Low Spin Four-co-ordinated Chromium Nitrosyl Dialkylamides and Alkoxides

By D. C. Bradley* and C. W. Newing

(*Department of Chemistry, Queen Mary College, Mile End Road, London, E.*1)

Summary Some diamagnetic nitrosyl chromium dialkylamides and alkoxides have been prepared containing four-co-ordinated chromium(II).

Compound	Colour	Volatility (sublimation temp.) at 10^{-4} mm.Hg)	NO stretching frequency (cm^{-1})
$Cr(NO)(NPr^i_2)_3$	Orange	75°	1641
$Cr(NO)(2,6\text{-dimethylpiperidide})_3$ ..	Brown	90°	1673
$Cr(NO)(NPr^i_2)(OBu^t)_2)$	Orange	52° (m.p. 61—62)	1683
$Cr(NO)[N(SiMe_3)_2]_3$	Deep purple	110°	1698
$Cr(NO)(OBu^t)_3$	Orange-red	40° (m.p. 62—63)	1707
$Cr(NO)(OPr^i)_3$	Red	90°(m.p. 108—110)	1720

Previous work[1] showed that bulky ligands would constrain chromium to co-ordination numbers of three or four, and *X*-ray structural determination[2] confirmed that in the trigonal complexes $M[N(SiMe_3)_2]_3$ (M = Cr and Fe) there is little room for additional ligands. We have now found that trisdialkylamido-chromium(III) compounds CrL_3 [L = NPr^i_2, $N(SiMe_3)_2$, and 2,6-dimethylpiperidide] react with nitric oxide forming coloured diamagnetic mononitrosyls $Cr(NO)L_3$ (see Table) which are soluble in organic solvents and can be sublimed *in vacuo*. These compounds were characterized by elemental analyses and mass (all gave parent molecular ions), n.m.r., i.r., and electronic spectra. Their chemical stability was further demonstrated by the substitution of dialkylamido-groups by t-butoxide or isopropoxide without loss of nitric oxide. The tris-t-butoxide $Cr(NO)(OBu^t)_3$ was also obtained by the action of nitric oxide on $LiCr(OBu^t)_4$[1] whilst from the Bu^tOH–$Cr(NO)(NPr^i_2)_3$ reaction some $Cr(NO)(NPr^i_2)(OBu^t)_2$ was isolated. The properties of these compounds may be understood formally in terms of NO^+ bonded to Cr^{II} in a four-co-ordinated covalent complex having local C_{3v} symmetry. An 18-electron valency group may be achieved by π-electron donation from the three dialkylamido-nitrogens to chromium whilst the CrNO system should be stabilized by π-electron donation from d^4-chromium (d_{xz}, d_{yz}) to the degenerate antibonding π^* orbitals of NO^+. On this basis increased ligand (L)$\rightarrow$chromium π-donation should lower the NO stretching frequency and the data in the Table indicate the following order of π-donor ability:—

$$NPr^i_2 > 2,6\text{-dimethylpiperidide} > N(SiMe_3)_2 > OBu^t > OPr^i.$$

The position of $N(SiMe_3)_2$ in this series is indicative of delocalization of the nitrogen lone pair into vacant silicon *d*-orbitals and this ligand may also act as a π-acceptor in competition with NO^+. The NO frequency in $Cr(NO)(NPr^i_2)(OBu^t)_2$ is close to the weighted average (1685 cm^{-1}) of $Cr(NO)(NPr^i_2)_3$ and $Cr(NO)(OBu^t)_3$. The isopropoxide $Cr(NO)(OPr^i)_3$ gave n.m.r. and mass spectral data indicative of some dimerization which is consistent with its relatively low volatility.

The monomeric species $Cr(NO)L_3$ represents an important new class of transition metal compound and suggests that isoelectronic species containing other metals and diatomic ligands (*e.g.* CO, CN^-, N_2 *etc.*) may be stabilized by bulky dialkylamido- or alkoxo-ligands.

We thank the Owens-Illinois Company of Toledo, Ohio for financial support.

(*Received, January* 1*st*, 1970; *Com.* 004.)

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