eluent) were isolated by column chromatography on silica (hexane/ CH_2Cl_2 or hexane/ethyl acetate mixtures as eluent). Spectroscopic data for the complexes are given in Tables 5 and 6 respectively. Reaction yields and isomer ratios are given in Tables 4b. Analytical data are given in Table 3.

(ii) $L = {}^tBuNC$ ($R = CH_3, C_2H_5, C_3H_7, C_6H_5$). As above, $Re_2(CO)_9(L)$ in RCN was treated with Me_3NO . After complete reaction of the starting material the two products, identified by TLC, were separated as above. Spectroscopic data for the complexes are given in Tables 5 and 6, reaction yields and isomer ratios in Table 4a. Analytical data for the complexes are given in Table 3.

(iii) $L = PR'_3$ ($R' = O\text{-}o\text{-tol}, CH_2C_6H_5; R = CH_3$). A solution of $Re_2(CO)_9(L)$ in RCN was treated with Me_3NO . After complete reaction of the starting material the two products, identified by TLC, were separated as above. Spectroscopic data for the new complexes are given in Tables 5 and 6, reaction yields and isomer ratios in Table 4a and analytical data in Table 3.

Reaction of $Re_2(CO)_9(L)$ and tBuNC in C_6H_6 . ($L = RCN$ where $R = CH_3, C_2H_5, C_3H_7, C_6H_5; {}^tBuNC; P(O\text{-}o\text{-tol})_3; P(CH_2C_6H_5)$)

$Re_2(CO)_9(L)$ (0.17 mmol) and tBuNC (0.19 mmol) were dissolved in C_6H_6 (15 ml) at $\sim 0^\circ\text{C}$. Addition of PdO (5 mg) to the mixture at 25°C resulted in complete reaction within 2.5 h (Table 3) as shown by the relevant changes in the IR spectra. The only product observed by TLC was purified by column chromatography on silica (hexane/ethyl acetate mixtures as eluent). Spectroscopic data for the new complexes are given in Tables 1 and 2, reaction yield and isomer ratios in Table 4b and analytical data in Table 3.

Synthesis of $Re(CO)_4(RCN)I$ ($R = CH_3, C_2H_5$)

(a) *Dimer cleavage.* $1,2-Re_2(CO)_8(CH_3CN)_2$ (0.1 mmol) was treated with I_2 (1.1 equiv.) in CH_2Cl_2 (20 ml); the solution was then stirred for 30 min. After treatment with aqueous sodium thiosulphate, the CH_2Cl_2 layer was dried over anhydrous $MgSO_4$ and filtered through Celite. After solvent removal under vacuum the product was characterised as $Re(CO)_4(CH_3CN)I$ by IR spectroscopy ($\nu(CO)/C_6H_6; 2116m, 2020vs, 1951s$).

(b) *Monomer substitution.* $Re(CO)_5I$ (0.1 mmol) was treated with Me_3NO (1.1 equiv.) in CH_3CN (20 ml). Only partial reaction occurred. The product was isolated by column chromatography on silica (ethyl acetate/hexane mixtures as eluent) and characterised as $Re(CO)_3(CH_3CN)_2I$ by IR spectroscopy ($\nu(CO)/CH_2Cl_2; 2042m, 1942s, 1914vs$) [12].

Table 6a

 ^1H NMR spectroscopic data for the complexes $\text{Re}_2(\text{CO})_8\text{LL}'$

