Bis(organoimido)-complexes of Tungsten(VI): The Crystal and Molecular Structures† of Tetrachlorobis(t-butylamine)bis(t-butylimido)bis(μ-*p*-tolylimido)-ditungsten(VI) and Tetrachlorobis(μ-phenylimido)-bis(t-butylamine)bis(t-butylimido)ditungsten(VI)

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The tungsten(VI) organoimido complexes $[\{WCl_4(NR)\}_2]$ (R = Ph, C_6H_4Me-*p*, Pr^i, or Me) were treated with the silylamines Me_3SiNHR'' (R'' = Ph, Bu^t, Pr^i, or Et) to form the dimeric complexes $[\{WCl_2(NR)(NR'')(NH_2R'')\}_2]$, containing terminal and bridging organoimido ligands, *cis*-oriented chloro ligands, and co-ordinated amine. $[\{WCl_2(NPh)(NBu^t)(NH_2Bu^t)\}_2]$ was also obtained from the reaction of $[\{WCl_4(NPh)\}_2]$ with NH_2Bu^t. Spectral studies suggest that these complexes arise from two *cis*-oriented organoimido groups by an inter-ligand proton-transfer process which proceeds regardless of the size of the group R. The structure of $[\{WCl_2(NC_6H_4Me\text{-}p)(NBu^t)(NH_2Bu^t)\}_2]$ was determined by *X*-ray crystallography and shown to have distorted edge-shared bioctahedral geometry with terminal t-butylimido groups and bridging unsymmetrical arylimido groups and with the longer W–N bridge bonds *trans* to the terminal t-butylimido group. The t-butylamine ligands are involved in intramolecular N–H ··· Cl bridging within the dimeric unit, which explains some striking features found in the ^1H n.m.r. spectrum. Full details are also given of the crystal structure of $[\{WCl_2(NPh)(NBu^t)(NH_2Bu^t)\}_2]$.

Although complexes of Group 6 transition metals containing *cis*-dioxo ligands are well known,[1] comparatively less is known about the isoelectronic bis(organoimido) species containing the $M(NR)_2$ (R = alkyl or aryl) unit.[2] Since the organoimido group may function as a two-electron donor with a 'bent' configuration (MNC < 180°) or as a four-electron donor $M{\equiv}NR$ with a linear configuration, the two organoimido ligands could contribute four, six, or eight electrons with interesting stereochemical consequences. In addition, the organoimido groups can act as bridging ligands to two (μ) or three (μ_3) different metals, thereby forming dinuclear or trinuclear complexes.

To date a few bis(organoimido) complexes of Group 6 metals have been isolated, including $[M(NBu^t)_2(OSiMe_3)_2]$ (M = Cr, W, or Mo)[3] and $[Mo(NPh)_2(S_2CNEt_2)_2]$.[4] In the latter complex one phenylimido group is considerably bent (MNC 139°) and the other is closer to linear (MNC 169°), in keeping with the 18-electron configuration for the molybdenum. Dimers containing both bridging and terminal organoimido groups have been structurally identified in $[\{M(NBu^t)(\mu\text{-}NBu^t)Me_2\}_2]$ (M = Mo or W)[5,6] and $[\{Mo(NR')(\mu\text{-}NR')(OBu^t)_2\}_2]$ (R′ = Ph or C_6H_4Me-*p*)[7] in both of which the metals are five-co-ordinated and the bridges are markedly unsymmetrical. *X*-Ray studies showed that $[W(NBu^t)_2(NHBu^t)_2]$ is mononuclear; a full structural analysis was precluded by disorder, although n.m.r. studies showed that the two imido groups are equivalent in solution, perhaps due to fluxional behaviour.[8] Other known bis(organoimido)tungsten(VI) complexes include $[W(NEt)_2(NEt_2)_2]$[9] and $[W(NBu^t)_2(pfp)(NH_2Bu^t)]$ (H_2pfp = perfluoropinacol),[10] the latter having been structurally characterised. These compounds were obtained using a variety of synthetic approaches but no general preparative method for synthesizing bis(organoimido)metal complexes has yet emerged.

Recently we reported that mono-organoimidotungsten complexes may conveniently be prepared from the reactions of $WOCl_4$ with organic isocyanates[11] and that for niobium and tantalum the complexes $[MCl_3(NR)(NH_2R)_2]$ could be obtained from reactions of the pentachlorides with the silylamines Me_3SiNHR (R = Et, Pr^i, or Bu^t).[12] It seemed reasonable to apply these methods to the synthesis of bis(organoimido)tungsten(VI) complexes and we report here the results of these investigations. A preliminary account of one of the complexes has already been published.[13]

Results and Discussion

Dimeric Complexes.—Reactions involving WO_2Cl_2 or $[WO_2Cl_2L_2]$ with organic isocyanates did not produce the desired bis(organoimido)tungsten compounds but the dimeric compound $[\{WCl_4(NPh)\}_2]$ reacted with either NH_2Bu^t or $Me_3SiNHBu^t$ to form $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$ (1) as orange-yellow crystals. The ^1H n.m.r. spectrum of (1) gave two equally intense singlets for the Bu^t protons and surprisingly an AX pattern for an NH_2 group with doublets at δ 3.38 and 6.26 (Table 1). In the ^{13}C spectrum, the two resonances at δ 55.49 and 71.95 could be assigned to the quaternary carbons of NH_2Bu^t and NBu^t respectively.

