Site Selectivity Studies on Heterobimetallic Complexes: Substitution Reactions of $(\eta^5\text{-}C_5H_5)MM'(CO)_8$ (M = Mo, W; M′ = Mn, Re)

Wayne L. Ingham and Neil J. Coville*

Applied Chemistry and Chemistry Technology Centre, Department of Chemistry, University of the Witwatersrand, Johannesburg, P.O. WITS 2050, South Africa

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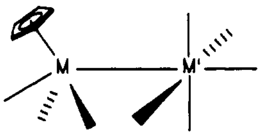
Synthesis of the heterobimetallic dimers $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ (M = Mo, W; M′ = Mn, Re) has been achieved by photochemical procedures from $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ and $M_2(CO)_{10}$ (5–10%), by reaction of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ and $M'(CO)_5X$ (X = I, Br) (15–25%) and by reaction of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ and $M'(CO)_5CF_3SO_3$ (45–95%). Reaction of $(\eta^5\text{-}C_5H_5)MRe(CO)_8$ (M = Mo, W) with L (L = $P(OMe)_3$, PMe_2Ph, $PMePH_2$, PPh_3, $P(CH_2C_6H_5)_3$, $P(p\text{-}C_6H_4OMe)_3$, *t*-BuNC, 2,6-$Me_2C_6H_3NC$, $C_6H_{11}NC$, $C_6H_5CH_2NC$) under Me_3NO, PdO, and thermal conditions yields $(\eta^5\text{-}C_5H_5)MRe(CO)_{8-n}L_n$ ($n = 1, 2$) (20–90% yield). Cleavage reactions of the substituted product with Br_2, performed in an NMR tube (CD_3CN), revealed that replacement of CO had occurred on the Re atom. The complexes ($n = 1$) were obtained as the *axial* isomer and/or the *equatorial* isomer and were characterized by IR and NMR spectroscopy. Reaction of $(\eta^5\text{-}C_5H_5)MMn(CO)_8$ (M = Mo, W) with RNC (R = 2,6-$Me_2C_6H_3$, *t*-Bu, $C_6H_5H_2$, C_6H_{11}) only gave $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ and $Mn_2(CO)_{10-x}RNC_x$ ($x = 1$–4). Reaction with L (L = $P(OMe)_3$, PMe_3, PMe_2Ph, PPh_3) gave homonuclear dimers as well as $(\eta^5\text{-}C_5H_5)MMn(CO)_7L$ in which substitution had occurred on Mn. The results could be interpreted in terms of the steric and electronic requirements of L *as well as* the steric requirements of the metal fragments. An analysis of the spectra of the new $(\eta^5\text{-}C_5H_5)MM'(CO)_7L$ complexes revealed that $\Delta(^{31}P_{ax-eq})$, i.e., the difference in ^{31}P positions for *axial* and equatorial isomers, gave a measure of the steric size of the metal fragments.

Introduction

The ready availability or a range of heterobimetallic metal carbonyl dimer complexes[1] permits an exploration of their CO substitution chemistry. Given the presence of two CO containing metal fragments in a bimetallic complex, it is clear that the substitution reaction could occur at either of the metal centers. Numerous studies have been performed to investigate the factors that influence (i) the direction of the substitution reaction and (ii) the final thermodynamic products obtained in the reaction.[2] From the studies performed to date, it appears that the site of CO substitution can generally be predicted from a knowledge of the reactivity patterns of related monomeric complexes.[3] However, the size of the second metal atom and its associated ligands can influence the final isomer composition.[4] To further investigate the influence of metal fragments on product isomer distributions in metal dimer complexes, we have undertaken a study of the CO substitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ (M = Mo, W; M′ = Mn, Re),[5,6] **1–4**, with a range of ligands (phosphines, phosphites, isocyanides). It is to be noted that only one other investigation of the substitution chemistry of $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ complexes has been reported; namely a photolytic investigation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ with PR_3 to produce $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_4PR_3$.[7]



1 (M = Mo, M′ = Re)
2 (M = W, M′ = Re)
3 (M = Mo, M′ = Mn)
4 (M = W, M′ = Mn)

Our main objectives in this study were (i) to determine the nature of the products produced in the CO substitution reaction using a variety of strategies to induce the substitution reaction and (ii) to compare the product distribution with other dimer complexes containing the "$M(CO)_5$" (M = Re, Mn) fragment, e.g. $Re(CO)_5$,[8] $Mn(CO)_5$,[2] $(\eta^5\text{-}C_5H_5)Fe(CO)_2$,[4,9] and hence relate the influence of steric and electronic factors associated with the various metal fragments to the product distribution.

Experimental Section

General Procedures. All reactions were routinely carried out under nitrogen in solvents degassed and distilled from appropriate drying agents prior to use. Chemicals were purchased from various sources: $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, Strem Chemicals; $Ag(CF_3SO_3)$, Me_3NO, and $W(CO)_6$, Aldrich Co. Ltd.; RNC (*t*-BuNC, 2,6-$Me_2C_6H_3NC$ (XyNC), $C_6H_5CH_2NC$ (BzNC), and $C_6H_{11}NC$ (CyNC)), Fluka; PR_3 ligands, Strem, Merck, and Aldrich. Literature procedures were used to prepare $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$,[10] $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNBu\text{-}t)X$ (X = Br, I),[11] $M(CO)_{4-n}(CNBu\text{-}t)_nX$ (M = Mn, Re; X = Br, I; $n = 1, 2$),[12] $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W),[13] Li-

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* Author to whom correspondence should be addressed.

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Table I. Analytical Data for Selected $(\eta^5\text{-}C_5H_5)MM'(CO)_{8-n}L_n$ (M = Mo, W; M′ = Mn, Re; *n* = 1,2) Complexes

complex	anal.[a]/% C	H	N	mp/°C
$CpMoMn(CO)_7P(OMe)_3$	33.58 (33.61)	2.45 (2.63)		
$CpMoRe(CO)_7(t\text{-}BuNC)$	32.48 (32.59)	2.10 (2.25)	2.23 (2.24)	127 dec
$CpMoRe(CO)_6(t\text{-}BuNC)_2$	36.56 (37.01)	3.32 (3.40)	4.12 (4.11)	102–105
$CpMoRe(CO)_6(BzNC)_2$	43.10 (43.26)	2.44 (2.55)	3.80 (3.74)	111–113
$CpMoRe(CO)_7PPh_3$	44.43 (44.73)	2.47 (2.50)		170 dec
$CpMoRe(CO)_7PBz_3$	46.67 (46.76)	2.97 (3.09)		136–138
$CpWRe(CO)_7(t\text{-}BuNC)$	29.25 (28.58)	2.00 (1.98)	1.93 (1.96)	127 dec
$CpWRe(CO)_6(BzNC)_2$	38.53 (38.72)	2.13 (2.29)	3.32 (3.35)	119–121
$CpWRe(CO)_7P(OMe)_3$	23.65 (23.85)	1.79 (1.87)		89–95
$CpWRe(CO)_7PPh_3$	40.36 (40.33)	2.17 (2.26)		177 dec
$CpWRe(CO)_7PBz_3$	42.24 (42.36)	2.68 (2.80)		140–142

[a] Found; calculated values in parentheses.