L	L'	Iso-mer ^a	δ (ppm) ^{b,c}			
CH_3CN	$\text{C}_2\text{H}_5\text{CN}$	2,6	0.32 [t, CH_3 (7.5)]	0.67 [s, CH_3]	1.22 [q, CH_2 (7.6)]	
		2,3	0.21 [t, CH_3 (7.6)]	0.57 [s, CH_3]	1.11 [q, CH_2 (7.6)]	
CH_3CN	$\text{C}_3\text{H}_7\text{CN}$	2,6	0.37 [t, CH_3 (7.3)]	0.59 [s, CH_3]	0.77 [m, CH_2 (7.4)]	1.22 [t, CH_2 (7.0)]
		2,3	0.42 [dt, CH_3 (6.4, 1.5)]	0.73 [s, CH_3]	0.84 [tq, CH_2 (7.6, 1.2)]	
			1.36 [dt, CH_2 (7.0, 0.8)]			
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,6	0.70 [s, CH_3]	6.5–7.2 [m, C_6H_5]		
		2,3	0.74 [s, CH_3]	6.5–7.0 [m, C_6H_5]		
$^i\text{BuNC}$	CH_3CN	2,6	0.52 [s, CH_3]	0.88 [s, CH_3]		
		2,3	0.65 [s, CH_3]	0.98 [s, CH_3]		
$^i\text{BuNC}$	$\text{C}_2\text{H}_5\text{CN}$	2,6	0.25 [t, CH_3 (7.6)]	0.91 [s, CH_3]	1.13 [q, CH_2 (7.6)]	
		2,3	0.27 [t, CH_3 (7.6)]	0.96 [s, CH_3]	1.18 [q, CH_2 (7.3)]	
$^i\text{BuNC}$	$\text{C}_3\text{H}_7\text{CN}$	2,6	0.35 [t, CH_3 (6.2)]	0.72 [q, CH_2 (7.8)]	1.15 [t, CH_2 (7.2)]	
		2,3	0.39 [t, CH_3 (7.2)]	0.76 [q, CH_2 (7.9)]	1.26 [t, CH_2 (7.0)]	
$^i\text{BuNC}$	$\text{C}_6\text{H}_5\text{CN}$	2,6	0.90 [s, CH_3]	6.58–6.81 [m, C_6H_5]		
		2,3	0.94 [s, CH_3]	6.56–6.84 [m, C_6H_5]		
$^i\text{BuNC}$	$^i\text{BuNC}$	2,6	0.85 [s, CH_3]			
		2,3	0.89 [s, CH_3]			
CH_3CN	$\text{P}(\text{O}-o\text{-tol})_3$	1,6	0.44 [s, CH_3]	2.36 [s, CH_3]	6.74–7.04 [m, C_6H_4]	7.67 [d, C_6H_4 (8.03)]
CH_3CN	$\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3^*$	1,6	0.59 [s, CH_3]	3.29 [d, CH_2 (8.5)]	7.15–7.02 [m, C_6H_5]	
$^i\text{BuNC}$	$\text{P}(\text{O}-o\text{-tol})_3$	1,6	0.79 [s, CH_3]	2.35 [s, CH_3]	6.83–7.00 [m, C_6H_4]	7.64 [d, C_6H_4 (8.02)]
$^i\text{BuNC}$	$\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$	1,6	0.86 [s, CH_3]	3.27 [d, CH_2 (8.7)]	7.12–6.96 [m, C_6H_5]	

^a I = 2,3-, 2,6- or 1,6- $\text{Re}_2(\text{CO})_8\text{L}_2$ isomer. ^b Coupling constant (Hz). ^c Recorded in C_6D_6 relative to TMS.

Table 6b
 ^{13}C NMR spectroscopic data for the complexes $\text{Re}_2(\text{CO})_8\text{LL}'$

