Square Planar and Tetrahedral Chromium(II) Complexes; Crystal Structure Determinations

By D. C. BRADLEY, M. B. HURSTHOUSE,* C. W. NEWING, and A. J. WELCH
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary The novel compound $Cr[N(SiMe_3)_2]_2(THF)_2$ has been prepared and characterised, and shown by *X*-ray crystal analysis to have the *trans*-square planar configuration; this contrasts with $Cr(NO)[N(SiMe_3)_2]_3$ which has been found to possess a pseudo-tetrahedral (C_{3v}) structure.

MOST Cr^{II} compounds are considered to have distorted octahedral geometries.[1] Rare exceptions are the 7-co-ordinate species $[Cr(CO)_2(diars)_2X]X$,[2] and the distorted tetrahedral complexes $CrX_2[(Ph)_3PO]_2$, (X = Br, I).[3] *X*-Ray powder photography has shown[4] the bis-β-diketonate to be isostructural with the square planar nickel(II) analogue.[5]

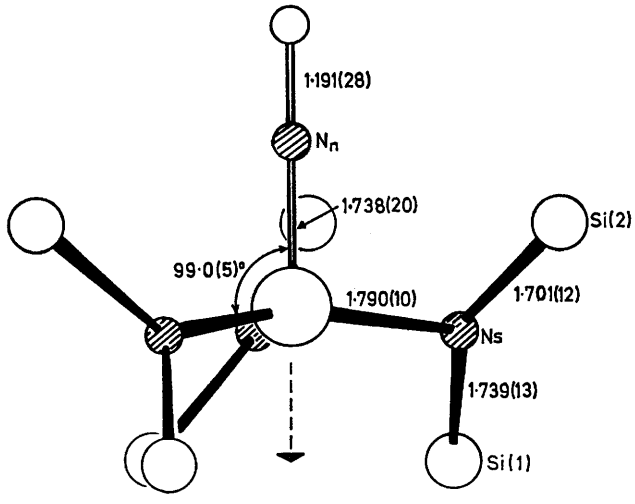

FIGURE 1. $Cr(NO)[N(SiMe_3)_2]_3$ *in a axis projection. The carbon atoms are omitted for clarity.*

Recently we isolated the novel compound $Cr(NO)[N(SiMe_3)_2]_3$ which was diamagnetic and appeared to be an example of low spin tetrahedral chromium(II).[6] In attempting to prepare bis(trimethylsilylaminato)chromium(II) by the reaction of chromium(II) chloride with $LiN(SiMe_3)_2$ in tetrahydrofuran, we also isolated the extremely oxygen-sensitive, crystalline $Cr[N(SiMe_3)_2]_2(THF)_2$. The compound was paramagnetic (μ_{eff} = 4·93 B.M.; 298—299 K) and the electronic spectrum showed two weak shoulders at *ca.* 19,800 and 25,600 cm^{-1} with broad bands at 33,330 and 38,400 cm^{-1}. These results suggested but did not prove the presence of square planar chromium(II).

In order to obtain details of the geometry of these compounds, we have determined their structures by single-crystal *X*-ray analysis.

Crystal data: $Cr[N(SiMe_3)_2]_2(THF)_2$, *M* 516·98, triclinic, a = 16·87(3), b = 11·45(1), c = 10·87(1) Å, α = 85·04(12), β = 122·47(13), γ = 117·57(15)°, U = 1534 Å^3, D_m not measured, Z = 2, D_c = 1·12, μ(Cu-K_α) = 46·8 cm^{-1}, space-group $P\bar{1}$. $Cr(NO)[N(SiMe_3)_2]_3$, *M* 543·17, rhombohedral, a = 11·44(1) Å, α = 96·48(10)°, U = 1465 Å^3, D_m not measured, Z = 2, D_c = 1·23, μ(Cu-K_α) = 57·4 cm^{-1}, space-group $R3c$.

Intensity data for both compounds were recorded on a G.E. XRD6 manual diffractometer using the stationary crystal-stationary counter technique and Cu-K_α radiation. For the tetrahydrofuran compound, 2631 reflections out of a total of 2709 measured up to a 2θ value of 105° had significant intensities. In the case of the nitrosyl compound, 737 out of 925 reflections measured up to 2θ = 120° were significant.

