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RHENIUM(I) ISOCYANIDE COMPLEXES

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Summary

Two series of rhenium(I) isocyanide complexes having the general formulas $Re(CO)_{5-n}L_nBr$ and $[Re(CO)_{6-n}L_n]PF_6$ (L = CNMe, CNtol) are described. The former compounds are formed from $Re(CO)_5Br$ by direct carbonyl replacement using thermal or photolytic conditions, the extent of the reaction being determined by reaction temperature and time. An interesting conversion of *fac*-$Re(CO)_3L_2Br$ to *mer,trans*-$Re(CO)_3L_2Br$ on heating is noted. The third possible isomer having this stoichiometry, *mer,cis*-$Re(CO)_3L_2Br$, forms in photolytic reactions of $Re(CO)_5Br$ and L. Three possible $Re(CO)_2L_3Br$ isomers were isolated, thermal reactions (toluene reflux) giving the *mer,cis* and *fac* isomers, photolytic reactions giving all three isomers. Isomers were generally separated by chromatography and their geometries ascertained from infrared data. More forcing reaction conditions eventually give $Re(CO)L_4Br$, then ReL_5Br and $[ReL_6]Br$ (L = CNtol only) or $[Re(CO)L_5]Br$. The other ionic complexes are prepared from the substituted carbonyl halide, $Re(CO)_{5-n}L_nBr$, and added ligands in the presence of a halide acceptor. Generally, all reactions are much less facile than corresponding reactions in the manganese carbonyl series. Spectroscopic and electrochemical data are reported.

Introduction

Little study has been accorded to rhenium(I) isocyanide complexes, in contrast to substantial recent work on the congener element, manganese [1,2]. In 1956, Hieber and Schuster [3] reported that $Re(CO)_5Cl$ and *p*-tolyl isocyanide * yielded an ionic complex, $[Re(CO)_4(CNtol)_2]Cl$, when refluxed in petroleum ether (100°C). A complex of analogous stoichiometry $Re(CO)_4(CNtol)_2I$ has recently been reported, and interestingly it is said to be a non-electrolyte [4]. The same paper reported $Re(CNtol)_5I$ (and also $Re(CNtol)_4I_3$ and $Re(CNtol)_3I_3$) as products of the reaction of K_2ReI_6 and the isocyanide. Several $[Re(CNR)_6]X$

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* CNtol refers to *p*-tolyl isocyanide throughout this paper.

complexes (R = Et, tol; X = several anions) have been described, obtained by reactions of rhenium halides and the isocyanide sometimes followed by anion exchange [5,6]. The ionic complex $[Re(CO)_2(CNtol)_4]I$ is reported to be formed from $[Re(CO)_2I_4]^-$ and CNtol. A number of rhenium(I) complexes having unusual stoichiometries, containing both phosphines (triphenylphosphine or 1,2-bis(diphenylphosphino)ethane) and isocyanide ligands are known [7,8]. In addition to these reports on rhenium(I) complexes, there are several papers concerned with rhenium(II) [9,10] and rhenium(III) [4,8,9] isocyanide complexes.

The lack of effort on rhenium isocyanide chemistry, and some confusing previous results, encouraged consideration of further work; and having been involved in the recent work on manganese isocyanide complexes [1,2] we were interested in pursuing this study. It was also our hope that some interesting contrasts in chemical behaviour of these elements would arise; indeed this was found to be the case.

Experimental

Methyl isocyanide [11], *p*-tolyl isocyanide [12], $Re(CO)_5Br$, $Re_2(CO)_8Br_2$ and $Re(CO)_5Cl$ [13] were prepared by the cited literature methods. Tetrahydrofuran was dried by distillation from $LiAlH_4$. Other reagents, commercially available, were used without further treatment.

Infrared spectra were run on a Beckman IR-10 (± 5 cm^{-1}). Mass spectra were recorded using an AEI MS-9 spectrometer. Electrochemical measurements were made using a three electrode configuration, with stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (KCl) reference electrode. Voltage and current were controlled with a PAR Model 170 electrochemical system, incorporating compensation for internal resistive potential drop. Solutions of substrate concentrations of $\sim 1 \times 10^{-3}$ *M* in either dichloromethane or acetonitrile were used; tetrabutylammonium perchlorate (0.1 *M*) was chosen as a base electrolyte. Sweep rates were varied from 50—200 mV/sec. Data from these studies are given in Table 1.

Analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of $Re(CO)_4(CNtol)Br$

To a 50 ml toluene suspension of $Re_2(CO)_8Br_2$ (0.25 g, 0.33 mmol) was added *p*-tolyl isocyanide (0.08 ml, 0.66 mmol). After stirring for 16 h at room temperature the solvent was removed and the residue dissolved in CH_2Cl_2. Filtration, followed by slow evaporation of the solvent gave the product as a white solid (0.26 g, 80%; m.p. 132—134°C).

Anal. (By mass spectrometric parent peak match.) Found: 496.911000. $C_{12}H_7{}^{81}BrNO_4{}^{187}Re$ calcd.: 496.90991 *. Infrared (CH_2Cl_2 solution): ν(CN) 2185m; ν(CO) 2105w, 2022vs, 1960vs cm^{-1}.

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* Some analyses were accomplished by parent peak match in the mass spectrum. When this was done extra care was taken to insure that a pure sample was being analyzed. Purification was accomplished by crystallization to constant m.p., and checked by infrared and NMR spectra. Also absence of other volatile complexes was defined by the absence of specific molecular ion peaks in the mass spectrum.