The difference $\delta_\alpha - \delta_\beta$ (Δ) obtained from the ^{13}C n.m.r. spectra of t-butylimidometal complexes has been used as an indication of the electron density on the nitrogen.[14] The quartenary resonance, δ_α, of the NBu^t group is shifted downfield by a decrease in electron density on the nitrogen and in compound (1) both δ_α and Δ (41.4) are larger than in other bis(t-butylimido)tungsten(VI) compounds, $[W(NBu^t)_2X_2]$ (X = $NHBu^t$ or $OSiMe_3$), referred to above. This suggests a greater degree of triple bond character ($W{\equiv}NBu^t$) in compound (1). The ^1H n.m.r. spectrum at 400 MHz revealed $^1J(^{15}NH)$ coupling of 67 Hz in the NH_2 group and enabled us to determine the ^{15}N resonance as δ 52.5 using the INEPT

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Physical data for bis(organoimido) complexes of tungsten(VI)

			Analysis^b (°C)			I.r. (ν/cm^{-1})			
Dimeric complex^a	Colour	M.p. (°C)	C	H	N	ν(NH)	ν(W–Cl)	^{1}H N.m.r.^{c,d}	^{13}C N.m.r.^{d,e}
(**1**) $[\{WCl_2(NPh)(NBu^t)(NH_2Bu^t)\}_2]\cdot\frac{1}{6}C_6H_6$	Yellow	85—90 (decomp.)	35.5 (35.8)	5.7 (5.2)	8.5 (8.4)	3 250, 3 140	308, 265 (*cis*)	1.28, 1.37 (2 s, 18 H, Bu^t); 3.38, 6.26 (br d, NH_2); 6.80—7.50 (m, 5 H, Ph)	30.0 (Me_3); 55.49 (NH_2C); 71.95 (N–C, terminal); 120.6 (*o*-Ph); 124.8 (*p*-Ph); 127.2 (*m*-Ph); 162.9 (*i*-NPh, bridge)
(**2**) $[\{WCl_2(NC_6H_4Me\text{-}p)(NBu^t)(NH_2Bu^t)\}_2]\cdot 1.6CHCl_3$	Yellow		31.7 (31.6)	4.6 (4.6)	7.0 (7.0)	3 248, 3 144, 3 077	307, 268 (*cis*)	1.29 (s, 9 H, Bu^t); 1.34 (s, 9 H, CMe_3); 2.26 (s, 3 H, Me); 3.35 [d, 1 H, ^2J(HH) 12, NH]; 6.22 [d, 1 H, ^2J(HH) 12, NH]; 6.79, 7.21 [AB, 4 H, J(AB) 8, C_6H_4]	
(**3**) $[\{WCl_2(NPh)_2(NH_2Ph)\}_2]\cdot\frac{1}{6}C_6H_6$	Yellow	178—180	42.6 (42.0)	3.2 (3.3)	7.7 (7.7)	3 275, 3 150	308, 260 (*cis*)	3.80 (s, br, 1 H, NH); 6.35—7.40 (m, 16 H, Ph and NH)	116.1, 119.6, 121.3, 122.4, 122.9, 126.3, 127.3, 128.2, 144.8 (*i*-NH_2Ph); 145.6 (*i*-NPh, terminal); 163.4 (*i*-NPh, bridge)
(**4**) $[\{WCl_2(NPh)(NCHMe_2)(NH_2CHMe_2)\}_2]\cdot\frac{5}{6}C_6H_6$	Orange-yellow	114 (decomp.)	35.1 (35.2)	4.4 (4.8)	8.9 (8.5)	3 245, 3 145	310, 265 (*cis*), 305, 278	1.20 (d, 12 H, Me_2); 3.10—3.70 (m, 1 H, NH_2CH); 4.80—5.40 (m, 1 H, NCH); 6.60—7.55 (m, 5 H, Ph); 8.15 (s, br, 2 H, NH_2)	22.6, 23.3, 24.7 (Me_2); 51.0, 51.9 (NH_2CH); 64.5 (NCH); 120.6, 121.3, 125.1, 125.8, 127.4, 127.7, 129.2 (Ph); 151.2 (*i*-NPh, terminal); 163.0 (*i*-NPh, bridge)
(**5**) $[\{WCl_2(NPh)(NEt)(NH_2Et)\}_2]\cdot\frac{1}{3}C_6H_6$	Yellow	105 (decomp.)	29.6 (29.6)	4.1 (4.1)	9.5 (9.4)	3 240, 3 190	312, 280 (*cis*)	0.90—1.60 (2 t, 6 H, Me); 2.75—4.05 (m, 3 H, NH_2CH_2 and NH); 4.40—5.15 (m, 2 H, NCH_2); 6.55—7.60 (m, 6 H, Ph and NH)	17.6 (Me); 57.8 (NH_2CH_2); 63.9 (NCH_2); 127.8 (*o*-Ph) 128.3 (*m*-Ph); 129.2 (*p*-Ph); 151.1 (*i*-NPh, terminal)
(**6**) $[\{WCl_2(NCHMe_2)_2(NH_2CHMe_2)\}_2]$	Pale yellow	118—121	25.5 (25.3)	5.3 (5.4)	9.4 (9.8)	3 225, 3 175	310, 250 (*cis*)	1.12—1.75 (2 d, 18 H, Me_2); 3.10—3.70 (m, 1 H, NH_2CH); 4.55—5.75 (m, br, 3 H, NCH and NH), 6.75 (br, 1 H, NH)	22.8, 23.7, 24.2, 24.8, 27.1 (Me_2); 52.0 (NH_2CH); 64.8 (NCH)
(**7**) $[\{WCl_2(NCHMe_2)(NBu^t)(NH_2Bu^t)\}_2]\cdot\frac{1}{3}C_6H_6$	Colourless	250 (decomp.)	30.3 (30.7)	6.4 (6.1)	8.8 (9.0)	3 200, 3 150	310, 270 (*cis*)	1.25 (d, 6 H, Me_2); 1.40 (s, 9 H, Bu^t); 1.56 (s, 9 H, Me_3); 3.68 (br, NH); 4.62—5.60 (m, 1 H NCH); 6.74 (br, NH)	24.6, 25.1 (Me_2); 30.9 (Me_3) 54.9 (NH_2C); 67.8 (NCH); 69.2 (NC)
(**8**) $[\{WCl_2(NCHMe_2)(NEt)(NH_2Et)\}_2]$	Colourless	138—141 (decomp.)	20.9 (21.0)	4.6 (4.8)	10.6 (10.5)	3 225, 3 175	308, 260 (*cis*)	1.10—1.70 (m, 12 H, Me and Me_2); 2.90—3.80 (m, 3 H, NH_2CH_2 and NH); 4.60—5.50 (m, br, 2 H, NCH and NH); 5.90—6.35 (q, 2 H, NCH_2)	15.9, 17.9, 19.7, 20.0 (Me); 23.0, 24.2 (Me_2); 44.9, 45.5 (NH_2CH_2); 63.8, 66.5, 67.4 (NCH_2 and NCH)
(**9**) $[\{WCl_2(NMe)(NBu^t)(NH_2Bu^t)\}_2]$	Colourless	167—173 (decomp.)	25.1 (25.3)	4.8 (5.4)	9.6 (9.8)	3 240, 3 180	310, 264 (*cis*)	1.40 (s, 9 H, Bu^t); 1.60 (s, 9 H, Bu^t); 2.80—3.60, 5.63—5.90 (br, 2 H, NH_2); 6.00 (s, 3 H, NMe)	29.5, 30.9 (Me_3); 54.6 (NH_2C); 62.9 (NMe); 70.3 (NC)
(**10**) $[\{WCl_2(NMe)(NCHMe_2)(NH_2CHMe_2)\}_2]\cdot\frac{1}{3}C_6H_6$	Pale yellow	114—118 (decomp.)	23.3 (23.3)	5.2 (4.9)	9.9 (10.2)	3 235, 3 100	305, 260 (*cis*)	1.05—1.60 (overlapping d, 12 H, Me_2); 2.9 (br, NH); 3.10—3.75 (m, 1 H, NH_2CH); 4.50—5.50 (m, 1 H, NCH); 6.04 (s, 3 H, NMe); 8.00—8.40 (br, NH)	21.4, 22.5, 23.6, 24.4, 25.4 (Me_2); 51.9 (NH_2CH); 62.1 (NMe); 64.1 (NCH)

