Synthesis of Arylthallium Complexes using Organomercury Compounds. Crystal and Molecular Structures of $[NMe_4][Tl(C_6H_4N{=}NPh\text{-}2)Cl_3]$ and $[Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$

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The reaction of $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$ or $[Hg(C_6H_4CH_2NMe_2\text{-}2)_2]$ with $[NMe_4]_2[TlCl_5]$ (1:2) affords $[NMe_4][Tl(C_6H_4N{=}NPh\text{-}2)Cl_3]$ or $[NMe_4][Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_3]$ respectively. These two anionic complexes react with $NaClO_4$ to give the neutral compounds $[Tl(C_6H_4N{=}NPh\text{-}2)Cl_2]$ and $[Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$. The crystal structure of $[NMe_4][Tl(C_6H_4N{=}NPh\text{-}2)Cl_3]$ shows a distorted trigonal bipyramidal geometry around the thallium atom, if the rather weak interaction between thallium and the farther N atom [2.786(8) Å] is included. The nitrogen and carbon atoms occupy axial and equatorial sites, respectively, and a five-membered TlC_2N_2 ring is observed. The Tl–Cl distances are normal, with $Tl\text{–}Cl_{ax}$ [2.575(3) Å] longer than $Tl\text{–}Cl_{eq}$ [2.500(4) and 2.427(3) Å]. The crystal structure of $[Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ consists of a dimer with two asymmetric chlorine bridges [Tl–Cl 2.530(4) and 2.937(3) Å]. The chelating ligand again gives rise to a five-membered ring, here TlC_3N. Each thallium atom has a distorted trigonal bipyramidal environment in which the axial positions are occupied by the nitrogen atom of the aryl ligand [Tl–N 2.513(8) Å] and the weakly bonded bridging chlorine. The equatorial sites are occupied by the carbon atom of the aryl ligand [Tl–C 2.127(10) Å], the other bridging chlorine, and a terminal chlorine [Tl–Cl 2.392(3) Å].

Structural data on organothallium compounds are scarce. As far as we know no monoarylthallium derivative has been structurally characterized,[1] despite the great number of such compounds obtained by thallation reactions.[2] The probable reason is that such reactions are usually designed as intermediate steps in organic syntheses, the organothallium compound rarely being isolated.

We therefore consider that more investigations of synthetic routes to isolable organothallium complexes are worthwhile. We are studying the use of organomercury compounds as transmetallating agents in the synthesis of new organometallic compounds that are not accessible, or are not easily prepared, from the classical Grignard or organolithium reagents. This synthetic method has several advantages over the use of the classical reagents; the main one is the possibility of preparing functionalized derivatives. Thus, we have previously reported the synthesis of aryl derivatives of rhodium,[3] palladium,[4] platinum,[5] gold,[6] and tin[7] by treating halides or halogeno complexes of these metals with the corresponding arylmercury compounds, most of which could not be prepared by other methods. One additional advantage arises from the selectivity of the transmetallation reaction. Thus, it is very difficult to prepare partially arylated or mixed diaryl complexes using lithium or magnesium reagents, but we have succeeded in synthesizing mono- or homo- and hetero-diaryl complexes.[3–7] One disadvantage of the use of mercurials is their limited arylation power which can only lead to mono- or di-aryl complexes.[3–7]

In spite of the fact that organomercury derivatives have been used for the synthesis of vinyl- and aryl-thallium(III) derivatives[2a,8] we believe that this synthetic route has still undiscovered possibilities in the chemistry of thallium (and also of other metals). We report here the synthesis of some neutral and anionic monoarylthallium(III) derivatives containing the ligands 2-(phenylazo)phenyl and 2-(dimethylaminomethyl)phenyl.