Table II. Reaction Conditions and Product Yields for the Photochemical Reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $Re_2(CO)_{10}$

	experiment 1	2	3
$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$/mg	10	10	10
$Re_2(CO)_{10}$/mg	2	10	50
yield/%[a]	14.3	12.0	3.5

[a] As determined by ^1H NMR spectroscopy after 2 h of reaction.

$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$,[14] and $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNBu\text{-}t)]$.[15] Complexes were characterized using a Brucker IFS 80 FTIR spectrometer, Brucker AC 200 FT NMR spectrometer, and Varian MAT CH5 mass spectrometer. Melting points were determined on a Köffler Hot stage melting point apparatus. Elemental analyses for the new compounds were performed at the Division of Energy and Technology, CSIR, Pretoria, RSA, and are presented in Table I. Photochemical experiments were performed with a 125-W Hanovia lamp (Table II).

Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNBu\text{-}t)Tf$ and $M'(CO)_{5-n}(CNBu\text{-}t)_nTf$ (M′ = Mn, Re; Tf = CF_3SO_3; *n* = 0, 1). $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNBu\text{-}t)Br$ or $M'(CO)_{5-n}(CNBu\text{-}t)_nBr$ (*n* = 0, 1; 0.2 mmol) was dissolved in CH_2Cl_2 (20 mL). $Ag(CF_3SO_3)$ (1.1 equiv) was added and the suspension stirred vigorously for 2 h. The yellow precipitate was removed by filtration through cotton wool and the solvent removed under vacuum. The resultant products were identified by comparison with reference IR data ($M'(CO)_5Tf$[16,17]) or comparison with the IR spectra of the related halogen compounds [ν(CO) for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNBu\text{-}t)Tf$, 2185, 2095, 2000, 1953, and 1975 cm^{-1}; ν(CO) for $Re(CO)_4(CNBu\text{-}t)Tf$, 2188, 2082, 1997, and 1955 cm^{-1}] and were used in the synthesis of the mixed-metal dimer products in the reactions below.

Reaction of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) with $M'(CO)_5Tf$ (M′ = Mn, Re). A solution of $M'(CO)_5Tf$ (M′ = Mn, Re) (1.1 equiv) in THF (10 mL) was slowly added to a solution of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) (0.5 mmol) in THF (20 mL). The reaction was monitored by IR spectroscopy and taken to be complete on disappearance of the characteristic ν(CO) absorptions of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W). The solvent was then removed under reduced pressure. The dimer product was extracted from the resultant brown solid with CH_2Cl_2 (50 mL) and filtered through celite. Crystallization from either CH_2Cl_2/hexane or CH_3CN/hexane mixtures gave the required products: $(\eta^5\text{-}C_5H_5)MoMn(CO)_8$ (55%); $(\eta^5\text{-}C_5H_5)MoRe(CO)_8$ (95%); $(\eta^5\text{-}C_5H_5)WMn(CO)_8$ (45%); $(\eta^5\text{-}C_5H_5)WRe(CO)_8$ (70%). Spectroscopic data for the dimers are given in Tables III and IV.

Reaction of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ with $Re(CO)_4(CNBu\text{-}t)Tf$. A solution of $Re(CO)_4(CNBu\text{-}t)Tf$ (1.1 equiv) in THF (10 mL) was slowly added to a solution of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ (0.5 mmol) in THF (20 mL). The reaction was monitored by IR spectroscopy and taken to be complete on disappearance of the characteristic ν(CO) absorptions of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ (1785–1730 cm^{-1}). After solvent removal under reduced pressure, the products were extracted from the solid brown residue into CH_2Cl_2 (50 mL) and filtered through Celite. Crystallization was achieved from either CH_2Cl_2/hexane mixtures or C_6H_6/hexane mixtures and gave the required product, $(\eta^5\text{-}C_5H_5)MoRe(CO)_7(t\text{-}BuNC)$, in 90% yield. Spectroscopic data for the new complex are given in Tables III and IV.

Reaction of $(\eta^5\text{-}C_5H_5)MMn(CO)_8$ (M = Mo, W) with $P(OMe)_3$, PMe_3, PMe_2Ph, and PPh_3. A solution of $(\eta^5\text{-}C_5H_5)MMn(CO)_8$ (0.1 mmol) and $P(OMe)_3$ (1.1 equiv) in CH_2Cl_2 or CH_3CN (20 mL) was prepared. Me_3NO (1.5 equiv) was added as a solid and the solution stirred vigorously in the dark for 1 h. Three products were identified in the reaction mixture and isolated by column chromatography on silica (C_6H_6/hexane mixtures as eluent). The products were characterized by IR and NMR spectroscopy as $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (20%) and $Mn(CO)_8[P(OMe)_3]_2$ (35%), and a new product, $(\eta^5\text{-}C_5H_5)MMn(CO)_7[P(OMe)_3]$ (20%), was characterized by elemental analysis (Table I) and NMR and IR spectroscopy (Tables III and IV). The other ligands were reacted in a similar manner with the dimers and the products isolated and then characterized by NMR and IR spectroscopy (see Tables III and IV).

Reaction of $(\eta^5\text{-}C_5H_5)MRe(CO)_8$ (M = Mo, W) with RNC (R = *t*-Bu, Xy, Cy, Bz). A solution of $(\eta^5\text{-}C_5H_5)MRe(CO)_8$ (0.2 mmol) and *t*-BuNC (1.1 equiv) in toluene (20 mL) was heated to reflux in the dark. The reaction was monitored by IR spectroscopy and continued until all the starting material had been consumed. The solvent was reduced to 2 mL under reduced pressure and the products isolated by column chromatography on silica (C_6H_6/hexane mixtures as eluent). A major yellow fraction was eluted from the column and characterized as $(\eta^5\text{-}C_5H_5)MRe(CO)_7(CNBu\text{-}t)$ (55% yield). Two minor fractions were also obtained from the column and characterized as $(\eta^5\text{-}C_5H_5)MRe(CO)_6(CNBu\text{-}t)_2$ (10%) and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ (5%) by IR and NMR spectroscopy. Other isonitrile ligands were also reacted with the dimer complexes and the new complexes isolated similarly in comparable yields. Spectroscopic data for the new complexes are listed in Tables III and IV.