L	L'	Isomer ^a	L(NC)	L(R)	δ (ppm) ^b		CO
					L'(R)	L(R)	
CH_3CN	$\text{C}_2\text{H}_5\text{CN}$	2,6		1.3	9.2, 11.5		189.5, 197.7, 208.0
		2,3		1.4	9.4, 12.0		189.4, 199.6, 201.6
CH_3CN	$\text{C}_3\text{H}_7\text{CN}$	2,6	129.7	1.2	12.9, 18.5, 19.4, 126.3		189.5, 197.7, 208.1
		2,3		1.3	12.9, 18.6, 19.4		189.4, 199.9, 201.7
CH_3CN	$\text{C}_6\text{H}_5\text{CN}$	2,6	128.9	29.7	110.1, 132.0, 133.9		188.6, 197.4, 207.1
		2,3	129.1	30.2	110.1, 133.6, 137.4		189.2, 200.0, 201.3
$^i\text{BuNC}$	$\text{C}_2\text{H}_5\text{CN}$	2,6	130.3	29.7, 57.7	9.1, 11.4		188.4, 196.6, 206.4
		2,3		29.8, 57.5	10.9, 11.4		188.2, 196.9, 200.6
$^i\text{BuNC}$	$\text{C}_3\text{H}_7\text{CN}$	2,6	129.7	29.7, 57.8	12.9, 18.5, 19.3		188.3, 196.6, 206.4
		2,3		29.8, -	12.9, 18.6, 19.3		188.2, 196.8, 200.6
$^i\text{BuNC}$	$\text{C}_6\text{H}_5\text{CN}$	2,6	129.0	29.7, 57.8	110.0, 132.4, 133.6		188.3, 196.6, 205.9
		2,3	129.1	29.8, -	132.4, 133.5		191.5, 197.2, 200.4
CH_3CN	$\text{P(O-}o\text{-tol)}_3$	2,6	129.4	1.0	17.1, 121.2, 121.3, 124.6, 125.1, 131.8, 132.0		200.1, 200.2, 202.9, 207.9
		2,6	128.2	2.3, 2.4	41.8, 42.3, 130.0, 130.2, 130.5, 131.4, 131.8		189.1, 196.2, 203.7, 203.8, 205.47
$^i\text{BuNC}$	$\text{P(O-}o\text{-tol)}_3$	2,6	127.2	29.5	17.1, 121.1, 124.9, 125.1, 130.4, 131.7, 132.0,		197.1, 199.1, 199.3
					151.1, 151.2		
$^i\text{BuNC}$	$\text{P(CH}_2\text{C}_6\text{H}_5)_3$	2,6	127.3	29.7, 57.5	41.1, 41.7, 129.1, 130.2, 130.3, 130.7, 130.8,		198.4, 201.8
					135.4, 135.5		

^a I = 2,3- or 2,6- $\text{Re}_2(\text{CO})_8\text{L}_2$ isomer. ^b Recorded in C_6D_6 relative to TMS. ^c CH_3CN not observed except 2,6- $\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})(\text{C}_3\text{H}_7\text{CN})$, 126.3 ppm.

Table 7

Comparisons of products obtained from the reactions of monomeric and dimeric Re complexes with $\text{Me}_3\text{NO}/\text{CH}_3\text{CN}$ and $\text{PdO}/^1\text{BuNC}$

Reactants	$\text{Me}_3\text{NO}/\text{CH}_3\text{CN}$	$\text{PdO}/^1\text{BuNC}$
	$\text{Re}(\text{CO})_5(\text{CH}_3\text{CN})(\text{L}')\text{X}^a$ (%)	$\text{Re}(\text{CO})_5(^1\text{BuNC})(\text{L}')\text{X}^a$ (%)
$\text{Re}(\text{CO})_5\text{I}/\text{Re}(\text{CO})_4(\text{RNC})\text{I}$	7 ^b	5 ^c
$\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4(\text{RNC})$	33 ^b	0 ^b
$\text{Re}(\text{CO})_5\text{I}/^1\text{Re}(\text{CO})_4(\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3)\text{I}$	0	0
<i>ax</i> - $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4(\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3)$	0	0
$\text{Re}(\text{CO})_5\text{I}/\text{Re}(\text{CO})_4(\text{C}_2\text{H}_5\text{CN})\text{I}$	10	8
$\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4(\text{C}_2\text{H}_5\text{CN})$	33	0

^a L' = RNC, $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ or $\text{C}_2\text{H}_5\text{CN}$; X = I or $\text{Re}(\text{CO})_5$. ^b R = ¹Bu. ^c R = 2,6-(CH_3)₂ C_6H_3 .

