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Preliminary communication

NO_2 as a single electron oxidant

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SUMMARY

Nitrogen dioxide has been shown to possess powerful oxidative properties which are a major effect in certain nitrosylation reactions; it has also been shown to provide a route to dicationic substituted manganese carbonyl salts.

Recently we reported[1] on the use of nitrosylhexafluorophosphate as a convenient method for bringing about single electron oxidation of transition metal compounds. We now find that nitrogen dioxide possesses similar oxidative properties, suggesting similar scope and diversity of NO_2 as an oxidant for organometallic compounds in various solvents without the solubility problems encountered with $NOPF_6$. Thus, paralleling our previous $NOPF_6$ work, reaction of *cis*-$[Mo(CO)_2(DPE)_2]$ with NO_2 gas in warm chloroform solution gives *trans*-$[Mo(CO)_2(DPE)_2]^+$ almost instantly, and $[(Cp)Fe(CO)_2]_2$ is oxidised by NO_2 under similar conditions to give the known[2] cation $[(Cp)Fe(CO)_3]^+$ after 15 min*.

Since NO_2 is considerably more reactive towards transition metal compounds than nitric oxide, our results indicate that many nitrosylation reactions which utilise nitric oxide yield oxidised by-products unless completely anaerobic conditions are maintained. Thus we have reinvestigated several reported nitrosylation reactions involving nitric oxide. $[Mn(CO)_3L_2Br]$ ($L = P(OPh)_3$) has been reported[3] to give $[Mn(NO)_2L_2Br]$ with NO gas. We find that with NO in the presence of small amounts of air, an immediate darkening of colour occurs in a variety of solvents, giving the oxidised product *fac*-$[Mn(CO)_3L_2Br]^+$ as an oil. This product is identified from analogous ν(CO) bands in the infrared spectra of the series *fac*-$[Mn(CO)_3L_2Br]^+$ ($L = PMe_2Ph$, $AsMe_2Ph$; L_2 = DPE, DPM), which we have prepared by $NOPF_6$ oxidation of the corresponding $[Mn(CO)_3L_2Br]$ compounds[1].

We find that *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ also reacts with NO gas in refluxing cyclohexane under anaerobic conditions to give the dinitrosyl species,

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* Cp = Cyclopentadienyl, DPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$

$[Mn(NO)_2L_2Br]$ ($L = P(OMe)_2Ph$) after 10 min. The increased reactivity of *mer-cis*-$[Mn(CO)_2L_3Br]$ towards nitric oxide, compared to the reaction times reported for $[Mn(CO)_3L_2Br]$ to form $[Mn(NO)_2L_2Br]$, can be explained on steric grounds[4]. Again, if any oxygen is present in the system, an instantaneous oxidation of *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ occurs, giving the deep red coloured cation, *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]^+$ which can also be prepared directly from *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ and NO_2 in a variety of organic solvents. *Mer-trans*-$[Mn(CO)_2L_3Br]^+$ ($L = P(OMe)_2Ph$) reacts further with $P(OMe)_2Ph$ in refluxing chloroform solution to give *cis*-$[Mn(CO)_2L_4]^+$, which rapidly undergoes oxidation with NO_2, yielding *trans*-$[Mn(CO)_2L_4]^{2+}$ at room temperature. Similarly, *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)]^+$ (prepared[5] by the action of $AgClO_4$ on *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$ in warm acetonitrile solution) is oxidised by NO_2 in dichloromethane solution to give *mer-trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)]^{2+}$

$[Mn(CO)_4(PPh_3)]_2$ has been reported[6] to react with NO gas to give a mixture of $[Mn(NO)(CO)_4]$ and $[Mn(NO)(CO)_3(PPh_3)]$ in solution. With NO_2 gas, however, no product is isolated from the darkened reaction solution unless a strongly coordinating solvent is used. Thus in acetonitrile solution the reaction gives entirely *cis*-$[Mn(CO)_4(PPh_3)(CH_3CN)]^+$. This can be related to the reported[7] reaction of $[Mn_2(CO)_{10}]$ with $NOPF_6$ to give $[Mn(CO)_5(CH_3CN)]^+$ in the same solvent.

IR data of these compounds are given in Table 1.

TABLE 1

IR DATA OF CARBONYL AND NITROSYL COMPOUNDS

Compound	*Medium*	*ν(CO) cm⁻¹*	*ν(NO) cm⁻¹*
$[Mn(NO)_2\{P(OMe)_2Ph\}_2Br]$	$CHCl_3$		1727s, 1676s
mer-trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]PF_6$	$CHCl_3$	2065w, 1981s	
cis-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]PF_6$	$CHCl_3$	1991s, 1937s	
trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_4](PF_6)_2$	$CHCl_3$	2054w, 1993s	
cis-$[Mn(CO)_4(PPh_3)(CH_3CN)]PF_6$	$CHCl_3$	2112m, 2044sh, 2028s, 1992m	
mer-cis-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)]ClO_4$	CH_2Cl_2	1985s, 1915s	
mer-trans-$[Mn(CO)_2\{P(OMe)_2Ph\}_3(CH_3CN)](PF_6)_2$	CH_2Cl_2	2093w, 2014s	

The similarity in oxidising properties of $NOPF_6$ and NO_2 may arise from the fact that dinitrogen tetroxide behaves as nitrosyl nitrate in organic donor solvents[8]. We are extending the range of these reactions to produce new cationic transition metal compounds.

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