Complexes containing the ligand $C_6H_4CH_2NMe_2\text{-}2$ such as $[Tl(C_6H_4CH_2NMe_2\text{-}2)X(X')]$ ($X = X' = RCO_2$; $X = Cl$, $X' = RCO_2$), characterized by ^1H and ^{13}C n.m.r. spectroscopy, and $[Tl(C_6H_4CH_2NMe_2\text{-}2)_2Cl]$, have been obtained by transmetallation reactions using $[Pd(C_6H_4CH_2NMe_2\text{-}2)_2]$ or $[Li(C_6H_4CH_2NMe_2\text{-}2)]$, respectively.[9] A compound reported as $2,4\text{-}X(R)C_6H_3N{=}NC_6H_4R\text{-}4$ [$X = Tl(O_2CCF_3)_2$; R = H or Me] has been obtained by metallation of the azo-compound with $Tl(O_2CCF_3)_3$.[10]

Results and Discussion

Synthesis.—The compound $[NMe_4]_2[TlCl_5]$[11] reacts with $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$[12a] or with $[Hg(C_6H_4CH_2NMe_2\text{-}2)_2]$[12b] in molar ratio 2:1 in refluxing ethanol to give $[NMe_4][Tl(C_6H_4N{=}NPh\text{-}2)Cl_3]$ (**1**) or $[NMe_4][Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_3]$ (**2**), respectively. The by-product of both processes is the insoluble halo complex $[NMe_4]_2[Hg_2Cl_6]$.

To account for the nature of the products and the molar ratio of the reagents used we propose a two-step process (Scheme).

$$[TlCl_5]^{2-} + [HgR_2] \longrightarrow [TlRCl_3]^- + [HgR(Cl)] + Cl^- \quad (1)$$

$$[HgR(Cl)] + \tfrac{1}{2}Cl^- \longrightarrow \tfrac{1}{4}[Hg_2Cl_6]^{2-} + \tfrac{1}{2}[HgR_2] \quad (2)$$

$$[TlCl_5]^{2-} + \tfrac{1}{2}[HgR_2] \longrightarrow [TlRCl_3]^- + \tfrac{1}{4}[Hg_2Cl_6]^{2-} + \tfrac{1}{2}Cl^-$$

Scheme. R = $C_6H_4N{=}NPh\text{-}2$ or $C_6H_4CH_2NMe_2\text{-}2$

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† Tetramethylammonium trichloro(2-phenylazophenyl)thallate(III) and dichloro(2-dimethylaminomethylphenyl-*C'N*)thallium(III).

Supplementary data available: complete bond lengths and angles, H-atom co-ordinates, thermal parameters, and structure factors have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 53734.

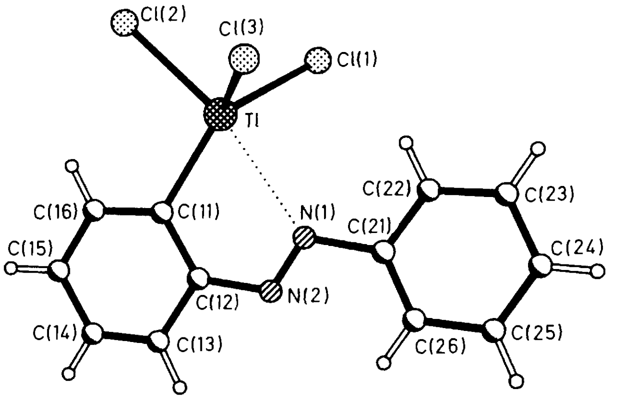

Figure 1. The anion of complex (**1**) in the crystal, showing the atom numbering scheme and the weak Tl···N interaction. Radii are arbitrary

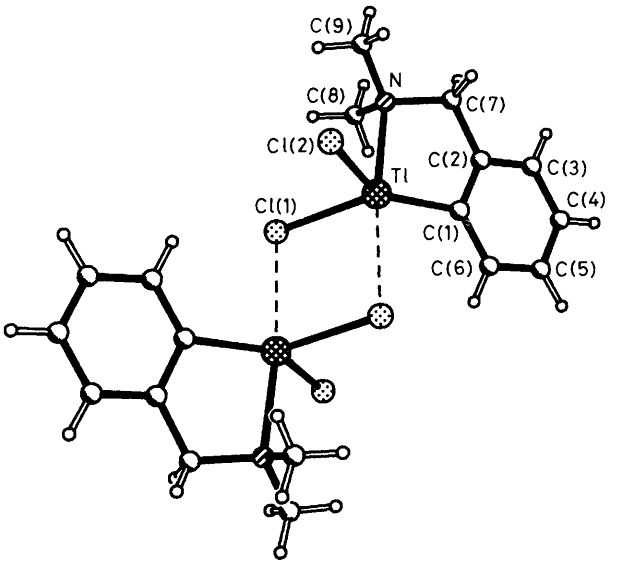

Figure 2. The dimer of complex (**4**) in the crystal, showing the numbering scheme of the asymmetric unit and the weaker Tl···Cl interactions. Radii are arbitrary

