

## The Molecular Structures of Some Cyclopentadienyl Nitrosyl Complexes

By M. A. BUSH\* and G. A. SIM

(Chemical Laboratory, University of Sussex, Brighton, BN1 9QJ)

and G. R. KNOX, M. AHMAD, and C. G. ROBERTSON

(Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1)

NUCLEOPHILIC displacement of chloride from cyclopentadienyldinitrosyl-chloro-chromium can lead to mononuclear or binuclear products. Simple replacement occurs with isocyanate ion. The green compound  $C_5H_5Cr(NO)_2NCO$ , m.p. 105–106°, has i.r. peaks at 1818 (s) and 1783 (vs)  $cm^{-1}$  (nitrosyl), and absorption at 2250 (s) and 1343 (w)  $cm^{-1}$  indicates a Cr–NCO grouping. Stable intermediate mononuclear species cannot be isolated when the nucleophilic reagent is alkoxide or dialkylamide. Thus lithium dimethylamide produces a mixture of *cis*- and *trans*-di- $\mu$ -dimethylamido-bis(cyclopentadienylnitrosylchromium); the red *trans*-isomer, m.p. 269.5° (decomp.),  $\nu_{NO}$  1634  $cm^{-1}$ , exhibits a single  $^1H$  n.m.r.  $CH_3$  signal at  $\tau$  6.79 and is distinguished from the red-brown *cis*-isomer, m.p. 265° (decomp.),  $\nu_{NO}$  1640  $cm^{-1}$ , which has two singlets at  $\tau$  6.45 and 7.26 for the methyl group in different environments.

Crystals of *trans*-di- $\mu$ -dimethylamido-bis(cyclopentadienylnitrosylchromium) are orthorhombic, space group *Pccn*, with four molecules of  $[C_5H_5Cr(NO)NMe_2]_2$  in a cell of dimensions  $a = 14.94$ ,  $b = 11.53$ ,  $c = 9.69$  Å. The intensities of 713 *X*-ray reflections were obtained from Weissenberg photographs (Cu- $K_\alpha$  radiation) by visual estimation.

Crystals of *cis*-di- $\mu$ -dimethylamido-bis(cyclopentadienylnitrosylchromium) are monoclinic, space group *P2<sub>1</sub>/c*, with four molecules in a cell of dimensions  $a = 8.52$ ,  $b = 14.73$ ,

$c = 14.72$  Å,  $\beta = 114^\circ 51'$ . The intensities of 1612 *X*-ray reflections were obtained from Weissenberg photographs (Cu- $K_\alpha$  radiation) by measurement with a scanning microdensitometer.

Crystals of cyclopentadienyldinitrosyl-isocyanatochromium are monoclinic, space group *P2<sub>1</sub>/m*, with two molecules in a unit cell of dimensions  $a = 6.18$ ,  $b = 9.00$ ,  $c = 7.52$  Å,  $\beta = 94^\circ 54'$ . *X*-Ray reflections in the range  $0 < 2\theta \leq 54^\circ$  (Mo- $K_\alpha$  radiation) were measured by means of a Hilger-Watts Y290-PDP8 four-circle diffractometer, and after averaging four sets of equivalent reflections 817 independent intensities were obtained.

Atomic co-ordinates were obtained from electron-density distributions, and subsequently refined by full-matrix least-squares calculations. The final values of *R* for the *cis*- and *trans*-isomers of  $[C_5H_5Cr(NO)NMe_2]_2$  are 0.105 and 0.114, respectively. The current value of *R* for the isocyanate complex is 0.05, and refinement of this structure is continuing. Details of the molecular structures are shown in the Figures.

The molecule of *trans*- $[C_5H_5Cr(NO)NMe_2]_2$  is situated on a crystallographic centre of symmetry, and the (CrN)<sub>2</sub> ring is therefore exactly planar. The (CrN)<sub>2</sub> ring in the *cis*-isomer is only slightly puckered, for the fold about the N–N vector is  $177.8 \pm 0.8^\circ$ .

The Cr–Cr separations of 2.72 and 2.67 Å in the *cis*- and

*trans*-isomers of  $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$  are notably shorter than the Cr–Cr distance of 2.950 Å in *trans*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SPh}]_2$ ,<sup>1</sup> and the contraction of the metal–metal bond on substituting  $\text{NR}_2$  for SR in the bridging position is much greater in these *planar*  $(\text{CrX})_2$  systems ( $\Delta \approx 0.25$  Å) than

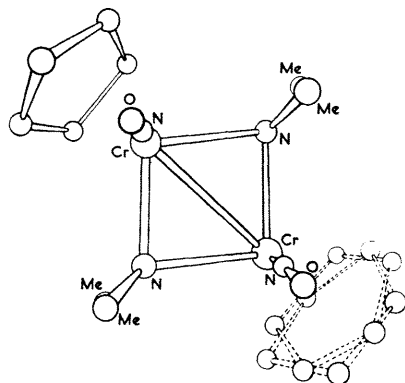


FIGURE 1. Molecular structure of *cis*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$ . Dimensions are: Cr–Cr  $2.72 \pm 0.01$  Å; Cr–N(bridging)  $2.01 \pm 0.01$  Å; Cr–C  $2.26 \pm 0.01$  Å; Cr–N(nitrosyl)  $1.63 \pm 0.01$  Å; N–O  $1.22 \pm 0.02$  Å; N–CH<sub>3</sub>  $1.50 \pm 0.02$  Å; Cr–N–Cr  $85.0 \pm 0.4^\circ$ ; N–Cr–N (bridging N)  $95.1 \pm 0.4^\circ$ ; Cr–N–O  $169.1 \pm 0.9^\circ$ .