TABLE 1

CYCLIC VOLTAMMETRY DATA [a]

	$E_{p,a}$ [b] (vs. SCE)		$E_{p,a} - E_{p,c}$ (V)	
	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN
A. $Re(CO)_{5-n}L_nX$ compounds				
1. $Re(CO)_4(CNtol)Br$	1.90	1.78		
fac-$Re(CO)_3(CNtol)_2Br$	1.68, 2.17	(dec.) [c]		
mer,trans-$Re(CO)_3(CNtol)_2Br$	insoluble			
mer,cis-$Re(CO)_2(CNtol)_3Br$	1.33, 1.75	(dec.) [c]		
trans-$Re(CO)(CNtol)_4Br$	1.04, 1.60	(dec.) [c]		
$Re(CNtol)_5Br$	0.51 [d], ~1.31	0.54 [d]	110	70
2. *fac*-$Re(CO)_3(CNtol)_2Cl$	1.73, 2.20	1.56, 2.05		
trans-$Re(CO)(CNtol)_4Cl$	1.03, 1.60			
$Re(CNtol)_5Cl$	0.50 [d], 1.32		110	
3. $Re(CO)_4(CNMe)Br$	2.01			
fac-$Re(CO)_3(CNMe)_2Br$	1.61, 2.14	1.50		
mer,trans-$Re(CO)_3(CNMe)_2Br$	insoluble			
mer,cis-$Re(CO)_2(CNMe)_3Br$	1.25, 1.70	1.14, 1.59		
trans-$Re(CO)(CNMe)_4Br$	0.87, 1.35			
B. $[Re(CO)_{6-n}(CNR)_n]PF_6$				
1. $[Re(CNtol)_6]PF_6$	1.20 [d], 1.98			
$[Re(CNC_6H_4OMe)_6]PF_6$	1.10 [d], 1.73	0.95 [d], 1.65	160	100
$[Re(CO)(CNtol)_5]PF_6$	1.41 [d], 2.26	1.28 [d], 2.04	140	90
2. $[Re(CO)(CNMe)_5]PF_6$	1.18 [d], ~1.8		80	
cis-$[Re(CO)_2(CNMe)_4]PF_6$	1.70 [d], ~2.6		130	
fac-$[Re(CO)_3(CNMe)_3]PF_6$	2.21		120	

[a] Obtained using a PAR-170 Electrochemical System, for solutions ~5 × 10^{-3} *M* in compound, 0.1 *M* in Bu_4NClO_4. [b] Except as indicated by (*d*) the systems are not chemically reversible, anodic and cathodic currents being unequal. The first values of $E_{p,a}$ given corresponds to the 1*e* oxidation processes $Re(CO)_{5-n}L_nX \rightarrow [Re(CO)_{5-n}L_nX]^+ + e$ or $[Re(CO)_{6-n}L_n]^+ \rightarrow [Re(CO)_{6-n}L_n]^{2+} + e$. In several cases, a second 1*e* oxidation was observed and its potential is also given. [c] Evidence for disproportionation or decomposition noted. [d] Chemically reversible, integrated currents for anodic and cathodic processes being equal. In these cases voltages recorded are $1/2(E_{p,a} + E_{p,c})$.

Preparation of fac-$Re(CO)_3(CNtol)_2Br$

Bromopentacarbonylrhenium (0.75 g, 1.8 mmol) and *p*-tolyl isocyanide (0.50 ml, 4.4 mmol) were refluxed in 150 ml tetrahydrofuran for 20 h. The solvent was removed, and the off-white solid, *fac*-$Re(CO)_3(CNtol)_2Br$ (1.01 g, 94%; m.p. 165–166°C) was washed with Skelly B.

Found: mol. wt. (mass spec.) 585.9681. $C_{19}H_{14}N_2O_3{}^{81}Br^{187}Re$ calcd.: 585.97284. Infrared (CH_2Cl_2 solution) ν(CN): 2195w, 2160m; ν(CO) 2040s, 1996s, 1938s cm^{-1}.

A longer reaction time (6 days), using a larger excess of the isocyanide, gave the same product; no evidence for further substitution was obtained.

Preparation of fac-$Re(CO)_3(CNtol)_2Cl$

Similarly, $Re(CO)_5Cl$ was treated with excess *p*-tolyl isocyanide for 4 h to give the pale-yellow product in 90% yield (m.p. 169°C).

Found: C, 43.29; H, 2.83. $C_{19}H_{14}ClN_2O_3Re$, calcd.: C, 42.26; H, 2.61%. Infrared (CH_2Cl_2 solution): ν(CN) 2195w, 2160m; ν(CO) 2035s, 1992s, 1935s cm^{-1}.

Preparation of mer,trans-$Re(CO)_3(CNtol)_2Br$

A sample of *fac*-$Re(CO)_3(CNtol)_2Br$ (0.60 g, 1.03 mmol) was refluxed in 50 ml octane for 2 h. The *mer,trans* isomer was collected as a yellow precipitate (0.44 g, 73%; m.p. 198.5—199.6°C) and washed with CH_2Cl_2. The product is only very slightly soluble in CH_2Cl_2 and THF, and insoluble in hexane, acetone, and acetonitrile.

This product was not obtained on heating the solid *fac*-$Re(CO)_3(CNtol)_2Br$.

Found: C, 38.88; H, 2.50; N, 4.84. $C_{19}H_{14}BrN_2O_3Re$ calcd.: C, 39.05; H, 2.41; N, 4.79%. Infrared (nujol mull): ν(CN) 2100s, 2160w; ν(CO) 2030m, 1950s, 1910s cm^{-1}.

Reaction of $Re(CO)_5Br$ *and CNtol in toluene; preparation of* $Re(CO)_2(CNtol)_3Br$, $Re(CO)(CNtol)_4Br$, *and* $Re(CNtol)_5Br$

A mixture of $Re(CO)_5Br$ (3.0 g, 7.4 mmol) and CNtol (3.6 ml, 30 mmol) was refluxed in 75 ml toluene for 20 h to give a yellow-brown solution. The solvent was removed to give a yellow solid. This was extracted in a Soxhlet extractor for 16 h using diethyl ether, giving a green solution. A yellow ether-insoluble solid remained; this was crystallized from CH_2Cl_2/diethyl ether to give yellow crystals of *trans*-$Re(CO)(CNtol)_4Br$, (2.83 g, 50% yield; m.p. 223—224.5°C).