Similar reactions were performed in the presence of Me_3NO, in CH_2Cl_2 or CH_3CN as solvent, at room temperature in the dark, and yielded the desired products, e.g., $(\eta^5\text{-}C_5H_5)MRe(CO)_7(CNBu\text{-}t)$ (~70%), as well as $(\eta^5\text{-}C_5H_5)MRe(CO)_6(CNBu\text{-}t)_2$ (10%) and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (7%). The PdO-catalyzed reaction (room temperature) also gave a similar product distribution viz. $(\eta^5\text{-}C_5H_5)MRe(CO)_7(CNR)$ (65% yield), $(\eta^5\text{-}C_5H_5)MRe(CO)_6(CNR)_2$ (7% yield), and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (12% yield).

Reaction of $(\eta^5\text{-}C_5H_5)MRe(CO)_8$ (M = Mo, W) with PR_3 (PR_3 = $P(OMe)_3$, PMe_2Ph, $PMePh_2$, PPh_3, PBz_3, $P(p\text{-}C_6H_4OMe)_3$). A solution of $(\eta^5\text{-}C_5H_5)MRe(CO)_8$ (0.1 mmol) and PR_3 (1.1 equiv) in toluene (20 mL) was prepared and heated at 90 °C in the dark. The reaction was monitored by IR spectroscopy and continued until all starting material had been consumed. The solvent was reduced to 2 mL and a yellow product isolated by column chromatography (silica; C_6H_6/hexane mixtures as eluent) and characterized as $(\eta^5\text{-}C_5H_5)MRe(CO)_7PR_3$ (45% yield) by IR and NMR spectroscopy (see Tables III and IV). $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (25%) and $Re_2(CO)_8(PR_3)_2$ (20%) were also isolated from the reaction mixture. Similar reactions were performed in the presence of Me_3NO (1.5 equiv) in CH_2Cl_2 or CH_3CN (20 mL) at room temperature. The required products $(\eta^5\text{-}C_5H_5)MoRe(CO)_7PR_3$ were obtained in 40–60% yields.

NMR Experiments: Reaction of $(\eta^5\text{-}C_5H_5)MoM(CO)_8$ (M = Mn, Re) with Me_3NO and *t*-BuNC in CD_3CN. $(\eta^5\text{-}C_5H_5)MoM(CO)_8$ (10 μmol) was dissolved in CD_3CN or C_6D_6 (0.4 mL) in an NMR tube. The *t*-BuNC or Me_3NO was added in aliquots (0.5 equiv) and the reaction monitored by IR and NMR spectroscopy. Results of the study are given in the discussion.

Cleavage Reactions of $(\eta^5\text{-}C_5H_5)MRe(CO)_{8-x}(RNC)_x$ (M = Mo, W; R = *t*-Bu, Xy; *x* = 1, 2) with Br_2. A solution of $(\eta^5\text{-}C_5H_5)MRe(CO)_{8-x}(RNC)_x$ (*x* = 1, 2) (0.03 mmol) in C_6D_6 (0.4 mL) was reacted with a solution of Br_2 (1.0 equiv) in C_6D_6 in an NMR tube. The products were identified as $(\eta^5\text{-}C_5H_5)M(CO)_3Br$ and *cis*-$Re(CO)_{5-x}(RNC)_xBr$ (*x* = 1, 2) by comparison with independently synthesized authentic materials.

Cleavage Reactions of $(\eta^5\text{-}C_5H_5)MM'(CO)_7PR_3$. (M = Mo, W; M′ = Mn, Re) with Br_2. A solution of $(\eta^5\text{-}C_5H_5)MM'(CO)_7PR_3$ (0.3 mmol) in C_6D_6 (0.4 mL) was reacted with Br_2 (1.1 equiv) in C_6D_6 in an NMR tube.

M′ = Mn; PR_3 = $P(OMe)_3$. Two products were obtained and identified by comparison with independently prepared samples and characterized as $(\eta^5\text{-}C_5H_5)M(CO)_3Br$ and *cis*-$Mn(CO)_4P(OMe)_3Br$.

M′ = Re; PR_3 = $P(OMe)_3$, $P(CH_2C_6H_5)_3$, $P(C_6H_5)_3$. Two or three products were obtained, as detected by NMR spectroscopy. Two of these

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Table III. Infrared Data for the Complexes $CpMM'(CO)_{8-n}L_n$[a,b] (M = Mo, W; M′ = Mn, Re; n = 0, 1, 2)

L	ν(CN)/cm^{-1}	ν(CO)/cm^{-1}							
$CpMoMn(CO)_7L$									
CO		2087 m	2045 w	2010 m	1993 vs		1977 (sh) br	1891 m, br	
$P(OMe)_3$			2056 w	2018 m	1995 vs		1963 m	1885 (sh)	1876 m
$CpMoRe(CO)_7L$									
CO[c]		2112 m	2070 (sh)	...	2007 vs		1963 s	1891 (sh)	1873 m
CO		2106 m	2064 w	2019 (sh)	2002 vs		1968 s, br	1894 (sh)	1875 m, br
t-BuNC	2188 w		2075 m	2020 (sh)	1995 vs		1953 vs	1880 m	1865 m
XyNC	2154 w		2062 m	2022 (sh)	1990 vs		1953 vs	1880 m	1860 m
CyNC	2198 w		2076 m	2025 (sh)	1993 vs		1950 vs	1878 m	1858 m
BzNC	2201 w		2076 m	2025 (sh)	1993 vs		1953 vs	1879 m	1858 m
CH_3CN[c]			2084 w	2033 vw	1995 vs		1948 vs	1871 m	1847 (sh)
Py[d]			2075 w	2022 m	1984 vs		1943 s	1880 m, br	
$P(OMe)_3$			2078 m	2013 w	...	1973 vs	1951 s	1873 m	1860 m
PMe_2Ph			2073 m	...	1983 s, br	...	1946 s, br	1868 m	1845 m
$PMePh_2$			2071 m	2014 (sh)	1983 s	1957 (sh)	1947 vs	1874 m	1851 m
PPh_3			2069 w	2011 m	1981 s	1961 vs	1949 (sh)	1876 m, br	
PBz_3			2074 m	2028 w	1989 s	1976 s	1949 vs, br	1870 m	1841 m
$P(p\text{-}C_6H_4OMe)_3$			2073 w	...	1989 s	1975 s	1946 vs	1868 m	1844 m
$CpWMn(CO)_7L$									
CO		2090 m		2026 w	1995 vs	1979 (sh)		1900 (sh)	1887 m
$P(OMe)_3$			2056 w	...	1995 w	...	1959 vs	1887 m	1870 m
$PMePh_2$			2046 w	...	1995 m	...	1951 vs	1882 m	1864 m
$CpWRe(CO)_7L$									
CO[c]		2112 m		2045 w	2007 vs		1960 s	1881 m	1863 m
CO		2113 m		2044 w	2008 vs		1964 s	1888 m	1867 m
t-BuNC	2192 m		2078 w	...	1995 vs		1947 vs	1872 m	1852 m
XyNC	2130 m		2074 m	2046 w	1995 vs		1953 vs	1870 m	1854 m
CyNC	2198 m		2078 m	2040 w	1992 vs		1949 vs	1872 m	1852 m
BzNC	2204 m		2078 m	...	1995 vs		1949 vs	1860 m	1852 m
CH_3CN[c]			2083 m	2035 w	1994 vs		1944 vs	1868 m	1845 m
Py[d]			2076 w	2023 w	1984 vs		1942 s	1863 s	1846 m
$P(OMe)_3$			2080 w	2014 (sh)	1972 vs	...	1949 s	1872 m	1856 m
PMe_2Ph			2074 w	2023 m	1991 s	1942 s	1933 (sh)	1871 m	1846 m
$PMePh_2$			2072 w	2011 m	1981 s	1957 (sh)	1943 vs	1869 m	1847 m
PPh_3			2068 w	...	1981 s	1960 vs	1945 s	1868 m	1847 m
PBz_3			2073 m	...	1989 s	1974 s	1944 vs, br	1861 m	1834 m
$P(p\text{-}C_6H_4OMe)_3$			2067 w	2025 w	1980 s	1957 vs	1942 s	1869 m	1847 m
$CpMoRe(CO)_6L_2$									
XyNC		2158 w	2124 w	2032 w	2012 s	1968 s	1940 s, br	1867 m	1845 m
CyNC		2212 m	2194 m	2060 (sh)	2038 s	1974 s	1922 s, br	1868 m	1844 m
BzNC		2200 m	2173 m	2041 w	2021 s	1959 s	1940 vs	1860 m	1844 m
CH_3CN[c]				2033 (sh)	2002 s	1948 m, br	1888 s, br	1775 s	
Py[d]				2035 w	2021 m	1919 s, br	1895 vs	1776 s	
$CpWRe(CO)_6L_2$									
XyNC		2164 m	2132 m	2014 (sh)	2017 s	1964 s	1938 s	1859 m	1842 m
CyNC		2209 m	2193 m	2068 w	2039 s	1975 s	1947 s, br	1875 w	1858 m
BzNC		2201 m	2162 m	2040 w	2019 s	1958 s	1936 vs	1837 m, br	
CH_3CN[c]				2032 (sh)	2002 m, br	1941 s, br	1884 vs, br	1773 s	
Py[d]				2038 (sh)	2022 s	1921 s, br	1889 vs, br	1775 s	