The symmetrization reaction (2) has been demonstrated independently.[6g]

The anionic complexes (**1**) and (**2**) can be used as starting products for the synthesis of new organothallium compounds; thus they react with $NaClO_4$ giving the neutral compounds $[Tl(C_6H_4N{=}NPh\text{-}2)Cl_2]$ (**3**) and $[Tl(C_6H_4CH_2NMe\text{-}2)Cl_2]$ (**4**), respectively.

Compound (**3**) can also be prepared by treatment with aqueous KCl of $[Tl(C_6H_4N{=}NPh\text{-}2)(O_2CCF_3)_2]$ which, in turn, is obtained by direct thallation of azobenzene with $[Tl(O_2CCF_3)_3]$ in trifluoroacetic acid.[10]

Van Koten and co-workers[9] reported the compounds $[Tl(C_6H_4CH_2NMe_2\text{-}2)(O_2CR)_2]$ and $[Tl(C_6H_4CH_2NMe_2\text{-}2)(O_2CR)Cl]$ (R = Me, Et, or Pr^i), related to complex (**4**), as the products of the transmetallation reactions between *cis*-$[Pd(C_6H_4CH_2NMe_2\text{-}2)_2]$ and $Tl(O_2CR)_3$ or, respectively, between $[\{Pd(O_2CR)_2\}_3]$ and $[Tl(C_6H_4CH_2NMe_2\text{-}2)_2Cl]$. However, the products were not isolated. The same authors reported the synthesis of $[Tl\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}Cl_2]$ as the product of the reaction between $TlCl_3$ and $[Tl\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}_2Cl]$. This thallium complex was, in turn, obtained in 25% yield by treating $TlCl_3$ with $[Li\{(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4\}]$. The use of organomercury compounds is more convenient because of the better overall yield and the simple reaction conditions (no protective atmosphere is required).

I.R. and N.M.R. Spectra.—The solid state i.r. spectra of complexes (**1**)—(**4**) show absorptions corresponding to the presence of the aryl groups. The thallium salts (**1**) and (**2**) show, in addition, a strong band from NMe_4^+ at around 950 cm^{-1} that disappears for the neutral complexes (**3**) and (**4**). Each pair of complexes has a very similar pattern of bands in the 300—200 cm^{-1} region, which should be assignable to ν(Tl–Cl).[13] Thus, the anionic complexes have three medium-intensity bands [(**1**) 287, 245, and 220; (**2**) 275, 240, and 210 cm^{-1}] while the neutral ones show two bands [(**3**) 310s, 225m; (**4**) 300s, 230s cm^{-1}].

The presence of direct aryl–thallium bonding was confirmed by the observation of long-range $^{203,205}Tl$–H coupling constants in the ^1H n.m.r. spectra. Thus, complex (**1**) shows a doublet of multiplets centred at δ 7.90 [*J*(TlH) = 887 Hz] assignable to the proton *ortho* to the thallium atom. The low solubility of complex (**3**) precludes observation of the *ortho*-H signals, which appear centred at δ 7.89 [*J*(TlH) = 908] and 7.85 [*J*(TlH) = 903 Hz] for complexes (**2**) and (**4**) respectively. The other aryl protons are clearly observed for $C_6H_4CH_2NMe_2$-2 complexes (**2**) and (**4**) as five multiplets, four of which, appearing around δ 6.2, 6.6, 7.0, and 7.5, can be assigned to two protons coupled to thallium; the fifth, at 8.10 for (**2**) and 8.24 for (**4**), corresponds to an uncoupled proton.