Found: C, 52.04; H, 3.77; N, 7.43. $C_{33}H_{28}BrN_4ORe$ calcd.: C, 51.97; H, 3.70%. Infrared (CH_2Cl_2 solution): ν(CN) 2080s, 2040sh; ν(CO) 1880m cm^{-1}.

After concentration, the ether soluble fraction was put into a 2 × 13 cm acidic alumina column and developed with ether. A colorless fraction eluting first yielded 0.16 g (3%) of *mer,cis*-$Re(CO)_2(CNtol)_3Br$; this product was recrystallized from CH_2Cl_2/diethyl ether (m.p. 127—128.5°C).

Found (mass spec.): 675.03576. $C_{26}H_{21}N_3O_2{}^{81}Br^{187}Re$ 675.03576. Infrared (CH_2Cl_2 solution): ν(CN) 2180w, 2105s, 2040w; ν(CO) 1985s, 1905s cm^{-1}. Further elution of the chromatographic column using diethyl ether gave a broad yellow band, which on evaporation gave a yellow solid. Crystallization of the residue from acetone/Skelly B gave yellow crystals of $Re(CNtol)_5Br$ (0.62 g, 10%; m.p. 146—147°C).

Found: C, 56.58; H, 4.21; N, 8.11. $C_{40}H_{35}BrN_5Re$ calcd.: C, 56.40; H, 4.14; N, 8.22%. Infrared (CH_2Cl_2 solution): 2070s, 2035m cm^{-1}.

Following elution of $Re(CNtol)_5Br$, a small amount of $Re(CO)(CNtol)_4Br$ was eluted with chloroform.

Reaction of $Re(CO)_5Cl$ *and CNtol in toluene: preparation of* $Re(CO)(CNtol)_4Cl$, $Re(CNtol)_5Cl$, *and* $[Re(CNtol)_6]PF_6$

A mixture of $Re(CO)_5Cl$ (0.60 g, 1.7 mmol) and CNtol (0.97 g, 8.3 mmol) was refluxed in toluene for 15 h. Evaporation of the solvent, followed by recrystallization of the residue from CH_2Cl_2/diethyl ether gave yellow crystals of *trans*-$Re(CO)(CNtol)_4Cl$ (0.62 g, 52% yield; m.p. 226—227°C).

Found: C, 55.35; H, 4.01; N, 7.90. $C_{33}H_{28}ClN_4ORe$ calcd.: C, 55.18; H, 3.93; N, 7.80%. Infrared (CH_2Cl_2 solution): ν(CN) 2080s, 2050(sh); ν(CO) 1880m cm^{-1}.

After removing the solvent from the filtrate, the residue was extracted with benzene, leaving a small amount of yellow solid, which after metathesis with NH_4PF_6, gave $[Re(CNtol)_6]PF_6$, identified by its infrared spectrum.

The residue obtained on evaporation of the benzene filtrate was put onto a 2 × 13 cm acidic alumina column with a minimum of CH_2Cl_2. A pale-yellow band eluting with CH_2Cl_2 was identified as $Re(CO)(CNtol)_4Cl$ by its infrared spectrum. A broad yellow band was eluted next. Evaporation left a yellow solid from which crystallization from acetone/Skelly B gave yellow crystals of $Re(CNtol)_5Cl$ (0.23 g, 17% yield; m.p. 149—150.5°C).

Found: C, 59.47; H, 4.43; N, 8.59. $C_{40}H_{35}ClNRe$ calcd.: C, 59.50; H, 4.37; N, 8.67%. Infrared (CH_2Cl_2 solution) ν(CN) 2070s, 2035m.

Preparation of $[Re(CNtol)_6]X$ and $[Re(CO)(CNtol)_5]X$ ($X = Br, PF_6$)

A mixture of $Re(CO)_5Br$ (0.75 g, 1.85 mmol) and CNtol (2.3 ml, 19.6 mmol) was heated at 113°C for 16 h (no solvent). A residue was left which partially dissolved in ethanol. Filtration followed by addition of diethyl ether gave a yellow-brown solid which upon recrystallization from CH_2Cl_2/diethyl ether gave yellow crystalline $[Re(CNtol)_6]Br$ (0.19 g, 11%); m.p. 223—226°C).

The cation, which is known with other anions, was then converted to the PF_6^- salt by metathesis with NH_4PF_6 (infrared (CH_2Cl_2 solution): ν(CN) 2080s, 2040(sh) cm^{-1}.)

The undissolved portion of the original sample was dissolved in ethanol and NH_4PF_6 (0.41 g, 2.5 mmol) added. After removal of ethanol, the residue was extracted with CH_2Cl_2 and the solution filtered. Tan crystals of $[Re(CO)(CNtol)_5]PF_6$ (0.46 g, 26%) were collected after addition of diethyl ether (m.p. 109—110°C).

Found: C, 52.18; H, 3.78, N, 7.33. $C_{41}H_{35}F_6N_5OPRe$ calcd.: C, 52.12; H, 3.73; N, 7.41%. Infrared (CH_2Cl_2 solution): ν(CN) 2130(sh), 2105s; ν(CO) 1975 cm^{-1}.

Preparation of $Re(CO)_4(CNMe)Br$

A solution of $Re_2(CO)_8Br_2$ (0.25 g, 0.33 mmol) and MeNC (0.036 ml, 0.66 mmol) in 100 ml tetrahydrofuran was stirred for 2 h at 25°C. Solvent was then removed. The residue was dissolved in CH_2Cl_2 and the solution filtered. Addition of petroleum ether precipitated the tan product, which could be recrystallized from the same solvent mixture (0.26 g, 93% yield); m.p. 142—143°C).
Found: mol. wt. (mass spec.) 420.87895. $C_6H_3{}^{81}BrNO_4{}^{187}Re$ calcd.: 420.87860. Infrared (CH_2Cl_2 solution): ν(CN) 2240m; ν(CO) 2118m, 2018vs, 1960vs cm^{-1}.