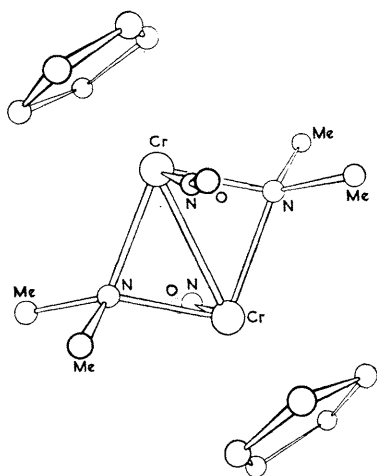


FIGURE 2. Molecular structure of *trans*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$ . Dimensions are: Cr–Cr  $2.67 \pm 0.01$  Å; Cr–N(bridging)  $2.00 \pm 0.01$  Å; Cr–C  $2.26 \pm 0.01$  Å; Cr–N(nitrosyl)  $1.63 \pm 0.02$  Å; N–O  $1.23 \pm 0.02$  Å; N–CH<sub>3</sub>  $1.56 \pm 0.02$  Å; Cr–N–Cr  $84.3 \pm 0.5^\circ$ ; N–Cr–N (bridging N)  $95.7 \pm 0.5^\circ$ ; Cr–N–O  $169.1 \pm 1.3^\circ$ .

in the *nonplanar*  $(\text{FeX})_2$  systems of various bridged iron carbonyls ( $\Delta \approx 0.14$  Å).<sup>2</sup> The Cr–N bridging bonds in the *cis*- and *trans*-isomers are shorter by about 0.18 Å than the Cr–N distance of 2.185 Å in diethylenetriaminechromium tricarbonyl,<sup>3</sup> and the single-bond radius of 1.48 Å which was assigned to chromium in that complex does not appear to be appropriate in the bridged complexes. The Cr–N(isocyanate) bond length in  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCO}$ , 1.98 Å, is only

slightly shorter than the average length (2.01 Å) of the Cr–N bridging bonds in  $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$ , and it is therefore arguable that the Cr–N(isocyanate) bond may be essentially single, for the Cr–N bridging bonds unquestionably lack any multiple-bond character.

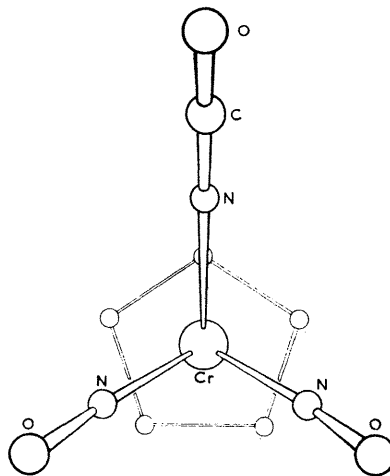
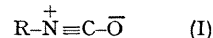


FIGURE 3. Molecular structure of  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCO}$ . Dimensions are: Cr–N(nitrosyl)  $1.72 \pm 0.01$  Å; N–O  $1.16 \pm 0.01$  Å; Cr–N(isocyanate)  $1.98 \pm 0.01$  Å; N–C  $1.13 \pm 0.02$  Å; C–O  $1.18 \pm 0.02$  Å; Cr–C  $2.20 \pm 0.01$  Å; Cr–N–O  $171.0 \pm 0.6^\circ$ ; Cr–N–C  $180.0 \pm 1.1^\circ$ ; N–C–O  $178.6 \pm 1.6^\circ$ .

The Cr–N(nitrosyl) bond lengths in *cis*- and *trans*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$  (1.63 Å) and *trans*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{SPh}]_2$  (1.66 Å)<sup>1</sup> are, as expected, shorter than those in  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCO}$  (1.72 Å) and  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$  (1.71 Å).<sup>4</sup> All these bonds must have appreciable multiple-bond character, and they are much shorter than the Cr–N(isocyanate) distance of 1.98 Å. The Cr–N–O angles are close to  $170^\circ$ , and these departures from linearity of the metal–nitrosyl groupings are highly significant. The chromium–isocyanate fragment, on the other hand, is very closely linear with Cr–N–C and N–C–O angles of  $180.0^\circ$  and  $178.6^\circ$ , respectively.

Both the linearity of the CrNCO grouping and the probably significant contraction of the C–N distance (1.13 Å) from the value of 1.207 Å in HNCO suggest that (I) is the predominant canonical form. Though  $d\pi$  back-donation to the nitrosyl groups is undoubtedly the principal route for the removal of the excess of negative charge from the chromium atom in  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{NCO}$ , (I) may contribute by an inductive mechanism.



In the crystal structure of *cis*- $[\text{C}_5\text{H}_5\text{Cr}(\text{NO})\text{NMe}_2]_2$  one of the cyclopentadienyl rings proved to be randomly distributed over two orientations in the same plane. Similar disorder has been reported in other cyclopentadienyl derivatives.<sup>4,5</sup>

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