Reactions of *tert*-Butyl Isocyanate and Trimethylsilyl Azide with Imidoamido Compounds of Chromium, Molybdenum and Tungsten†

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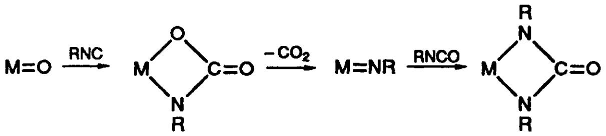
tert-Butyl isocyanate and $Cr(NBu^t)_2(NHBu^t)_2$ react to form a complex containing the dianion of *N,N′,N″*-tri-*tert*-butylbiuret $Cr(NBu^t)_2\{[Bu^tNC(O)]_2NBu^t\}$. The crystal structure of its hydrogen-bonded adduct with $[Bu^t(H)NC(O)]_2NBu^t$ has been determined and the ligand found to bind its three N atoms, whereas in solution the ^1H NMR spectrum indicates a six-membered chromium metallacyclic structure. Interaction of $Mo(NBu^t)_2(NHBu^t)_2$ and of $Cr(NBu^t)_2[NH(C_6H_3Cl_2\text{-}2,6)]_2$ with Bu^tNCO, gives $\overline{M[N(Bu^t)C(O})(NHR)]_2(NBu^t)_2$ (M = Cr, R = $C_6H_3Cl_2$-2,6; M = Mo, R = Bu^t) confirmed by the crystal structure of the molybdenum compound as having N,O bonding in a four-membered metallacycle. The previously described tungsten analogue has been reformulated as having the same structure. In all these reactions Bu^tNCO is inserted into the M–N bond of the MNHR groups and not into that of the MNR imido groups. The tungsten ureato(1 −)-*N,O* compound reacts with HCl in Et_2O to give $WCl_3(NBu^t)(NHBu^t)[OC(NHBu^t)_2]$ and the crystal structure confirms an octahedral structure with unidentate O-bonded di-*tert*-butylurea. Interaction of $M(NBu^t)_2(NHBu^t)_2$, M = Cr or W, with $SiMe_3(N_3)$ gives, respectively, the azido species $Cr(NBu^t)_2(N_3)_2$ and $[W(NBu^t)_2(N_3)(NH_2Bu^t)]_2(\mu\text{-}N_3)_2$. The structure of the latter has been confirmed by X-ray crystallography.

In reactions of the tetraphenylphosphonium salts of the ions $[RuO_2Cl_3]^-$ and $[MO_2Cl_4]^{2-}$, M = Ru and Os, with *tert*-butyl isocyanate the $[PPh_4]^+$ salts of the nitrido ureato anions $[MN\{Bu^tNC(O)NBu^t\}Cl_2]^-$ were obtained and the structures confirmed by X-ray diffraction.[1] It was proposed that the metallacycle was formed by insertion of Bu^tNCO into an unisolable $Ru(NBu^t)$ imido intermediate. Such insertions into unisolable imido intermediates obtained from carbamato-*N,O* metallacycles formed in [2 + 2] cycloadditions from M=O species, equation (1), have been proposed in other cases.[2] The last step of equation (1) has also been proposed to explain imido exchanges in interactions of organic isocyanates with $[Mo(\eta^5\text{-}C_5H_4Me)(NPh)(\mu\text{-}NPh)]_2$.[3] Finally, the direct reaction of $Os(\eta^6\text{-arene})(NBu^t)$ with Bu^tNCO has been shown[4a] in a diagram as giving a ureato complex, while a similar insertion reaction of $Mo(NR)_2(OBu^t)_2$, R = 2,6-$Pr^i{}_2C_6H_3$, and PhNCO has been reported recently[4b] as giving a bis(ureato) complex. Another ureato complex has been made by interaction of $W(C_5Me_5)(NC_6H_4Me\text{-}p)_2(CH_2SiMe_3)$ with *p*-tolyl isocyanate and structurally characterised.[4c]



(1)

Ureato (or urylene) complexes, formally derived from doubly deprotonated ureas, $[RNC(O)NR]^{2-}$, have, of course, been made in other ways, *e.g.* by reactions of zerovalent metal carbonyl and alkene compounds with organic isocyanates and azides.[5]

In the earlier work[1] we also reported the reaction of $W(NBu^t)_2(NHBu^t)_2$ with Bu^tNCO and formulated the product as the ureato compound $W(NHBu^t)_2[Bu^tNC(O)NBu^t]_2$ only on the basis of spectroscopic data since suitable crystals for X-ray diffraction were unobtainable, and by analogy with the other insertions into the M=NR bond. In extending this work we were somewhat surprised to find that (*i*) $M(NBu^t)_2X_2$ (M = Mo or W, X = Cl or $OSiMe_3$; M = Cr, X = Cl, $OSiMe_3$ or CH_2SiMe_3) did not react with Bu^tNCO under the same conditions, (*ii*) interaction of the chromium analogue, $Cr(NBu^t)_2(NHBu^t)_2$,[6a] and Bu^tNCO gave a complex derived from the previously unknown 1,3,5-tri-*tert*-butylbiuret, $[Bu^t(H)NC(O)]_2NBu^t$ (H_2L), while the compound $Mo(NBu^t)_2(NHBu^t)_2$[6b] gave a product that appeared to be the analogue of the tungsten insertion product on the basis of IR and ^1H NMR spectra at 90 MHz. However, X-ray-quality crystals of the molybdenum compound were obtained and, as discussed below, the structure is that of the product of Bu^tNCO insertion into the $Mo(NHBu^t)$ amido bonds, *i.e.* $\overline{Mo[N(Bu^t)C(O})NHBu^t]_2(NBu^t)_2$. Since ^1H NMR studies at 270 MHz showed that the spectra of the two compounds were almost identical, the structure of the tungsten compound is now reformulated.

It is now also evident that for all three compounds $M(NBu^t)_2(NHBu^t)_2$, M = Cr, Mo or W, insertion of Bu^tNCO into the $M(NHBu^t)$ bond occurs. Although one case of RNCO insertion into transition-metal M(NHR) bonds, discussed later, was cited,[5b] insertions into dialkylamido, $M(NR_2)$, bonds are well established.[5b,7] An insertion of PhNCO into the $NHBu^t$ groups of a main-group compound, $B(NBu^t)(NHBu^t)$, is, however, known (ref. 7, p. 590).

Analytical and physical data for new compounds are given in Table 1.

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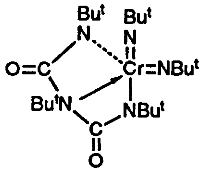
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)* C	H	N	Other
1 $Cr(NBu^t)_2\{[Bu^tNC(O)]_2NBu^t\}$	Red	141	57.7	10.1	15.0	7.3
			(57.0)	(9.7)	(15.1)	(6.9) O
2 $Mo[N(Bu^t)C(O)(NHBu^t)]_2(NBu^t)_2$	Yellow	130	52.1	9.4	13.8	
		(decomp.)	(53.8)	(9.7)	(14.5)	
3 $Cr(NBu^t)_2[NH(C_6H_3Cl_2\text{-}2,6)]_2$	Red	128	44.5	5.2	10.0	26.1
			(46.5)	(5.0)	(10.8)	(27.5) Cl
4 $Cr\{N(Bu^t)C(O)[NH(C_6H_3Cl_2\text{-}2,6)]\}_2(NBu^t)_2$	Red	135	50.8	6.3	11.2	19.5
			(50.4)	(6.2)	(11.8)	(20.0) Cl
5 $WCl_3(NBu^t)(NHBu^t)[OC(NHBu^t)_2]$	Yellow	163	34.2	6.5	9.2	17.0
			(32.4)	(6.6)	(9.4)	(17.6) Cl
6 $Cr(NBu^t)_2(N_3)_2$	Red	169	34.3	6.6	40.0	
			(34.5)	(6.5)	(40.3)	
7 $[W(NBu^t)_2(N_3)(NH_2Bu^t)]_2(\mu\text{-}N_3)_2$	Yellow	178	29.4	6.0	24.9	
			(29.8)	(6.0)	(26.1)	

* Calculated values in parentheses; for mass spectral data see Experimental section.



