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Preliminary communication

A simple route to new cationic carbonyl compounds of manganese and rhenium

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SUMMARY

$[Mn(CO)_3(CH_3CN)_3]PF_6$ has been prepared and shown to be a useful precursor for a potentially wide range of new cationic manganese carbonyl compounds. The corresponding rhenium compound has also been prepared.

The formation and reactions of cationic transition metal solvolysed species are currently subject to increasing interest. One commonly used procedure for the preparation of these solvent-containing salts is given in Eqn. (1) and involves

$$L_yMX_n + nAgY \xrightleftharpoons{\text{solvent}} [L_yM(\text{solvent})_n]^{n+}nY^- + nAgX \qquad (1)$$

$$(M = \text{metal};\ X = Cl,\ Br \text{ or } I)$$

treatment of a metal halide complex with a silver salt containing a poorly coordinating anion Y, ($Y = ClO_4$, PF_6, BF_4 etc.) in some suitable solvent. Formation of the solvolysed species is then favoured by the precipitation of the highly insoluble silver halide salts, lability of the metal halide ligands and good donor solvents.

Following our studies on the substitution reactions of the manganese carbonyl bromide system[1] we have observed that solvolysis of $[Mn(CO)_5Br]$ readily occurs in refluxing acetonitrile without the aid of other reagents, to give the tris-nitrile derivative, *fac*-$[Mn(CO)_3(CH_3CN)_3]^+$ (I). The cation has been isolated from ethanol–water mixtures in almost quantitative yield as the PF_6 salt and is electronically equivalent and isosteric with molecular $[Mo(CO)_3(CH_3CN)_3]$[2]. The possible lability of the acetonitrile ligands has prompted us to investigate the potential of $[Mn(CO)_3(CH_3CN)_3]PF_6$ as a ready route into cationic manganese carbonyl compounds, the chemistry of which is fairly limited. Treatment of a refluxing chloroform solution of (I) with an excess of propylamine has resulted in rapid substitution yielding *fac*-[Mn(CO)$_3$(propylamine)$_3$]PF$_6$. Similar treatment of (I) with pyridine or dimethylphenylphosphine only effected replacement of two acetonitrile ligands to give *fac*-[Mn(CO)$_3$L$_2$(CH$_3$CN)]PF$_6$, (L = C$_5$H$_5$N or PMe$_2$Ph), whereas trimethylphosphite and diethyl sulphide gave *fac*-[Mn(CO)$_3$L(CH$_3$CN)$_2$]PF$_6$, (L = P(OMe)$_3$ or Et$_2$S). The *fac* configuration of the carbonyl ligands has been inferred from the intensity of the ν(CO) bands in the infrared spectra[3]. We are at present extending the range of reactions of (I) in attempts to correlate the type of product formed with the σ-donor and/or steric properties of the ligands L.

The degree of substitution in these compounds can also be varied by the use of different solvent systems. For example, the reaction of (I) with stoichiometric quantities of trimethylphosphite in refluxing acetonitrile gives [Mn(CO)$_2${P(OMe)$_3$}$_2$(CH$_3$CN)$_2$]PF$_6$ (II), with mutually *cis* bonded carbonyl groups, and *mer-cis*-[Mn(CO)$_2${P(OMe)$_3$}$_3$(CH$_3$CN)]PF$_6$ (III). The compounds (II) and (III) can also be prepared from [Mn(CO)$_{5-x}${P(OMe)$_3$}$_x$Br], (x = 2 or 3) using AgPF$_6$ in acetonitrile solution and are members of a complementary range of precursors for mixed ligand manganese carbonyl cations. Thus *mer-cis*-[Mn(CO)$_2${P(OMe)$_3$}$_3$Br] rapidly reacts with AgPF$_6$ in warm acetonitrile solution to give (III), or under reflux conditions to give (II). Similar reaction of *mer-trans*-[Mn(CO)$_3${P(OMe)$_3$}$_2$Br] in refluxing acetonitrile solution also gives (II) although *mer-trans*-[Mn(CO)$_3${P(OMe)$_3$}$_2$(CH$_3$CN)]PF$_6$ is formed at lower temperatures. The substitution of the phosphite ligand in *mer-cis*-[Mn(CO)$_2${P(OMe)$_3$}$_3$Br] and of the carbonyl ligand in *mer-trans*-[Mn(CO)$_3${P(OMe)$_3$}$_2$Br] suggests that steric factors play a role in these solvolysis reactions. The structural assignments of the phosphite-substituted carbonyl cations are inferred from infrared data[1] and assume that the carbonyl group *trans* to Br does not migrate during solvolysis.

TABLE 1

IR DATA OF CARBONYL SALTS

Compound[a]	*ν(CO)*[b]			*ν(CN)*[c]	
fac-[Mn(CO)$_3$(CH$_3$CN)$_3$]PF$_6$	2060s	1982s (br)		2328s,	2300m
fac-[Re(CO)$_3$(CH$_3$CN)$_3$]PF$_6$	2045s,	1956s (br)		2325m,	2296s
fac-[Mn(CO)$_3$(propylamine)$_3$]PF$_6$	2032s,	1930s (br)			
fac-[Mn(CO)$_3$(C$_5$H$_5$N)$_2$(CH$_3$CN)]PF$_6$	2050s,	1965s,	1953s	2312w,	2287s
fac-[Mn(CO)$_3$(PMe$_2$Ph)$_2$(CH$_3$CN)]PF$_6$	2034s,	1972m,	1945m	2323w,	2293w
fac-[Mn(CO)$_3$(Et$_2$S)(CH$_3$CN)$_2$]PF$_6$	2055s,	1982s,	1967 (sh)	2324m,	2294s
fac-[Mn(CO)$_3${P(OMe)$_3$}(CH$_3$CN)$_2$]PF$_6$	2064s,	1997s,	1965s	2332m,	2304m
cis-[Mn(CO)$_2${P(OMe)$_3$}$_2$(CH$_3$CN)$_2$]PF$_6$	1988s,	1919s		2314m,	2288m
mer-cis-[Mn(CO)$_2${P(OMe)$_3$}$_3$(CH$_3$CN)]PF$_6$	1996s,	1927s		2330w,	2296w
mer-trans-[Mn(CO)$_3${P(OMe)$_3$}$_2$(CH$_3$CN)]PF$_6$	2083w,	2001s,	1975m	2320w,	2292w

[a] All compounds reported here have been confirmed by elemental analysis and conductivity measurements. [b] CHCl$_3$ solution. [c] Nujol mull. These bands are proportionately very much weaker than the ν(CO) bands[6].

Comparable reactions with $[Re(CO)_5Br]$ indicate that the solvolysis process is slower than for the corresponding manganese compound. In refluxing acetonitrile, solvolysis of $[Re(CO)_5Br]$ proceeds only as far as the reported[4] compound $[Re(CO)_3(CH_3CN)_2Br]$ after 4 h. However, in the presence of $AgPF_6$, this reaction results in the initial formation of $[Re(CO)_5(CH_3CN)]PF_6$[5] and finally *fac*-$[Re(CO)_3$-$CH_3CN)_3]PF_6$ in almost quantitative yield, opening the way to similar cationic species for rhenium.

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