[a] Recorded in CH_2Cl_2. [b] Cp = η^5-C_5H_5. [c] Recorded in CH_3CN. [d] Recorded in pyridine.

products were characterized as $(\eta^5\text{-}C_5H_5)M(CO)_3Br$ and *cis*-$Re(CO)_4(PR_3)Br$ while the third complex was characterized as *trans*-$Re(CO)_4(PR_3)Br$.

Results

The synthesis of the dimer complexes $(\eta^5\text{-}C_5H_5)MM'(CO)_8$ (M = Mo, W; M′ = Mn, Re), **1**–**4**, have been reported in the literature but in modest yields.[1c,9,18] We have also obtained poor yields from the photolytic reaction of a mixture of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $Re_2(CO)_{10}$ in the mass ratios 5:1, 1:1, and 1:5 in C_6D_6 (Table II).

The reaction of the sodium and lithium salts of $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ (M = Mn, W)[13,14] with $M'(CO)_5X$ (M′ = Mn, Re; X = halogen) also resulted in the formation of the heteronuclear dimer in low yields (15–20%, see Table II). However replacement of $M(CO)_5X$ by $M(CO)_5CF_3SO_3$[16,17] results in good to almost quantitative formation of complexes **1**–**4** (see Table V). Isolation of the required heteronuclear dimer from the reaction mixture was simplified by the addition of a slight excess of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$. This resulted in reduced amounts of the dimer, $M_2(CO)_{10}$, being formed, and the low solubility of the other byproduct, $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$, in acetonitrile simplified its separation from the remaining reaction mixture. The heteronuclear dimer was separated from the above homonuclear dimers in solution by recrystallization from CH_2Cl_2/Hexane mixtures or CH_3CN, obviating the extensive chromatographic separation otherwise required to obtain the pure heteronuclear dimers.

Substitition of the heteronuclear dimers **1** and **2** by L (phosphines, phosphites, and isonitriles) was achieved by refluxing **1** or **2** in toluene in the presence of the ligand. Mono- and disubstituted products $(\eta^5\text{-}C_5H_5)MoRe(CO)_{8-x}L_x$ (x = 1, 2) as well as the homonuclear dimers $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ and $Re_2(CO)_{10-x}L_x$ were obtained and characterized by elemental analyses and IR and NMR spectroscopy (see below). Similar substituted products were obtained when the decarbonylating agent Me_3NO was added to the dimers in CH_2Cl_2 or CH_3CN

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Table IV. ^{1}H and ^{31}P NMR Data for the Complexes CpMM′(CO)$_{8-n}$L$_n$^{a,b} (M = Mo, W; M′ = Mn, Re; *n* = 0, 1, 2)

