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Preliminary communication

Cationic nitrosyls of Ni, Co and Group VI metals

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In a continuation of our studies[1] of the preparation of cationic nitrosyls which are isoelectronic with known neutral species we have investigated the reactions of the nitrosonium ion, NO^+, with carbonylphosphine complexes of Ni, Co and the Group VI metals. By this method we have succeeded in synthesising cationic species isoelectronic with $Co(NO)L_3$, $Co(NO)(CO)L_2$, $Fe(NO)_2L_2$ and $V(NO)(CO)_3L_2$ (where L are phosphine ligands such as $P(C_6H_5)_3$).

The reactions of $Ni(CO)_2L_2$, where L = $P(C_6H_5)_3$, $P(C_6H_5)_2(CH_3)$ and $P(C_6H_5)(CH_3)_2$, with $NOPF_6$ in methanol/toluene mixtures lead to the formation of $[Ni(NO)L_3]PF_6$ by a reaction involving disproportionation. The new complexes are deep blue-violet crystalline solids which have nitrosyl stretching frequencies which are considerably higher than those of the isoelectronic cobalt compounds $Co(NO)L_3$ (Table 1). If the reaction between $Ni(CO)_2[P(C_6H_5)_3]_2$ and $NOPF_6$ is carried out in benzene only a mixture is formed which contains $\{Ni(NO)[P(C_6H_5)_3]_3\}PF_6$, and a red-brown complex which has one carbonyl stretching frequency at 2080 cm^{-1} as well as a nitrosyl band at 1795 cm^{-1}. Although a complete separation of the species cannot be made we tentatively formulate the red-brown complex as $\{Ni(NO)(CO)[P(C_6H_5)_3]_2\}PF_6$ on the basis of its infrared spectrum, and on its reactions with $(C_6H_5)_3P$ and chloroform which give, with evolution of carbon monoxide, $\{Ni(NO)[P(C_6H_5)_3]_3\}PF_6$ and $Ni(NO)[P(C_6H_5)_3]_2Cl$[2] respectively. $\{Ni(NO)(CO)[P(C_6H_5)_3]_2\}PF_6$ is the first example of a carbonyl nitrosyl of nickel.

The species $\{Ni(NO)[P(C_6H_5)_3]_3\}PF_6$ reacts slowly with chloroform to afford $Ni(NO)[P(C_6H_5)_3]_2Cl$, and with tertiary phosphines or phosphites to give compounds of the type $\{Ni(NO)[P(C_6H_5)_3]_2[P(OC_6H_5)_3]\}PF_6$. With halide ions similar displacements of $P(C_6H_5)_3$ from $\{Ni(NO)[P(C_6H_5)_3\}PF_6$ can be effected to give the species $Ni(NO)[P(C_6H_5)_3]_2X$ (X = Br or I). With methoxide ion, however, the reaction is complex. Stoichiometric amounts of sodium methoxide in methanol/chloroform react to give the

TABLE 1

Complex	*$\nu(NO)$ $(cm^{-1}$*	*$\nu(CO)$ (cm^{-1})*	*Medium*
$[Ni(NO)(PPh_3)_3]PF_6$	1795s		Nujol
$[Ni(NO)(CO)(PPh_3)_2]PF_6$	1795s	2080s	Nujol
$\{Ni(NO)(PPh_3)_2[P(OPh)_3]\}PF_6$	1810s		Nujol
	1815s		$CHCl_3$
$Co(NO)(PPh_3)_3$	1640s		KBr
$Co(NO)(CO)(PPh_3)_2$	1714s	1958vs	CCl_4
$[Co(NO)_2(PPh_3)_2]PF_6$	1840s, 1785s		Nujol
	1850s, 1795s		CH_2Cl_2
$[Co(NO)_2(diphos)]PF_6$	1860s, 1795s		Nujol
	1853s, 1800s		$CHCl_3$
$Co(NO)_2(diphos)Br$	1840, 1755s		$CHCl_3$
$Co(NO)(diphos)(THF)$	1640s		Nujol
$Fe(NO)_2(PPh_3)_2$	1723s, 1679s		CCl_4
$Fe(NO)_2(diphos)$	1726s, 1679s		CCl_4
$[Mo(NO)(CO)_3(diphos)]PF_6$	1727s	2105s, 2037s	CH_2Cl_2
$[W(NO)(CO)_3(diphos)]PF_6$	1719s	2097s, 2021s	CH_2Cl_2
$[Cr(CO)_4(diphos)]PF_6$		2090s, 2015s, 1978s	CH_2Cl_2

known purple complex $Ni(NO)[P(C_6H_5)_3]_2(OCH_3)$ whereas excess methoxide ion produces a white, but as yet uncharacterised, nickel complex.

