Contribution from the Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, FRG

Preparation and Crystal Structure of Thallium 2,4,6-Tris(trifluoromethyl)phenoxide, a Compound of Thallium(I) with Coordination Number 2 at the Thallium Atom

Herbert W. Roesky,* Mario Scholz, Mathias Noltemeyer, and Frank T. Edelmann

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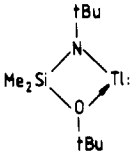
The reaction of $C_6H_2(CF_3)_3Li$ and $(Me_3Si)_2O_2$ results in the formation of $C_6H_2(CF_3)_3OSiMe_3$ (**5**), which is converted by hydrogen chloride to the phenol $C_6H_2(CF_3)_3OH$ (**4**). **4** reacts with $TlOC_2H_5$ to give the title compound $[C_6H_2(CF_3)_3OTl]_2$ (**6**). Mass spectroscopic and X-ray structural analyses confirm the dimeric structure with Tl(I) of coordination number 2. $[C_6H_2(CF_3)_3OTl]_2$ crystallizes in the space group $P2_1/c$ with a = 1257.5 (7) pm, b = 946.1 (7) pm, c = 1060.9 (5) pm, and β = 101.41 (4)°.

Introduction

There has been considerable recent interest in low-coordination-number species of group 13, 14, 15, and 16 elements.[1] Molecules containing these elements with coordination numbers 1 and 2 have been prepared. In the case of thallium compounds, the lowest coordination number so far structurally characterized by X-ray analysis is 3. Tl(I) halides show similarities in color and solubility to the corresponding silver compounds. TlF, like AgF, is soluble in water. The other halides of Tl are insoluble. We were interested in the preparation of a Tl(I) compound of coordination number 2. This could be achieved by using an electron-withdrawing, bulky ligand. We now report the structure and physical properties of such a compound.

Results and Discussion

Thallium(I) is found in different compounds with every coordination number between 3 and 12.[2] Thallium(I) with a lower coordination number has been postulated by Veith et al.[3] and others[4] in compounds of type **1** and **2**; however, no structural data are known.



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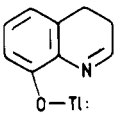

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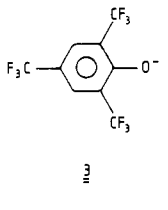
A ligand with suitable steric demand and electron-withdrawing properties is 2,4,6-tris(trifluoromethyl)phenoxide (**3**), a ligand that has not yet been reported in the literature. 2,4,6-Tris(trifluoromethyl)phenol (**4**) is synthesized in two steps by the reaction of bis(trimethylsilyl)peroxide with (2,4,6-tris(trifluoromethyl)phenyl)lithium in Et_2O to yield the compound **5**, followed by treatment of **5** with dry HCl gas. After distillation, **4** is obtained as a colorless oily liquid in 63% yield.



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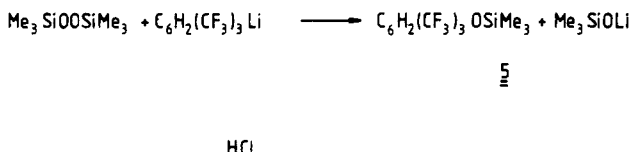
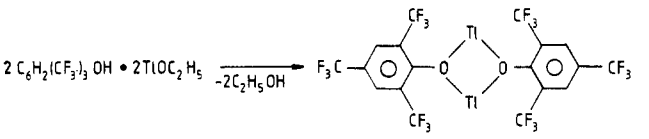


4 can be used directly to synthesize the thallium compound **6**. A solution of **4** in THF was added to a solution of $TlOC_2H_5$ in THF. The compound that forms, thallium(I) 2,4,6-tris(trifluoromethyl)phenoxide (**6**, 80% yield), is a white solid which is not stable to moisture and air.