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Results and Discussion

Biuret Complex of Chromium(VI).—The interaction of $Cr(NBu^t)_2(NHBu^t)_2$ with Bu^{t}NCO leads to red crystals of the very moisture-sensitive complex $Cr(NBu^t)_2L$ **1**, L = $[Bu^tNC(O)]_2NBu^{t\,2-}$. We have been unable to obtain crystals of **1** suitable for X-ray diffraction study, but crystals of the hydrogen-bonded adduct of **1** with free biuret were obtained in an early preparation when the sensitivity of **1** to moisture had not been appreciated. White crystals of free biuret, formed by hydrolysis of **1**, were obtained simultaneously. Under strictly anhydrous conditions, including flaming of glassware, **1** can be obtained in a pure state.

The structure of the adduct $\mathbf{1}\cdot H_2L$ is shown in Fig. 1; selected bond lengths and angles are given in Table 2. In the complex the biuret ligand co-ordinates through all three nitrogens with the 'outer', anionic nitrogens giving shorter [*ca.* 2.01(2) Å] distances than the 'inner' [2.13(1) Å]. Within the ligand, the dihedral angle between the two halves of the 'butterfly' CrNCNCN system is 49.20°. The largest angle in the CrN_5 co-ordination sphere is N(2)–Cr–N(3), at 141.7(3)°, and the next, N(1)–Cr–N(5) at 119.4(7)°. The co-ordination geometry can thus be described either as distorted square pyramidal, with one of the imido groups [at N(4)] axial and the biuret taking three adjacent sites in the base, or trigonal bipyramidal with N(2) and N(3) defining the axial sites. In either case the two imido functions are chemically different. The geometry is strongly distorted of course, by the restricted bites of the terdentate ligand, but the molecule has an approximate plane of symmetry passing through C(4), N(4), Cr, N(2), C(2). It is pertinent that, owing to a pseudo-symmetrical alignment of the complex molecule in the unit cell, correlation effects (see Experimental section) reduce the accuracy of some bond lengths and angles in this species, and it is not possible to discuss the bonding in the co-ordinated ligand in any detail. The crystal structure also contains one molecule of free ligand per molecule of complex, and this is hydrogen bonded to an oxygen atom of the co-ordinated ligand (see Fig. 1). Although this hydrogen-bonded biuret is positioned generally in the unit cell, high thermal motion and/or disorder in the Bu^t groups in particular required the use of bond-length contraints in the refinement. This feature is almost certainly also responsible for the poor diffracting power of the crystal, the small number of observed data, and the low precision of the structure determination in general. Nevertheless, the overall identification of the complex and definition of the co-ordination geometry at the metal are clear.

Table 2 Selected bond lengths (Å) and angles (°) for compound **1** as its adduct of the biuret

N(1)–Cr	2.013(19)	N(2)–Cr	2.129(10)
N(5)–Cr	2.011(16)	N(4)–Cr	1.644(9)
N(3)–Cr	1.637(12)		
N(2)–Cr–N(1)	62.4(9)	N(5)–Cr–N(1)	119.4(7)
N(5)–Cr–N(2)	65.9(8)	N(4)–Cr–N(1)	133.0(10)
N(4)–Cr–N(2)	107.3(5)	N(4)–Cr–N(5)	110.7(9)
N(3)–Cr–N(1)	97.9(10)	N(3)–Cr–N(2)	141.7(3)
N(3)–Cr–N(5)	103.8(9)	N(3)–Cr–N(4)	110.7(5)
C(10)–N(1)–Cr	100.4(13)	C(1)–N(1)–Cr	133.4(16)
C(10)–N(2)–Cr	90.5(10)	C(20)–N(2)–Cr	85.1(13)
C(2)–N(2)–Cr	126.6(6)	C(20)–N(5)–Cr	96.0(15)
C(5)–N(5)–Cr	144.1(13)	C(4)–N(4)–Cr	154.0(9)
C(3)–N(3)–Cr	175.0(17)		

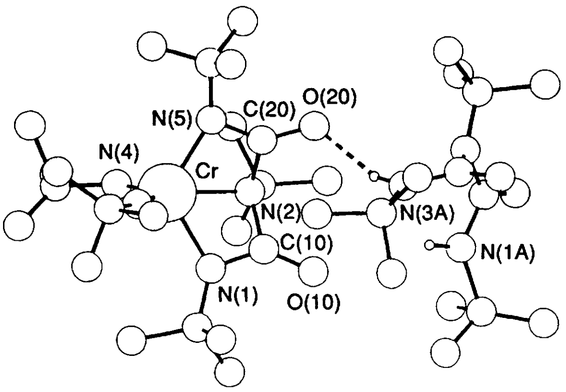
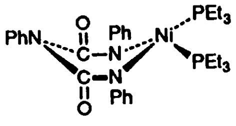


Fig. 1 The structure of $Cr(NBu^t)_2\{[Bu^tNC(O)]_2NBu^t\}$ in its adduct with $[Bu^t(H)NC(O)]_2NBu^t$

The Cr–N distances to the imido nitrogens are very similar, although the Cr–N–C angles are quite different. An 18e count for this metal is obtained if both are considered to be 4e donors, although with the availability of additional electron density from the biuret amide nitrogens N(1) and N(5) various canonicals can be written, including representation of N(3) and N(4) imido groups as either linear, 4e, or bent, 2e, ligands.

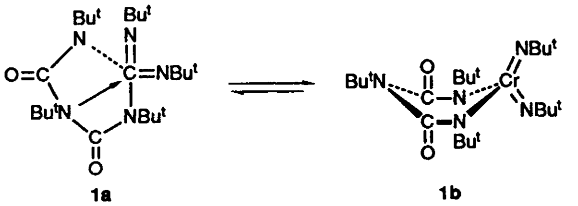


A

Although complexes of biuret, $[H_2NC(O)]_2NH$, and of doubly deprotonated biuret, *e.g.* $Cr\{[HNC(O)]_2NH\}_2$ have long been known,[8] as far as we are aware complexes of alkyl-substituted biurets are unknown. The only complex comparable to **1** is the planar nickel(II) compound, $Ni\{[PhNC(O)]_2NPh\}(PEt_3)_2$, made by Hoberg *et al.*[9a] by reaction of bis(cycloocta-1,5-diene)nickel(0), PEt_3 and PhNCO. X-Ray study showed this to have a six-membered metallacyclic ring in the boat form, **A**. An amorphous polymeric chromium compound was formulated similarly, but on the basis only of analyses.[9b]