Relative reaction rates

(i) Carbonyl activation by Me_3NO : $\text{Re}(\text{CO})_5\text{I}/\text{Re}(\text{CO})_4\text{LI}$ mixtures (L = $\text{C}_2\text{H}_5\text{CN}$, ¹BuNC, *trans*- $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$). Complexes $\text{Re}(\text{CO})_5\text{I}$ (0.02 mmol) and $\text{Re}(\text{CO})_4\text{LI}$ (0.02 mmol) were dissolved in CH_3CN (5 ml) and solid Me_3NO (1 equiv., 0.02 mmol) was added. The mixture was stirred for 30 min, then the solvent was removed under reduced pressure. The products were extracted from the residue in CH_2Cl_2 (2 × 5 ml) and the extract filtered through Celite. After removing the solvent under reduced pressure the residue was dissolved in C_6D_6 and the ¹H and ³¹P NMR spectra recorded. The results are reported in Table 7.

(ii) Similar solutions to those described above were prepared in C_6D_6 in an NMR tube and treated with ¹BuNC (1 equiv.) in the presence of PdO catalyst (0.1 equiv.). The reactions were monitored by ¹H and ³¹P NMR spectroscopy and the results are given in Table 7.

Results and discussion

A series of known $\text{Re}_2(\text{CO})_9(\text{L})$ starting materials were synthesised by reaction of $\text{Re}_2(\text{CO})_{10}$ with L in the presence of Me_3NO (L = CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, $\text{C}_3\text{H}_7\text{CN}$, $\text{C}_6\text{H}_5\text{CN}$, $\text{P}(\text{CH}_2\text{Ph})_3$, $\text{P}(\text{O}-o\text{-tol})_3$) [6,10] or PdO (¹BuNC) [9]. Spectroscopic data, obtained with the above complexes, were in agreement with the earlier studies confirming the equatorial substitution (RCN, ¹BuNC) and predominantly axial substitution (group 15 donor ligands) of the products [9]. Product yields were high (> 60%) except for L = $\text{C}_6\text{H}_5\text{CN}$, where difficulties were experienced with removal of the high boiling solvent.

Reaction of $\text{Re}_2(\text{CO})_9(\text{L})$ with Me_3NO and L (L = CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, $\text{C}_3\text{H}_7\text{CN}$, $\text{C}_6\text{H}_5\text{CN}$)

The reaction was monitored by TLC and IR spectroscopy. The disappearance of the A_1 absorption band of the starting material at $\pm 2105\text{ cm}^{-1}$ was used to monitor the reaction. Two new products were formed in the reaction as determined by TLC. These were separated by column chromatography and characterised by elemental analyses, and IR and NMR spectroscopy. Since the analytical

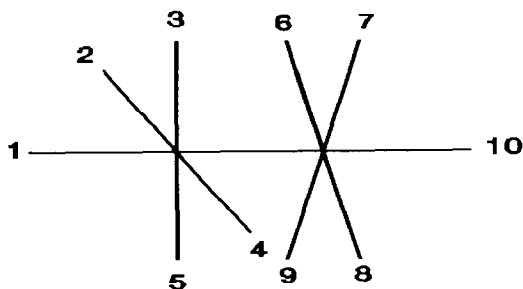


Fig. 2. The systematic numbering scheme used for $M_2(CO)_{10}$.

data (Table 3), as well as the reaction stoichiometry (1:1) are consistent with di-substituted product formation, the products are expected to be two of the five isomers shown in Fig. 1. Electronic factors [13] suggest that the *cis* substituted products, **d** and **e** in Fig. 1 will be formed. The first product eluted from the column was **d**, and the second was **e**, as determined by comparative IR spectroscopy (comparison with 2,3- and 2,6- $Re_2(CO)_8(^1BuCN)_2$) [9]; for numbering scheme see Fig. 2) and chemical reactions (see below). The major differences between the 2,3- and 2,6-isomers relate to the positions of the strong bands at $2000\text{--}2020\text{ cm}^{-1}$ and $1890\text{--}1910\text{ cm}^{-1}$.

