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

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Monoimido complexes of chromium(V) have been obtained by chlorination of $Cr^{VI}(NBu^t)_2Cl_2$ to give an oil, '$Cr(NBu^t)Cl_3$,' which on dissolution in tetrahydrofuran (thf) or dimethoxyethane and crystallising or by interaction with nitrogen or phosphorus ligands gives adducts of stoichiometry $Cr(NBu^t)Cl_3L_2$, *e.g.* L = thf, quinuclidine, $PMe_3$, *etc.*; the X-ray structure of $Cr(NBu^t)Cl_3(EtPh_2P)_2$ shows the six-coordinate compound to have *trans* phosphine and *mer* chloro groups.

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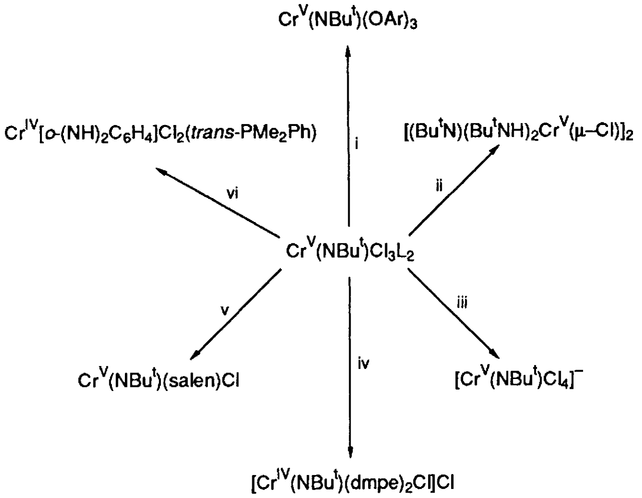
Chromium(V) is a relatively uncommon oxidation state in isolable compounds. The main examples[1a,b] are $Cr^VO$ species with ligands such as $Cl^-$, $O_2^{2-}$, α-hydroxy-carboxylates, Schiff's bases,[1c] perfluoropinacolates[1d] and the pentamethylcyclopentadienyl, $(C_5Me_5)CrOBr_2$;[1e] porphyrin compounds[1f] of $Cr^VO$ and $Cr^VN$ and $N_4$ macrocyclic compounds of $Cr^VO$[1g] are also known.

We now report the synthesis of the first family of chromium(V) imido complexes, $Cr(NBu^t)Cl_3L_2$, L = tetrahydrofuran (thf), quinuclidine, $PMe_3$, $PMe_2Ph$, $PEtPh_2$ and $L_2$ = $Me_2PCH_2CH_2PMe_2$ (dmpe) and $MeOCH_2CH_2OMe$ (dme). The crystalline compounds are obtained by initial chlorination of $Cr(NBu^t)_2Cl_2$[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-$Me_2C_6H_3OLi$, thf; ii, $Bu^tNHSiMe_3$, $CH_2Cl_2$; iii, $(Ph_3P)_2NCl$ or $Ph_4PCl$, $CH_2Cl_2$; iv, Na–Hg, dmpe, thf; v, $Na_2(salen)$ (salen = *N,N'*-ethylenebissalicylideneaminato), MeCN; vi, L = $PMe_2Ph$, 1,2-$(H_2N)_2C_6H_4$, $Et_3N$, toluene. All reactions at ambient temperature.

taining $Cr(NBu^t)Cl_3$. Dissolution of this oil in $CH_2Cl_2$ 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 ($\mu_{eff}$ = 1.62–1.75 $\mu_B$ by Evans' method in $CH_2Cl_2$) close to the $d^1$ spin-only value. X-Band EPR spectra have bands with $<g_{av}>$ = 2.084–2.088 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 $M^V(NR)Cl_3L_2$. The similar molybdenum and tungsten compounds such as *mer,trans*-Mo(N-$C_6H_4Me)Cl_3(PEtPh_2)_2$,[3] $W(NPh)Cl_3(PPh_3)_2$[4a] and $W(NPh)Cl_3(PMe_3)_2$[4b] have been structurally characterised. Related compounds are $Re(NMe)Cl_3(PEtPh_2)_2$[5] and *mer,cis*-$Ta(NPh)Cl_3(thf)(PEt_3)$;[6] the vanadium compound[7] $V(NBu^t)Cl_3$(2,2'-bipyridine) has not been structurally characterised.

An X-ray study‡ shows (Fig. 1) that $Cr(NBu^t)Cl_3(PEtPh_2)_2$ has the *mer*-$Cl_3$,*trans*-$PR_3$, 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–P$d_\pi$–$d_\pi$ bonding; a similar distribution of bond lengths was found for $W(NPh)Cl_3(PPh_3)_2$.[4a]

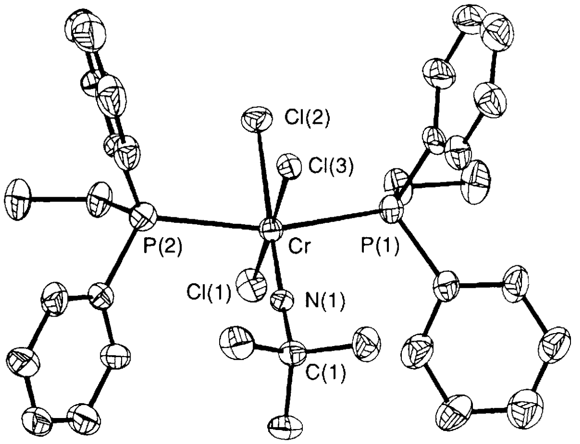


**Fig. 1** The structure of $Cr(NBu^t)Cl_3(PEtPh_2)_2$. Selected bond lengths (Å) and angles (°) are: Cr–N(1) 1.634(7), Cr–Cl(1) 2.330(4), Cr–Cl(2) 2.381(4), Cr–Cl(3) 2.303(4), Cr–P(1) 2.477(4), Cr–P(2) 2.480(4); N(1)–Cr–Cl(1) 96.6(3), N(1)–Cr–Cl(2) 173.3(2), N(1)–Cr–Cl(3) 87.8(3), N(1)–Cr–P(1) 99.7(3), 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).

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 $PMe_2Ph$ in toluene are reduced photolytically ($t_{\frac{1}{2}}$ *ca.* 15 min) or thermally (reflux, $t_{\frac{1}{2}}$ *ca.* 12 h) to give $CrCl_3(PR_3)_3$ and the corresponding phosphineimine.

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

‡ *Crystal data*: $C_{32}H_{39}Cl_3CrNP_2$, $M_r$ = 709.966. Monoclinic, $a$ = 8.378(2), $b$ = 17.973(4), $c$ = 22.075(5) Å, $\beta$ = 97.93(2)°, $V$ = 3292.7 Å$^3$, space group $P2_1/n$, $Z$ = 4, $D_c$ = 1.432 g cm$^{-3}$, $F(000)$ = 1164, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$(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.