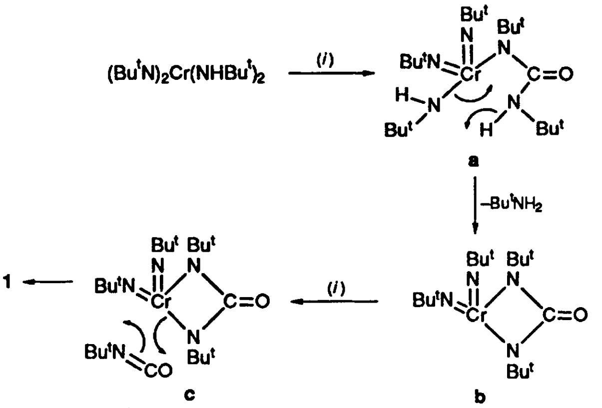
The IR spectrum of compound **1** has a single C=O stretch at 1712 cm^{-1} (*cf.* the above nickel complex[9a] at 1645 cm^{-1}) which is within the range for *N,N′,N″*-trisubstituted biurets.[10] The ^1H NMR spectrum in $[^2H_8]$toluene at 25 °C shows four singlets with intensity values 1:1:2:1 at δ 1.79, 1.41, 1.34 and 1.26, respectively. We assign the line at δ 1.41 to a 'linear' $CrNBu^t$ group and that at δ 1.26 to a 'bent' imido by comparison with data for linear and bent imido groups in the compounds $[Li_2M(NBu^t)_4]_2$, M = Cr,[6a] Mo or W.[6b] These lines are solvent dependent and in $CHCl_3$ they shift to δ 1.69 and 1.52 respectively. Such solvent dependency for MNR groups has been noted previously, *e.g.* for $Cr(NBu^t)_2Cl_2$ a shift from δ 1.14 in C_6D_6 to 1.60 in $CDCl_3$.[6a] The two imido lines of **1** show no change up to +80 °C suggesting that there is no linear–bent imido interconversion. The remaining two peaks of ratio 2:1 can be assigned, respectively, to the two $CrNBu^t$ groups (δ 1.34) and the central NBu^t group (δ 1.79) of the ligand L. Both these peaks are less solvent dependent than those of the $Cr(NBu^t)$ imido groups: in $CDCl_3$ they appear at δ 1.30 and 1.67, respectively. The equivalence of the outer NBu^t groups of the biuret ligand is consistent with the approximate mirror plane in the structure found in the solid state. On cooling to the lowest accessible temperature (−88 °C) only the band assigned to the central NBu^t of the ligand broadens and virtually disappears at −68 °C: the other singlet for the two $CrNBu^t$ groups remains. Although it is difficult to obtain spectra of **1** entirely free from H_2L, impurity lines can be recognised from the ^1H NMR spectra of the free biuret over the temperature range studied.

The fact that the band assigned to the central NBu^t group shows temperature dependence leads us to suggest that in solution there is an equilibrium between two forms **1a** and **1b**, equation (2).The predominant form **1b** has the six-membered ring as in Hoberg's nickel complex,[9a] and four-co-ordination for Cr^{VI}. Since **1a** has two four-membered rings in the solid, release of strain in solution seems likely to give the favoured **1b**.



1a **1b** (2)

It is of interest that the two $CrNBu^t$ terminal imido groups in compound **1b** remain inequivalent, although in other distorted-tetrahedral molecules, $Cr(NBu^t)_2X_2$, X = Cl, $NHBu^t$,[6a] $OSiMe_3$,[11a] $C_6H_2Me_3$-2,4,6 and $C_6H_3Me_2$-2,6,[11b] CH_2SiMe_3, CH_2CMe_3 and CH_2CMe_2Ph,[11c] the two NBu^t groups are equivalent according to ^1H NMR spectra, and by X-ray data where available, *e.g.* for $Cr(NBu^t)_2(C_6H_2Me_3\text{-}2,4,6)_2$.[11b] The difference might be due to electronic factors such as variation in M=N multiple bonding but more likely it arises from steric factors: as a result of non-flexibility of the ring, the $CrNBu^t$ imido groups above and below the CrL plane might not be magnetically equivalent. No ^1H NMR data were reported for the nickel complex.[9a]



Scheme 1 (*i*) Bu^tNCO

For the nickel complex **A**, Hoberg *et al.*[9a] gave only the overall reaction (3). They proposed an intermediate with a N,C-

$$PhNCO + Ni^0 + PEt_3 \longrightarrow (Et_3P)_2Ni(Ph_3N_3C_2O_2) \quad (3)$$

bonded five-membered metallacycle as in an isolated nickel complex with tetramethylethylenediamine as ligand; insertion of the nitrene PhN produced by decarbonylation of PhNCO into the Ni–C bond of the ring gave the product.

In view of the work discussed later, it appears that the initial step in the formation of compound **1** is insertion into the chromium–amido bond. In addition to the precedents[5b,7] for insertion into MNR_2 bonds noted earlier, which lead to $\overline{M[N(R)C(O}){NR_2}]$ moieties (see below), there are two examples for the insertion of PhNCO into the amido bond of transition metals in both cases giving N-bonded, unidentate PhNC(O)NHPh groups for *trans*-$MH(NHPh)(PR_3)_2$ (M = Pt, R = Et;[12a] M = Pd, R = C_6H_{11}[12b]).

A possible reaction sequence is shown in Scheme 1. The elimination of Bu^tNH_2 from the intermediate **a** seems reasonable. Proton transfers from bis(*tert*-butylamido)tungsten halides to give *tert*-butylimido *tert*-butylamine complexes have been reported,[13a] as have transfers from an unisolable intermediate, $Ir(\eta^5\text{-}C_5H_5)(NHBu^t)_2$, to give $Ir(\eta^5\text{-}C_5H_5)(NBu^t)$,[13b] and from $Mo(OBu^t)_2(NR)(NHR)(NHBu^t)$ to give $Mo(OBu^t)_2(NBu^t)(NR)$, R = $2,6\text{-}Pr^i{}_2C_6H_3$.[4b] Co-ordination of Bu^tNCO to the four-co-ordinate species **b** in Scheme 1 then leads to the biuret complex **1**. An alternative pathway could involve an initial intermediate with a $Cr[N(Bu^t)C(O)NHBu^t]_2$ moiety which subsequently undergoes elimination of NH_2Bu^t.

Since the only *N,N′,N″*-biurets with alkyl groups are those with Me and Et,[8a,10] we attempted to make the *tert*-butyl by the Lewis-acid-catalysed route used for the aryls[14] using $SnCl_4$, $BF_3(OEt_2)$ or $AlCl_3$. However, only the 1,5-di-*tert*-butylbiuret,[8a] $[Bu^tHNC(O)]_2NH$, was obtained and identified by ^1H NMR spectroscopy ($CDCl_3$): δ 1.42 (18 H, NBu^t) and 4.14 (3 H, NH); in C_6D_6 the NBu^t band occurs at 1.28. We have obtained the tri-*tert*-butylbiuret only by hydrolysis of **1** as noted earlier and the nature of which was confirmed in the X-ray structure, Fig. 1. Hydrolysis of the nickel compound[9a] gives the triaryl-substituted biuret.

Ureato(1 −) *Complexes of* Cr, Mo *and* W.—The reaction of $Mo(NBu^t)_2(NHBu^t)_2$ and Bu^tNCO produces yellow crystals of **2** which are very air and moisture sensitive. The structure was determined by X-ray crystallography. A diagram of the molecule is shown in Fig. 2; selected bond lengths and angles are given in Table 3.