The 1H NMR spectra also revealed that in every instance the 2,6- $Re_2(CO)_8(NCR)_2$ isomer absorptions occurred upfield relative to the 2,3-isomer absorptions. The ^{13}C NMR ligand absorption data were less helpful in correlating the isomer type with the position of the ligand absorption (Table 6a). Further, the ^{13}C CO data gave fewer absorptions than expected for the 2,3-isomer (4 resonances in a 4:2:1:1 ratio expected; 3 observed). Since both isomers show the same number of ^{13}C CO absorptions, the position of the lowest field absorption (± 208 ppm for the 2,6-isomer; ± 200 ppm for the 2,3-isomer) can be used to differentiate between the isomers. This absorption presumably corresponds to the CO *trans* to the RCN or CO ligands.

The 2,3- and 2,6-isomers were independently treated with 1BuNC to confirm their geometries. 2,6- $Re_2(CO)_8(NCCH_3)_2$ was treated in a NMR tube with an excess of 1BuNC (10 equiv.) in C_6D_6 at $75^\circ C$. The reaction was monitored by 1H NMR spectroscopy and during a 2 h period the starting material was converted entirely into the known complex 2,6- $Re_2(CO)_8(CN^1Bu)_2$ ($\delta = 0.85$ ppm [9]) and free CH_3CN ($\delta = 0.63$ ppm). Addition of Br_2 in C_6D_6 to the above reaction mixture resulted in formation of a *cis*- $Re(CO)_4(CN^1Bu)Br$ ($\delta = 0.85$ ppm [14]).

Reaction of 2,3- $Re_2(CO)_8(NCCH_3)_2$ with 1BuNC under the conditions described for the 2,6-isomer, gave a product solution with NMR spectrum resonances at $\delta = 0.89$ ppm (2,3- $Re_2(CO)_8(CN^1Bu)_2$) [9], overlapping with free 1BuNC) and $\delta = 0.63$ ppm (free CH_3CN). Further treatment of the above solution with Br_2 gave one new product with NMR parameters corresponding to *cis*- $Re(CO)_3(CN^1Bu)_2Br$ ($\delta = 0.86$ ppm [14]). All the above data (spectroscopic, analytical, chemical) are consistent with the isomer assignments proposed.

Of importance in the above study was the 2,6:2,3 product isomer ratio, which in all cases was found to be 2:1. Since there are four equatorial CO ligands in the $Re(CO)_5$ fragment *cis* to the M–M bond but only two equatorial CO ligands in the

$\text{Re}(\text{CO})_4\text{L}$ fragment *cis* to the M–M bond in $\text{Re}_2(\text{CO})_9\text{L}$, it appears that a statistical product distribution has been obtained in the reaction.

Our data are to be contrasted with those in an earlier report on the reaction of $\text{Re}_2(\text{CO})_{10}$ with R_3NO (R = Me, Et) and two equivalents of RCN, in which only one major isomer, 2,6- $\text{Re}_2(\text{CO})_8(\text{NCR})_2$ was identified [6b]. Although our NMR data are reasonably consistent with the earlier reported NMR data, our IR data suggest that a mixture of the 2,3- and 2,6-isomers had indeed been produced. We repeated the above reaction of $\text{Re}_2(\text{CO})_{10}$ with two equivalents of Me_3NO in a solution of RCN, and observed the same isomer ratio (1:2) as detected by stepwise RNC addition.