[a] Inclusion of solvent molecules supported by n.m.r. spectra. [b] Calculated values given in parentheses. [c] Spectra obtained in $CDCl_3$. [d] br = Broad, m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [e] C_6H_6 assignments: *ortho*, *meta*, tentative (*meta* based on δ 128.5) *para* made from relative peak height.

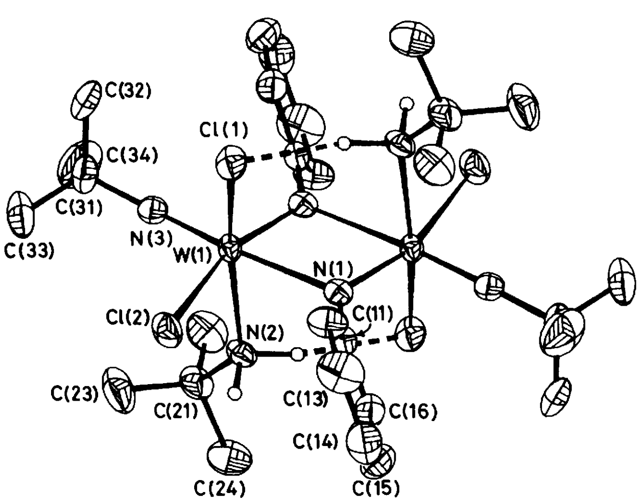

Figure 1. Molecular structure of (1)

technique. This is similar to the value (δ 66.1) obtained for the co-ordinated $\mathrm{NH_2Bu^t}$ in $[\{\mathrm{WCl_2(NHBu^t)(NH_2Bu^t)}\}_2]$.[15]

Although ^{15}N resonances for the organoimido nitrogen in (**1**) could not be obtained, the ^{14}N n.m.r. spectrum gave a signal at δ 404 which is in the region characteristic of terminal, linear organoimido groups.[16,17] In the ^{13}C n.m.r. spectrum of (**1**) the phenylimido *ipso*-carbon resonance occurred at δ 162.9, which is downfield from that found previously for terminal phenylimido ligands (*ca.* δ 148),[18] and in view of the crystal structure determination[13] it appears that δ 162.9 corresponds to the chemical shift for a μ-bridging phenylimido group. The i.r. spectrum of (**1**) gave two N–H stretching frequencies (3 250 and 3 140 cm^{-1}), confirming non-equivalence of the $\mathrm{NH_2}$ protons whilst two W–Cl stretching vibrations (308 and 265 cm^{-1}) suggested a *cis*-dichloride configuration.[19] These spectroscopic data are all consistent with the dimeric molecular structure (Figure 1).

The *p*-tolylimido derivative $[\{\mathrm{WCl_2(\mu\text{-}NC_6H_4Me\text{-}}p\mathrm{)(NBu^t)(NH_2Bu^t)_2}\}_2]$ (**2**) was obtained by the reaction of $[\{\mathrm{WCl_4(NC_6H_4Me\text{-}}p\mathrm{)}\}_2]$ and $\mathrm{Me_3SiNHBu^t}$ and its crystal structure (Figure 2) showed that, as in (**1**), the arylimido groups are μ-bridging and the t-butylimido groups terminal. The relevant bond distances and bond angles for (**1**) and (**2**) are given in Table 2. In both molecules the overall edge-shared bioctahedral geometry is considerably distorted and the arylimido bridges are markedly unsymmetrical with the longer W–NR′ (R′ = Ph or $\mathrm{C_6H_4Me\text{-}}p$) bond being *trans* to the terminal t-butylimido group. The tungsten atoms are displaced out of the plane containing the two chlorines towards the t-butylimido nitrogen. Short W–N distances and large WNC angles for the $\mathrm{NBu^t}$ groups indicate a considerable degree of π interaction with high triple-bond character (four-electron donor). The bridging arylimido groups can be considered as forming a double bond to one tungsten and a dative bond to the other, the longer W←NR′ distances being greater than the $\mathrm{W \leftarrow NH_2Bu^t}$ distances. The W=NR′ double bonds exert a *trans* influence on the W–Cl bond in the equatorial plane of the molecules. The W–Cl(2) distances of 2.470(5) Å in compound (**2**) can be compared with the W–Cl distance *trans* to the linear *p*-tolylimido group in $[\mathrm{WCl_5(NC_6H_4Me\text{-}}p\mathrm{)}]^-$ of 2.465(5) Å.[16] The orientation of the $\mathrm{NH_2Bu^t}$ ligands with one N–H bond towards the opposite axial chlorine and N···Cl distances which are slightly less than the sum of the van der Waals radii for these atoms suggest that N–H···Cl hydrogen bonding is occurring across the dimers. This would account for the relatively low-field chemical shift of one of the $\mathrm{NH_2}$ protons in the ^{1}H n.m.r. spectra of (**1**) and (**2**). Similar interactions across binuclear species have been observed in $[\{\mathrm{WCl_2(NHBu^t)(NH_2Bu^t)}\}_2]$ (N–H···Cl)[15] and $[\{\mathrm{WCl_2(OR)_2(ROH)_2}\}_2]$ (RO–H···OR).[20]