Both structures were solved by Patterson and Fourier techniques, and refined by full-matrix least-squares. Current *R* values are *ca.* 0·12 for the THF compound, and *ca.* 0·07 for the nitrosyl compound.

The structures found are shown in Figures 1 and 2, which include some of the more important bond lengths and angles.

The $Cr(NO)[N(SiMe_3)_2]_3$ molecule has space-group-imposed C_3 symmetry, with a linear Cr–N–O system. Thus the CrN_4 unit is strictly a trigonal pyramid, but the N_n–Cr–N_S angle of *ca.* 99° gives it a pseudo-tetrahedral appearance. The shortness of the Cr–N_n bond suggests that the NO group is acting in its π-acceptor mode, and this is borne out by the slight lengthening of the N_n–O bond compared with that in the free NO molecule. If the ligand is considered to be NO^+, the chromium atom is formally in the oxidation state (+2).

The $CrNSi_2$ group is planar to within 0·05 Å, and makes a dihedral angle of *ca.* 35° with the ON_nCrN_S plane. The Cr–N_S bond is somewhat shorter than that found for tris-(hexamethyldisilylaminato)chromium(III),[9] in which the lone pair on the nitrogen atom is believed to interact with empty metal *d* orbitals. This implies considerable π-interactions between the Cr atom and the silylamine

nitrogen atoms in the nitrosyl compound, probably influenced by the strong electron withdrawing property of the NO ligand. This type of interaction gives the chromium atom access to 18 electrons.

The N_S–Si bonds, the difference between which is barely significant, both lie in the region which implies N → Si $p\pi$–$d\pi$ interactions. The Si–C bond lengths and C–Si–C angles are in good agreement with standard values.

For $Cr[N(SiMe_3)_2]_2(THF)_2$ the Cr^{II} co-ordination is confirmed as *trans*-square planar. The Cr, N, and O atoms are planar to within 0·03 Å. The $CrNSi_2$ and $CrOC_2$ groups are also planar to within 0·01 Å ($CrNSi_2$) and 0·005 Å ($CrOC_2$), and make dihedral angles of *ca.* 73° and 56° respectively with the CrN_2O_2 plane.

As far as we can ascertain, there are no reliable data with which to compare our values for the square planar Cr^{II}–N bonds. The short N–Si bonds suggest π-bonding as strong as in the free ligand,[7] and this would suggest little, if any, nitrogen → metal π-interaction. The Cr–O bonds are also difficult to classify in the absence of comparable data, but these too do not appear to be unusually short. The planarity of the $CrOC_2$ groups is therefore very interesting. This may be due to the short α-methylene–silyl–methyl contacts which would be set up should the oxygen atoms adopt tetrahedral geometry. This symmetrical co-ordination of THF has been reported before.[8] The $SiMe_3$ and THF ring bond lengths and angles are all normal.

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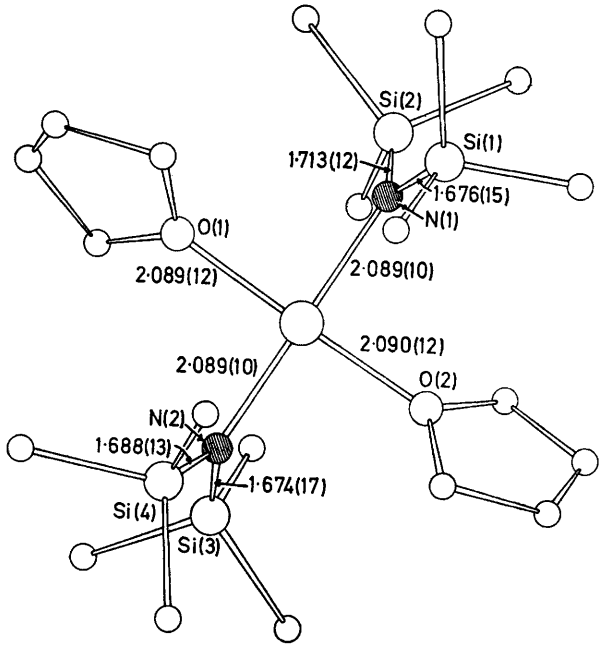

FIGURE 2. $Cr[N(SiMe_3)_2]_2(THF)_2$, *viewed normal to the molecular plane.*

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