Reaction of $\text{Re}_2(\text{CO})_9(\text{NCCH}_3)$ with Me_3NO and L (L = $\text{C}_2\text{H}_5\text{CN}$, $\text{C}_3\text{H}_7\text{CN}$, $\text{C}_6\text{H}_5\text{CN}$)

Reactions similar to those described above were performed to establish whether the isomer ratio would be influenced by the nitrile ligand added to the Re dimer. Two isomers of $\text{Re}_2(\text{CO})_8(\text{NCCH}_3)$ (L) in a 1:2 ratio, were isolated in every instance and were characterised by elemental analyses, and IR and ^1H NMR spectroscopy as the 2,3- and 2,6-isomers. (When L = $\text{C}_6\text{H}_5\text{CN}$ high thermal conditions were needed to remove solvent and this distorted the initial product distribution as the less stable 2,3-isomer decomposed during this process.) No influence of the addition of the second nitrile is thus apparent, consistent with kinetic studies on Me_3NO induced substitution reactions [15].

Reaction of $\text{Re}_2(\text{CO})_9(\text{CN}^t\text{Bu})$ with Me_3NO and L (L = CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, $\text{C}_3\text{H}_7\text{CN}$, $\text{C}_6\text{H}_5\text{CN}$)

Similar reactions to those described above were performed to establish the influence of the $^t\text{BuNC}$ ligand on the product isomer distribution. In this instance two products were observed, but in a 1:5 ratio (^1H NMR spectroscopy). The isomers were characterised by IR and NMR spectroscopy and chemical reactions, as described for earlier reactions. Further reaction of the isomer mixture with $^t\text{BuNC}$ at elevated temperatures gave 2,3- and 2,6- $\text{Re}_2(\text{CO})_8(\text{CN}^t\text{Bu})_2$ in a 1:5 ratio. Thus the different strategies using Me_3NO or PdO and $^t\text{BuNC}$ can yield different dimer isomer compositions.

Reaction of $ax\text{-Re}_2(\text{CO})_9\text{L}$ (L = $\text{P}(\text{O}-o\text{-tol})_3$, $\text{P}(\text{CH}_2\text{Ph})_3$) with Me_3NO and CH_3CN

Reaction of $ax\text{-Re}_2(\text{CO})_9\text{L}$ with Me_3NO in CH_3CN gave only one new product, as detected by TLC and NMR spectroscopy. Cleavage of the dimer with Br_2 in an NMR tube, resulted in the appearance of two absorptions in the ^1H NMR spectrum, corresponding to those of independently prepared *cis*- $\text{Re}(\text{CO})_4(\text{NCCH}_3)\text{Br}$ ($\delta = 0.14$) and *cis*- $\text{Re}(\text{CO})_4\text{LBr}$ (L = $\text{P}(\text{CH}_2\text{Ph})_3$, δ 3.30 (d, CH_3 , $J(\text{PH}) = 9$); 6.93–7.16 (m, aromatic); L = $\text{P}(\text{O}-o\text{-tol})_3$, δ 2.26 (s, CH_3); 6.77–7.42 (m, aromatic)) [16]. This reaction confirmed that substitution had occurred on the unsubstituted Re atom. Since *trans*- $\text{Re}(\text{CO})_4\text{LBr}$ converts to *cis*- $\text{Re}(\text{CO})_4\text{LBr}$ [17], it is not possible to establish conclusively that the 1,6- rather than the 2,6-isomer had been formed in the initial reaction. IR spectra also do not help in this regard (see Table 5). Again the initially attached group 15 ligand plays a major role in the Me_3NO reaction in influencing isomer composition, directing reactivity to the second metal centre.