The molecule has a distorted-octahedral structure with two

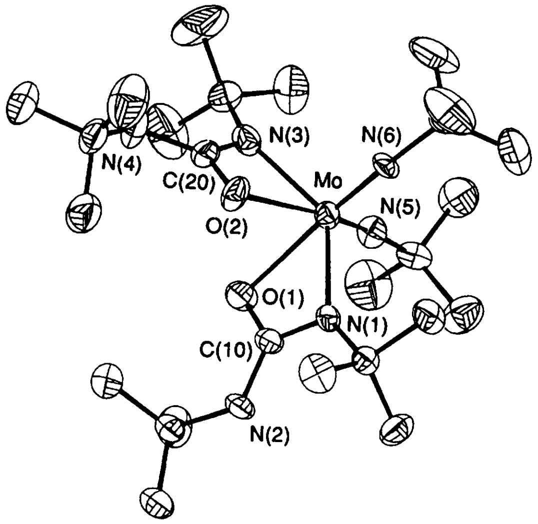
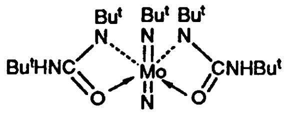


Fig. 2 The structure of $\overline{\mathrm{Mo[N(Bu^t)C(O}}\mathrm{)(NHBu^t)]_2(NBu^t)_2}$

Table 3 Selected bond lengths (Å) and angles (°) for compound 2

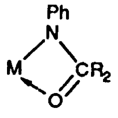
O(1)–Mo	2.297(8)	O(2)–Mo	2.203(9)
N(1)–Mo	2.089(9)	N(3)–Mo	2.124(10)
N(5)–Mo	1.672(9)	N(6)–Mo	1.738(8)
O(2)–Mo–O(1)	76.1(4)	N(1)–Mo–O(1)	59.6(3)
N(1)–Mo–O(2)	87.2(4)	N(3)–Mo–O(1)	83.7(4)
N(3)–Mo–O(2)	58.9(4)	N(3)–Mo–N(1)	135.9(3)
N(5)–Mo–O(1)	88.9(4)	N(5)–Mo–O(2)	159.1(3)
N(5)–Mo–N(1)	97.8(5)	N(5)–Mo–N(3)	105.7(5)
N(6)–Mo–O(1)	162.3(3)	N(6)–Mo–O(2)	92.6(4)
N(6)–Mo–N(1)	107.0(4)	N(6)–Mo–N(3)	102.2(4)
N(6)–Mo–N(5)	105.2(5)	C(10)–N(1)–Mo	96.2(7)
C(1)–N(1)–Mo	139.5(6)	C(20)–N(3)–Mo	94.5(7)
C(3)–N(3)–Mo	139.2(7)	C(5)–N(5)–Mo	170.4(8)
C(6)–N(6)–Mo	159.7(8)		



2

cis imido functions and two chelating (N,O) ureato ligands. The main distortion from octahedral metal geometry arises from the small bite (*ca.* 60°) of the ureato ligand. For these, the oxygen functions are each *trans* to the imido group, so the molecule has a pseudo-two-fold axis of symmetry. However, the $MoO_2N_2N'_2$ geometry shows differences in what might be expected to be chemically equivalent bonds and this may partly be a reflection of some bonding asymmetry. If the ureato ligand is considered as a 1e,2e (N,O) ligand, then an 18e configuration will be achieved with only one of the two imido functions behaving as a 4e donor. Both Mo–N–C groups are bent, but Mo–N(6)–C(6) has the smallest angle [159.7(8)°] and Mo–N(6) is significantly longer than Mo–N(5), suggesting that N(6) has more '2e character' than N(5). It is then rather perplexing to find that Mo–O(2), *trans* to the stronger bonding imido group, has a shorter length than Mo–O(1). It is possible that, in view of the presence of so many substituent Bu^t groups, steric effects are quite large, and these may be affecting metal–ligand bond lengths.

It is clear that compound 2 is formed by insertion of Bu^tNCO into the Mo–N amido bonds. At 90 MHz in $CDCl_3$ the ^1H NMR spectrum of the tungsten analogue[1] showed only two bands in a 2:1 ratio which were assigned, respectively, to the four NBu^t groups of two ureato(2–) ligands and two $WNHBu^t$ groups; compound 2 had a similar spectrum. The overlapping and inadequate resolution of bands and the sensitivity of the line positions to solvent were not recognised earlier. In C_6D_6 or $[^2H_8]$toluene (25 °C, 270 MHz) there are three bands for both compounds at δ 1.46, 1.33 and 1.32 (Mo) and 1.52, 1.38 and 1.33 (W), in a 1:1:1 ratio in each case. Comparison of the spectra with those of similar *tert*-butylimido compounds of Mo and W[6b,11a] and with 1,3-di-*tert*-butylurea allows assignments, respectively, to imido $MNBu^t$, ureato $MNBu^t$ and ureato $NHBu^t$. There is no change in the spectra over the range –60 to 100 °C. We advise that imido and amido ^1H NMR spectra should be obtained in C_6D_6 or $[^2H_8]$toluene and the sensitivity of bands to $CHCl_3$ borne in mind.



B

The IR spectra for the two compounds have very similar bands in the NH and C=O stretching region (see Experimental section) and the latter bands are *ca.* 100 cm^{-1} lower than for the free urea, consistent with C–O–M co-ordination.

A third compound of this type was also obtained by interaction of $Cr(NBu^t)_2[NH(C_6H_3Cl_2\text{-}2,6)]_2$ 3 and Bu^tNCO, namely $\overline{\mathrm{Cr\{N(Bu^t)C(O}}\mathrm{)[NH(C_6H_3Cl_2\text{-}2,6)]\}_2(NBu^t)_2}$ 4. The difference from the reaction of Bu^tNCO with $Cr(NBu^t)_2(NHBu^t)_2$ is presumably due to electronic factors.

Compounds of the present type do not seem to have been structurally characterised. For Ti, Zr and Hf, insertions of PhNCO into the M–N bonds of dialkylamides such as $Ti(NMe_2)_4$ have led to compounds formulated on the basis of spectra as having chelate $MN(Ph)C(O)NMe_2$,[15a] *cf.* **B**, or unidentate $MN(Ph)C(O)NMe_2$[15b] groups.

Before obtaining the crystal structure of compound 2, we had protonated $\overline{\mathrm{W[N(Bu^t)C(O}}\mathrm{)(NHBu^t)]_2(NBu^t)_2}$ with HCl in Et_2O in the hope of obtaining a cationic species that might have thrown some light on the structure. Analyses, spectra and X-ray crystallography showed that the yellow crystalline product is $WCl_3(NBu^t)(NHBu^t)[OC(NHBu^t)_2]$ 5 which has an O-bonded, 1,3-di-*tert*-butylurea ligand. The molecular structure is given in Fig. 3, with selected bond lengths and angles in Table 4. The tungsten geometry is octahedral with a *mer*-Cl_3 arrangement and with the O-bonded urea ligand *trans* to the imido function. As a result the W–O bond is quite long. With all ligands assigned conventional electron-donation counts, the metal atom has 16e. Two further electrons could be donated by the $NHBu^t$ ligand and this would explain the short W–N(2) distance of 1.894(7) Å.

The spectra are in accord with the structure determined. The IR spectrum has N–H and C–O stretches. The latter is lowered compared to that of the free urea in agreement with unidentate O bonding of ureas.[16] The ^1H NMR spectrum has three singlets at δ 1.63, 1.53 and 1.43 in a 1:1:2 ratio which can be assigned, respectively, to the $WNBu^t$, $WN(H)Bu^t$ and urea $N(H)Bu^t$ groups.

It is evident that excess of HCl protonates one of the $WNBu^t$ imido groups and the $WNBu^t$ groups of the $W[N(Bu^t)C(O)(NHBu^t)]$ rings leading to displacement of one urea molecule and co-ordination of chloride ion.