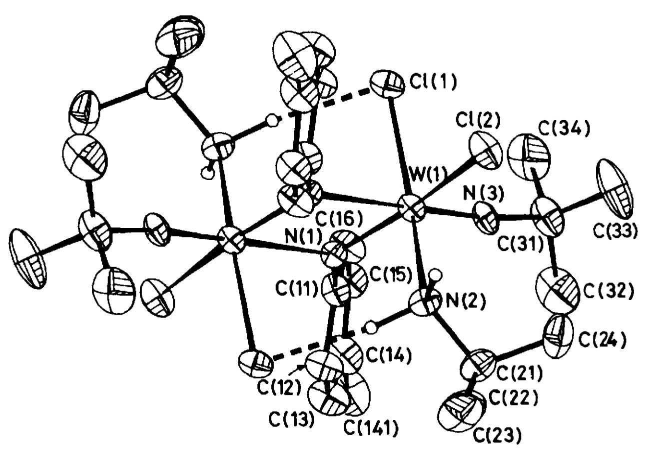

Figure 2. Molecular structure of (2)

Table 2. Selected bond lengths (Å) and angles (°) for complexes (**1**) and (**2**)

	(1)	(2)
W–Cl(1)	2.396(3)	2.403(5)
W–Cl(2)	2.463(4)	2.470(5)
W–N(1)	2.317(6)	2.293(9)
W–N(1a)	1.890(6)	1.870(9)
W–N(2)	2.210(6)	2.236(10)
W–N(3)	1.736(7)	1.729(10)
Cl(1)–W(1)–Cl(2)	86.4(2)	86.3(2)
N(1)–W(1)–Cl(1)	85.8(2)	86.3(3)
N(1)–W(1)–Cl(2)	86.7(3)	87.4(3)
N(1)–W(1)–N(1a)	76.3(3)	75.1(3)
N(1a)–W(1)–Cl(1)	97.9(3)	97.5(3)
N(1a)–W(1)–Cl(2)	161.6(2)	161.8(2)
N(1a)–W(1)–N(2)	92.1(3)	92.9(3)
N(1a)–W(1)–N(3)	100.3(2)	102.5(3)
N(2)–W(1)–Cl(1)	158.8(2)	158.6(2)
N(2)–W(1)–Cl(2)	78.6(2)	78.3(3)
N(2)–W(1)–N(1)	78.5(3)	78.3(4)
N(3)–W(1)–Cl(1)	93.3(2)	92.1(4)
N(3)–W(1)–Cl(2)	97.3(3)	95.2(4)
N(3)–W(1)–N(1)	175.8(2)	176.9(3)
N(3)–W(1)–N(2)	103.3(3)	103.9(5)
W(1)–N(1)–C(11)	126.0(4)	126.4(7)
W(1)–N(1a)–C(1a)	130.1(4)	128.7(7)
W(1)–N(2)–C(21)	128.9(5)	130.1(7)
W(1)–N(3)–C(31)	169.3(5)	172.8(8)
W(1)–N(1)–W(1a)	103.7(3)	104.9(5)

Hydrogen-1 n.m.r. studies of the reaction between $[\{\mathrm{WCl_4(NR')}\}_2]$ (R′ = Ph or $\mathrm{C_6H_4Me\text{-}}p$) and two equivalents of $\mathrm{Me_3SiNHBu^t}$ in $\mathrm{CDCl_3}$ show the initial formation of $\mathrm{Me_3SiCl}$ with broad resonances in the region for NH and t-butyl peaks. This suggests the formation of intermediates containing $\mathrm{NHBu^t}$ groups and this was confirmed by a ^{13}C n.m.r. spectrum obtained after the addition of silylamine, which showed a resonance at 63 p.p.m. characteristic of t-butylamino groups. The ^{1}H n.m.r. spectra of the yellow precipitate formed in the reactions carried out in toluene and discussed above were also indicative of a mixture of compounds containing $\mathrm{NHBu^t}$ groups. The first stages of the reaction appear to be as in equations (1)—(3). The formation of $[\{\mathrm{WCl_2(\mu\text{-}NR')(NBu^t)(NH_2Bu^t)}\}]$ by α-H exchange as in equation (4) could then

$$[\{WCl_4(NR')\}_2] + 2Me_3SiNHBu^t \longrightarrow 2[WCl_4(NR')\{NHBu^t(SiMe_3)\}] \tag{1}$$

$$[WCl_4(NR')\{NHBu^t(SiMe_3)\}] \longrightarrow [WCl_3(NR')(NHBu^t)] + Me_3SiCl \tag{2}$$

$$[WCl_3(NR')(NHBu^t)] + Me_3SiNHBu^t \longrightarrow [WCl_2(NR')(NHBu^t)_2] + Me_3SiCl \tag{3}$$

$$2[WCl_2(NR')(NHBu^t)_2] \xrightarrow{\Delta} [\{WCl_2(NR')(NBu^t)(NH_2Bu^t)\}_2] \tag{4}$$

(1) $R' = Ph$

(2) $R' = C_6H_4Me$-*p*

occur when the reaction mixture is heated, or stirred for a longer period. A similar α-H exchange occurs in the equilibrium (5)

$$[W(NBu^t)_2(NH_2Bu^t)\{OC(Y)_2C(Y)_2O\}] \rightleftharpoons [W(NBu^t)(NHBu^t)_2\{OC(Y)_2C(Y)_2O\}] \tag{5}$$

where the position of the equilibrium depends on the electronic properties of Y. When Y = CF_3, the equilibrium lies towards the bis(t-butylimido) compound whereas the predominant species in solution when Y = Ph or Me is the bis(t-butylamido) compound.[21] This is consistent with the formation of **(1)** and **(2)** in reaction (4) where the less π-donating chlorines favour the formation of the bis(imido) compound. With two organoimido groups a maximum of three π bonds is possible and it is the arylimido group which adopts a bent geometry and bridges another tungsten.

The dialkylamido ligands in $[TaCl_3(NMe_2)(NHMe_2)]$ and $[\{TaCl_2(NMe_2)_3\}_2]$ are oriented *cis* due to their high *trans* influence,[22] so that a *cis*-bis(amido) precursor is preferred in the above reactions. The presence of *cis*-orientated t-butylamido ligands should then allow proton transfer to form the t-butylimido and -amine ligands, reaction (4), as well as give rise to *cis*-orientated dichloro ligands.