L	δ(^{1}H)/ppm [J/Hz] Cp	other	aromatic^c	δ(^{31}P)/cm^{-1}
		CpMoMn(CO)$_7$L		
CO^d	5.48			
	4.46			
P(*n*-Bu)$_3$	ax 4.84	0.94 (m), 1.61 (m), 1.38 (m), 1.85 (m)		...
P(OMe)$_3$	ax 4.77	3.19 (d) [J_{PH} = 12]		187.8
PMe$_3$	ax 4.75	ax 0.91 (d) [J_{PH} = 5]		35.9
PMe$_2$Ph	ax 4.75	ax 1.21 (d) [J_{PH} = 9]	7.14–6.74	31.1
PPh$_3$	ax 4.79		7.32–6.87	26.7
CD$_3$CN^d	5.36			
		CpMoRe(CO)$_7$L		
CO^e	5.44			
	4.54			
t-BuNC^f	eq 5.36	1.47 (s, CH$_3$)		
	eq 4.79	0.82 (s, CH$_3$)		
XyNC	eq 4.78	2.04 (s, CH$_3$)	6.67–6.45	
CyNC	eq 4.82	2.86 (m, CH), 1.35–1.05 (m, CH$_2$) 0.91–0.71 (m, CH$_2$)		
BzNC	eq 4.77	3.74 (s, CH$_3$)	7.03–6.78	
P(OMe)$_3$	eq 4.81	3.29 (d, CH$_2$) [J_{PH} = 12]		114.1
	ax 4.85	3.11 (d, CH$_2$) [J_{PH} = 12]		120.1
PMe$_2$Ph	ax 4.79	1.47 (d, CH$_3$) [J_{PH} = 9]	7.76–6.98	−34.2
PMePh$_2$	eq 4.82	1.98 (d, CH$_3$) [J_{PH} = 9]	7.38–6.52	*g*
	ax 4.86	1.97 (d, CH$_3$) [J_{PH} = 9]		−14.1
PPh$_3$	ax 4.83		7.57–6.96	8.6
PBz$_3$	ax 4.81	3.31 (d, CH$_2$) [J_{PH} = 8]	7.15–7.08	
P(*p*-C$_6$H$_4$OMe)$_3$	ax 4.88	3.17 (s, CH$_3$)	7.56–6.72	
CD$_3$CN	eq 5.35^d			
Py	eq 4.90		6.44 (p), 5.98 (o)^h 8.14 (m)	
		CpWMn(CO)$_7$L		
CO	4.47			
P(OMe)$_3$	eq 4.69	3.33 (d, CH$_3$) [J_{PH} = 12]		*g*
	ax 4.75	3.20 (d, CH$_3$) [J_{PH} = 12]		192.6
PMePh$_2$	eq 4.68	1.70 (d, CH$_3$) [J_{PH} = 8]		...
	ax 4.74	1.76 (d, CH$_3$) [J_{PH} = 8]	7.22–6.71	...
		CpWRe(CO)$_7$L		
CO	4.52			
t-BuNC	eq 4.77	0.86 (s, CH$_3$)		
XyNC	eq 4.74	2.07 (s, CH$_3$)	6.67–6.45	
CyNC	eq 4.77	2.89 (m, CH), 1.38–1.18 (CH$_2$, m) 0.92–0.70 (CH$_2$, m)		
BzNC	eq 4.73	3.75 (s, CH$_3$)	7.03–6.77	
P(OMe)$_3$	eq 4.78	eq 3.15 (d, CH$_3$) [J_{PH} = 12]		112.5
	ax 4.82	ax 3.11 (d, CH$_3$) [J_{PH} = 12]		120.7
PMe$_2$Ph	eq 4.75	1.52 (d, CH$_3$) [J_{PH} = 9]	7.30–6.95	−35.8
	ax 4.83	1.88 (d, CH$_3$) [J_{PH} = 9]	7.38–6.95	...
PMePh$_2$	ax 4.77	2.04 (d, CH$_3$) [J_{PH} = 8]	7.43–6.99	−15.3
PPh$_3$	eq 4.78		7.48–6.98	5.9
	ax 4.84		7.65–6.93	15.1
PBz$_3$	eq 4.77	eq 3.36 (d, CH$_2$) [J_{PH} = 8]		−12.3
	ax 4.81	ax 3.23 (d, CH$_2$) [J_{PH} = 8]	7.01–7.18	4.1
P(*p*-C$_6$H$_4$OMe)$_3$	eq 4.84	eq 3.18 (s, CH$_3$)	7.81–6.64	1.0
	ax 4.90	ax 3.17 (s, CH$_3$)	7.82–6.64	9.3
		CpMoRe(CO)$_6$L$_2$		
t-BuNC^d	dieq 5.07	1.54 (s, CH$_3$)		
	dieq 5.04	0.95 (s, CH$_3$)		
XyNC	dieq 5.02	2.18 (s, CH$_3$)	6.72–6.52	
CyNC	dieq 5.03	3.13 (m, CH), 1.42–1.19 (m, CH$_2$) 0.96–0.88 (m, CH$_3$)		
BzNC	dieq 5.00	3.91 (s, CH$_2$)	7.05–6.84	
CD$_3$CN^d	dieq 5.12			
		CpWRe(CO)$_6$L$_2$		
t-BuNC	dieq 4.99	0.98 (s, CH$_3$)		
XyNC	dieq 4.97	2.20 (s, CH$_3$)	6.73–6.49	
CyNC	dieq 5.08	3.10 (m, CH), 1.53–1.27 (m, CH$_2$) 1.19–0.81 (m, CH$_2$)		
BzNC	dieq 4.95	3.93 (s, CH$_2$)	7.05–6.85	

[a] Recorded in C$_6$H$_6$/ppm relative to TMS internal standard. [b] Cp = η^5-C$_5$H$_5$. [c] Multiplet range quoted, for ax/eq isomer mixtures. [d] Recorded in CD$_3$CN. [e] ^{13}C, C$_6$D$_6$ (ppm relative to TMS), (η^5-C$_5$H$_5$)MoRe(CO)$_7$: 91.4 (η^5-C$_5$H$_5$), 191.6 (ax ReCO), 181.8 (eq ReCO), 227.0 (cis MoCO), 235.1 (trans MoCO). [f] ^{13}C, C$_6$D$_6$ (ppm relative to TMS), (η^5-C$_5$H$_5$)MoRe(CO)$_7$(*t*-BuNC): 91.0 (η^5-C$_5$H$_5$), 164.6 (ax ReCO), 192.6 (cis–eq ReCO), 194.4 (trans–eq ReCO), 228.5 (cis MoCO), 237.2 (trans MoCO), 30.1 (CH$_3$), 87.5 (C—N), 134.3 (C≡N). [g] Not detected. [h] m = meta, p = para, and o = ortho.

Table V. Percent Yield from the Metathetical Dimer Formation Reactions

	yield/%		
M′(CO)$_5$X^a	Na[(η^5-C$_5$H$_5$)-Mo(CO)$_3$]	Li[(η^5-C$_5$H$_5$)-Mo(CO)$_3$]	Na[(η^5-C$_5$H$_5$)-W(CO)$_3$]
X = Cl	15–20	...	...
X = Br	15–25	40–63	15–20
X = I	15–25	5–10	20–25
X = Tf	75–95	...	55–65

[a] M′ = Mn, Re.

under milder conditions (room temperature). No formation of the homonuclear dimers was observed under these conditions, and yields of up to 75% were obtained when the reaction was performed in CH$_3$CN. In the absence of L, (η^5-C$_5$H$_5$)MRe(CO)$_7$(CH$_3$CN) was identified in the reaction mixture (Tables II and III).

The catalyzed substitution of CO on the dimers by L (isonitrile) was achieved by using a PdO catalyst, which is known to assist decarbonylation reactions.[19] The disubstituted product could be obtained by addition of a second equivalent of isonitrile ligand to the reaction mixture or by addition of 2 equiv of isonitrile to the parent heteronuclear dimers **1** and **2** (PdO catalyst at room temperature).

Thermal CO substitution of **3** and **4** in the presence of isonitrile ligands (RNC) in refluxing toluene resulted in the formation of only the homonuclear dimers [(η^5-C$_5$H$_5$)M(CO)$_3$]$_2$ and Mn$_2$(CO)$_{10-x}$(RNC)$_x$ (x = 0, 1, 2, 3). No substituted heteronuclear dimer products were detected, e.g., by in situ ^{1}H NMR spectroscopy. The formation of Mn$_2$(CO)$_9$(RNC) *and* Mn$_2$(CO)$_{10}$ suggests that some M–M′ bond fragmentation must have occurred prior to substitution. Under catalytic conditions (PdO), no substituted heteronuclear dimer species were detected either.