Preparation of fac-$Re(CO)_3(CNMe)_2Br$

A solution of $Re(CO)_5Br$ (0.74 g, 1.8 mmol) and NeNC (1.0 ml, 18 mmol) in 125 ml tetrahydrofuran was refluxed for 42 h. Infrared monitoring of the solution indicated complete conversion to the product in ~16 h; no further reaction occurred after that time. The solvent was removed, the residue dissolved in CH_2Cl_2 and filtered. Addition of petroleum ether to this solution precipitated the product as a white solid which was recrystallized in the same solvent mixture (0.51 g, 65% yield; m.p. 176—177°C).

Found: mol. wt. (mass spec.) 433.91092. $C_7H_6{}^{82}BrN_2O_3{}^{187}Re$ calcd. 433.91026. Infrared (CH_2Cl_2 solution): ν(CN) 2230m, 2210m; ν(CO) 2038s, 1982s, 1928s cm^{-1}.

Preparation of mer,trans-Re(CO)$_3$(CNMe)$_2$Br

A sample of *fac*-Re(CO)$_3$(CNMe)$_2$Br (0.40 g, 0.92 mmol) was refluxed in 20 ml mesitylene for 30 min, during which time a yellow precipitate formed. This precipitate was filtered and washed with CH_2Cl_2 (0.28 g, 70% yield). This compound was insoluble in common organic solvents, and did not melt up to 290°C.

Found: C, 19.16; H, 1.33; N, 6.54. $C_7H_6BrN_2O_3Re$ calcd.: C, 19.45; H, 1.40; N, 4.68%. Infrared (Nujol mull): ν(CN) 2165s; ν(CO) 2040m, 1960s, 1880s cm^{-1}.

Photolysis of Re(CO)$_5$Br and MeNC in tetrahydrofuran: preparation of trans-Re(CO)(CNMe)$_4$Br, and Re(CO)$_2$(CNMe)$_3$Br (three isomers)

Bromopentacarbonylrhenium (2.00 g, 4.92 mmol) and MeNC (1.08 ml, 19.7 mmol) were dissolved in 175 ml tetrahydrofuran. The solution was irradiated using a GE H 100-PSP 44-4 Mercury Lamp (Pyrex flask) for 22 h until most of the initially formed Re(CO)$_3$(CNMe)$_2$Br had disappeared (according to the infrared spectrum). The volume of the solution was reduced to 15 ml and a precipitate collected by filtration and washed with acetone. This product, *trans*-Re(CO)(CNMe)$_4$Br, was further purified by crystallization from CH_2Cl_2/diethyl ether (0.33 g, 22%). It did not melt up to 290°C.

Found: mol. wt. (mass spec.) 459.97351. $C_9H_{12}{}^{81}BrN_4O^{187}Re$ calcd.: 459.97351. Infrared (CH_2Cl_2 solution): ν(CN) 2130vs(br); ν(CO) 1858m(br) cm^{-1}.

The filtrate obtained above was evaporated and the residue place on a 3.3 X 23 cm acidic alumina chromatographic column in $CHCl_3$. Following elution of a small amount of Re(CO)$_3$(CNMe)$_2$Br, a broad pale yellow band eluted with 1/1 (v/v) CH_2Cl_2/$CHCl_3$. This band was collected and the solvent evaporated. Fractional crystallization of this product from CH_2Cl_2/diethyl ether gave as the predominant fraction white crystals of *mer,cis*-Re(CO)$_2$(CNMe)$_3$Br (0.26 g, 15% yield, m.p. 222—223°C).

Found: mol. wt. (mass spec.) 446.94116. $C_8H_9{}^{81}BrN_3O_2{}^{187}Re$ calcd.: 446.94190. Infrared (CH_2Cl_2 solution): ν(CN) 2220w, 2180(sh), 2160s; ν(CO) 1980s, 1829s cm^{-1}.

Further concentration of this solution led to crystallization of the pure second isomer, *fac*-Re(CO)$_2$(CNMe)$_3$Br as pale yellow needles (0.035 g, 2% yield, m.p. ~176°C); upon melting the compound resolidifies as the *mer,cis* isomer which remelts at 220—221°C.

Found: mol. wt. (mass spec.) 446.94201. $C_8H_9{}^{81}BrN_3O_2{}^{187}Re$ calcd.: 446.94190. Infrared (CH_2Cl_2 solution): ν(CN) 2240m, 2195m, 2130s; ν(CO) 1980s, 1930s cm^{-1}.

A third fraction from this fractional crystallization gave pale yellow-green crystals of another compound, probably the third possible isomer, *mer,trans*-Re(CO)$_2$(CNMe)$_3$Br; this was never obtained completely free of the *fac*-isomer, however (m.p. ~140°C).

Infrared (CH_2Cl_2 solution): ν(CN) 2200w, 2160(sh), 2130(br), ν(CO) 1915m(br).

Photolysis of Re(CO)$_5$Br and MeNC(2); isolation of mer,cis-Re(CO)$_3$(CNMe)$_2$Br (and other products)

A larger scale reaction, carried less to completion, gave the above named complex. Photolysis of 3.00 g (7.40 mmol) $Re(CO)_5Br$ and 1.22 ml (22.4 mmol) MeNC in 225 ml tetrahydrofuran was run for 21 h; at this time some disubstituted complex was still seen to be present according to the infrared data. Solvent was removed and the residue extracted with acetone; insoluble $Re(CO)(CNMe)_4$-Br (0.32 g, 9% yield) remained. (This compound was identified by its infrared spectrum.) Evaporation of the acetone solution gave a residue; this was crystallized from CH_2Cl_2/diethyl ether and gave as a preliminary fraction 1.53 g of *mer,cis*-$Re(CO)_2(CNMe)_3Br$ (46% yield). The material still remaining in the acetone solution was then chromatographed on a 1.5 × 52 cm alumina column with CH_2Cl_2. A small amount of $Re(CO)_4(CNMe)Br$ eluted first. Next a new compound believed to be *mer,cis*-$Re(CO)_3L_2Br$, eluted. This white crystalline product was recrystallized from $CHCl_3$/diethyl ether (0.2 g, 6%); m.p. 178.5–179.5°C).