Interactions of Trimethylsilyl Azide.—Since $SiMe_3(N_3)$ is also a cumulene, reactions with $M(NBu^t)_2(NHBu^t)_2$, M = Cr or W, were studied. For chromium the product is red $Cr(NBu^t)_2(N_3)_2$ 6 and for tungsten the bridged species $[W(NBu^t)_2(N_3)(NH_2Bu^t)]_2(\mu\text{-}N_3)_2$ 7. The N-bonded azides have stretches at 2084

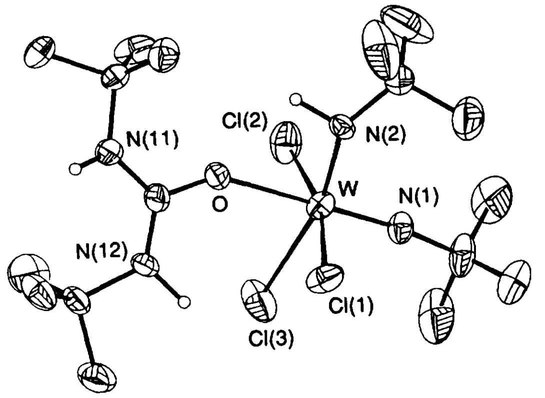


Fig. 3 The structure of $\mathrm{WCl_3(NBu^t)(NHBu^t)[OC(NHBu^t)_2]}$

Table 4 Selected bond lengths (Å) and angles (°) for compound **5**

Cl(1)–W	2.397(4)	Cl(2)–W	2.380(4)
Cl(3)–W	2.446(4)	O–W	2.212(6)
N(1)–W	1.717(7)	N(2)–W	1.894(7)
Cl(2)–W–Cl(1)	165.6(1)	Cl(3)–W–Cl(1)	85.0(2)
Cl(3)–W–Cl(2)	85.0(2)	O–W–Cl(1)	83.5(2)
O–W–Cl(2)	85.5(2)	O–W–Cl(3)	85.8(2)
N(1)–W–Cl(1)	95.7(3)	N(1)–W–Cl(2)	95.5(3)
N(1)–W–Cl(3)	95.3(3)	N(1)–W–O	178.6(2)
N(2)–W–Cl(1)	92.8(3)	N(2)–W–Cl(2)	93.9(3)
N(2)–W–Cl(3)	164.1(2)	N(2)–W–O	78.3(3)
N(2)–W–N(1)	100.6(3)	C(10)–O(1)–W	144.7(5)
C(01)–N(1)–W	168.7(5)	C(02)–N(2)–W	144.7(5)
C(101)–N(11)–C(10)	128.9(7)	C(102)–N(12)–C(10)	129.8(8)

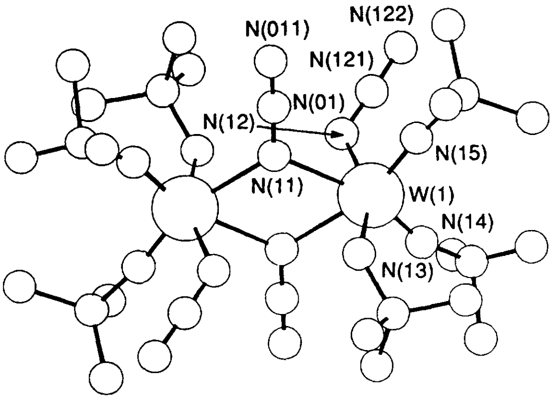


Fig. 4 The structure of $\mathrm{[W(NBu^t)_2(N_3)(NH_2Bu^t)]_2(\mu\text{-}N_3)_2}$

Table 5 Selected bond lengths (Å) and angles (°) for compound **7**

Molecule 1		Molecule 2	
N(11)–W(1)	2.357(16)	N(21)–W(2)	2.295(16)
N(12)–W(1)	2.156(14)	N(22)–W(2)	2.130(17)
N(13)–W(1)	2.185(14)	N(23)–W(2)	2.204(15)
N(14)–W(1)	1.734(16)	N(24)–W(2)	1.767(16)
N(15)–W(1)	1.794(15)	N(25)–W(2)	1.758(14)
N(11B)–W(1)	2.270(16)	N(21B)–W(2)	2.329(16)
N(12)–W(1)–N(11)	80.3(6)	N(22)–W(2)–N(21)	80.2(6)
N(13)–W(1)–N(11)	78.0(6)	N(23)–W(2)–N(21)	80.6(6)
N(13)–W(1)–N(12)	157.0(6)	N(23)–W(2)–N(22)	154.4(5)
N(14)–W(1)–N(11)	159.6(5)	N(24)–W(2)–N(21)	159.2(5)
N(14)–W(1)–N(12)	95.8(7)	N(24)–W(2)–N(22)	97.9(7)
N(14)–W(1)–N(13)	101.8(7)	N(24)–W(2)–N(23)	94.1(7)
N(15)–W(1)–N(11)	91.0(7)	N(25)–W(2)–N(21)	95.3(7)
N(15)–W(1)–N(12)	95.9(6)	N(25)–W(2)–N(22)	94.6(7)
N(15)–W(1)–N(13)	92.2(7)	N(25)–W(2)–N(23)	103.9(6)
N(15)–W(1)–N(14)	109.4(8)	N(25)–W(2)–N(24)	105.5(7)
N(11)–W(1)–N(11B)	66.8(6)	N(21)–W(2)–N(21B)	64.9(6)
N(12)–W(1)–N(11B)	81.6(6)	N(22)–W(2)–N(21B)	80.1(6)
N(13)–W(1)–N(11B)	82.8(6)	N(23)–W(2)–N(21B)	76.6(6)
N(14)–W(1)–N(11B)	93.0(7)	N(24)–W(2)–N(21B)	94.3(6)
N(15)–W(1)–N(11B)	157.7(5)	N(25)–W(2)–N(21B)	160.0(5)
N(01)–N(11)–W(1)	120.7(12)	N(02)–N(21)–W(2)	121.8(12)
N(121)–N(12)–W(1)	125.5(13)	N(221)–N(22)–W(2)	128.9(16)
C(13)–N(13)–W(1)	130.3(12)	C(23)–N(23)–W(2)	128.2(11)
C(14)–N(14)–W(1)	161.8(16)	C(24)–N(24)–W(2)	170.4(11)
C(15)–N(15)–W(1)	172.3(12)	C(25)–N(25)–W(2)	168.3(11)

(Cr) and 2093 (W) $\mathrm{cm^{-1}}$, respectively, while the μ-($\mathrm{N_3}$) stretch in the tungsten compound is at 2049 $\mathrm{cm^{-1}}$.[17] The structure of **7** was confirmed by X-ray study. A diagram of the molecule is shown in Fig. 4; bond lengths and angles are given in Table 5. The unit cell contains two crystallographically independent centrosymmetric dimeric molecules with double azido bridges. These are characterised by a slight asymmetry and relatively long W–N distances of 2.36(2), 2.33(2) Å and 2.27(2), 2.30(2) Å. The apparent weakness of these bonds presumably arises from their *trans* positioning to the imido groups in the distorted octahedral $\mathrm{WN_6}$ co-ordination. These groups are in a mutually *cis* arrangement and the W–N distances are slightly longer than usual.

If the bridging azides are formally recognised as three-electron donors *i.e.* W–N→W, and all imido groups as 4e donors, the electron count on each metal would be 20e. The general lengthening of all W–N(imido) bonds suggests that the reduction in electron donation is distributed. Within the relatively high limits of experimental error (see Experimental section), all other geometry parameters are normal.

It seems likely that in both cases $\mathrm{M(NBu^t)_2(N_3)_2}$ is formed together with $\mathrm{SiMe_3(NHBu^t)}$. For tungsten the $\mathrm{NH_2Bu^t}$ could arise from hydrolysis of the latter by adventitious water or by the four-co-ordinate azide acting as a Lewis acid, co-ordinating the amine and promoting hydrogen transfer [equation (4)]. The

$$\mathrm{W[NH(Bu^t)(SiMe_3)]_2} \longrightarrow \mathrm{W(NH_2Bu^t) + (Me_3Si)_2NBu^t} \quad (4)$$

tungsten reaction could be expected to proceed beyond the bis(azide) stage owing to the greater tendency of $\mathrm{W^{VI}}$ to become octahedral [*cf.* ref. 13(*a*) for imido–amine species].