Complex (**4**) shows the presence of two doublets assignable to the CH_2 group [δ 3.70, *J*(TlH) = 39 Hz] and to the NMe_2 group [2.56, *J*(TlH) = 12 Hz]. In complex (**2**) the NMe_2 resonance appears as a singlet (δ 2.39) while the corresponding signal from the CH_2 group is an apparent doublet with the high-field resonance obscured by the intense NMe_4 signal at δ 3.40.

Crystal Structures of Complexes (**1**) *and* (**4**).—In both complexes the aryl ligand produces a five-membered chelate ring *via* the co-ordination of a nitrogen atom. The co-ordination geometries are also the same, being distorted trigonal bipyramidal.

In complex (**1**) (Figure 1), two chlorine atoms and the aryl carbon atom occupy the equatorial positions while the other chlorine and the co-ordinated nitrogen atom of the azo group occupy axial sites. The crystal structure of complex (**4**) (Figure 2) consists of a dimer with two asymmetric chlorine bridges. The distorted trigonal bipyramidal environment of each thallium atom is attained with the axial positions occupied by the nitrogen atom and the weakly bonded bridging chlorine. The equatorial sites are occupied by the carbon atom and the terminal and the more strongly bonded bridging chlorine atoms.

The axial/equatorial position of the aryl ligands is required by their small 'bite' angles [complex (**1**) 66.6(3); (**4**), 77.2(3)°], which are even smaller than the ideal 90°. The axial location of the nitrogen atom in both complexes is that expected for the most electronegative ligand donor atom.

The Tl–N distance in complex (**1**), 2.786(8) Å, is much longer than in complex (**4**), 2.513(8) Å. It seems that one of the axial ligands in these complexes tends to be weakly bonded to thallium; in complex (**4**) the stronger Tl–N bond is opposite the weakly bonded bridging chlorine atom, whereas in (**1**) the Tl–N bond is long. Shorter Tl–N bond distances have been found in $[TlCl_3(phen)]$ (phen = 1,10-phenanthroline) [2.348(8) and 2.380(8) Å].[14] However, similar values have been reported in $[TlMe_2(phen)(OClO_3)]$ (2.57 Å).[15] The Tl···N(1) interaction in (**1**) is associated with considerable distortion of the angles N(2)–C(12)–C(11) (126.2), N(1)–N(2)–C(12) (115.6), and N(2)–N(1)–C(21) (114.5°).

The Tl–Cl range of bond lengths, 2.43—2.94 Å, is quite wide. As expected, the Tl–Cl_{ax} bond in complex (**1**) [2.575(3) Å] is longer than Tl–Cl_{eq} bonds [2.500(4) and 2.427(3) Å]. The difference between the two Tl–Cl_{eq} bond lengths might be rationalized as a consequence of the angle Cl(3)–Tl–C(11) [118.9(3)°] being smaller than Cl(1)–Tl–C(11) [135.9(3)°]. The three well separated ν(Tl–Cl) bands in the solid-state i.r. spectra of (**1**) and (**2**) could be associated with the three significantly different Tl–Cl bond distances.

The Tl–Cl_{eq} bond length in complex (**4**) [2.392(3) Å] is shorter than in (**1**) [2.500(4) and 2.427(3) Å]. The anionic nature of this complex, which should decrease the strength of the $p_\pi(Cl)\rightarrow p_\pi(Tl)$ bonding, could be the main reason for the lengthening of the Tl–Cl_{eq} bonds. We have observed a similar relationship between the charge of gold(III) complexes and the strength of the Au–Cl bond, as deduced from i.r. spectroscopy.[6b]

