

t-Butylimido Complexes of Chromium(v). X-Ray Crystal Structure of t-Butylimidotrichlorobis(ethyldiphenylphosphine)chromium(v)

Andreas A. Danopoulos,^a Bilquis Hussain-Bates,^b Michael B. Hursthouse,^{* b} Wa-Hung Leung^a and Geoffrey Wilkinson^{* a}

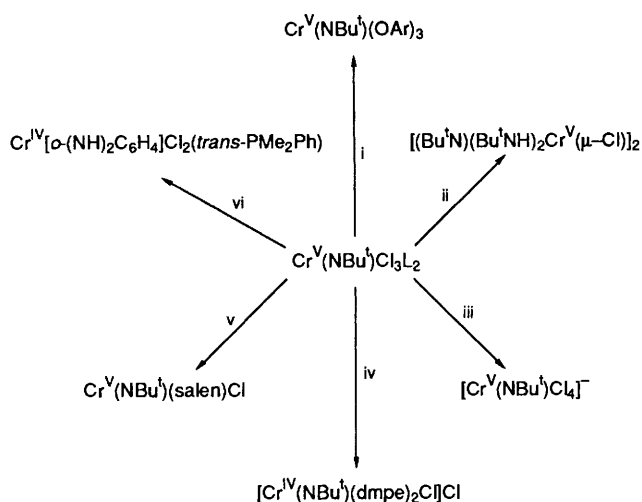
^a Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK

^b Chemistry Department, Queen Mary and Westfield College, London E1 4NS, UK

Monoimido complexes of chromium(v) have been obtained by chlorination of $\text{Cr}^{\text{VI}}(\text{NBU}^t)_2\text{Cl}_2$ to give an oil, ' $\text{Cr}(\text{NBU}^t)\text{Cl}_3$,' which on dissolution in tetrahydrofuran (thf) or dimethoxyethane and crystallising or by interaction with nitrogen or phosphorus ligands gives adducts of stoichiometry $\text{Cr}(\text{NBU}^t)\text{Cl}_3\text{L}_2$, e.g. $\text{L} = \text{thf}$, quinuclidine, PMe_3 , etc.; the X-ray structure of $\text{Cr}(\text{NBU}^t)\text{Cl}_3(\text{EtPh}_2\text{P})_2$ shows the six-coordinate compound to have *trans* phosphine and *mer* chloro groups.

Chromium(v) is a relatively uncommon oxidation state in isolable compounds. The main examples^{1a,b} are CrVO species with ligands such as Cl^- , O_2^{2-} , α -hydroxy-carboxylates, Schiff's bases,^{1c} perfluoropinacolates^{1d} and the pentamethylcyclopentadienyl, $(\text{C}_5\text{Me}_5)\text{CrOBr}_2$;^{1e} porphyrin compounds^{1f} of CrVO and Cr^{VN} and N_4 macrocyclic compounds of CrVO ^{1g} are also known.

We now report the synthesis of the first family of chromium(v) imido complexes, $\text{Cr}(\text{NBU}^t)\text{Cl}_3\text{L}_2$, $\text{L} = \text{tetrahydrofuran (thf)}$, quinuclidine, PMe_3 , PMe_2Ph , PEtPh_2 and $\text{L}_2 = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) and $\text{MeOCH}_2\text{CH}_2\text{OMe}$ (dme). The crystalline compounds are obtained by initial chlorination of $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$ in CH_2Cl_2 at room temperature; removal of solvent leaves a non-crystallisable brown oil, evidently con-



Scheme 1 Reagents and conditions: L = thf or dme; i, 2,6-Me₂C₆H₃OLi, thf; ii, Bu^tNHSiMe₃, CH₂Cl₂; iii, (Ph₃P)₂NCl or Ph₄PCl, CH₂Cl₂; iv, Na-Hg, dmpe, thf; v, Na₂(salen) (salen = N,N'-ethylenebissalicylideneaminato), MeCN; vi, L = PMe₂Ph, 1,2-(H₂N)₂C₆H₄, Et₃N, toluene. All reactions at ambient temperature.

taining Cr(NBu^t)Cl₃. Dissolution of this oil in CH₂Cl₂ and addition of N and P ligands or dissolution in thf or dme and crystallisation gives the green or red-brown (phosphine) adducts.† These are moderately moisture and air sensitive; they have magnetic moments ($\mu_{\text{eff}} = 1.62\text{--}1.75 \mu_{\text{B}}$ by Evans' method in CH₂Cl₂) close to the d¹ spin-only value. X-Band EPR spectra have bands with $\langle g_{\text{av}} \rangle = 2.084\text{--}2.088$ and the phosphine complexes show superhyperfine coupling of ca. 30 G (1 G = 10⁻⁴ T).

The series completes the group 6 monoimido species of general stoichiometry M^V(NR)Cl₃L₂. The similar molybdenum and tungsten compounds such as *mer,trans*-Mo(N-C₆H₄Me)Cl₃(PEtPh₂)₂,³ W(NPh)Cl₃(PPh₃)₂^{4a} and W(NPh)Cl₃(PMe₃)₂^{4b} have been structurally characterised. Related compounds are Re(NMe)Cl₃(PEtPh₂)₂⁵ and *mer,cis*-Ta(NPh)Cl₃(thf)(PEt₃);⁶ the vanadium compound⁷ V(NBu^t)Cl₃(2,2'-bipyridine) has not been structurally characterised.