The known complex cations $[Co(NO)_2L_2]^+$ [3] L = PPh_3, $(PhO)_3P$ and PPh_2Me, or L_2 = $Ph_2PCH_2CH_2PPh_2$(diphos), are conveniently prepared in near-quantitative yields from $Co(NO)(CO)L_2$ and $NOPF_6$ in methanol/toluene mixtures. The triphenylphosphine cation reacts with bromide ion to give $Co(NO)_2[P(C_6H_5)_3]Br$ [3]. However, the corresponding diphos cation reacts to give a compound of the formulation $Co(NO)_2$(diphos)Br, the infrared spectrum (ν(NO)) of which differs from that of $[Co(NO)_2(diphos)]^+$ (Table 1). $Co(NO)_2$(diphos)Br is soluble in non-polar solvents such as ether and benzene and is a non-electrolyte in nitromethane. It may either contain a monodentate diphos ligand, or be another example of a complex containing two nitrosyl ligands, one of which is coordinated as formally NO^+, and the other as formally NO^- [4]. The reaction of $Co(NO)_2[P(C_6H_5)_3]_2^+$ with $NaBH_4$ in THF gives the mononitrosyl $Co(NO)[P(C_6H_5)_3]_3$ [5] with evolution of ammonia which is presumably formed by the reduction of one of the coordinated NO ligands. The corresponding reaction of $[Co(NO)_2(diphos)]^+$, however, yields a complex which on the basis of elemental analysis may be formulated as Co(NO) (diphos) (THF). If this reaction is carried out in the presence of excess ligand L then mixed complexes of the type Co(NO) (diphos)L are obtained.

It has been shown recently that *cis*-$Mo(CO)_2(diphos)_2$ can be oxidised by the nitrosonium ion. In CH_2Cl_2 both *cis*- and *trans*-$Mo(CO)_2(diphos)_2^+$ have been prepared, whereas in nitromethane the dication $[cis\text{-}Mo(CO)_2(diphos)_2]^{2+}$ was formed[6]. We have found that in methanol/toluene mixtures the oxidation leads exclusively to $[trans\text{-}M(CO)_2(diphos)_2]^+$ (M = Cr, Mo or W), whereas the *cis*-monocations are the sole products in acetonitrile. The isomerisation of the *trans*- to *cis*-monocations can be effected by addition of a catalytic amount of $NOPF_6$ to the *trans* isomers in acetonitrile.

In contrast to the reactions of $M(CO)_2(diphos)_2$, the species $M(CO)_4(diphos)$ ($M = Mo$ and W), react with the nitrosonium ion in methanol/toluene, or in acetonitrile, to give the new cationic carbonylnitrosyls $[M(CO)_3(NO)diphos]^+$. The yellow, air-stable, crystalline complexes are the first examples of cationic carbonyl nitrosyls of Group VI elements. They react with halides, X , in acetone solution to give compounds of the type $M(CO)_2(NO)(diphos)X$[7] and with other ligands such as diphos to give, as yet, uncharacterised products.

In contrast to the Mo and W complexes, $Cr(CO)_4(diphos)$ is oxidised by $NOPF_6$ in methanol/toluene mixtures to give deep purple, $[Cr(CO)_4(diphos)]PF_6$. In acetonitrile, however, $NOPF_6$ reacts with $Cr(CO)_4(diphos)$ to form the known dinitrosyl $[Cr(NO)_2(CH_3CN)_4][PF_6]_2$[8].

REFERENCES

1 B.F.G. Johnson and J.A. Segal, *J. Organometal. Chem.*, 31 (1971) C79.
2 R.D. Feltham, *Inorg. Chem.*, 3 (1964) 166.
3 T. Bianco, M. Rossi and L. Uva, *Inorg. Chim. Acta*, 3 (1969) 443.
4 J.M. Waters and K.R. Whittle, *Chem. Commun.*, (1971) 518.
5 W. Beck and K. Lottes, *Chem. Ber.*, 98 (1965) 2657.
6 R.H. Riemann and E. Singleton, *J. Organometal. Chem.*, 32 (1971) C44.
7 W.R. Robinson and M.E. Swanson, *J. Organometal. Chem.*, 35 (1972) 315.
8 N.G. Connelly and L.F. Dahl, *Chem. Commun.*, (1970) 880.