The bridging Tl–Cl bond distances in (**4**) are appreciably different [2.530(4) and 2.937(3) Å] and, as expected, longer than Tl–Cl_{eq}. The longest bond should correspond to a weak interaction for which ν(Tl–Cl) woud lie below the range of our i.r. spectrophotometer,[13b,c] thus explaining the observation of only two ν(Tl–Cl) bands in the i.r. spectra of (**3**) and (**4**). A weak dimer has also been found in the complex [$TlCl_3$(phen)],[14] and similar weak Tl···Cl interactions (3.046 and 3.119 Å) in [$Tl(mes)_2$][$TlCl_3$(mes)] (mes = 2,4,6-$Me_3C_6H_2$).[16] Complexes (**3**) and (**4**) are not soluble enough for the molecular weight to be measured. The complexes [$Tl(C_6H_4CH_2NMe_2\text{-}2)X(X')$] (X = X′ = RCO_2; X = Cl, X′ = RCO_2) have been proposed to be four-co-ordinate in solution.[9]

The thallium atom in complex (**1**) is out of the plane formed by the three equatorial ligands (by 0.35 Å) in the direction of the more strongly bonded axial ligand. This geometry is similar to that assumed to occur in intermediate five-co-ordinate species formed in substitution reactions of tetrahedral compounds. In complex (**4**) the thallium atom is almost in the equatorial plane (deviation 0.04 Å).

The differences that can be observed in the angles in the equatorial planes can be rationalized using the isovalent hybridization concept.[17] Thus, two chlorine atoms, which are the more electronegative equatorial donor atoms in both complexes, will demand greater *p* character of the thallium hybrids and the Cl–Tl–Cl angles will be smaller [complex (**1**), 98.1(1); (**4**), 97.0(1)°] than the Cl–Tl–C angles [(**1**), 118.9(3), 135.9(3); (**4**) 118.7(3), 144.3(3)°]. Similar effects were observed in the anion $[TlCl_3(mes)]^-$.[16]

In solution, complexes (**1**) and (**2**) behave as 1:1 electrolytes according to the equation $\Lambda = A + B\sqrt{c}$ [Λ = equivalent conductivity; *c* = equivalent concentration; complex (**1**) $B = -184$; (**2**), $B = -151$, in nitromethane].[18] Complexes (**3**) and (**4**) are non-conducting in acetone solution.

The reactions of organomercurials with $[NMe_4]_2[TlCl_5]$ offer a selective and high-yield synthesis of monoarylthallium derivatives. These complexes could react with organomercurials bearing a different aryl group to give mixed diorganothallium compounds, analogously to our studies of gold(III) and tin(IV) complexes. We are currently investigating this possibility and we have so far been able to prepare the compound [$Tl(C_6H_4N{=}NPh\text{-}2)(C_6H_4CH_2NMe_2\text{-}2)Cl$] by reaction of (**1**) with [$Hg(C_6H_4CH_2NMe_2\text{-}2)_2$].

Experimental

Infrared spectra were recorded in the range 4 000—200 cm^{-1} on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets; ^1H n.m.r. spectra in $CDCl_3$ solutions (δ with respect to $SiMe_4$) on a Bruker AC 200 spectrometer. Conductivities were measured with a Philips 9501 conductimeter on acetone solutions. Melting points were determined on a Reichert apparatus and are uncorrected. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyser.

Reactions were carried out with magnetic stirring and without special precautions against light or atmospheric moisture unless otherwise stated. The starting complexes [$Hg(C_6H_4N{=}NPh\text{-}2)_2$],[12a] [$Hg(C_6H_4CH_2NMe_2\text{-}2)_2$],[12b] and $[NMe_4]_2[TlCl_5]$[11] were prepared by literature methods. Single crystals of (**1**) and (**4**) were obtained by slow diffusion of n-hexane into saturated solutions of the complexes in dichloromethane.

[NMe_4][$Tl(C_6H_4N{=}NPh\text{-}2)Cl_3$] (**1**).—The salt $[NMe_4]_2$-[$TlCl_5$] (787 mg, 1.50 mmol) and [$Hg(C_6H_4N{=}NPh\text{-}2)_2$] (423 mg, 0.75 mmol) were refluxed in ethanol (15 cm^3) for 6 h. The solvent was evaporated to dryness and the residue recrystallized from dichloromethane–diethyl ether giving orange complex (**1**). Yield: 85%. M.p. 169 °C. Λ_M = 82 Ω^{-1} cm^2 mol^{-1} (Found: C, 34.00; H, 3.80; N, 7.50. Calc. for $C_{16}H_{21}Cl_3N_3Tl$: C, 33.95; H, 3.75; N, 7.40%). ^1H N.m.r.: δ 3.38 (s, 12 H, NMe_4), 6.9—7.9 (several multiplets), 7.90 [dm, 1 H, *o*-H, *J*(TlH) = 887 Hz], and 8.4 (m) and 9.15 (m) ($C_6H_4N{=}NPh$-2, all aryl protons except *ortho*-H).