Reaction of $\text{Re}_2(\text{CO})_9\text{L}$ ($\text{L} = \text{CH}_3\text{CN}$, $\text{C}_3\text{H}_7\text{CN}$, $\text{C}_6\text{H}_5\text{CN}$, $\text{P}(\text{CH}_2\text{Ph})_3$, $\text{P}(\text{O}-o\text{-tol})_3$) with ${}^1\text{BuNC}$ in the presence of PdO

The thermal reaction between $\text{Re}_2(\text{CO})_9(\text{NCCH}_3)$ and ${}^1\text{BuNC}$ ($> 70^\circ\text{C}$, C_6H_6) cleanly yielded $\text{Re}_2(\text{CO})_9(\text{CN}{}^1\text{Bu})$. At lower temperatures little reaction occurs. However, reaction of $\text{Re}_2(\text{CO})_9(\text{NCCH}_3)$ with ${}^1\text{BuNC}$ at 25°C in the presence of PdO cleanly and rapidly leads to the synthesis of one new product, 2,6- $\text{Re}_2(\text{CO})_8(\text{NCCH}_3)(\text{CN}{}^1\text{Bu})$. The isomer was identified by IR and NMR spectroscopy (Tables 3 and 4). Further, reaction with Br_2 in C_6D_6 in an NMR tube resulted in the formation of only two new product absorptions corresponding to $\text{Re}(\text{CO})_4(\text{NCCH}_3)\text{Br}$ ($\delta = 0.14$ ppm) and $\text{Re}(\text{CO})_4(\text{CN}{}^1\text{Bu})\text{Br}$ ($\delta = 0.89$ ppm [9]). Addition of ${}^1\text{BuNC}$ (4 equiv.) to the NMR tube and heating at 50°C for 90 min resulted in the disappearance of the absorption at $\delta = 0.14$ ppm, and further growth of the absorption at $\delta = 0.85$ ppm. Only one isomer was also produced when the other $\text{Re}_2(\text{CO})_9\text{L}$ complexes, including $\text{Re}_2(\text{CO})_9(\text{CN}{}^1\text{Bu})$ [9], were reacted with ${}^1\text{BuNC}$. The PdO reaction thus provides a clean route to disubstituted products in which the two substituents are on different Re atoms. This is to be contrasted with the Me_3NO assisted reactions described above.

Reaction of $\text{Re}(\text{CO})_4\text{LBr}/\text{Re}(\text{CO})_5\text{Br}$ mixtures with L ($\text{L}' = {}^1\text{BuNC}$, CH_3CN , $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$)

To determine whether the metal fragment substituent played a role in the substitution reactions of $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4\text{L}$, equimolar mixture of $\text{Re}(\text{CO})_5\text{I}$ and $\text{Re}(\text{CO})_4\text{LI}$ were treated with one equivalent of L' ($\text{L}' = {}^1\text{BuNC}$, CH_3CN) in the presence of PdO or Me_3NO . The product analysis was performed by NMR spectroscopy and the results are given in Table 7. As expected, reaction occurred predominantly, if not exclusively, on $\text{Re}(\text{CO})_5\text{I}$. However, a comparison of the results with those obtained on the equivalent dimers (Table 7) revealed the following.

(i) Reaction of the monomer mixtures with Me_3NO or PdO gave similar results.

(ii) Reaction of the dimers with PdO and Me_3NO gave completely contrasting results compared with those for the monomer reactions. Thus, reaction of $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_4\text{L}$ ($\text{L} = {}^1\text{BuNC}$, EtCN) with $\text{Me}_3\text{NO}/\text{CH}_3\text{CN}$ gave 33% $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})\text{L}$, while reaction of the $\text{Re}(\text{CO})_5\text{I}/\text{Re}(\text{CO})_4\text{LI}$ mixture with Me_3NO gave 7–10% $\text{Re}_3(\text{CO})_3(\text{CH}_3\text{CN})\text{LI}$. However, for the PdO reaction the reverse was observed — no disubstituted $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_3\text{LL}'$ product was obtained in the reaction while small amounts of $\text{Re}_3(\text{CO})_3\text{LL}'\text{I}$ were produced (Table 7).