Experimental

The general procedures and instrumentation have been described.[1,6b] Microanalyses were by Pascher, Remagen, MEDAC plc, Brunel University, and Imperial College Laboratories. Infrared spectra were recorded in Nujol mulls unless otherwise stated, mass spectra by electron impact (EI) and ^{1}H NMR spectra at 90 or 270 MHz are referenced to $\mathrm{SiMe_4}$.

Commercial chemicals were from Aldrich. Amides, LiNHR, were made in hexane from $\mathrm{NH_2R}$ and $\mathrm{LiBu^t}$ in hexanes. The compound $\mathrm{(Bu^tNH)_2CO}$ was made by interaction of $\mathrm{NH_2Bu^t}$ and CO in the presence of selenium.[18]

$\mathrm{Cr(NBu^t)_2\{[Bu^tNC(O)]_2NBu^t\}}$ **1**.—It is essential that the reactants and solvents and also glassware are thoroughly dried to avoid partial product hydrolysis. To freshly sublimed $\mathrm{Cr(NBu^t)_2(NHBu^t)_2}$[6a] (0.7 g, 2.1 mmol) in hexane (40 $\mathrm{cm^3}$) was added $\mathrm{Bu^tNCO}$ (3.6 $\mathrm{cm^3}$, 30 mmol) and the mixture refluxed for 12 h. After removal of volatiles under vacuum, the residue was extracted with hexane (2 × 30 $\mathrm{cm^3}$). The extract was filtered, concentrated (10 $\mathrm{cm^3}$) and cooled (−20 °C) to give fine red needles. Yield: 0.6 g, 60%. In the initial preparations the free tri-*tert*-butylbiuret was also obtained along with red crystals. The latter were hand picked and mounted for X-ray study as the hydrogen-bonded biuret adduct of **1**.

Table 6 Crystal data, details of intensity measurements and structure refinements *

Compound	1	2	5	7
Formula	$C_{20}H_{45}CrN_5O_2\cdot C_{12}H_{29}N_3O_2$	$C_{26}H_{54}MoN_6O_2$	$C_{17}H_{39}Cl_3N_4OW$	$C_{24}H_{54}N_{18}W_2$
M	686.99	578.69	605.731	962.51
Space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	12.002(3)	10.534(4)	8.627(2)	19.716(3)
b/Å	14.537(2)	16.340(9)	18.151(2)	9.322(7)
c/Å	13.607(3)	19.397(4)	17.184(3)	22.794(8)
β/°	108.87(3)	97.80(3)	100.47(1)	106.39(4)
U/Å^3	2246.46	3307.83	2631.39	4019.13
Z	2	4	4	4
D_c/g cm^{-3}	1.016	1.162	1.529	1.591
F(000)	756	1240	1208	1888
μ/cm^{-1}	2.83	4.135	48.04	58.81
Total no. of reflections	8788	14 555	11 605	11 563
No. of unique reflections	3968	7926	3956	6670
No. of observed reflections [$F_o > 3\sigma(F_o)$]	2159	2269	2471	3181
No. of refined parameters	529	218	283	445
Final R	0.0628	0.0519	0.0345	0.0421
Final R'	0.0667	0.0534	0.0353	0.0437

* Details in common: monoclinic; weighting scheme $w = 1/\sigma^2(F)$.

Table 7 Fractional atomic coordinates ($\times 10^4$) for compound **1**

Atom	x	y	z	Atom	x	y	z
Cr	507(2)	0	2177(1)	C(32)	1835(13)	963(12)	149(12)
O(10)	2114(12)	1211(10)	4705(12)	C(33)	1274(14)	−519(13)	−303(14)
O(20)	2072(13)	−1125(11)	4690(14)	O(10A)	3338(7)	12(13)	8472(6)
N(1)	1066(15)	1187(12)	2939(16)	C(10A)	3669(9)	−28(18)	7737(9)
N(3)	1233(7)	72(13)	1347(7)	N(1A)	3774(12)	799(12)	7251(14)
N(5)	1047(13)	−1202(10)	2906(12)	C(1A)	3787(15)	1827(14)	7702(17)
C(20)	1402(21)	−866(19)	3834(22)	C(11A)	3963(17)	2434(13)	6898(16)
C(1)	1277(18)	2076(14)	2617(17)	C(12A)	4673(16)	1971(13)	8697(16)
C(2)	−194(9)	4(16)	4304(9)	C(13A)	2417(14)	1870(13)	7492(16)
C(3)	1857(11)	53(18)	585(9)	N(2A)	3942(12)	−785(12)	7245(13)
C(4)	−1984(10)	51(14)	635(9)	C(2A)	3658(14)	−1700(11)	7562(12)
C(5)	1386(15)	−2176(12)	2759(15)	C(21A)	4390(15)	−1829(13)	8737(14)
C(11)	475(16)	2322(12)	1498(14)	C(22A)	4029(15)	−2423(12)	6852(14)
C(12)	2588(17)	2157(14)	2674(18)	C(23A)	2429(15)	−1867(14)	7532(17)
C(13)	1139(15)	2858(12)	3338(16)	C(20A)	4906(6)	−549(5)	6835(6)
C(51)	2649(15)	−2267(13)	2814(16)	O(20A)	5940(6)	−545(5)	7366(6)
C(52)	1024(16)	−2764(12)	3517(16)	N(3A)	4545(6)	−344(5)	5797(6)
C(53)	668(17)	2415(14)	1779(15)	C(3A)	5249(9)	−14(19)	5133(9)
C(41)	−1936(17)	679(14)	−98(15)	C(31A)	4464(9)	64(17)	4042(9)
C(42)	−3040(10)	−62(21)	957(11)	C(32A)	6190(15)	−654(13)	5571(16)
C(43)	−2029(18)	−918(13)	135(16)	C(33A)	5867(15)	895(13)	5165(15)
C(21)	350(9)	−26(18)	5491(8)	N(2)	758(6)	31(14)	3798(6)
C(22)	−874(14)	822(13)	4035(16)	N(4)	−919(7)	−15(15)	1568(7)
C(23)	−1023(14)	−848(12)	3958(16)	C(10)	1425(14)	890(12)	3903(14)
C(31)	3129(10)	58(19)	1106(10)				

IR: 1712 cm^{-1} (CO). ^{1}H NMR (CDCl$_3$, 20 °C), δ 1.30 (s, 18 H, CrNBu^t), 1.52 (s, 9 H, bent CrNBu^t), 1.67 (s, 9 H, central NBu^t) and 1.69 (s, 9 H, linear CrNBu^t); ([^{2}H$_8$]toluene, 20 °C), δ 1.26 (s, 9 H, bent CrNBu^t), 1.34 (s, 18 H, CrNBu^t), 1.41 (s, 9 H, linear CrNBu^t) and 1.79 (s, 9 H, central CrNBu^t); small peaks due to the hydrolysis product [Bu^{t}NHC(O)]$_2$NBu^t may also be present at δ 1.19 and 1.56 in [^{2}H$_8$]toluene.

The biuret can be obtained by addition of 2 equivalents of water to compound **1** in MeCN when the red solution becomes yellow over *ca.* 5 h. Evaporation and extraction of the residue with hexane followed by concentration and cooling gave colourless crystals, m.p. 133–134 °C, which are hygroscopic and become amorphous on standing in air. IR: 3311s, 1685s, 1666s, 1523s, 1262s, 1201m, 1099s, 1021s and 801s cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C), δ 1.33 (s, 18 H, NHBu^t), 1.44 (s, 9 H, NBu^t) and 5.30 (br, 2 H, NH).