Thermal substitution of **3** and **4** in the presence of group 15 donor ligands (PR$_3$) resulted in the formation of fragmentation products similar to those obtained with RNC, viz. [(η^5-C$_5$H$_5$)M(CO)$_3$]$_2$ and Mn(CO)$_{10-x}$(PR$_3$)$_x$ (x = 0, 1, 2). The Me$_3$NO-induced reaction did yield the required product, (η^5-C$_5$H$_5$)MoMn(CO)$_7$(PR$_3$), in ~20% yield (see Experimental Section). No PdO- or [(η^5-C$_5$H$_5$)M(CO)$_3$]$_2$-catalyzed carbonyl substitution of **3** and **4** was observed with phosphine ligands, consistent with the results obtained for **1** and **2**.

Discussion

Synthesis. The dramatic differences in the yields of heteronuclear dimer obtained when the halogen in Re(CO)$_5$X is replaced by the triflate group suggests that different mechanisms are responsible for (η^5-C$_5$H$_5$)MM′(CO)$_8$ formation. It has been reported that metathetical reactions involving organometallic ions may not proceed by simple ion exchange reactions but could involve radicals.[20] For instance radical species have been detected in the synthesis of M$_2$(CO)$_{10}$ (M = Mn, Re) from [Re(CO)$_6$]$^+$ with

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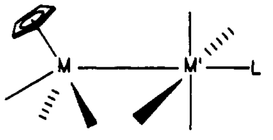
$[Mn(CO)_5]^-$,[21] with product yields dependent on the selectivity of the radical fragment toward hetero- or homonuclear dimer formation. It can be argued that the weakly bound triflate group (readily substituted by poor donor ligands,[16,22,23] e.g., H_2O, THF, etc.) is displaced so readily in solution by nucleophilic $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ that the radical path, which competes with the ion exchange pathway, is effectively eliminated. This results in the higher yields of the required dimer being formed.

Characterization of the Substituted Products. (a) Halogen Cleavage Reactions. In order to identify the site of substitution in $(\eta^5\text{-}C_5H_5)MM'(CO)_9L$, i.e., whether the L group was attached to M or M', the substituted dimers were reacted with Br_2 in an NMR tube. The resultant monomer fragments were then identified by IR and NMR spectroscopy as $(\eta^5\text{-}C_5H_5)M(CO)_3Br$[13] and $M(CO)_4LBr$[12] showing that the ligand occupied a site on the M' fragment of the heteronuclear dimer.

The cleavage reactions also provided information on the site (*axial* versus *equatorial* i.e. **5** or **6**) of substitution at the Re atom. Thus, cleavage of the substituted dimers $(\eta^5\text{-}C_5H_5)MRe(CO)_4PR_3$ resulted in the formation of *cis*- and *trans*-$Re(CO)_4(PR_3)Br$, which were identified from their ^1H and ^{31}P NMR spectra.[12a,12b,24]



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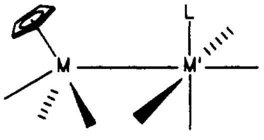

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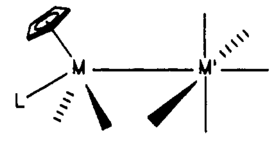

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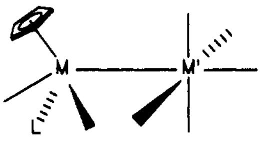

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(b) Synthesis. Attempts to synthesize the M-substituted dimer (**7** or **8**) from $Na[(\eta^5\text{-}C_5H_5)M(CO)_2(CNBu\text{-}t)]$ and $Re(CO)_5Tf$ were unsuccessful,[25] resulting in only the formation of complex reaction mixtures. The only substituted heteronuclear dimer (5% yield) identified by ^1H NMR and IR spectroscopy in the reaction mixture was $(\eta^5\text{-}C_5H_5)MRe(CO)_7(CNBu\text{-}t)$.

The Re-substituted heteronuclear dimer $(\eta^5\text{-}C_5H_5)MoRe(CO)_7(t\text{-}BuNC)$ was successfully prepared by the metathetical reaction of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ and $Re(CO)_4(CNBu\text{-}t)Tf$ in excellent yield (90%) with spectroscopic properties identical to those for the product obtained from the reaction of **1** and *t*-BuNC.

(c) Analysis of Mass Spectral Data. Mass spectral data for the series $(\eta^5\text{-}C_5H_5)MoRe(CO)_{8-x}(CNBu\text{-}t)_x$ ($x = 0, 1, 2$) confirmed that substitution had occurred at the Re atom in the new products. Metal–metal bond dissociation appears to dominate in these complexes in the mass spectrometer since the major fragment observed in the spectra when $x = 1, 2$ is the monometallic $Re(CO)_2(CNBu\text{-}t)^+$ fragment.

(d) X-ray Data. Confirmation of the stereochemistry of the substituted dimer products was obtained from the X-ray crystal structure determinations of $(\eta^5\text{-}C_5H_5)MoRe(CO)_7(CNBu\text{-}t)$, where the RNC ligand was found to occupy an *equatorial* site on the Re center,[6a] and $(\eta^5\text{-}C_5H_5)MoMn(CO)_7P(OMe)_3$, where the phosphite ligand was found to occupy an *axial* site on the Mn center.[6b] These structures provided reference samples for correlating spectral properties with the structure of the substituted dimers.

Table VI. Initial Percent *Axial* Isomer Formed from Reaction of Dimers with L in the Presence of Me_3NO[a]

L	yield/%			
	$X = A^b$	$X = B^c$	$X = C^d$	$X = D^e$
$P(OMe)_3$	>95	30	0	86
$PMePh_2$			44	90
$P(O\text{-}o\text{-}tol)_3$			10	99
PPh_3	>95	58	71	99
PBz_3		90	40	94
$P(p\text{-}C_6H_4OMe)_3$		70		

[a] Reaction yield for the reaction $Re(CO)_5X + L \rightarrow Re(CO)_4LX$ as determined by ^{31}P or ^1H NMR spectroscopy. [b] $A = (\eta^5\text{-}C_5H_5)Mo(CO)_3$. [c] $B = (\eta^5\text{-}C_5H_5)W(CO)_3$. [d] $C = Re(CO)_5$.[2] [e] $D = Mn(CO)_5Re(CO)_4L$.[2]

(e) Analysis of the NMR Data. The presence of the C_5H_5 ring and the RNC and the PR_3 ligands permits a ready evaluation of the degree of substitution on the dimers by NMR spectroscopy.