[NMe_4][$Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_3$] (**2**).—This compound was prepared as described above as a white solid. Yield: 77%. M.p. 112 °C. Λ_M = 101 Ω^{-1} cm^2 mol^{-1} (Found: C, 29.35; H, 4.70; N, 5.85. Calc. for $C_{13}H_{24}Cl_3N_2Tl$: C, 30.10; H, 4.65; N, 5.40%). ^1H N.m.r.: δ 2.39 (s, 6 H, NMe_2), 3.40 (s, 12 H, NMe_4), 3.69 (see Discussion section; 1 H, CH_2), 6.19 (m), 6.60 (m), 6.99 (m), and 7.54 (m) (2 H, $C_6H_4CH_2NMe_2$-2), 7.89 [dm, 1 H, *o*-H, *J*(TlH) = 908 Hz], and 8.10 (m, 1 H, $C_6H_4CH_2NMe_2$-2).

[$Tl(C_6H_4N{=}NPh)Cl_2$] (**3**).—Complex (**1**) (100 mg, 0.18 mmol) and $NaClO_4{\cdot}H_2O$ (27 mg, 0.19 mmol) were allowed to react in acetone (10 cm^3) at room temperature for 6 h. The solvent was evaporated and the residue recrystallized from dichloromethane–hexane yielding yellow-orange complex (**3**). Yield: 72%. M.p. 180 °C. Λ_M = 5 Ω^{-1} cm^2 mol^{-1} (Found: C, 32.00; H, 2.10; N, 6.05. Calc. for $C_{12}H_9Cl_2N_2Tl$: C, 31.60; H, 2.00; N, 6.15%). ^1H N.m.r.: multiplets corresponding to aryl protons coupled to thallium at δ 7.2, 7.4, 7.7, and 8.2 (see Discussion section).

[$Tl(C_6H_4CH_2NMe_2\text{-}2)Cl_2$] (**4**).—This compound was similarly prepared from (**2**) as a white solid. Yield: 89%. M.p. 148 °C. Λ_M = 0 (Found: C, 26.70; H, 3.10; N, 3.45. Calc. for $C_9H_{12}Cl_2NTl$: C, 26.40; H, 2.95; N, 3.4%). ^1H N.m.r.: 2.56 [d, 6 H, NMe_2, *J*(TlH) = 12 Hz], 3.70 [d, 2 H, CH_2, *J*(TlH) = 39], 6.25 (m), 6.59 (m), 7.07 (m), and 7.64 (m) (2 H, $C_6H_4CH_2NMe_2$-2), 7.85 [dm, 1 H, *o*-H, *J*(TlH) = 903 Hz], and 8.24 (1 H, $C_6H_4CH_2NMe_2$-2).

Crystal Structure Determination of Complex (**1**).—*Crystal data.* $C_{16}H_{21}Cl_3N_3Tl$, M_r = 566.1, monoclinic, space group $P2_1/n$, a = 9.722(3), b = 8.199(3), c = 25.832(8) Å, β = 92.43(3)°, U = 2 057 Å^3, Z = 4, D_c = 1.83 Mg m^{-3}, λ(Mo-K_α) = 0.710 69 Å, μ = 8.3 mm^{-1}, $F(000)$ = 1 080. Crystal size 0.65 × 0.15 × 0.02 mm (orange plate).