The use of bulky groups to achieve inter-ligand proton transfer is well known in metal–carbon bond chemistry where neopentyl or trimethylsilylmethyl groups generate alkylidene ligands (M=CHR) (R = Bu^t or $SiMe_3$) when suitable steric congestion is present.[23] Clearly the environment is less cluttered in the present case but an NH proton is more acidic than a CH proton so it was of interest to establish whether less bulky amido precursors would also generate the imido linkage.

Reactions between four equivalents of the silylamines Me_3SiNHR (R = Ph, $CHMe_2$, or Et) and the tetrachloro(phenylimido)tungsten dimer similarly led to darkening of the solution and precipitation of the complexes $[\{WCl_2(NPh)(NR)(NH_2R)\}_2]$ which were assigned structures on the basis of spectral analogies to $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$ (Table 3). In particular, the ^{13}C n.m.r. spectrum of $[\{WCl_2(NPh)(\mu\text{-}NPh)(NH_2Ph)\}_2]$ **(3)** showed *ipso*-carbon resonances at δ 163.4 and 145.6, characteristic of bridging and terminal phenylimido ligands, while the *ipso*-carbon resonance of co-ordinated aniline appeared at 144.8. In the i.r. spectrum inequivalent NH proton bands occurred at 3 275 and 3 150 cm^{-1} while *cis*-dichloro ligands were indicated by absorptions of equal intensity at 308 and 260 cm^{-1}.

$[\{WCl_2(NPh)(NCHMe_2)(NH_2CHMe_2)\}_2]$ **(4)** showed *ipso*-carbon resonances at δ 163.0 and 151.2 and two isopropylamine methine-carbon resonances at δ 51.9 and 51.0, indicating a mixture of isomers and thus no preference in the complex for bridging and terminal ligands. The isopropylimido methine carbon was not resolved into two resonances. For $[\{WCl_2(NPh)(NEt)(NH_2Et)\}_2]$ **(5)** an *ipso*-carbon resonance at δ 151.1 and single resonances for the ethylimido and amine ligands suggested only one isomer where the phenylimido ligand is terminal. Both the isopropyl and ethyl complexes exhibited *cis*-dichloro ligands in the i.r. spectra, the former showing two sets of bands which is consistent with the isomeric mixture proposed.

Table 3. Crystal data for complexes (1) and (2)

Compound	**(1)**	**(2)**
Formula	980.26	1 486.03
M	$C_{28}H_{48}Cl_4N_6W_2\cdot\frac{1}{6}C_6H_6$	$C_{30}H_{52}Cl_4N_6W_2\cdot 1.6CHCl_3$
Crystal system	Monoclinic	Triclinic
a/Å	10.063(3)	10.303(4)
b/Å	14.189(3)	11.466(4)
c/Å	13.287(3)	12.813(3)
α/°	90.0	91.408(3)
β/°	97.40(2)	101.173(2)
γ/°	90.00	105.145(4)
U/Å^3	1 881.4	1 428.9
Space group	$P2_1/n$	$P\bar{1}$
Z	2[a]	1[a]
D_c/g cm^{-3}	1.730	1.727
μ/cm^{-1}	65.55	45.78
F(000)	952	724
Data collection		
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 28	1.5, 27
Total data	4 962	6 496
Total unique	3 363	6 226
Total observed [$I > 1.5\sigma(I)$]	3 168	5 196
Refinement		
No. of parameters	184	301
Weighting scheme coefficient g[b]	0	0.0004
Final R	0.031	0.0404
Final R'	0.033	0.0421

[a] Both dimers are sited on centres of symmetry. [b] $w = 1/[\sigma^2(F_o) + gF_o^2]$.

Further reactions of various silylamines with the organoimido complexes $[\{WCl_4(NR)\}_2]$ (R = $CHMe_2$ or Me) also gave complexes consistent with the formulation $[WCl_2(NR)(NR'')(NH_2R'')]$ (R'' = Bu^t, $CHMe_2$, or Et) based on their spectral characteristics. In particular the ^{13}C n.m.r. spectrum of $[\{WCl_2(NCHMe_2)(NBu^t)(NH_2Bu^t)\}_2]$ **(7)** showed resonances pertaining to a single isomer in which the t-butylimido ligand is expected to be terminal based on $[\{WCl_2(\mu\text{-}NPh)(NBu^t)(NH_2Bu^t)\}_2]$ **(1)**.[13] In contrast to the *ipso*-carbon resonances distinguishing between bridging and terminal modes in $[\{WCl_2(NPh)(\mu\text{-}NPh)(NH_2Ph)\}_2]$ **(3)**, the methine-carbon resonances of $[\{WCl_2(NCHMe_2)(\mu\text{-}NCHMe_2)(NH_2CHMe_2)\}_2]$ **(6)** appear as a single resonance. $[\{WCl_2(NCHMe_2)(NEt)(NH_2Et)\}_2]$ **(8)** showed several isopropylimido methine-carbon resonances, several ethylamine methylene-carbon resonances, and only one ethylimido methylene-carbon resonance, consistent with no particular preference for the bridging organoimido ligand.

A single resonance in the ^{13}C n.m.r. spectrum for each of the imido and amine α-carbon resonances of $[\{WCl_2(NMe)(NBu^t)(NH_2Bu^t)\}_2]$ **(9)** suggests only one isomer in which a terminal t-butylimido ligand is preferred. Only one set of resonances was similarly resolved for $[\{WCl_2(NMe)(NCHMe_2)(NH_2CHMe_2)\}_2]$ **(10)** in which a bridging methyl-

Table 4. Fractional atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	50	1 170	58	N(2)	−2 153(4)	1 037(3)	−253(4)
Cl(1)	2 248(2)	1 140(1)	997(1)	C(21)	−3 148(6)	1 612(5)	−992(6)
Cl(2)	−661(2)	1 991(1)	1 533(1)	C(22)	−2 808(8)	1 478(5)	−2 056(5)
N(1)	−311(4)	−222(3)	893(3)	C(23)	−3 087(8)	2 632(5)	−665(7)
C(11)	−718(6)	−297(4)	1 836(4)	C(24)	−4 535(7)	1 203(6)	−883(8)
C(12)	149(7)	−82(5)	2 695(5)	N(3)	387(5)	2 166(3)	−625(4)
C(13)	−287(10)	−229(6)	3 643(6)	C(31)	870(8)	3 033(5)	−1 045(7)
C(14)	−1 570(10)	−530(6)	3 724(6)	C(32)	2 372(9)	2 995(5)	−904(8)
C(15)	−2 426(9)	−705(5)	2 874(6)	C(33)	428(12)	3 868(5)	−456(10)
C(16)	−2 009(7)	−605(5)	1 937(5)	C(34)	378(10)	3 113(7)	−2 154(7)