Assignment of the spectra to the presence of *axial* and *equatorial* isomers, **5** and **6** (L = phosphine, phosphite), proved possible when mixtures of the isomers were detected in solution. Assignments were based on the ^1H and ^{31}P NMR spectral data of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_4P(OMe)_3$, which contains an axial $P(OMe)_3$ substituent (see above). On steric grounds[26] larger phosphines will also occupy the *axial* position. This suggests that for the Mo–Re and W–Mn complexes the major amount of isomer (>95%) detected by NMR spectroscopy will again be the *axial* isomer. The NMR (^1H, ^{31}P) spectra of the W–Re dimers revealed the presence of both *axial* and *equatorial* isomers in measurable amounts. Assuming the assignments suggested above, the percent *axial* isomer observed immediately at the end of the reaction (see experimental) was as follows: $P(OMe)_3$, 30%; PPh_3, 58%; $P(p\text{-}C_6H_4OMe)_3$, 70%; PBz_3, 90%. This sequence again suggests the dominance of steric effects in establishing the isomer ratio of **5** and **6**. Data for the axial/equatorial mixtures $M(CO)_5M'(CO)_4L$ (M,M' = Mn,Re)[2] are also shown in Table VI and support this general conclusion.

The NMR data listed in Table IV indicate that the C_5H_5 ^1H resonance occurs *downfield* for the *axial* isomer relative to the *equatorial* isomer while a *reverse* trend occurs for the ^{31}P resonance of the ligand.

It is to be noted that all isonitrile (and acetonitrile) substituted derivatives yield only one isomer as detected by ^1H NMR spectroscopy (Table IV). This isomer is the equatorial isomer, established conclusively from the X-ray structural determination of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Re(CO)_4(CNBu\text{-}t)$. This isomer is expected on both electronic and steric[27] grounds.

(f) Analysis of the IR Data. An analysis of the IR spectra of $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_4L$ reveals that the isomers can be differentiated by this technique. Although the *equatorial* and *axial* isomers exhibit six and seven ν(CO) resonances, respectively, the difference between the two spectra relates to (i) a weak band at ~2020 cm^{-1} associated with the *equatorial* isomer and (ii) a change in the band profile in the 2000–1950-cm^{-1} region. IR spectra to indicate these differences are shown in Figure 1a–d which also indicates the influence of solvent effects on the spectra.

Notwithstanding that the pure isomers can be differentiated by IR spectroscopy, when the IR spectrum of a mixture of isomers is recorded, little information on the isomer composition is available. This is clearly indicated in Figure 2a,b.

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Table VII. ^{31}P Data for $Re(CO)_4LX$ Complexes[a]

			δ/ppm										
			X = A[d]		X = B[e]		X = C[f]		X = D[g]		X = E[h]		X = F[i]
L	θ/deg[b]	pK_a[c]	t	c	a[j]	e[k]	a[j]	e[k]	a[j]	e[k]	a[j]	e[k]	a[j]
$P(OMe)_3$	107	2.6	111.1	100.7	120.1	114.1	120.7	112.5	120.6	112.6	126.7	115.1	130.6
$P(OMe)_2Ph$	120	2.64	128.1	122.2									140.5
$P(OPh)_3$	128	−2	105.2	91.8									119.7
$P(O\text{-}i\text{-}Pr)_3$	130	4.08	101.0	90.9					108.3	105.3	113.7	107.8	119.5
$P(OMe)Ph_2$	132	2.69	104.5	93.5									113.7
$PMePh_2$	136	4.57	−10.0	−25.2	−14.1		−15.3		−9.3	−19.4	−7.3	−21.7	−6.4
$P(O\text{-}o\text{-}tol)_3$	141	−1.83	101.4	88.3					108.7		113.5	98.2	115.7
PPh_3	145	2.37	13.3	−4.9	8.6		15.1	5.9	14.7		16.2	1.2	18.1
$P(p\text{-}C_6H_4OMe)_3$	145						1.0	−9.3					
PBz_3	165		5.1	−18.6			4.1	−12.3	4.5	−16.1	6.6	−17.4	6.1

[a] ^{31}P data measured in C_6D_6 relative to H_3PO_4 (δ = 0 ppm). [b] Tolman cone angle.[26] [c] Data obtained from ref 32. [d] A = I.[24] Data refer to cis (c) and trans (t) isomers. [e] B = $(\eta^5\text{-}C_5H_5)Mo(CO)_3$. [f] C = $(\eta^5\text{-}C_5H_5)W(CO)_3$. [g] D = $Mn(CO)_5$.[2] [h] E = $Re(CO)_5$.[2] [i] F = $Re(CO)_4L$.[3] [j] a = axial. [k] e = equatorial.

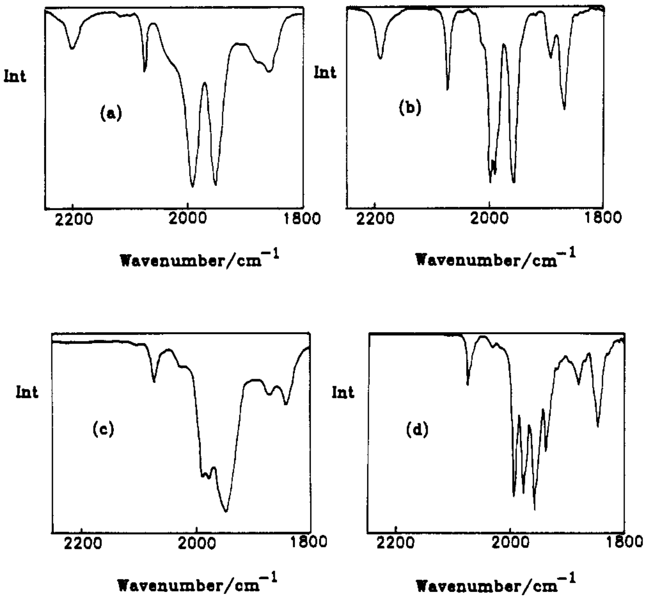

Figure 1. IR spectra: (a) *eq*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7(CNBz)$ recorded in CH_2Cl_2; (b) *eq*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7CNBz$ recorded in hexane; (c) *ax*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7(PBz_3)$ recorded in CH_2Cl_2; (d) *ax*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7(PBz_3)$ recorded in hexane.

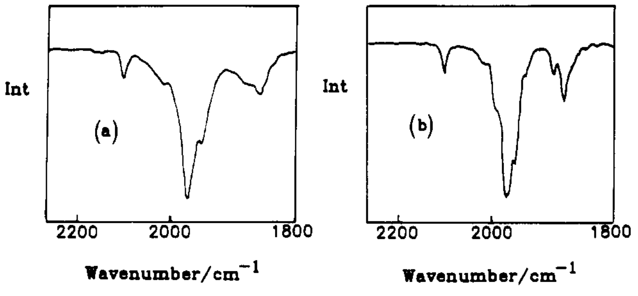

Figure 2. IR spectra: (a) *ax*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7[P(OMe)_3]$ recorded in CH_2Cl_2; (b) *ax*-$(\eta^5\text{-}C_5H_5)MoRe(CO)_7[P(OMe)_3]$ recorded in hexane.

