Acetonitrilecarbonyl and Acetonitrilenitrosyl Metal Cations from the Reactions of the Nitrosonium Ion, NO$^+$, with Transition-metal Organometallics in Acetonitrile

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Summary The reactions of $NOPF_6$ in acetonitrile with (π-PhMe)$Cr(CO)_3$ and $M_2(CO)_{10}$ (M = Mn and Re) lead to the formation of $[Cr(NO)_2(MeCN)_4][PF_6]_2$ and $[M(CO)_5(MeCN)][PF_6]$, respectively, which are valuable new organometallic reagents as exemplified by a variety of reactions.

THOUGH many transition-metal nitrosyl complexes are known, very few have been made by the direct use of salts of the nitrosonium cation, NO$^+$. The reactions of $NOHSO_4$ with (π-C_5H_5)$Re(CO)_3$ to form the $[(\pi\text{-}C_5H_5)Re(CO)_2(NO)]^+$ cation[1] and of $NOBF_4$ with $Ir(CO)Cl[Ph_3P]_2$ to give the five-co-ordinated iridium cation $[Ir(CO)(NO)Cl(Ph_3P)_2]^+$,[2] have been reported. In order to synthesize certain new metal nitrosyl complexes which can be used as operational tests of existing and newly-formulated stereochemical and bonding principles, the reactions of $NOPF_6$ with a number of organometallic transition metal complexes have been carried out. We report the unexpected results of several of these reactions to illustrate the scope and potential diversity of $NOPF_6$ in acetonitrile solution for the preparation of new metal–acetonitrile complexes which are useful intermediates for the convenient synthesis of many other metal complexes.‡

Attempts to prepare $[(\pi\text{-PhMe})Cr(CO)_2(NO)]PF_6]$, which would be formally electronically equivalent to $[(\pi\text{-}C_5H_5)Mn(CO)_2NO][PF_6]$, by the reaction of ($\pi$-$C_5H_5$Me)$Cr(CO)_3$ and $NOPF_6$ in acetonitrile have led instead to the isolation of $[Cr(NO)_2(MeCN)_4][PF_6]_2$, (I). This yellow, diamagnetic, crystalline complex is soluble in polar solvents; the solutions slowly decompose in air. Conductivity measurements in acetone and elemental analysis§ confirm the formulation of the compound as a 2:1 electrolyte. Its i.r. spectrum (Table), which establishes the presence both of metal-co-ordinated acetonitrile and of the hexafluorophosphate anion, exhibits only one stretching frequency in the region associated with metal-co-ordinated nitric oxide. This sharp absorption band shows no visible splitting in either acetonitrile or Nujol mull thereby indicating that the two nitrosyl groups are *trans*-oriented about the octahedral-like chromium atom of the $[Cr(NO)_2(MeCN)_4]^{2+}$ cation.

The acetonitrile ligands are easily replaced by a variety of other ligands. For example, the reaction of (I) with $As(S_2CNEt_2)_3$, which functions as a source of the diethyldithiocarbamate ligand,[3] leads to the formation of the known *cis*-dinitrosyl $Cr(NO)_2(S_2CNEt_2)_2$.[4] This molecular complex may be separated from the $Cr(S_2CNEt_2)_3$, also formed in the reaction, by column chromatography. Treatment of (I) with $Na_2S_2C_2(CN)_2$ and $[Ph_4As]Cl$ affords the dark-brown, diamagnetic, crystalline complex $[Ph_4As]_2[Cr(NO)_2\{S_2C_2(CN)_2\}_2]$ (II). This new complex cannot be made by the methods used to prepare the analogous molybdenum and tungsten species.[5] The dichloromethane-solution i.r. spectrum of (II) shows two bands, at 1775 and 1678 cm^{-1}, indicating a *cis*-(octahedral-like) arrangement of the two nitrosyl ligands. These nitrosyl frequencies are considerably higher than those in the corresponding molybdenum and tungsten salts suggesting the lesser tendency of the chromium atom in these homologues to back-donate electron density into the antibonding π^*_{NO} orbitals.

The known complex $[(\pi\text{-}C_5H_5)Mn(CO)_2NO][PF_6]$ may be easily prepared by warming (π-C_5H_5)$Mn(CO)_3$ and $NOPF_6$ in acetonitrile for 3—5 min. On being precipitated with ether the complex is isolated in essentially quantitative yields. This new method therefore represents a considerable improvement over the established preparation[6] in terms of both time and yield.

The decacarbonyls of manganese and rhenium have been found to react with $NOPF_6$ in acetonitrile to form PF_6 salts of the new cations $[M(CO)_5(MeCN)]^+$ [M = Mn, (III), and Re, (IV)] which are electronically equivalent and presumably isosteric with molecular $Mo(CO)_5(MeCN)$.[7]

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‡ Since completion of this communication we have learned that Dr. W. A. G. Graham and Mr. N. Okamoto of the University of Alberta are investigating reactions similar to those reported here. Their results will be published at a later date.

§ Elemental analyses for all new complexes are in excellent agreement with the calculated analyses.

These white crystalline complexes are air stable, diamagnetic, and soluble in polar solvents to give solutions unstable to air. The similar i.r. spectra of (III) and (IV) in acetone solution (Table) show the well known three-band spectral pattern of carbonyl stretching modes ($2A_1 + E$) characteristic of C_{4v}–$4mm$ symmetry for these simple manganese and rhenium acetonitrile pentacarbonyl cations. The occurrence of these absorption bands at higher frequencies compared to those of the neutral molecular molybdenum analogue reflects the larger C–O bond orders in the carbonyl ligands of each cation due to less dissipation of electron density from the more positively charged metal atom into the empty π^*_{CO} orbitals. Upon heating, these complexes decompose to re-form the dimetal decacarbonyls which may be isolated by sublimation.

	Medium	ν_{CO} (cm^{-1})	ν_{NO} (cm^{-1})	ν_{CN} (cm^{-1})	Ref.
$[Cr(NO)_2(MeCN)_4][PF_6]_2$	Nujol mull		1797(vs)	2300(m), 2328(m sh)	This work
$[Cr(NO)_2(MeCN)_4][PF_6]_2$	MeCN		1781(vs)		This work
$Cr(NO)_2(S_2CNEt_2)_2$	KBr disc		1785(vs), 1660(vs)		Ref. 4
$[Ph_4As]_2[Cr(NO)_2\{S_2C_2(CN)_2\}_2]$	CH_2Cl_2		1775(vs), 1678(vs)	2200(s)	This work
$[Mn(CO)_5(MeCN)][PF_6]$	Me_2CO	2140(w), 2061(vs), 2043(sh)			This work
$[Re(CO)_5(MeCN)][PF_6]$	Me_2CO	2159(w), 2050(vs), 2021(sh)			This work
$Mo(CO)_5(MeCN)$	Hexane	2085(w), 1948(vs), 1931(s)			Ref. 7

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