Found: C, 19.52; H, 1.21; N, 6.42. $C_7H_6BrN_2O_3Re$ calcd.: C, 19.45; H, 1.40; N, 6.48%. Infrared ($CHCl_3$ solution): ν(CN) 2175s; ν(CO) 2080vw, 2050w, 1990s, 1930s cm^{-1}.

The next band to elute from the column contained *fac*-$Re(CO)_3(CNMe)_2Br$, (0.31 g, 10% yield) characterized by its infrared spectrum. Finally, a small amount (0.32 g) of a mixture *mer,cis*-$Re(CO)_2(CNMe)_3Br$ and *trans*-$Re(CO)$-$(CNMe)_4Br$ eluted. This mixture was not separated.

Photolysis of $Re(CO)_5Br$ and MeNC(3); isolation of $[Re(CO)(CNMe)_5]X$

A mixture of $Re(CO)_5Br$ (0.40 g, 0.98 mmol) and MeNC (0.60 ml, 11 mmol) in 80 ml tetrahydrofuran was irradiated for 22 h. The solution volume was reduced and a solid collected by filtration. The solid was dissolved in acetone and treated with an aqueous acetone solution of NH_4PF_6. The insoluble product, $[Re(CO)(CNMe)_5]PF_6$, was filtered and recrystallized from CH_2Cl_2/diethyl ether as an off-white solid (0.28 g, 50%; m.p. 213°C (dec.)).

Found: C, 23.22; H, 2.58; N, 12.29. $C_{11}H_{15}F_6N_5OPRe$ calcd.: C, 23.41; H, 2.68; N, 12.41%. Infrared (CH_2Cl_2 solution): ν(CN) 2190s, 2160s, 2140(sh); ν(CO) 1950m cm^{-1}.

The original filtrate contained $Re(CO)_3(CNMe)_2Br$ and $Re(CO)_2(CNMe)_3Br$ isomers, and $Re(CO)(CNMe)_4Br$ which were not separated.

Reaction of $Re(CO)_5Br$ and MeNC in toluene; preparation of mer,cis-$Re(CO)_2$-$(CNMe)_3Br$

A mixture of $Re(CO)_5Br$ (0.40 g, 0.98 mmol) and MeNC (1.0 ml, 20 mmol) was refluxed in toluene, while the progress of the reaction was monitored by IR. At 4 h only *fac*-$Re(CO)_3(CNMe)_2Br$ was observed; after 24 h *mer,cis*-$Re(CO)_2$-$(CNMe)_3Br$ was first observed and its concentration increased until the last of the *fac*-$Re(CO)_3(CNMe)_2Br$ had disappeared at 120 h. At this time the reaction was stopped, the solvent evaporated, and the residue extracted with CH_2Cl_2. Precipitation of 0.15 g (35% yield) of a solid occurred with addition of diethyl ether. An infrared spectrum indicated that this was primarily *mer,cis*-$Re(CO)_2$-$(CNMe)_3Br$, with a small amount of *fac*-$Re(CO)_2(CNMe)_3Br$ also present. Separation was not persued further.

Preparation of [Re(CO)(CNtol)$_5$]PF$_6$

• This complex, described earlier in this paper, was also prepared by a standard route from Re(CO)(CNtol)$_4$Br (0.25 g, 0.33 mmol), CNtol (0.22 ml, 1.8 mmol) and AgPF$_6$ (0.14 g, 0.55 mmol) in 60 ml acetone. After stirring 66 h at ambient temperature, the solution was filtered and solvent was removed. The residue that remained was dissolved in CH_2Cl_2 and after filtration, diethyl ether was added. Several crops of white crystals of the product [Re(CO)(CNtol)$_5$]PF$_6$ were obtained (0.22 g, 70%). Identification was made by m.p. and infrared spectrum.

Preparation of trans-[Re(CO)$_2$(CNtol)$_4$]PF$_6$

Carbon monoxide was bubbled through a 50 ml benzene solution of Re(CO)(CNtol)$_4$Br (0.30 g, 0.39 mmol) and $AlCl_3$ (0.28 g, 2.1 mmol) for 66 h. The white solid formed was collected by filtration and washed with water. The solid was next dissolved in acetone and a metathesis reaction carried out with an aqueous acetone solution of NH_4PF_6. The white product was filtered off, dried and recrystallized from CH_2Cl_2/diethyl ether (0.018 g, 5% yield; m.p. 195—196°C).

Found: C, 48.18; H, 3.91. $C_{34}H_{28}F_6N_4O_2PRe$ calcd.: C, 47.72; H, 3.30%. Infrared (CH_2Cl_2 solution): ν(CN) 2115s; ν(CO) 1995 m cm^{-1}.

From the original benzene filtrate 0.15 g (60%) of unreacted starting material was recovered.

Preparation of cis-[Re(CO)$_2$(CNtol)$_4$]PF$_6$

To a suspension of *mer,trans*-Re(CO)$_3$(CNtol)$_2$Br (0.25 g, 0.43 mmol) in 75 ml tetrahydrofuran was added CNtol (0.10 ml, 0.85 mmol). After 15 min in which no change appeared to occur, AgPF$_6$ (0.13 g, 0.52 mmol) was added, causing an immediate darkening. After stirring 16 h, the solution was filtered, the solvent removed, and the residue extracted with benzene leaving a small amount of an insoluble salt. Addition of petroleum ether to the benzene solution followed by slow evaporation gave a white flocculant precipitate of the product (0.29 g, 89%; m.p. 71.5—73°C).

Found: C, 47.61; H, 3.32; N, 6.36. $C_{34}H_{28}F_6N_4O_2PRe$ calcd.: C, 47.22; H, 3.30, N, 6.55%. Infrared (CH_2Cl_2 solution): ν(CN) 2200w, 2150m, 2120s; ν(CO) 2005m, 1990m cm^{-1}.

This product was also obtained in the more straightforward reaction between *mer,cis*-Re(CO)$_2$(CNtol)$_3$Br, AgPF$_6$ and CNtol in tetrahydrofuran. Identification was made from infrared data.