Table 5. Fractional atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	252	57	3 763	C(31)	1 864(13)	−764(12)	2 116(10)
Cl(1)	2 101(3)	1 879(2)	4 244(2)	C(32)	1 762(18)	−2 098(13)	2 040(13)
Cl(2)	−889(3)	1 250(3)	2 495(2)	C(33)	1 360(16)	−260(16)	1 071(11)
N(1)	−712(7)	758(6)	5 033(6)	C(34)	3 359(14)	−19(16)	2 536(13)
C(11)	−1 522(9)	1 606(9)	4 897(8)				
C(12)	−961(11)	2 810(10)	4 744(10)	C(1)	6 715(21)	2 782(19)	1 068(17)
C(13)	−1 794(12)	3 608(11)	4 646(11)	Cl(11)	5 834(7)	1 422(7)	333(6)
C(14)	−3 175(11)	3 203(11)	4 685(10)	Cl(12)	6 701(11)	3 917(9)	227(8)
C(15)	−3 720(11)	1 991(11)	4 771(9)	Cl(13)	5 427(20)	2 993(20)	1 760(13)
C(16)	−2 905(10)	1 187(11)	4 902(9)	Cl(14)	6 528(20)	2 995(21)	2 175(12)
C(141)	−4 060(14)	4 090(13)	4 578(12)	C(2)	1 443(18)	3 780(16)	2 012(15)
N(2)	−1 905(8)	−1 130(7)	3 354(7)	Cl(21)	783(17)	3 529(13)	697(9)
C(21)	−2 526(12)	−2 223(12)	2 582(11)	Cl(22)	447(30)	−5 799(31)	951(29)
C(22)	−2 380(15)	−1 871(15)	1 462(10)	Cl(23)	285(20)	4 683(12)	2 469(17)
C(23)	−4 017(13)	−2 669(15)	2 660(13)	Cl(24)	1 767(27)	4 899(14)	2 871(15)
C(24)	−1 781(15)	−3 163(12)	2 946(13)	Cl(25)	2 996(12)	4 754(17)	2 433(14)
N(3)	1 056(8)	−469(8)	2 859(6)	Cl(26)	3 130(16)	3 691(16)	1 766(14)

imido ligand is preferred. In general the α-carbon resonance position for these complexes does not distinguish between bridging or terminal imido ligands.

Experimental

Preparations and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-tube techniques.[24] Hydrocarbon and ether solvents were distilled from sodium benzophenone or sodium dihydronaphthylide and stored over 4Å molecular sieves. Dichloromethane was distilled from P_4O_{10} and stored over 4Å molecular sieves. $WOCl_4$ was prepared by reaction of WO_3 with thionyl chloride;[25] tetrachloro(phenylimido)- and tetrachloro(methylimido)-tungsten(VI) were prepared by treatment of $WOCl_4$ with the corresponding isocyanate in benzene.[11,18] Trimethylsilylamines were prepared by treating trimethylsilyl chloride with two equivalents of the appropriate primary amine and distilling the product.[26]

Infrared spectra were obtained from Nujol mulls between CsI plates using Perkin-Elmer 577 or 597 spectrometers. N.m.r. spectra were obtained using Bruker WP-80 and WH-400 or JEOL FX60 spectrometers.

Elemental analyses (C, H, N) were obtained either from the Microanalytical department at University College, London or from Dr. A. C. Campbell and associates at the University of Otago, New Zealand. Physical data for the bis(organoimido) complexes are presented in Table 1.

Tetrachloro(p-*tolylimido*)*tungsten*(VI).—*p*-Tolyl isocyanate (4.7 cm^3, 37.3 mmol) and $WOCl_4$ (12.7 g, 37.2 mmol) were heated in refluxing benzene (100 cm^3) for 18 h. Brown crystals were filtered from the cooled solution, washed with benzene and dried *in vacuo*. Yield 13.7 g, 85% (Found: C, 19.6; H, 1.8; Cl, 32.9; N, 3.2%; M^+, 430.888 388. $C_7H_7Cl_4NW$ requires C, 19.5; H, 1.6; Cl, 32.9; N, 3.25%; M^+, 430.887 390). I.r.: 1 585s, 1 352m, 1 305w, 1 289w, 1 258w, 1 213w, 1 172m, 1 115w, 1 019m, 942w, 830w, 811s, 721w, 533w, 436m, 378m, 364s, 337s, 330 (sh), 318 (sh), 305w, 281w cm^{-1}.

Tetrachlorobis(μ-*phenylimido*)-*bis*(*t-butylamine*)*bis*(*t-butylimido*)*ditungsten*(VI), (**1**).—*Method* (*A*). A solution of $Me_3SiNHBu^t$ (0.8 cm^3, 4.1 mmol) in benzene (30 cm^3) was added to $[\{WCl_4(NPh)\}_2]$ (0.85 g, 1.0 mmol) suspended in benzene (30 cm^3) and the mixture was stirred for 12 h. The product was deposited as a yellow crystalline solid which was filtered off, washed with benzene (2 cm^3), cooled with ice, and dried *in vacuo*. I.r.: 3 250w, 3 140m, 3 075w, 2 720vw, 2 700vw, 1 585m, 1 580w, 1 550w, 1 470s, 1 400w, 1 360s, 1 290m, 1 240s, 1 210s, 1 184s, 1 155m, 1 070w, 1 028m, 935w, 904s, 890m, 801w, 765s, 750m, 720m, 700s, 685s, 678s, 608w, 540w, 518w, 466m, 450w, 355w, 308s, 265s cm^{-1}.

Method (*B*). A suspension of $[\{WCl_4(NPh)\}_2]$ (1.05 g, 1.26 mmol) in pentane (25 cm^3) was treated with NH_2Bu^t (0.8 cm^3, 7.61 mmol) and stirred. After 20 h a yellow solid was formed in a yellow-orange solution. The solid was filtered off, washed with toluene, then heated in toluene to give an orange-red solution which on cooling deposited crystals of (**1**) as a toluene solvate.

