

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).

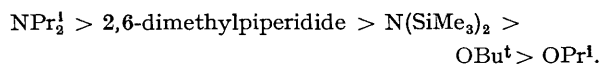
PREVIOUS work¹ showed that bulky ligands would constrain chromium to co-ordination numbers of three or four, and

of nitric oxide on $\text{LiCr}(\text{OBu}^t)_4$ ¹ whilst from the $\text{Bu}^t\text{OH}-\text{Cr}(\text{NO})(\text{NPr}_2)_3$ reaction some $\text{Cr}(\text{NO})(\text{NPr}_2)(\text{OBu}^t)_2$ 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_3^v symmetry. An 18-electron valency group may be achieved

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

X-ray structural determination² confirmed that in the trigonal complexes $\text{M}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{M} = \text{Cr}$ and Fe) there is little room for additional ligands. We have now found that trisdialkylamido-chromium(III) compounds CrL_3 [$\text{L} = \text{NPr}_2$, $\text{N}(\text{SiMe}_3)_2$, and 2,6-dimethylpiperidide] react with nitric oxide forming coloured diamagnetic mononitrosyls $\text{Cr}(\text{NO})\text{L}_3$ (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 $\text{Cr}(\text{NO})(\text{OBu}^t)_3$ was also obtained by the action

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:—



The position of $\text{N}(\text{SiMe}_3)_2$ 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 $\text{Cr}(\text{NO})(\text{NPr}_2^1)(\text{OBu}^t)_2$ is close to the weighted average (1685 cm^{-1}) of $\text{Cr}(\text{NO})(\text{NPr}_2^1)_3$ and $\text{Cr}(\text{NO})(\text{OBu}^t)_3$. The isopropoxide $\text{Cr}(\text{NO})(\text{OPr}^1)_3$ gave n.m.r. and mass spectral data indicative of some dimerization which is consistent with its relatively low volatility.

The monomeric species $\text{Cr}(\text{NO})\text{L}_3$ 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 alkoxy-ligands.

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¹ E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *Chem. Comm.*, 1968, 495.

² D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Comm.*, 1969, 14.