Preparation of fac-[Re(CO)$_3$(CNtol)$_3$]PF$_6$

A mixture of *fac*-Re(CO)$_3$(CNtol)$_2$Br (0.43 g, 0.74 mmol), AgPF$_6$ (0.21 g, 0.83 mmol), and CNtol (0.10 ml, 0.86 mmol) were dissolved in 60 ml acetone. After refluxing for 19 h, the solution was filtered and the volume was reduced to several ml. Ethanol was then added and the solution filtered and chilled to give a white solid. An infrared spectrum indicated this was a mixture of product and starting material. The latter was removed by washing with diethyl ether, and the product then recrystallized from ethanol (0.14 g, 25%; m.p. 203—204.5°C).

Found: C, 42.47, H, 2.54; N, 5.40. $C_{27}H_{21}F_6N_3O_3PRe$ calcd.: C, 42.30; H, 2.76; N, 5.48%. Infrared (CH_2Cl_2 solution): ν(CN) 2205w, 2165s, 2125w; ν(CO) 2050s, 2000s cm^{-1}, From the ether extract, ~0.14 g of a mixture of *fac*-$Re(CO)_3(CNtol)_2Br$ and product was obtained.

Preparation of cis-[Re(CO)$_2$(CNMe)$_4$]PF$_6$

To a 60 ml acetone solution of *mer,cis*-$Re(CO)_2(CNMe)_3Br$ (0.15 g, 0.34 mmol) was added $AgPF_6$ (0.14 g, 0.55 mmol). The resulting cloudy gray solution immediately turned clear upon addition of MeNC (0.5 ml, 9 mmol). After refluxing the solution for 18 h, the solvent was removed and the product extracted with CH_2Cl_2. Evaporation, followed by crystallization of the residue from hot ethanol gave the product as a white solid (0.10 g, 54% yield; m.p. 251—252.5°C).

Found: C, 21.66; H, 2.13; N, 9.95. $C_{10}H_{12}F_6N_4O_2PRe$ calcd.: C, 21.78; H, 2.19; N, 10.16%. Infrared (CH_2Cl_2 solution): ν(CN), 2190(sh), 2175s, 2160(sh); ν(CO) 2000s, 1962s cm^{-1}.

Preparation of fac-[Re(CO)$_3$(CNMe)$_3$]PF$_6$

A 50 ml tetrahydrofuran solution of $Re(CO)_5Br$ (0.18 g, 0.44 mmol) and MeNC (0.30 ml, 5.5 mmol) was refluxed for 7 h. To the resulting solution of *fac*-$Re(CO)_3(CNMe)_2Br$ was added $AgPF_6$ (0.17 g, 0.617 mmol). This mixture was refluxed for 16 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and filtered. Addition of Et_2O precipitated the product as a white solid. This was recrystallized from hot ethanol (0.20 g, 83% yield; m.p. 179—180°C.

Found: C, 20.17; H, 1.72; N, 7.79. $C_9H_9F_6N_3O_3PRe$ calcd.: C, 20.08; H, 1.68; N, 7.81%. Infrared (CH_2Cl_2 solution): ν(CN) 2260m, 2225s; ν(CO) 2050s, 1992s cm^{-1}.

Other reactions

Syntheses of a number of other cationic complexes $[Re(CO)_{6-n}L_n]PF_6$ were attempted by the standard routes but were unsuccessful. These included attempts to prepare *cis*- and *trans*-$[Re(CO)_4L_2]PF_6$, and *mer*-$[Re(CO)_3L_3]PF_6$ species (L = CNtol and CNMe). In several instances the infrared spectral monitoring was encouraging but workup did not yield desired products. Further work, possibly varying reactions conditions, is needed before any conclusions on these negative results should be reached.

Results and discussion

We have directed our study to reaction leading to syntheses of two types of complexes, $Re(CO)_{5-n}L_nX$ and $[Re(CO)_{6-n}L_n]^+$ (L = CNMe, CNtol). Complexes of the first type can be prepared using varied reaction conditions and stoichiometries from $Re(CO)_5X$ and the ligand. Compounds of the second type are obtained from $Re(CO)_{5-n}L_nX$ and either L or CO in the presence of a halide acceptor, this being a general reaction for synthesis of such species. In addition, the more fully substituted ionic complexes $[ReL_6]^+$ (L = CNtol only) and $[Re(CO)L_5]^+$ also arise in the direct ligand + $Re(CO)_5X$ reactions using forcing conditions.

An interesting aspect of this work is the severe conditions required to give the products desired. In general, considerably more forcing conditions are required than were seen in corresponding manganese carbonyl chemistry [1]. Though many products were similar to known manganese compounds, an interesting variations arises with $\mathrm{Re(CO)_{5-n}L_nBr}$ compounds since it is possible to isolate isomeric compounds for $n = 2$ and $n = 3$. Isomeric manganese complexes, $\mathrm{Mn(CO)_{5-n}L_nBr}$ had not been observed in the earlier work [1].

The equations below summarize the non-photolytic syntheses of the $\mathrm{Re(CO)_{5-n}L_nBr}$ compounds (L = CNMe, CNtol, expect as noted). Photolysis reactions are described later.

$$\mathrm{Re_2(CO)_8Br_2 + 2L \xrightarrow{25^\circ C} 2\ \mathit{cis}\text{-}Re(CO)_4(L)Br} \tag{1}$$

(same as Mn system)

$$\mathrm{Re(CO)_5Br + 2L \xrightarrow[16-20\ h]{THF,\ reflux} \mathit{fac}\text{-}Re(CO)_3L_2Br} \tag{2}$$

(no further reaction in refluxing THF; in contrast $\mathrm{Mn(CO)_5Br + L \rightarrow \cdots \rightarrow [MnL_6]^+}$ [1])

$$\mathrm{\mathit{fac}\text{-}Re(CO)_3L_2Br \xrightarrow[reflux]{octane} \mathit{mer,trans}\text{-}Re(CO)_3L_2Br\downarrow} \tag{3}$$