Tetrachlorobis(*t-butylamine*)*bis*(*t-butylimido*)*bis*(μ-p-*tolylimido*)-*ditungsten*(VI), (**2**).—A stirred suspension of $[\{WCl_4(NC_6H_4Me\text{-}p)\}_2]$ (4.2 g, 9.7 mmol) in toluene (30 cm^3) was treated with a solution of $Me_3SiNHBu^t$ (3.0 g, 19.4 mmol) in toluene (10 cm^3). After 19 h the mixture was heated to dissolve the orange-yellow solid present and then cooled in ice–water to give a yellow precipitate. The solid was filtered off, washed with toluene and dried *in vacuo* (4.0 g, 82%). Crystals suitable for *X*-ray diffraction were grown by diffusion of hexane into a chloroform solution of (**2**). I.r.: 3 248m, 3 144m, 3 077w, 1 600w, 1 552m, 1 496s, 1 400w, 1 360w, 1 290w, 1 242s, 1 231m, 1 183m, 1 156w, 1 107w, 1 028w, 1 017w, 935w, 898m, 890w, 827m, 802m, 755w, 662w, 635w, 570w, 474m, 454w, 355w, 307m, 268 cm^{-1}.

Dianilinetetrachlorobis(μ-phenylimido)bis(phenylimido)-ditungsten(VI), (**3**).—The compound $\mathrm{Me_3SiNHPh}$ (1.65 cm^3, 9.3 mmol) in benzene (30 cm^3) was added to a suspension of $[\{\mathrm{WCl_4(NPh)}\}_2]$ (1.9 g, 2.3 mmol) in benzene (50 cm^3) and the mixture was stirred for 12 h. The yellow insoluble product was filtered off, washed with benzene (5 cm^3), and dried *in vacuo*. I.r.: 3 275w, 3 150m, 3 075m, 1 600m, 1 580w, 1 560s, 1 550m, 1 540w, 1 520w, 1 490m, 1 210s, 1 140m, 1 130s, 1 070m, 1 065s, 1 020s, 1 000w, 910s, 890s, 795m, 770s, 760s, 750s, 740m, 720w, 690m, 685m, 675s, 670m, 660w, 630m, 590s, 560m, 540m, 520s, 470w, 440s, 410m, 380m, 360m, 308s, 300m, 275w, 260s, 250w cm^{-1}.

Tetrachlorobis(isopropylamine)bis(isopropylimido)bis(μ-phenylimido)-ditungsten(VI), (**4**).—To a suspension of $[\{\mathrm{WCl_4(NPh)}\}_2]$ (1.45 g, 1.7 mmol) in benzene (50 cm^3) was added $\mathrm{Me_3SiNHPr^i}$ (1.3 cm^3, 7.2 mmol) in benzene (30 cm^3) and the mixture was stirred for 14 h. The red solution was filtered, the volume reduced to *ca.* 20 cm^3 and on standing orange-yellow microcrystals of the complex were deposited which were filtered off, washed with benzene (10 cm^3), cooled with ice, and dried *in vacuo*. I.r.: 3 245w, 3 145m, 1 570m, 1 550m, 1 530m, 1 510w, 1 260s, 1 230s, 1 220s, 1 150m, 1 110w, 1 090s, 1 060s, 1 010m, 1 000w, 980w, 940w, 920w, 895s, 885s, 860w, 810m, 760s, 685s, 680s, 640w, 620m, 580s, 560s, 550m, 535w, 510s, 465s, 430w, 400w, 380w, 350w, 310s, 305s, 300s, 278s, 265s, 250m, 240m cm^{-1}.

Tetrachlorobis(ethylamine)bis(μ-ethylimido)-bis(phenylimido)ditungsten(VI), (**5**).—A solution of $\mathrm{Me_3SiNHEt}$ (1.7 cm^3, 11 mmol) in benzene (30 cm^3) was added to $[\{\mathrm{WCl_4(NPh)}\}_2]$ (1.9 g, 2.3 mmol) suspended in benzene (30 cm^3) and the mixture stirred for 12 h during which time the solution turned red-brown and the complex precipitated as a yellow microcrystalline solid. The product was filtered off, washed with benzene (5 cm^3), cooled with ice, and dried *in vacuo*. I.r.: 3 240s, 3 190m, 2 625w, 1 620w, 1 585m, 1 570m, 1 560m, 1 285m, 1 230s, 1 130w, 1 110m, 1 070m, 1 035m, 1 025m, 1 010w, 910m, 890m, 800w, 770s, 670w, 630w, 585m, 560w, 520w, 480w, 465m, 400w, 312s, 300m, 280w, 258 cm^{-1}.

Di-μ-chloro-hexachlorobis(isopropylimido)ditungsten(VI).—Isopropyl isocyanate (1.65 cm^3, 17 mmol) in benzene (20 cm^3) was added to $\mathrm{WOCl_4}$ (dimer) (5.8 g, 17.0 mmol) suspended in benzene (90 cm^3) and the mixture was refluxed for 18 h. The dark red solution was filtered while still hot and the volume reduced to *ca.* 30 cm^3. On the standing for several days dark red crystals of the product were formed which were filtered off and washed with benzene (10 cm^3). On drying *in vacuo* the material lost crystallinity leaving the complex as an orange powder, m.p. 158—160 °C (Found: C, 9.8; H, 2.1; N, 3.5. $\mathrm{C_6H_{14}Cl_8N_2W_2}$ requires C, 9.4; H, 1.8; N, 3.7%). I.r.: 1 650w, 1 580m, 1 240s, 1 230s, 1 150m, 1 105m, 1 070s, 950m, 935s, 880s, 860s, 810s, 680w, 610m, 540s, 480s, 400s, 370s, 330s, 300s, 280s cm^{-1}. ^{1}H N.m.r. ($\mathrm{CDCl_3}$): δ 1.70 (d, 6 H, $\mathrm{CH_3}$), 7.05 (septet, 1 H, CH). ^{13}C N.m.r. ($\mathrm{CDCl_3}$): δ 23.2 ($\mathrm{CH_3}$), 71.6 (CH).