This finding suggests that the metal fragment does influence the product distribution and can be used to modify reaction yields from that predicted from a knowledge of the constituent monomer fragments. Although steric effects are almost certain to play a role in influencing the product distribution ($\text{Re}(\text{CO})_5 > \text{I}$), electronic effects may also be important. Our results do not presently permit us to establish the relative importance of these two effects on the product distribution observed.

Conclusion

Reaction of $\text{Re}_2(\text{CO})_9\text{L}$ complexes with L' yields two types of isomers in which substitution occurs either at the $\text{Re}(\text{CO})_5$ or $\text{Re}(\text{CO})_4\text{L}$ fragment. The products

formed are dependent on the reaction procedure (Me_3NO assisted; PdO catalysed) and the L groups under consideration. This study thus shows that bimetallic isomer ratios can be influenced, by the (mild) reaction conditions and cannot necessarily be predicted from the chemistry of the monomer fragments. Bimetallic complexes containing metal-metal bonds which are not as strong as the Re-Re bond should also be susceptible to the same types of studies and potentially lead to novel complexes.

Acknowledgements

We wish to thank the FRD and the University for financial support.

References

- 1 N.J. Coville, in W.C. Troglor (Ed.), *Organometallic Radical Processes*, Vol. 4, Elsevier, Amsterdam, 1990, p. 106.
- 2 (a) D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982; (b) W.L. Gladfelter and G.L. Geoffroy, *Adv. Organomet. Chem.*, 18 (1980) 207.
- 3 (a) M.M. Olstead, H. Hope, L.S. Benner and A.L. Balch, *J. Am. Chem. Soc.*, 99 (1977) 5502; (b) C.P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 99 (1977) 6129.
- 4 See e.g. P. Johnston, G.J. Hutchings, L. Denner, J.C.A. Boeyens and N.J. Coville, *Organometallics*, 6 (1987) 1292.
- 5 A.M. Stolzenberg and F.L. Muetterties, *J. Am. Chem. Soc.*, 105 (1983) 822.
- 6 (a) U. Koelle, *J. Organomet. Chem.*, 155 (1978) 53; (b) L.K. Peterson, R.S. Dhani and F. Wade, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 291.
- 7 P.O. Nubel, S.R. Wilson and T.L. Brown, *Organometallics*, 2 (1983) 515.
- 8 M.O. Albers and N.J. Coville, *Coord. Chem. Rev.*, 53 (1984) 227.
- 9 G.W. Harris and N.J. Coville, *Organometallics*, 4 (1985) 908.
- 10 W.L. Ingham, A.E. Leins and N.J. Coville, *S. Afr. J. Chem.*, 44 (1991) 6.
- 11 A.C. Cope and E. Ciganek, *Org. Synth. Coll.*, 4 (1963) 612.
- 12 (a) M.F. Farone and K.F. Kraus, *Inorg. Chem.*, 9 (1970) 1700; (b) J.G. Dunn and D.A. Edwards, *J. Organomet. Chem.*, 27 (1971) 73.
- 13 G.W. Harris, J.C.A. Boeyens and N.J. Coville, *J. Chem. Soc., Dalton Trans.*, (1985) 2277.
- 14 N.J. Coville, P. Johnston, A.E. Leins and A.J. Markwell, *J. Organomet. Chem.*, 378 (1989) 401.
- 15 Y.-L. Shi, Y.-C. Gao, Q.-Z. Shi, D.L. Kershner and F. Basolo, *Organometallics*, 6 (1987) 1528.
- 16 (a) P.W. Jolly and F.G.A. Stone, *J. Chem. Soc.*, (1965) 5259; (b) J.-T. Moelwyn-Hughes, A.W.B. Garner and N. Gordon, *J. Organomet. Chem.*, 26 (1971) 373.
- 17 A.E. Leins and N.J. Coville, *J. Organomet. Chem.*, 407 (1991) 359.
- 18 G.W. Harris and N.J. Coville, *Organometallics*, 4 (1985) 908.