(Mesitylene reflux for L = CNMe; high yield with products precipitating from solution)

$$\mathrm{Re(CO)_5X + excess\ CNtol \xrightarrow[reflux,15-20\ h]{toluene}} \left\{ \begin{array}{l} \mathrm{\mathit{mer,cis}\text{-}Re(CO)_2L_3X} \\ \mathrm{\mathit{trans}\text{-}Re(CO)L_4X} \\ \\ \mathrm{ReL_5X} \\ \mathrm{[ReL_6]X\ (Cl\ only)} \end{array} \right. \tag{4}$$

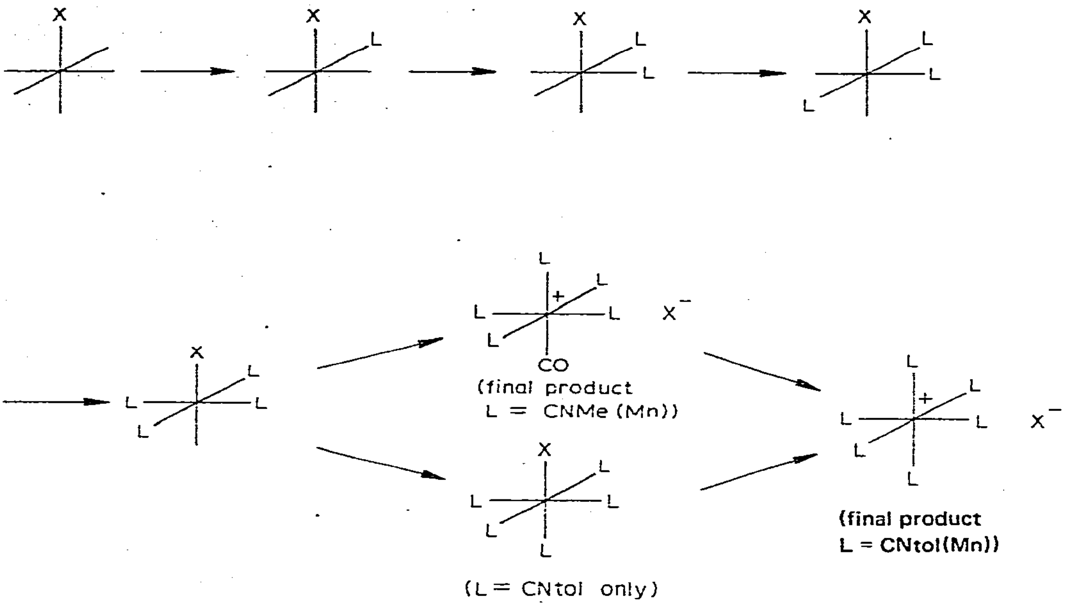
$$\mathrm{Re(CO)_5Br + excess\ CNMe \xrightarrow[reflux]{toluene}} \left\{ \begin{array}{l} \mathrm{\mathit{mer,cis}\text{-}Re(CO)_2L_3X\ (primarily)} \\ \\ \mathrm{\mathit{fac}\text{-}Re(CO)_2L_3X} \end{array} \right.$$

$$\mathrm{Re(CO)_5Br + CNtol \xrightarrow[113^\circ C]{no\ solvent}} \left\{ \begin{array}{l} \mathrm{[Re(CO)L_5]Br} \\ \\ \mathrm{[ReL_6]Br} \end{array} \right. \tag{5}$$

The reactions in refluxing tetrahydrofuran may be compared to the reactions of $\mathrm{Mn(CO)_5Br}$ in this solvent. It was reported [1] that 6 h of reflux produced $\mathrm{Mn(CO)_2L_3Br}$ using CNMe, and a mixture of $\mathrm{Mn(CO)L_4Br}$, $\mathrm{[Mn(CO)L_5]Br}$, and $\mathrm{[MnL_6]Br}$ for using CNPh. Longer reactions, 24 h, gave $\mathrm{Mn(CO)L_4Br}$ and $\mathrm{[Mn(CO)L_5]Br}$ for CNMe. In contrast, the final product of the reaction between $\mathrm{Re(CO)_5Br}$ and either CNMe or CNtol is $\mathrm{\mathit{fac}\text{-}Re(CO)_3L_2Br}$. Only at the higher reaction temperature available in refluxing toluene did the rhenium systems generate tri-, tetra-, or penta-isocyanide complexes. It is noted, in passing, that the reactions of CNtol with $\mathrm{Re(CO)_5X}$ appear somewhat more rapid than analogous reactions of CNMe. The same result was found for the manganese system. Similar to $Mn(CO)_5X$ chemistry, the reactions of $Re(CO)_5Cl$ are more facile than those of $Re(CO)_5Br$.

Apart from the kinetic differences in the two systems, rhenium and manganese carbonyl halide thermal reactions were very much the same. Sequential substitution of CO by L occurred up to addition of four equivalents of L; then replacement of either CO (only for L = CNtol) or X^- occurs. Initial CO substitutions are always *cis* to the halide and *cis* to other L (see Scheme 1).

SCHEME 1



The actual mechanisms of substitution which lead to these isolated products might be more complicated. For example, conversion of *fac*-$Re(CO)_3L_2Br$ to *mer,cis*-$Re(CO)_2L_3Br$ might occur via *mer,trans*-$Re(CO)_3L_2Br$. In the latter species, known to be formed from *fac*-$Re(CO)_3L_2Br$ on heating, mutually *trans*-CO groups would lead to labilization of a CO ligand [14]. A similar mechanism might apply to the conversion of *mer,cis*-$Re(CO)_2L_3Br$ to *trans*-$Re(CO)L_4Br$ via *mer,trans*-$Re(CO)_2L_3Br$. Although we have not attempted to test this hypothesis here, the isolation of the various isomeric $Re(CO)_3L_2Br$ and $Re(CO)_2L_3Br$ species in photolytic reactions might make possible such a test by a feature study of kinetics of these reactions.