Data collection and reduction. 5 619 Profile-fitted intensities[19] were registered on a Stoe-Siemens four-circle diffractometer using monochromated Mo-K_α radiation ($2\theta_{max.}$ 50°). Absorption corrections were based on ψ scans and plate faces 001 (transmission factors 0.27—0.82). A correction for slight crystal decay (1.5%, by repeated monitoring of three check reflections) was also applied. Merging equivalents gave 3 533 unique reflections (R_{int} 0.023), of which 2 403 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its

Table 1. Atomic co-ordinates (× 10^4) for complex (**1**)

Atom	*x*	*y*	*z*
Tl	5 156.5(4)	6 948.7(5)	6 174.3(2)
Cl(1)	4 167(3)	9 652(4)	6 072(2)
Cl(2)	2 939(3)	5 475(5)	6 420(1)
Cl(3)	6 110(4)	7 254(5)	7 083(1)
N(1)	7 661(9)	7 971(11)	5 801(3)
N(2)	8 119(10)	6 982(13)	5 519(4)
C(11)	6 068(10)	5 203(12)	5 678(4)
C(12)	7 311(11)	5 576(15)	5 437(4)
C(13)	7 847(11)	4 385(18)	5 093(5)
C(14)	7 143(13)	2 988(19)	4 996(6)
C(15)	5 978(14)	2 618(15)	5 238(5)
C(16)	5 429(12)	3 753(13)	5 570(4)
C(21)	8 531(11)	9 422(15)	5 884(5)
C(22)	8 017(12)	10 606(15)	6 178(5)
C(23)	8 746(14)	12 006(16)	6 291(6)
C(24)	10 028(13)	12 243(19)	6 101(5)
C(25)	10 559(12)	11 013(21)	5 801(6)
C(26)	9 752(15)	9 618(20)	5 690(6)
N(3)	9 649(10)	2 758(11)	2 534(4)
C(1)	9 568(16)	1 278(18)	2 849(6)
C(2)	8 274(15)	3 119(23)	2 323(6)
C(3)	10 632(15)	2 415(19)	2 118(6)
C(4)	10 170(15)	4 033(20)	2 872(9)

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

Tl–Cl(1)	2.427(3)	Tl–Cl(2)	2.575(3)
Tl–Cl(3)	2.500(4)	Tl–N(1)	2.786(8)
Tl–C(11)	2.138(10)	N(1)–N(2)	1.188(14)
N(1)–C(21)	1.470(14)	N(2)–C(12)	1.406(16)
Cl(1)–Tl–Cl(2)	97.1(1)	Cl(1)–Tl–Cl(3)	98.1(1)
Cl(2)–Tl–Cl(3)	95.5(1)	Cl(1)–Tl–N(1)	92.0(2)
Cl(2)–Tl–N(1)	168.5(2)	Cl(3)–Tl–N(1)	90.0(2)
Cl(1)–Tl–C(11)	135.9(3)	Cl(2)–Tl–C(11)	101.9(3)
Cl(3)–Tl–C(11)	118.9(3)	N(1)–Tl–C(11)	66.6(3)
Tl–N(1)–N(2)	111.2(7)	Tl–N(1)–C(21)	134.3(7)
N(2)–N(1)–C(21)	114.5(9)	N(1)–N(2)–C(12)	115.6(10)
Tl–C(11)–C(12)	120.2(7)	Tl–C(11)–C(16)	120.6(8)
C(12)–C(11)–C(16)	119.2(10)	N(2)–C(12)–C(11)	126.2(10)
N(2)–C(12)–C(13)	116.0(10)		

Table 3. Atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*x*	*y*	*z*
Tl	4 300.4(2)	3 396.7(3)	4 522.9(3)
Cl(1)	4 969(2)	4 954(3)	3 776(2)
Cl(2)	5 677(2)	2 139(3)	5 332(2)
N	3 482(5)	2 046(8)	3 046(6)
C(1)	2 871(6)	3 569(8)	4 205(7)
C(2)	2 278(6)	2 697(8)	3 537(7)
C(3)	1 326(7)	2 721(10)	3 291(8)
C(4)	1 004(8)	3 604(11)	3 713(9)
C(5)	1 573(8)	4 468(11)	4 353(8)
C(6)	2 529(8)	4 463(9)	4 612(7)
C(7)	2 638(8)	1 681(9)	3 127(9)
C(8)	3 223(8)	2 804(14)	2 165(8)
C(9)	4 024(9)	929(13)	3 036(10)