Table VIII. Analysis of the ^{31}P Data for $Re(CO)_4LX$ Complexes

	$\Delta(\delta(^{31}P_{ax-eq}))$/ppm				
L	X = A[a]	X = B[b]	X = C[c]	X = D[d]	X = *E*[e]
$P(OMe)_3$	11.6	10.4	8.2	8.0	6.0
$P(OMe)_2Ph$		5.9			
$P(OPh)_3$		13.4			
$P(O\text{-}i\text{-}Pr)_3$	5.9	10.1		3.0	
$P(OMe)Ph_2$		11.0			
$PMePh_2$	14.4	15.2		10.1	
$P(O\text{-}o\text{-}tol)_3$	15.3	13.1			
PPh_3	15.9	18.2	9.2		
$P(p\text{-}C_6H_4OMe)_3$			10.3		
PBz_3	24.0	23.7	16.4	20.6	

[a] A = $Re(CO)_5$.[2] [b] B = I.[24] Data refer to cis and trans isomers. [c] C = $(\eta^5\text{-}C_5H_5)W(CO)_3$. [d] D = $Mn(CO)_5$.[2] [e] E = $(\eta^5\text{-}C_5H_5)Mo(CO)_3$.

The Influence of Metal Fragments on the Product Distribution. One of the major objectives of this study was to assess the steric and electronic effects of the metal fragment [$(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$, $Mn(CO)_5$, $Re(CO)_5$] on the substitution reactions of the heterobimetallic complexes $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ (M = Mo, W; M′ = Mn, Re).

The mechanism of the substitution reaction is not known in detail and indeed will be different for the different methodologies employed in this work. However, it is proposed that all reactions proceed through a common intermediate $(\eta^5\text{-}C_5H_5)Mo(CO)_3M'(CO)_4$), involving CO loss from M′.[28,29] The CO loss is expected to occur from an *equatorial* position[30] on M′, and the incoming ligand, if small, is expected to occupy an *equatorial* position on M′ on electronic grounds. If L interacts sterically with the $(\eta^5\text{-}C_5H_5)M(CO)_3$ fragment, M–M′ bond cleavage to relieve the steric strain, *or* isomerization of L to give the axially substituted complex, can occur. In the case of $(\eta^5\text{-}C_5H_5)M(CO)_3Mn(CO)_4L$ (L = RNC) the isomerization route is not available.[4,8] Cleavage of the M–M′ bond results in the formation of $Mn(CO)_4L^\bullet$ radicals which then dimerize with other Mn radicals in solution to give $Mn_2(CO)_{10-x}L_x$ (x = 2). The $(\eta^5\text{-}C_5H_5)M(CO)_3Re(CO)_4L$ (L = RNC) complex, containing the larger Re atom, by contrast, can be isolated. When L = group 15 ligand the electronic properties permit the ligands to occupy *axial* sites and there is precedence for *ax/eq* isomerization in a wide range of metal carbonyl dimers.

The steric requirements of the various fragments composing the four heteronuclear bimetallic complexes thus rationalizes the "*inverse steric effect*" *in which smaller ligands such as isonitriles lead to decreased stability of a complex.* This is to be contrasted with typical complex stability studies in which increasing ligand size results in *decreased* complex stability.[31]

Comparative Analysis of the ^{31}P NMR Data. The ^{31}P data for a range of complexes $Re(CO)_4LX$ (X = I, $Mn(CO)_5$, $Re(CO)_5$, $Re(CO)_4L$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$) are listed in Table VII. For *ax*-$Re(CO)_4LX$ (L = $P(OMe)_3$) the ^{31}P resonance is found to move upfield for X, $Re(CO)_4P(OMe)_3$ > $Re(CO)_5$ > $Mn(CO)_5$ ~ $(\eta^5\text{-}C_5H_5)W(CO)_3$ ~ $(\eta^5\text{-}C_5H_5)Mo$-

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(28) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.
(29) Shen, J.-K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Organometallics* **1989**, *8*, 2144.
(30) (a) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160. (b) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1989**, *28*, 3524 and references cited therein.
(31) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

$(CO)_3$ > I. A comparison of the *equatorially* substituted $Re(CO)_4(P(OMe)_3)X$ complexes reveals a similar trend. Similar effects are seen for other L.

The *difference* between the *axial* and *equatorial* resonance positions for any one ligand, L, might be expected to reflect the steric constraints of the X fragment. An analysis of this data in which the difference in ^{31}P resonances between axial and equatorial isomers, (or cis and trans isomers for $Re(CO)_4(L)I$), $\Delta(\delta(^{31}P_{ax-eq}))$ has been determined and is shown in Table VIII. Two trends are to be noted.

(i) When the *steric* size of L is increased, there is a general *increase* in Δ. ($PBz_3 > P(OMe)_3$).

(ii) For both the $P(OMe)_3$ and the PBz_3 series the available data show Δ increases in the order $Re(CO)_5 > I > (\eta^5\text{-}C_5H_5)W(CO)_3 \sim Mn(CO)_5 > (\eta^5\text{-}C_5H_5)Mo(CO)_3$. These values are expected to reflect the steric size of the X group as experienced by $Re(CO)_4L$ and suggest, for instance, that $Re(CO)_5$ is sterically more demanding than $(\eta^5\text{-}C_5H_5)Mo(CO)_3$.

Conclusion

From the above study the following statements can be made.

(i) Substitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ occur predominantly if not exclusively at $M'(CO)_5$ for L = nitriles, isonitriles and group 15 donor ligands. This is true for all methodologies employed (thermal and PdO-catalyzed and Me_3NO-induced carbonylations).

(ii) Substitution of CO occurs to give *equatorially* substituted dimers for L = nitriles and isonitriles. In some instances (M = Mn, L = RNC) the substituted dimer is unstable and only the cis-substituted $Mn_2(CO)_8L_2$ complex is observed.

(iii) *Axial* products are always observed for L = group 15 donor ligands. A consideration of the *ax*/*eq* ratios for the $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_4L$ complexes indicates that the *axial* complex is favored for the Mo (>95%) over the W derivatives (30–90%, Table VI).

(iv) The $(\eta^5\text{-}C_5H_5)W(CO)_3Re(CO)_4L$ NMR data indicate that the initial (kinetic) *ax*/*eq* ratio obtained from the reaction of **2** with L in the presence of Me_3NO reflects the steric demand of the group 15 donor ligand, namely, $PBz_3 > P(p\text{-}C_6H_4OMe)_3 \sim PPh_3 > P(OMe)_3$.

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