Tetrachlorobis(isopropylamine)bis(μ-isopropylimido)-bis(isopropylimido)ditungsten(VI), (**6**).—A solution of $\mathrm{Me_3SiNHPr^i}$ (1.9 cm^3, 11 mmol) in benzene (20 cm^3) was added to $[\{\mathrm{WCl_4(NPr^i)}\}_2]$ (1.94 g, 2.5 mmol) in benzene (40 cm^3) and the mixture was stirred for 14 h. The green solution was filtered and the volume reduced to *ca.* 15 cm^3; on standing, the complex formed as pale yellow microcrystals which were filtered off, washed with benzene (5 cm^3), cooled with ice, and dried *in vacuo*. I.r.: 3 225m, 3 175m, 1 600m, 1 580m, 1 500w, 1 260s, 1 230s, 1 150s, 1 120s, 1 115m, 1 090s, 1 070s, 1 020m, 940m, 925m, 900m, 870m, 850s, 820s, 675m, 630s, 590s, 570m, 530w, 520m, 490w, 470m, 410s, 400m, 365m, 310s, 280w, 250m, 220s cm^{-1}.

Tetrachlorobis(μ-isopropylimido)-bis(t-butylamine)bis(t-butylimido)ditungsten(VI), (**7**).—To a solution of $[\{\mathrm{WCl_4(NPr^i)}\}_2]$ (1.7 g, 2.2 mmol) in benzene (40 cm^3) was added $\mathrm{Me_3SiNHBu^t}$ (1.8 cm^3, 9.1 mmol) in benzene (20 cm^3) and the mixture stirred for 14 h. The light green solution was filtered and the volume reduced until a colourless solid began to precipitate. On standing, the complex was obtained as colourless microcrystals which were filtered off, washed with ice-cold benzene (3 cm^3), and dried *in vacuo*. I.r.: 3 200s, 3 150s, 2 700s, 2 575s, 2 475s, 2 060s, 1 950w, 1 740w, 1 666s, 1 550m, 1 500s, 1 400s, 1 300s, 1 240s, 1 210s, 1 190m, 1 115m, 1 105w, 1 070w, 1 020w, 960m, 930s, 880s, 850s, 800m, 680m, 670w, 650w, 600w, 570w, 445s, 420w, 340s, 320m, 310w, 300w, 280w, 270m cm^{-1}.

Tetrachlorobis(ethylamine)bis(μ-ethylimido)-bis(isopropylimido)ditungsten(VI), (**8**).—A solution of $\mathrm{Me_3SiNHEt}$ (1.6 cm^3, 10.0 mmol) in benzene (20 cm^3) was added to a solution of $[\{\mathrm{WCl_4(NPr^i)}\}_2]$ in benzene (30 cm^3) and the mixture was stirred for 14 h. The complex precipitated as colourless microcrystals which were filtered off, washed with benzene (3 cm^3), cooled with ice, and dried *in vacuo*. I.r.: 3 225m, 3 175m, 1 560s, 1 540w, 1 300m, 1 280m, 1 260s, 1 225s, 1 150w, 1 125s, 1 100s, 1 065s, 1 030s, 920s, 890s, 865m, 800s, 690s, 650s, 640s, 580s, 560m, 520m, 500s, 470w, 400s, 380w, 340w, 308s, 280w, 260s cm^{-1}.

Tetrachlorobis(μ-methylimido)-bis(t-butylamine)bis(t-butylimido)ditungsten(VI), (**9**).—A solution of $\mathrm{Me_3SiNHBu^t}$ (1.8 cm^3, 9.3 mmol) in benzene (10 cm^3) was added to $[\{\mathrm{WCl_4(NMe)}\}_2]$ (1.6 g, 2.4 mmol) in benzene and the mixture was stirred for 14 h. After reducing the volume to *ca.* 10 cm^3, the colourless microcrystalline solid was filtered off, washed with benzene (2 cm^3) cooled with ice, and dried *in vacuo*. I.r.: 3 240m, 3 180m, 3 125w, 1 590m, 1 500m, 1 410m, 1 365s, 1 308s, 1 254s, 1 220s, 1 190s, 1 174m, 1 120s, 1 117s, 1 100m, 1 048w, 1 035w, 940w, 900m, 810w, 755s, 740s, 654s, 620m, 590m, 578w, 550w, 442w, 422m, 400m, 376w, 310s, 264s cm^{-1}.

Tetrachlorobis(isopropylamine)bis(isopropylimido)bis-(μ-methylimido)-ditungsten(VI), (**10**).—A solution of $\mathrm{Me_3SiNHPr^i}$ (0.5 cm^3, 2.8 mmol) in benzene (10 cm^3) was added to $[\{\mathrm{WCl_4(NMe)}\}_2]$ (0.5 g, 0.73 mmol) in benzene (40 cm^3) and the solution stirred for 14 h. The volume was reduced to *ca.* 10 cm^3 and the solution allowed to stand whereupon very pale yellow microcrystals of the complex were deposited. The product was washed with ice-cold benzene (1 cm^3) and dried *in vacuo*. I.r.: 3 235m, 3 100m, 1 600s, 1 490s, 1 365s, 1 300w, 1 258m, 1 210s, 1 158s, 1 085m, 1 014m, 935m, 800s, 720m, 680m, 670m, 460s, 410s, 370m, 305w, 260w cm^{-1}.

X-*Ray Crystallography*.—Crystals of (**1**) and (**2**) were sealed under nitrogen in thin-walled capillaries. Unit-cell parameters and intensity data were obtained using a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation as previously described.[27] Intensities were corrected for absorption on the basis of ψ-scan data.[28] The structures were solved *via* the heavy-atom method and refined by least-squares procedures. Non-hydrogen atoms were refined anisotropically, hydrogens included in calculated positions for (**1**) but experimentally located for (**2**). In both cases they were refined with group $U_{iso.}$ values (one each for phenyl, methyl, and amine). Unit weights were used for (**1**), whilst a weighting scheme $w = 1/[\sigma^2(F_o) + 0.0004\ F_o^2]$ gave good agreement analyses for (**2**). Complex (**2**) contains two disordered $CHCl_3$ molecules of crystallisation, which were represented by the central carbon and then four and six chlorine atoms with partial occupancy factors. Details of the crystal data and refinement procedures are given in Table 3. Final atomic fractional co-ordinates are given in Tables 4 and 5. Atomic scattering factors were taken from International Tables.[29]

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