

NOTE

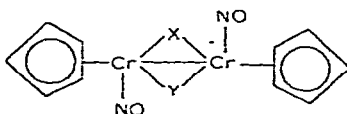
A CYCLOPENTADIENYLNITROSYLCHROMIUM COMPLEX WITH A BRIDGING AMIDO GROUP

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Binuclear chromium complexes in which the metal atoms are bridged by nitrogen containing ligands, *cf.* $[\text{C}_5\text{H}_5\text{Cr}(\text{NMe}_2)(\text{NO})]_2$ *i.e.* complex (I), are well known¹. Related complexes containing bridging carbonyl groups, *e.g.* $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, have attracted attention recently as examples of complexes in which different geometric isomers are observed in solution and in the solid state². Although few complexes containing bridging nitrosyl groups are known, $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]_2$ *i.e.* complex (II), was prepared some years ago³ and its geometric configuration both in solution and in the solid state is of interest in order that a direct comparison with structurally analogous complexes may be made. During the preparation of complex (II), a new, related derivative $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH}_2)$ *i.e.* complex (III), has been observed as a by-product, presumably formed by the unusual reduction of Cr-NO to Cr-NH₂ by sodium borohydride. This new complex appears to possess considerable stability and an X-ray crystallographic structure determination is in progress.

(I), X=Y=NMe₂; (II), X=Y=NO; (III), X=NO, Y=NH₂

EXPERIMENTAL

$(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH}_2)$ was prepared by adding a solution of NaBH₄ (3.0 g, 79 mmoles) in water (50 ml) dropwise over a period of 1 h to a mixture of $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ (8.5 g, 40 mmoles), water (150 ml) and thiophene-free benzene (150 ml) under nitrogen. After stirring for 20 h at room temperature, the reaction mixture was filtered by suction, the benzene layer separated and combined with several benzene extracts of the aqueous layer, and then filtered by gravity. Having removed solvent at ~30 mm from the filtrate, the residue was dissolved in a minimum of benzene and the red-brown solution chromatographed on a 2 × 40 cm alumina column. On elution with benzene, several bands of different colour appeared. The

first red-violet band, collected under nitrogen, was $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]_2$ as reported³. Further development of the column with benzene yielded a dark-green solution of the new complex (III), also collected under nitrogen. From this solution, solvent was removed under high vacuum and the resulting dark-green crystals washed with pentane (2×10 ml portions) and dried under high vacuum (0.12 g, 1% yield). The complex decomposed without melting up to 300° . (Found: C, 35.06; H, 3.65; N, 16.04. $\text{C}_{10}\text{H}_{12}\text{Cr}_2\text{N}_4\text{O}_3$ calcd.: C, 35.28; H, 3.56; N, 16.47%.)

Proton NMR spectrum

In carbon disulphide solution, using TMS as internal standard, a sharp resonance at τ 4.84 (relative intensity 9.8) due to ten equivalent π -cyclopentadienyl protons and a broad resonance at τ 8.77 (relative intensity 2.0) due to two equivalent μ -amido protons was observed.

IR Spectrum

In dichloromethane solution, absorptions were observed at 1684 [w, (sh)], 1644 (vs) and 1505 (m) cm^{-1} in the $\nu(\text{NO})$ region, and $\nu(\text{NH})$ absorptions at 3395 and 3323 cm^{-1} (KBr disc).

Proton NMR spectra were recorded on a Varian A56/60 spectrometer, IR spectra recorded on a Beckmann IR 12 spectrophotometer, and a Perkin Elmer Hitachi RMU-6E instrument used for the mass spectra (see below). Microanalyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

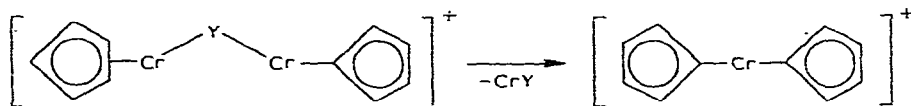
DISCUSSION

The structure of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH}_2)$ is confirmed by the spectroscopic results. The proton NMR spectrum, although very simple, shows the presence of two equivalent cyclopentadienyl groups, *cf.* $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]_2$, cyclopentadienyl resonance at τ 4.82 (chloroform solution)³. Although no general correlations of $-\text{NH}$ chemical shifts with molecular structure have so far been attempted because of the many complicating factors, monomeric monoethylamine in dilute carbon tetrachloride solution shows a $-\text{NH}_2$ resonance at τ 9.17⁴.

Group theoretical calculations predict two $\nu(\text{NO})$ (terminal) and one $\nu(\text{NO})$ (bridging) vibration for both the *cis*-isomer (symmetry C_2) and the *trans*-isomer (symmetry C_2) in the IR spectrum of complex (III) as observed. The positions of the terminal and bridging $\nu(\text{NO})$ absorptions in $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH}_2)$ are comparable with the $\nu(\text{NO})$ (terminal) absorption at 1672 cm^{-1} in $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2]_2$ and the $\nu(\text{NO})$ (bridging) absorption at 1505 cm^{-1} in the same complex³. The observed $\nu(\text{NH})$ absorptions are in excellent agreement with the relationship $\nu_{\text{sym}} = 345.53 + 0.876 \nu_{\text{asym}}$ observed for a wide range of primary amines⁵.

Some details of the mass spectrum of complex (III) are of interest. Observation of a parent ion and of a fragmentation pattern consistent with structure has proved to be possible with several chromium complexes. Thus $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2(\text{NO})$ shows a parent ion ($m/e=203$) and a fragmentation pattern derived from successive loss of two CO groups, the nitrosyl group and the cyclopentadienyl group from the parent ion, consistent with the mode of decomposition of ions derived from other metal carbonyl nitrosyl complexes⁶. In the spectrum of complex (II), ions corresponding to

P^+ , $(P-NO)^+$, $(P-2NO)^+$ and $(P-3NO)^+$ are observable before scission of the Cr-Cr bond occurs, thus supporting the structure of this complex as written with bridging nitrosyl groups *cf.* the mass spectrum of $[C_5H_5Cr(CO)_3]_2$ where no ions containing two Cr atoms are observed⁷. Identical behaviour is found in the spectrum of complex (III) *i.e.* ions P^+ , $(P-NO)^+$, $(P-2NO)^+$ and $(P-3NO)^+$ are observed, whereas systematic loss of NO groups does not occur in complex (I)⁸. However ions at $m/e=182$, 117, 65 and 52, corresponding to the cracking pattern of the positively charged chromocene ion, occur in all three complexes, arising at least partly in complex (III) via the decomposition



a metastable ion being observed at $m/e=133$ (calcd. 132.5).

ACKNOWLEDGEMENT

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