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Preliminary communication

A simple route to some carbonyl and metal phosphine salts using $NOPF_6$

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Few reactions have been reported utilising salts containing the nitrosonium ion, NO^+, as a single electron oxidant for transition metal systems. Treatment of nickel(II) amine complexes[1] and the decacarbonyls of manganese and rhenium[2] with $NOBF_4$ in methyl cyanide solution have given the oxidised products, namely nickel(III) amine, and manganese(I) and rhenium(I) carbonyls, all containing methyl cyanide bonded to the metal atom. In contrast, single electron oxidations of molybdenum(II) and molybdenum(III) cyanide salts[3] in non-aqueous media with NOCl have given molybdenum(III) and molybdenum(IV) cyanide salts with no solvent inclusion into the metal coordination sphere.

During our studies on the reactions of metal-nitrosyl complexes, we have found that $NOPF_6$ reacts rapidly with a series of metal carbonyl and metal phosphine compounds in poor coordinating solvents to give a variety of oxidised products, none of which contain NO as a ligand, or solvent molecules coordinated to the metal atom.

Yellow solutions of the neutral manganese(I) carbonyl complexes *trans*–$[Mn(CO)_3L_2Br]$ (I) ($L = P(CH_3)_2C_6H_5$, $As(CH_3)_2C_6H_5$) and *fac*–$[Mn(CO)_3L_2Br]$ (II) ($L = As(CH_3)_2C_6H_5$, $L_2 = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ {= DPE}, $(C_6H_5)_2PCH_2P(C_6H_5)_2$ {= DPM}) in benzene react rapidly with suspended $NOPF_6$ to give dark green solutions from which nitric oxide is evolved. After a few minutes dark green crystals of *fac*–$[Mn(CO)_3L_2Br]PF_6$ (III) are deposited from the reaction mixture. Conductivity measurements in acetone and elemental analysis on (III)* confirm our formulation of these new salts. The IR spectra of these complexes (see Table 1) exhibit three strong peaks, characteristic of C_s symmetry $[3(2A' + A'')]$, showing that the *fac*-isomer is formed in all cases. The ^1H NMR spectra of these compounds for $L = P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$ contained broad ill-defined bands due to their paramagnetism. The salts (III) were all found to be oxidising agents which react slowly with chloroform or hydrogen but rapidly with alcohols to give a complete reversion to the original stereochemistry or as in the case of *fac*– $\{Mn(CO)_3[As(CH_3)_2C_6H_5]_2Br\}PF_6$, a mixture of (I) and (II).

cis–$[Mo(CO)_2(DPE)_2]$ (IV) in CH_2Cl_2 reacts with $NOPF_6$ to form

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*All compounds reported here have been confirmed by elemental analysis and conductivity measurements.

TABLE 1

IR DATA OF CARBONYL AND RELATED SALTS

Compound	Medium	ν(CO)cm^{-1}	ν(M-H)cm^{-1}
fac-$\{Mn(CO)_3[P(CH_3)_2C_6H_5]_2Br\}PF_6$	nujol^a	2106 m, 2068 m, 2030 vs	
fac-$\{Mn(CO)_3[As(CH_3)_2C_6H_5]_2Br\}PF_6$	nujol^a	2119 s, 2080 s, 2022 vs	
fac-$[Mn(CO)_3(DPE)Br]PF_6$	nujol	2110 s, 2072 m, 2019 vs	
	CH_2Cl_2	2104 s, 2069 m, 2016 s	
fac-$[Mn(CO)_3(DPM)Br]PF_6$	nujol^a	2124 s, 2085 m, 2032 vs	
trans-$[Mo(CO)_2(DPE)_2]PF_6$ (V)	CH_2Cl_2	1878 vs	
cis-$[Mo(CO)_2(DPE)_2]PF_6$ (VI)	CH_2Cl_2	1948 vs, 1892 vs	
cis-$[Mo(CO)_2(DPE)_2](PF_6)_2$ (VII)	CH_2Cl_2	1969 s, 1907 m	
$[(\pi-C_5H_5)Fe(CO)_3]PF_6$ (VIII)	acetone	2130 vs, 2078 vs (Ref. 5)	
$\{(\pi-C_5H_5)Fe(CO)_2[P(OC_6H_5)_3]\}PF_6$ (IX)	CH_2Cl_2	2077 s, 2037 s (Ref. 5)	
$\{RhH[P(OCH_3)_3]_5\}(PF_6)_2$ (X)	nujol		1968 m

[a] Rapid reversion to the neutral complexes (I) and (II) occurred in solution when in contact with KBr plates.

trans-$[Mo(CO)_2(DPE)_2]PF_6$ (V) initially, with a concommitant solution colour change from yellow to red. This red solution further changed after a period of time to give a yellow solution containing the isomer *cis*-$[Mo(CO)_2(DPE)_2]PF_6$ (VI). Pure (V) and (VI) were isolated by decanting the solution from the $NOPF_6$ at a suitable stage during the reaction and crystallising in the presence of methanol. The isomerisation (V) → (VI) could not be effected by heating (V) in a variety of solvents but occurred rapidly in the presence of $NOPF_6$. The mechanism of this isomerisation, which seems to proceed via an oxidation-reduction process involving both NO^+ and solvent is under further investigation.

When (V) or (VI) were treated with $NOPF_6$ in nitromethane solution the stable dipositive cationic salt *cis*-$[Mo(CO)_2(DPE)_2](PF_6)_2$ (VII) was formed. We have been unable to isolate (VII) from the reactions of $NOPF_6$ with either (V) or (VI) in CH_2Cl_2 or $CHCl_3$ solutions.

The reaction of $NOPF_6$ with $[(\pi-C_5H_5)Fe(CO)_2]_2$ in dichloromethane has resulted in an asymmetric oxidative fission of the metal-metal bond to give $[(\pi-C_5H_5)Fe(CO)_3]PF_6$ (VIII). With the monosubstituted dimer $\{(\pi-C_5H_5)_2Fe_2(CO)_3[P(OC_6H_5)_3]\}$ and $NOPF_6$ in CH_2Cl_2, the salt $\{(\pi-C_5H_5)Fe(CO)_2[P(OC_6H_5)_3]\}PF_6$ (IX) is formed. The absence of any ν(CO) bands in the IR of the reaction solution other than those attributed to (IX) indicates that NO^+ preferentially attacks the iron atom of highest electron density. These oxidative fission reactions represent by far the simplest preparation of (VIII) and (IX) reported to date[4].

Treatment of $\{Rh[P(OCH_3)_3]_5\}PF_6$ with $NOPF_6$ in CH_2Cl_2 in the presence of $P(OCH_3)_3$, followed by methanol addition has given the hydride $\{RhH[P(OCH_3)_3]_5\}(PF_6)_2$ (X) in high yield, and the neutral platinum(0) complex $\{Pt[P(C_6H_5)_3]_4\}$ has been converted to the dipositive salt $\{Pt[P(C_6H_5)_3]_4\}(PF_6)_2$ in a similar manner. Further reactions of $NOPF_6$ are under way to study the general applicability of this reagent as an oxidant in organometallic chemistry.

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