Bis(tert-*butylimido*)*bis*[N,N′-*di*-tert-*butylureato*(1 −)-κN,O]*molybdenum*(VI) **2**.—To Mo(NBu^t)$_2$(NHBu^t)$_2$ (*ca.* 1.0 g) in hexane (40 cm^3) was added a 14-fold excess (*ca.* 1.7 cm^3) of Bu^{t}NCO and the mixture refluxed (12 h), after which volatiles were removed and the residue was extracted with hexane (2 × 30 cm^3). Filtration, concentration (to *ca.* 5 cm^3) and cooling gave yellow needles. Yield: 0.3 g, 30%. Mass spectrum: *m*/*z* 582 (M^+), 410 [M^+ − (Bu^{t}NH)$_2$CO] and 172 [(Bu^{t}NH)-CO$^+$]. IR: 3485, 3355 (NH) and 1543 cm^{-1} (CO stretch). ^{1}H NMR ([^{2}H$_8$]toluene, 25 °C), δ 1.32 (s, 18 H, ureato NHBu^t), 1.33 (s, 18 H, ureato NBu^t), 1.46 (s, 18 H, imido NBu^t) and 4.18 (br, 2 H, NH).

The tungsten analogue[1] has a similar NMR spectrum in C$_6$D$_6$ at 25 °C: δ 1.33 (s, 18 H, ureato NHBu^t), 1.38 (s, 18 H, ureato NBu^t), 1.52 (s, 18 H, imido NBu^t) and 4.20 (br, 2 H, NH). Neither spectrum at 270 MHz changed over the temperature range −60 to 100 °C.

Bis(tert-*butylimido*)*bis*(2,6-*dichlorophenylamido*)*chromium* (VI) **3**.—The compound Cr(NBu^t)$_2$Cl$_2$[6a] (0.7 g, 2.6 mmol) in toluene (20 cm^3) at −78 °C was slowly added to a well stirred

Table 8 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Mo	1325(1)	251(1)	2530(1)
O(1)	3405(6)	−47(4)	2979(4)
O(2)	1781(7)	−845(4)	1949(4)
N(1)	1721(6)	−452(5)	3434(4)
N(2)	3843(7)	−842(5)	3925(4)
N(3)	2095(7)	354(5)	1577(4)
N(4)	2943(9)	−776(6)	1032(5)
N(5)	1505(8)	1173(4)	2903(4)
N(6)	−306(6)	160(5)	2249(4)
C(10)	3003(9)	−458(6)	3450(5)
C(20)	2275(9)	−416(7)	1518(5)
C(1)	1036(8)	−943(6)	3907(5)
C(11)	1388(10)	−707(7)	4672(5)
C(12)	1253(10)	−1823(6)	3804(6)
C(13)	−389(9)	−771(7)	3717(6)
C(2)	5232(9)	−914(7)	3911(6)
C(21)	5758(11)	−1431(8)	4522(6)
C(22)	5526(11)	−1302(8)	3243(6)
C(23)	5841(10)	−100(7)	3974(6)
C(3)	2583(11)	985(7)	1148(6)
C(31)	2201(17)	869(9)	388(7)
C(32)	4017(12)	1031(9)	1301(9)
C(33)	2053(12)	1778(7)	1357(7)
C(4)	3031(12)	−1618(7)	904(6)
C(41)	3600(14)	−2048(8)	1554(7)
C(42)	3894(13)	−1709(9)	356(7)
C(43)	1761(13)	−1945(10)	657(8)
C(5)	1610(10)	1881(7)	3317(6)
C(51)	1164(13)	1687(8)	4010(6)
C(52)	800(13)	2532(7)	2969(7)
C(53)	2979(12)	2165(9)	3462(9)
C(6)	−1636(9)	397(6)	2030(5)
C(61)	−1664(12)	891(10)	1419(8)
C(62)	−2432(12)	−308(9)	1901(9)
C(63)	−2126(13)	875(10)	2586(8)

Table 9 Fractional atomic coordinates (× 10^4) for compound **5**

Atom	*x*	*y*	*z*
W	−1449(1)	7274(1)	57(1)
Cl(1)	738(8)	6748(5)	949(4)
Cl(2)	−3254(9)	8072(4)	−755(6)
Cl(3)	−1358(9)	8232(5)	1071(5)
O	407(19)	7917(9)	−371(10)
N(1)	−2866(21)	6755(11)	387(12)
N(2)	−1075(21)	6693(11)	−810(12)
N(11)	2210(25)	8636(13)	−752(13)
N(12)	1942(25)	8562(14)	572(13)
C(10)	1508(29)	8372(15)	−175(16)
C(01)	−4131(34)	6436(16)	767(21)
C(02)	−1561(35)	6029(17)	−1286(18)
C(11)	−5612(33)	6394(25)	120(23)
C(12)	−3556(40)	5693(19)	1134(23)
C(13)	−4461(46)	6972(21)	1380(25)
C(21)	−176(44)	5732(21)	−1610(31)
C(22)	−2956(51)	6183(25)	−1933(27)
C(23)	−2100(50)	5404(20)	−785(24)
C(102)	2884(29)	9205(15)	924(16)
C(101)	1833(31)	8492(16)	−1620(15)
C(111)	2252(34)	7723(15)	−1796(18)
C(112)	2915(34)	9012(17)	−1981(18)
C(113)	187(28)	8704(21)	−1932(17)
C(121)	2845(40)	9181(23)	1809(17)
C(122)	4569(27)	9154(18)	814(20)
C(123)	2174(42)	9902(18)	574(24)

suspension of $Li(C_6H_3Cl_2\text{-}2,6)$ (0.88 g, 5.2 mmol) in toluene (40 cm^3) at −78 °C. The deep red mixture was allowed to warm to room temperature and stirred for 12 h when volatiles were removed and the residue was extracted with hexane (2 × 30 cm^3). After filtration and concentration (15 cm^3), cooling (−78 °C) gave the red product. Yield: 0.8 g, 60%. The product is pure enough to use directly but can be recrystallised from hexane at −78 °C. ^1H NMR (C_6D_6), δ 1.31 (s, 18 H, imido NBu^t), 6.49 (t, 2 H, aromatic *p*-H), 7.23 (d, 4 H, aromatic *m*-H) and 9.10 (br, 2 H, NH).

Bis(tert-*butylimido*)*bis*[N-tert-*butyl*-N′-2,6-*dichlorophenylureato*(1−)-κN,O]*chromium*(VI) **4**.—To compound **3** (1.0 g, 1.9 mmol) in hexane (40 cm^3) was added an excess of Bu^tNCO (3.4 cm^3, 29 mmol) and the mixture refluxed for 12 h. Work-up as for **2** gave a microcrystalline solid. Yield: 0.6 g, 45%. Mass spectrum: *m*/*z* 714 (M^+) and 453 [$M^+ - Bu^tHNC(O)NH(C_6H_3Cl_2)$]. IR: 3352 (NH) and 1541 cm^{-1} (CO). ^1H NMR (C_6D_6, 20 °C), δ 1.16 (s, 18 H, ureato $NHBu^t$), 1.49 (s, 18 H, imido NBu^t), 4.20 (br, 2 H, NH) and 7.05 (m, 6 H, aromatic H).