A high yield conversion of *fac*-$Re(CO)_3L_2Br$ to the *mer,trans*-isomer was observed for both L = CNMe and CNtol in refluxing octane or mesitylene. Pure *mer,trans*-$Re(CO)_3L_2Br$ precipitates from solution, and can be analysed directly. No work on isomerizations was previously done with *fac*-$Mn(CO)_3(CNR)_2X$ compounds, although with other ligands such rearrangements are known [14]. Thus we attempted here to duplicate this reaction using *fac*-$Mn(CO)_3L_2Br$. This reactions was unsuccessful, only decomposition being noted.

Because the thermal reactions with $Re(CO)_5X$ and CNMe were sluggish, several photolytic reactions were also carried out. Equation 6 shows the results.

$$\mathrm{Re(CO)_5Br + CNMe} \xrightarrow[\text{various conditions}]{\mathrm{THF},\ h\nu} \left\{ \begin{array}{l} mer,cis\text{-}\mathrm{Re(CO)_3L_2Br} \\ fac\text{-}\mathrm{Re(CO)_3L_2Br} \\ mer,cis\text{-}\mathrm{Re(CO)_2L_3Br} \\ fac\text{-}\mathrm{Re(CO)_2L_3Br} \\ mer,trans\text{-}\mathrm{Re(CO)_2L_3Br} \\ trans\text{-}\mathrm{Re(CO)L_4Br} \\ \mathrm{[Re(CO)L_5]Br} \end{array} \right. \tag{6}$$

A variety of products ranging from di- to penta-substitution resulted. The actual products isolated and amounts obtained depended on $\mathrm{Re(CO)_5Br/CNMe}$ ratios and on the length of reaction time (and probably on other factors too.) Multiple substitution occurred, not unexpectedly. More interesting, however, is the generation of two new isomers through the photolytic reactions. From reactions which were interrupted while substantial amounts of disubstituted product were present, it was posssible to isolate *mer,cis*-$\mathrm{Re(CO)_3L_2Br}$. In longer reactions the new isomer, *mer,trans*-$\mathrm{Re(CO)_2L_3Br}$, was formed along with the other trisubstituted isomers. Apparently these isomers once formed are quite stable to isomerization. This low reactivity toward isomerization seems to accord with the lower reactivity of the rhenium complexes to further substitution.

All isomeric species were identified from observed patterns of absorptions in the ν(CO) and ν(CN) region of the infrared which conform to predictions by group theory. Some infrared data on analogous isomeric species with a different ligand are available for comparison [14,15].

As the rates of CO-substitution were slow, so also were reactions of $\mathrm{Re(CO)_{5-n}L_nBr}$ and either L or CO in the presence of a halide acceptor. This type of reaction is generally applied to the synthesis of cationic complexes, here $\mathrm{[Re(CO)_{5-n}L_{n+1}]^+}$ or $\mathrm{[Re(CO)_{6-n}L_n]^+}$. We used this route to prepare the complexes $\mathrm{[Re(CO)_{6-n}(CNtol)_n]^+}$ (n = 5, 4 *cis*- and *trans*-isomers; n = 3, *fac*-isomer) and $\mathrm{[Re(CO)_{6-n}(CNMe)_n]^+}$ (n = 4, *cis*-isomer; n = 3, *fac*-isomer) according to the eqns. 7—10.

$$trans\text{-}\mathrm{Re(CO)L_4Br} \xrightarrow[\mathrm{AgPF_6}]{+\mathrm{L}} \mathrm{[Re(CO)L_5]PF_6\ (L = CNtol)} \tag{7}$$

$$trans\text{-}\mathrm{Re(CO)L_4Br} \xrightarrow{+\mathrm{CO},\ \mathrm{AlCl_3},\ \mathrm{PF_6^-}} trans\text{-}\mathrm{[Re(CO)_2L_4]PF_6\ (L = CNtol)} \tag{8}$$

$$mer,cis\text{-}\mathrm{Re(CO)_2L_3Br} \xrightarrow[\mathrm{AgPF_6}]{+\mathrm{L}} cis\text{-}\mathrm{[Re(CO)_2L_4]PF_6\ (L = CNtol, CNMe)} \tag{9}$$

$$fac\text{-}\mathrm{Re(CO)_3L_2Br} \xrightarrow[\mathrm{AgPF_6}]{+\mathrm{L}} fac\text{-}\mathrm{[Re(CO)_3L_3]PF_6\ (L = CNtol, CNMe)} \tag{10}$$

The reaction of *mer,trans*-$\mathrm{Re(CO)_3L_2Br}$, $\mathrm{AgPF_6}$ and CNtol produced an unexpected product *cis*-$\mathrm{[Re(CO)_2L_4]PF_6}$ rather than the expected *mer*-$\mathrm{[Re(CO)_3L_3]PF_6}$. It seems likely that this result is a consequence of rapid replacement of a

CO by L in either *mer*-[$Re(CO)_3L_3$]PF_6 or perhaps in *mer,trans*-$Re(CO)_3L_2Br$. This facile replacement is probably a conseqeunce of the *trans*-CO arrangement of ligands; as was noted above, a characteristic of this ligand arrangement is facile CO replacement [14].

Cyclic voltammetry data on oxidations of both series of compounds are given in Table 1. The trends in $E_{1/2}$ values were generally the same as had been observed for similar manganese series. Thus progressive substitution of L for CO (in [$Re(CO)_{6-n}L_n$]PF_6 and in $Re(CO)_{5-n}L_nX$) lowered $E_{1/2}$ values between 0.4 and 0.6 V; an approximately linear relationship of $E_{1/2}$ and n was found. In keeping with the better donor power of CNMe vs. CNtol complexes of the former ligand were easier to oxidize.

Generally $E_{1/2}$ values recorded here were about 0.2 V greater than $E_{1/2}$ values of analogous manganese compounds. It is known that $E_{1/2}$ values correlate with HOMO energies calculated for the reactant complexes [16]. The higher $E_{1/2}$ values thus suggest a higher degree of stabilization of the HOMO orbitals, which are, primarily, the metal orbitals involved in π-interaction with the various ligands.

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