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THE PREPARATION AND REACTIVITY OF SOME CATIONIC RHENIUM CARBONYL COMPLEXES

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SUMMARY

The hexacarbonyl cation $Re(CO)_6^+$ reacts with nucleophiles of the type OR^- to give alkoxycarbonyl derivatives. The preparation of a new cationic ethylene complex $[Re(CO)_5C_2H_4]^+$ is described and its reactivity towards nucleophiles compared with that of $Re(CO)_6^+$.

The ability of certain cationic carbonyl derivatives to undergo nucleophilic addition at the coordinated carbon atom has been recognised as indicative of the activation of the CO ligand by a *formal* positive charge[1]. Several years ago Muetterties[2] demonstrated that the oxygen atom in $Re(CO)_6^+$ undergoes moderately fast exchange with the oxygen atom in water. He considered that this exchange might proceed through a carboxylic acid intermediate of the type $Re(CO)_5COOH$ by attack on a carbon by OH^-. We now report that contrary to previous observations[3], addition of OR^- to $Re(CO)_6^+$ occurs smoothly to give the expected ester derivatives. The complexes obtained were identical to those produced from the reaction of $NaRe(CO)_5$ with $ClCO_2R$ (see Table 1) and may be reconverted to the original cation by reaction with acid.

$$Re(CO)_6PF_6 \underset{HPF_6}{\overset{OR^-}{\rightleftharpoons}} Re(CO)_5CO_2R$$

TABLE 1

Compound	IR (cm^{-1})		^{1}H NMR (τ)
	ν(C≡O)	ν(C=O)	
$Re(CO)_5CO_2Me$	2142 w, 2034 vs, 2004 s[b]	1639 m	6.38 (singlet)[d]
$Re(CO)_5CO_2Et$	2140 w, 2034 vs, 2004 s[b]	1636 m	5.71 (quartet) 8.73 (triplet)[d]
$[Re(CO)_5C_2H_4]PF_6$	2168 m, 2070 vs[c]		4.92 (singlet)[e]
$Re_2O(CO)_{10}$[a]	2045 vs, 2015 w, 1984 s, 1936 m, 1895 w[b]		

[a] Characterised by mass spectrum. [b] In CCl_4. [c] In CH_3NO_2. [d] In C_6H_6. [e] In $(CD_3)_2CO$.

In the course of our studies of metal olefin compounds we have prepared the mono-substituted cation $[Re(CO)_5C_2H_4]^+$. This new ion was prepared by the reaction of ethylene at 110 atm with $Re(CO)_5Cl$ in the presence of anhydrous aluminium trichloride. It has been shown previously[4] that under more vigorous conditions (250 atm) the product is the disubstituted cation $[Re(CO)_4(C_2H_4)_2]^+$.

The monosubstituted ion has been fully characterised by analysis, and IR and NMR spectroscopy. In the IR spectrum bands at 2168 and 2070 cm^{-1} are readily assigned to CO stretching vibrations. This is very similar to the spectrum observed for the analogous manganese compound[5].

The NMR spectrum (100 MHz) in deuteroacetone shows only one resonance at τ 4.92 and a proton count carried out on a solution containing equimolar amounts of iodoform and the complex is consistent with the presence of only one ethylene per molecule. Two resonances are observed at τ 4.62 and 4.92 when ethylene is passed through a solution of the complex. The former is assigned to uncoordinated ethylene and the half peak height of the latter is unchanged indicating that the coordinated ethylene is not exchanging with the free ethylene. Attempts to produce analogous complexes with higher olefins by simple olefin exchange were not successful.

In a previous communication we reported that the relative activation of ligand sites towards nucleophilic reagents depended upon the metal employed[6]. It was therefore of interest to investigate the reactivity of ethylene coordinated to rhenium (I) and to compare its reactivity with that of $Re(CO)_6^+$. In contrast to the simple reactions exhibited by $Re(CO)_6^+$ with OR^- the corresponding reactions of $[Re(CO)_5C_2H_4]^+$ are complicated and attempts to isolate pure organometallic derivatives were unsuccessful. On several occasions small amounts of a volatile white solid were isolated. Because of the very small yields of this material it was not characterised, however, on the basis of mass spectral analysis this product appears to be a carbonyl oxide $Re_2(CO)_{10}O$. The IR spectra of this compound is complex in the region 1800–2000 cm^{-1} (Table 1). We suggest that a possible structure of this compound involves two $Re(CO)_5$ units linked by an oxygen atom.

EXPERIMENTAL

Reaction of $Re(CO)_6PF_6$ with sodium methoxide

To a solution of 0.036 g (0.67 mmole) sodium methoxide in 25 ml dry methanol at 0° was added 0.323 g (0.65 mmole) $Re(CO)_6PF_6$. After shaking the mixture at room temperature for 1 h, the solvent was removed and the compound extracted into ether. The white crystals obtained on concentrating the ether solution were recrystallised from benzene (0.109 g; 43.8%) m.p. 108–109°. (Found: C, 22.2; H, 1.1. $C_7H_3O_7Re$ calcd.: C, 21.8; H, 0.8%.) Mass spectrum: major ions, 386 [P, $Re(CO)_5CO_2Me$]; 355 (P–OMe) and five other peaks due to sequential loss of CO from (P–OMe).

Reaction of $Re(CO)_6PF_6$ with sodium ethoxide

Following the above method 0.322 g (0.64 mmole) of $Re(CO)_6PF_6$ yielded 0.120 g (46.7%) of $Re(CO)_5CO_2Et$ when reacted with sodium ethoxide [prepared from 0.015 g (0.63 mmole) sodium metal dissolved in ethanol] m.p. 69–70° (lit.[3] 69–70°). Mass spectrum: major ions, 400 [P, $Re(CO)_5CO_2Et$]; 355 (P–OEt); and five other peaks due to loss of CO from (P–OEt). Weak peaks are also observed corresponding to sequential loss of CO from the parent.

Reaction of $Re(CO)_5CO_2R$ $(R = Me, Et)$ *with* HPF_6

An ether solution of 0.059 g (0.15 mmole) $Re(CO)_5Me$ was shaken with two drops of 65% HPF_6. The white precipitate which formed was washed with ether and dried *in vacuo* (0.052 g, 67.8%). The product was identified as $Re(CO)_6PF_6$ by its IR spectrum. Similarly 0.065 g (0.16 mmole) of $Re(CO)_5CO_2Et$ gave 0.060 g (73.6%) of $Re(CO)_6PF_6$.

Preparation of $[Re(CO)_5C_2H_4]PF_6$

A mixture of 2.19 g (5.9 mmoles) of $Re(CO)_5Cl$, 1.60 g (12 mmoles) of freshly sublimed $AlCl_3$ and 70 ml dry cyclohexane were shaken under 110 atm of ethylene at 45° in an autoclave for 48 h. After cooling the solvent was removed and the residue added to 70 ml of water which had been acidified with two drops 6 *N* HCl. The insoluble white solid [shown to be $Re(CO)_5Cl$ from its IR spectrum] was filtered off and the aqueous solution concentrated to half volume. On the addition of a 15% solution of NH_4PF_6 the white complex precipitated out and was recrystallised from acetone/ether (0.72 g, 24%). (Found: C, 16.8; H, 0.8; P, 6.0. $C_7H_4F_6O_5PRe$ calcd.: C, 16.8; H, 0.85; P, 6.2%.)

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