An X-ray study‡ shows (Fig. 1) that Cr(NBu^t)Cl₃(PEtPh₂)₂ has the *mer*-Cl₃,*trans*-PR₃, geometry found for the Mo and W compounds.^{3,4} The Cr-Cl bond *trans* to the CrNBu^t function shows the expected lengthening compared to the other two mutually *trans* Cr-Cl bonds. The Cr-P bonds are long, indicating little or no tendency to Cr-Pd_π-d_π bonding; a

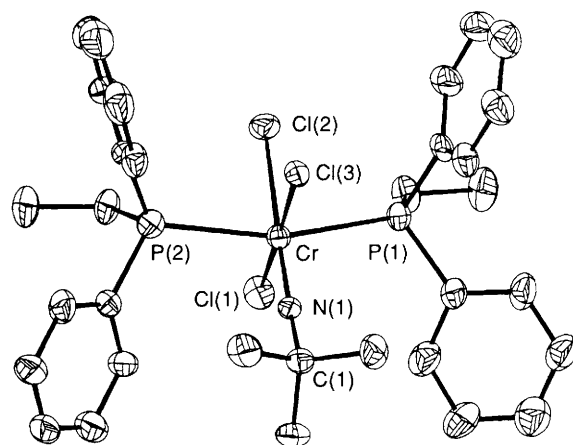


Fig. 1 The structure of Cr(NBu^t)Cl₃(PEtPh₂)₂. Selected bond lengths (Å) and angles (°) are: Cr-N(1) 1.634(7), Cr-Cl(1) 2.330(4), Cr-Cl(2) 2.381(4), Cr-Cl(3) 2.303(4), Cr-P(1) 2.477(4), Cr-P(2) 2.480(4); N(1)-Cr-Cl(1) 96.6(3), N(1)-Cr-Cl(2) 173.3(2), N(1)-Cr-Cl(3) 87.8(3), N(1)-Cr-P(1) 99.7(3), N(1)-Cr-P(2) 99.2(3), Cl(1)-Cr-Cl(3) 175.6(1), P(1)-Cr-P(2) 161.0(1), C(1)-N(1)-Cr 168.1(5).

similar distribution of bond lengths was found for W(NPh)Cl₃(PPh₃)₂.^{4a}

The thf or dme adducts are useful starting materials for syntheses of 4-, 5- and 6-coordinate species of chromium in v and lower oxidation states and a few examples are given in Scheme 1. The monophosphine adducts, e.g. of PMe₂Ph in toluene are reduced photolytically ($t_{\frac{1}{2}}$ ca. 15 min) or thermally (reflux, $t_{\frac{1}{2}}$ ca. 12 h) to give CrCl₃(PR₃)₃ and the corresponding phosphineimine.

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References

- (a) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, pp. 691, 695; (b) L. F. Larkworthy, N. B. Nolan and P. O'Brian in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 3, p. 931; (c) B. Rihter and J. Masnovi, *J. Chem. Soc., Chem. Commun.*, 1988, 35; (d) H. Nishino and J. K. Kochi, *Inorg. Chim. Acta*, 1990, **174**, 93; (e) D. B. Morse, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1988, **110**, 8234; (f) C-M. Che, J-X. Ma, W-T. Wong, T-F. Lai and C-K. Poon, *Inorg. Chem.*, 1988, **27**, 2547; L. A. Bottomley and F. L. Neely, *Inorg. Chem.*, 1990, **29**, 1860; (g) T. J. Collins, C. Slebodnick and E. B. Uffelman, *Inorg. Chem.*, 1990, **29**, 3433.
- Prepared by interaction of BCl₃ in hexane with Cr(NBu^t)₂(OSiMe₃)₂ in CH₂Cl₂ at 0°C, evaporation and sublimation of the solid (m.p. 68–70°C) *in vacuo*; see A. A. Danopoulos, W-H. Leung, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1990, **9**, in the press.
- C. Y. Chou, J. C. Huffman and E. A. Maatta, *Inorg. Chem.*, 1986, **25**, 822.
- (a) D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielsen and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2657; (b) A. J. Nielsen and J. M. Waters, *Aust. J. Chem.*, 1983, **36**, 243.
- D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.
- M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1982, **21**, 233.
- F. Preuss and W. Towae, *Z. Naturforsch., Teil B*, 1981, **36**, 1130.

† Satisfactory microanalyses and mass spectra have been obtained for these and other compounds shown in Scheme 1.

‡ *Crystal data*: C₃₂H₃₉Cl₃CrNP₂, $M_r = 709.966$. Monoclinic, $a = 8.378(2)$, $b = 17.973(4)$, $c = 22.075(5)$ Å, $\beta = 97.93(2)^\circ$, $V = 3292.7$ Å³, space group $P2_1/n$, $Z = 4$, $D_c = 1.432$ g cm⁻³, $F(000) = 1164$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu(\text{Mo-K}\alpha) = 6.43$ cm⁻¹. 5119 Data collected, 4567 unique, 2550 observed [$I > 2.5\sigma(I)$]. The structure was solved and developed *via* the Patterson/heavy-atom method and refined by full-matrix least-squares analysis with anisotropic displacement factors for non-hydrogen atoms. The phenyl rings were refined as idealised rigid hexagons and all hydrogen atoms were included in idealised positions with group U_{iso} coefficients. The final R , R_w values were 0.048, 0.050 for 330 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.