Table 4. Bond lengths (Å) and angles (°) for complex (**4**)

Tl–Cl(1)	2.530(4)	Tl–Cl(2)	2.392(3)
Tl–N	2.513(8)	Tl–C(1)	2.127(10)
Tl–Cl(1$^{\text{I}}$)	2.937(3)	N–C(7)	1.472(17)
N–C(8)	1.477(16)	N–C(9)	1.476(17)
C(1)–C(2)	1.392(11)	C(1)–C(6)	1.388(16)
C(2)–C(3)	1.399(14)	C(2)–C(7)	1.499(17)
C(3)–C(4)	1.376(19)	C(4)–C(5)	1.355(15)
C(5)–C(6)	1.400(18)		
Cl(1)–Tl–Cl(2)	97.0(1)	Cl(1)–Tl–N	96.1(2)
Cl(2)–Tl–N	97.7(2)	Cl(1)–Tl–C(1)	118.7(3)
Cl(2)–Tl–C(1)	144.3(3)	N–Tl–C(1)	77.2(3)
Cl(1)–Tl–C(1$^{\text{I}}$)	87.0(1)	Cl(2)–Tl–Cl(1$^{\text{I}}$)	88.1(1)
N–Tl–Cl(1$^{\text{I}}$)	173.0(2)	C(1)–Tl–C(1$^{\text{I}}$)	95.8(3)
Tl–Cl(1)–Tl$^{\text{I}}$	93.0(1)	Tl–N–C(7)	100.8(7)
Tl–N–C(8)	110.3(7)	C(7)–N–C(8)	110.2(8)
Tl–N–C(9)	113.8(6)	C(7)–N–C(9)	111.2(9)
C(8)–N–C(9)	110.2(11)	Tl–C(1)–C(2)	114.4(7)
Tl–C(1)–C(6)	124.3(6)	C(2)–C(1)–C(6)	121.2(9)
C(1)–C(2)–C(3)	118.8(10)	C(1)–C(2)–C(7)	122.1(9)
C(3)–C(2)–C(7)	119.0(8)	C(2)–C(3)–C(4)	119.1(9)
C(3)–C(4)–C(5)	122.6(12)	C(4)–C(5)–C(6)	119.5(12)
C(1)–C(6)–C(5)	118.9(9)	N–C(7)–C(2)	113.5(8)

Symmetry operator: I, $1 - x, 1 - y, 1 - z$.

author Professor G. M. Sheldrick). Cell constants were refined from 2θ values of 68 reflections in the range 20—22°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on *F*. The final *R* value was 0.055, with *R'* 0.045. Hydrogen atoms included using riding model; weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, with *g* 0.0003; 208 parameters; *S* 1.5; maximum shift/error 0.002; maximum electron density difference 1.5 e Å^{-3} near Tl.

Final atomic co-ordinates are presented in Table 1, with selected bond lengths and angles in Table 2.

Crystal Structure Determination of Complex (**4**).—*Crystal data.* $C_{14}H_{24}Cl_4N_2Tl_2$, $M_r = 770$, monoclinic, space group *C*2/*c*, *a* = 16.089(3), *b* = 10.621(3), *c* = 15.589(3) Å, β = 117.29(2)°, *U* = 2 367 Å^3, *Z* = 4, $D_c = 2.16$ Mg m^{-3}, μ(Mo-K_α) = 14.2 mm^{-1}, *F*(000) = 1 408. Colourless prism, 0.25 × 0.25 × 0.15 mm.

Data collection and reduction. As for complex (**1**), with the following differences. 4 116 Intensities, 2 082 unique (R_{int} 0.043), 1 809 observed. Absorption corrections assuming ellipsoidal form; transmissions 0.64—0.95. Crystal decay 23% (crystal became grey). Cell constants refined from 56 2θ values in the range 20—23°.

Structure solution and refinement. As for (**1**), with the following differences: *R* 0.044, *R'* 0.044, *g* 0.000 65; 118 parameters. Final atomic co-ordinates are given in Table 3, with derived bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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