(tert-*Butylamido*)(tert-*butylimido*)*trichloro*(N,N′-*di*-tert-*butylurea*-κO)*tungsten*(VI) **5**.—To $\overline{W[N(Bu^t)C(O)}(NHBu^t)]_2(NBu^t)_2$[1] (0.7 g, 1.0 mmol) in Et_2O (20 cm^3) at −78 °C was added an excess of a 1.0 mol dm^{-3} solution of HCl in Et_2O (5.0 cm^3) and the mixture allowed to warm to room temperature. After stirring (2 h) and removal of volatiles, extraction of the residue with CH_2Cl_2 (3 × 10 cm^3) gave a yellow solution which after concentration (to *ca.* 10 cm^3), filtration and cooling (−20 °C) gave rod-shaped crystals. Yield: 0.3 g, 47%. IR: 3458, 3326, 3269 (NH), 1615s, 1567, 1265s, 1205s, 1118m, 1048m, 802m and 752; ($CHCl_3$) 3460 (NH) and 1615 cm^{-1} (CO). ^1H NMR ($CDCl_3$, 25 °C), δ 1.43 [s, 18 H, $(Bu^tNH)_2CO$], 1.53 (s, 9 H, $NHBu^t$), 1.63 (s, 9 H, imido NBu^t), 4.2 (br, 1 H, $NHBu^t$) and 5.0 (br, 2 H, urea NH).

Bis(*azido*)*bis*(tert-*butylimido*)*chromium*(VI) **6**.—To freshly sublimed $Cr(NBu^t)_2(NHBu^t)_2$ (0.5 g, 1.5 mmol) in hexane (30 cm^3) was added $SiMe_3(N_3)$ (2.0 g, 17.3 mmol) and the solution refluxed for 12 h. On cooling, red needle crystals were obtained. Yield: 0.24 g, 58%. A second crop of crystals was obtained after concentration of the filtrate and cooling; overall yield *ca.* 90%. Mass spectrum: *m*/*z* 278 (M^+). IR: 2084 cm^{-1} (N_3). ^1H NMR ($CDCl_3$, 20 °C), δ 1.66 (s, 18 H, NBu^t).

Bis(μ-*azido*)-*bis*[*azido*(tert-*butylamine*)*bis*(tert-*butylimido*)-*tungsten*(VI)] **7**.—To $W(NBu^t)_2(NHBu^t)_2$ (1.0 g, 2.1 mmol) in hexane was added $SiMe_3(N_3)$ (3.7 g, 32 mmol). Work-up as for compound **6** gave a yellow precipitate which was collected, washed with hexane (10 cm^3) and extracted into CH_2Cl_2 (20 cm^3). After filtration and concentration (*ca.* 5 cm^3) addition of hexane (10 cm^3) and cooling (−20 °C) gave yellow crystals. Yield: 0.9 g, 45%. Mass spectrum (FAB): *m*/*z* 966 (M^+), 924 ($M^+ - N_3$) and 851 ($M^+ - Bu^tNH_2$). IR: 2093 (N_3) and 2049 cm^{-1} (N_3). ^1H NMR ($CDCl_3$, 20 °C), δ 1.37 (s, 9 H, Bu^tNH_2), 1.45 (s, 18 H, NBu^t) and 4.43 (br, 2 H, NH_2).

X-Ray Crystallography.—Crystals of all complexes were sealed under argon in thin-walled glass capillaries. Cell dimensions and one hemisphere of intensity data were recorded using a FAST TV area detector diffractometer following previously described procedures.[19] The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. An absorption correction was made in all cases using DIFFAST.[20] For two of the structures, refinement was not straightforward. Complex **1**, which crystallises in space group $P2_1$, has approximate mirror symmetry and the molecule lies in the unit cell such that the mirror plane is perpendicular to the *b* axis. This produced significant correlation effects and as a result the co-ordinates and associated bond lengths and angles of atoms related by this pseudo-mirror have high estimated standard deviations (e.s.d.s). It was not necessary to incorporate any restraints or contraints to core atoms to achieve stable

Table 10 Fractional atomic coordinates (× 10^4) for compound **7**

Atom	*x*	*y*	*z*
W(1)	896(1)	797(1)	461.5(3)
W(2)	4 519.2(4)	9 717(1)	9 134.1(3)
N(11)	−107(8)	1 014(12)	−390(5)
N(14)	1 482(9)	75(13)	1 110(6)
N(01)	−140(9)	1 955(12)	−771(6)
N(011)	−202(11)	2 808(15)	−1 137(7)
N(121)	1 724(12)	−351(14)	−347(8)
N(122)	2 238(14)	−234(21)	−524(11)
N(21)	5 387(8)	8 963(11)	9 979(6)
N(23)	3 865(9)	8 498(12)	9 601(6)
N(24)	3 801(9)	10 728(12)	8 685(6)
N(25)	4 719(9)	8 416(12)	8 632(6)
N(02)	5 489(9)	8 169(12)	9 938(6)
N(022)	6 279(12)	7 389(16)	9 889(8)
N(221)	5 416(10)	11 790(15)	8 686(7)
C(13)	193(12)	2 247(16)	1 501(7)
C(131)	−454(14)	3 126(20)	1 523(9)
C(132)	890(12)	3 052(17)	1 802(7)
C(133)	161(14)	797(17)	1 818(8)
C(14)	2 131(14)	−471(19)	1 540(10)
C(141)	2 303(21)	−1 779(28)	1 383(16)
C(142)	2 625(23)	539(33)	1 753(18)
C(143)	1 939(19)	−705(29)	2 189(11)
C(15)	1 618(9)	3 806(12)	182(6)
C(151)	1 795(13)	3 709(20)	−433(10)
C(152)	2 275(12)	4 019(17)	750(8)
C(153)	1 035(13)	5 019(15)	162(9)
C(23)	3 621(11)	6 972(15)	9 496(7)
C(231)	3 125(12)	6 831(17)	8 865(8)
C(232)	4 311(13)	6 045(15)	9 603(11)
C(233)	3 242(13)	6 557(18)	9 968(9)
C(24)	3 227(11)	11 471(16)	8 217(6)
C(241)	2 862(15)	12 531(23)	8 516(10)
C(242)	2 829(21)	10 532(28)	7 837(16)
C(243)	3 603(19)	12 352(31)	7 826(15)
C(25)	4 898(12)	7 675(18)	8 142(7)
C(251)	5 245(21)	6 394(29)	8 328(12)
C(252)	5 289(21)	8 573(31)	7 870(14)
C(253)	4 269(19)	7 383(32)	7 650(13)
N(12)	1 224(9)	−534(12)	−182(6)
N(13)	159(8)	1 949(11)	850(5)
N(15)	1 254(10)	2 436(13)	263(6)
N(22)	5 345(9)	11 157(13)	9 096(7)
N(222)	5 513(12)	12 428(18)	8 288(9)

refinement. The biuret molecule in this structure has no special orientation, and this counteracts the pseudo-symmetry in the other component. As mentioned in the discussion, however, bond-length constraints were applied for some C–C bonds in the strongly oscillating or disordered Bu^t groups. For compound **7**, normal anisotropic refinement produced physically unreasonable ellipsoids for some atoms and it was necessary to incorporate isotropic refinement for these. We could not identify any obvious reason for these problems which were present before and after absorption correction. It is pertinent that analogous features occurred in a set of data recorded using a different crystal and a CAD4 diffractometer. The structure contains two independent centrosymmetric molecules, and there is no obvious pseudo-symmetry.

Crystal data and other experimental details are given in Table 6, fractional atomic coordinates in Tables 7–10.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Croucher Foundation, Hong Kong, for a postdoctoral Fellowship (to H. L.), and the SERC for provision of X-ray facilities.

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Received 30*th September* 1992; *Paper* 2/05259H