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Preliminary communication

Synthesis and properties of $Re_2(CO)_8(NCO)_2$

ROGER B. SAILLANT
Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (U.S.A.)

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Kinetic data for ligand substitution reactions of the pseudohalide complex $Re(CO)_5NCO$ have been reported by Angelici and Faber[1]. The rate-determining and initial step of the reaction was shown to be the loss of carbon monoxide. Therefore, it seemed probable that $Re(CO)_5NCO$ in the absence of other suitably strong donor ligands would lose carbon monoxide and dimerize as observed for the rhenium pentacarbonyl halides[2]. This reaction does occur and the preliminary results are reported here.

Rhenium pentacarbonyl isocyanate was synthesized as previously described[1]. When $Re(CO)_5NCO$ (0.05 g, 0.14 mmole) was dissolved in cyclohexane[★] and refluxed under a stream of argon for 8 min, carbon monoxide evolved and a fine white crystalline solid (0.03 g, 65% yield) appeared upon cooling. Elemental analyses revealed the empirical formula $Re(CO)_4NCO$. (Found: C, 17.67, 18.25; N, 4.30, 4.12. C_5NO_5Re calcd.: C, 17.65; N, 4.12.) The solution phase molecular weight could not be obtained because the compound was only slightly soluble in appropriate solvents. A molecular ion having the Re_2 isotope pattern and centered at *m/e* 680, corresponding to $Re_2(CO)_8(NCO)_2^+$, was identified in the mass spectrum. Other ion fragments produced by the loss of 10 carbon monoxide units were also recorded.

The infrared spectra of this and related substances are given in Table 1 for the 1800–2300 cm^{-1} region. For $Re_2(CO)_8(NCO)_2$ the number of bands, their positions, and intensity ratios in the carbonyl stretching region strongly resemble those of the dimeric tetracarbonyl halides $M_2(CO)_8X_2$ where M = Mn, Tc, Re and X = Cl, Br, I[3]. The very strong absorption at 2197 cm^{-1} is assigned to the pseudoasymmetric NCO stretch. This frequency is significantly lower than others of the same assignment in Table 1 and suggests a difference in the coordination of the isocyanate ligand[4,5,6].

[★] All solvents were dry, air-free and distilled prior to use.

TABLE 1

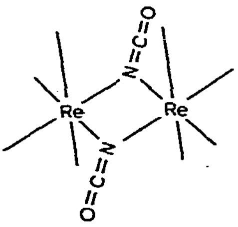
INFRARED DATA[a]

Compound	*Solvent*	$\nu_a(NCO)$	$\nu(CO)$
$Re(CO)_5NCO$[1]	CCl_4	2257m	2159w, 2048vs, 2020vw, 1995s
$Re_2(CO)_8(NCO)_2$	CH_2Cl_2	2197vs	2115w, 2031s, 1996m, 1956m
$Re_2(CO)_8Cl_2$	CH_2Cl_2	–	2117w, 2034s, 1999m, 1959m
$Re(CO)_4(PPh_3)NCO$	C_6H_{12}	2240m	2104w, 2016m(sh), 2000s, 1951s
$Re(CO)_3(PPh_3)_2NCO$	C_6H_{12}	2242m	2035s, 1955s, 1905s
$Re(CO)_3$(diphos)NCO[1]	$CHCl_3$	2250m	2035s, 1958s, 1916s

[a] All spectra of this study were recorded on a Perkin–Elmer 521 spectrophotometer calibrated to ± 1 cm^{-1} with indene. Relative intensities: w, weak; m, medium; s, strong; v, very; (sh), shoulder.

The Raman spectrum★ of a polycrystalline sample has been recorded from 200–2400 cm^{-1}. The Raman bands at 2205w and 1324m cm^{-1} have been tentatively assigned to the pseudoasymmetric and pseudosymmetric stretches respectively. However, the infrared spectrum of very concentrated CsI discs of $Re_2(CO)_8(NCO)_2$ has not revealed the infrared component of the pseudosymmetric stretch in the 1330 cm^{-1} region. A comparison of the infrared and Raman spectra shows almost complete extinction of complementary modes, suggesting a center of symmetry for the molecule. A more thorough discussion of the infrared and Raman spectra awaits the results of ^{15}N labelling experiments which will assist in the assignment of the isocyanate deformation and Re–N stretching modes[7].

The substance is dimeric and the bridging linkage is presumed to involve the isocyanate ligands. The ambidentate ligands thiocyanate and selenocyanate are known to form bridging linkage isomers of the type M–NCX–M[8], but structures of this type are unknown for transition metal isocyanate complexes. However, complexes are known in which an isocyanate bridges two metal atoms via the nitrogen atom[5,6,9]. Therefore, a structure is proposed in which two octahedra share a common edge and the isocyanate nitrogens function as one atom bridges (the CO ligands are omitted for clarity).



★Obtained by Professor R.C. Taylor of the University of Michigan, Ann Arbor, Michigan, on a Spex 1401 Spectrophotometer.

This bridging linkage is observed to be unstable in the presence of nucleophiles. The dimer in chloroform readily adds carbon monoxide forming the parent carbonyl isocyanate. In addition, triphenylphosphine reacts under mild conditions to give the mono- and di-substituted derivatives in Table 1. These reactions may proceed via nucleophilic attack at either a coordinatively saturated rhenium with subsequent rupture of one isocyanate—metal bond, or an open coordination site produced through an equilibrium ring opening process.

$$1/2\ Re_2(CO)_8(NCO)_2 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Re(CO)_5NCO$$

$$Re_2(CO)_8(NCO)_2 + PPh_3 \rightarrow Re(CO)_4PPh_3(NCO) + Re(CO)_3(PPh_3)_2NCO$$

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