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In the FI (field ionization) mass spectrum, a dimer at m/e 502 (100%) was seen in the gas phase. Unambiguous structural assignment was made by the X-ray structural investigation. The two phenyl groups (Figure 1) are in the same plane, and the TlOTlO four-membered ring is necessarily planar and lies approximately (if one considers the angle between least-squares planes Tl(1)O(1)Tl(1a)O(1a) and C(11)–C(16)) perpendicular to the phenyl groups. The dihedral angles Tl(1)–O(1)–C(11)–C(16) = 96.6° and Tl(1)–O(1)–C(11)–C(12) = 85.5° and O(1a)–Tl(1)–O(1)–C(11) = 172.2°, however, deviate from 90° (180°), respectively, because the O(1)–C(11) bond is bent 6.2° away from the four-membered-ring plane. This can also be seen from the deviations of 14 pm for C(11) and 43 pm for C(14) from the four-membered-ring plane. The average Tl–O bond lengths (246.5 pm) (Table I) may be compared with those of 259.5 pm in $Tl(O\text{-}t\text{-}Bu)_3Sn$.[5] However, the latter compound has a coordination number of 3 around thallium. The measured Tl^I–O distance may be compared to that of 284 pm calculated from ionic radii.[6] The O(1)–Tl(1)–O(1a) angle (70.8 (4)°) is small compared to the corresponding oxygen angle within the four-membered ring (Tl(1)–O(1)–Tl(1a) = 109.2 (4)°) (Table II).

Experimental Section

All manipulations and measurements were carried out under an inert atmosphere of dry N_2 by using Schlenk techniques.

Reagents were purified according to standard methods. $TlOC_2H_5$ (Merck) was used as received.

^1H and ^{19}F NMR spectra were obtained on a Bruker WP 80 SY (80.13 and 75.39 MHz) spectrometer. Infrared spectra were recorded

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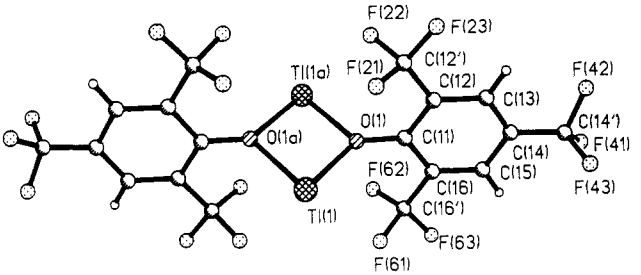

Figure 1. Molecular structure of $[C_6H_2(CF_3)_3OTl]_2$.

Table I. Selected Bond Distances (pm) and Angles (deg) in $[C_6H_2(CF_3)_3OTl]_2$

Tl(1)-O(1)	246.9 (8)	Tl(1)-O(1a)	246.1 (10)
O(1)-C(11)	129.8 (16)	O(1)-Tl(1a)	246.1 (10)
O(1)-Tl(1)-O(1a)	70.8 (4)	Tl(1)-O(1)-C(11)	125.1 (7)
Tl(1)-O(1)-Tl(1a)	109.2 (4)	C(11)-O(1)-Tl(1a)	125.2 (7)
O(1)-C(11)-C(12)	123.0 (11)	O(1)-C(11)-C(16)	120.8 (12)

Table II. Atomic Coordinates ($\times 10^4$) of $[C_6H_2(CF_3)_3OTl]_2$ and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2)

	x	*y*	*z*	*U*(eq)[a]
Tl(1)	780 (1)	450 (1)	1796 (1)	64 (1)
O(1)	-959 (7)	662 (9)	248 (9)	55 (3)
C(11)	-1858 (10)	1128 (12)	520 (11)	45 (4)
C(12)	-2580 (12)	265 (13)	1014 (13)	54 (5)
C(13)	-3526 (13)	779 (16)	1316 (16)	70 (6)
C(14)	-3800 (14)	2167 (17)	1123 (15)	73 (6)
C(15)	-3111 (12)	3079 (15)	612 (13)	64 (5)
C(16)	-2179 (11)	2578 (13)	283 (12)	51 (4)
C(12')	-2222 (15)	-1254 (17)	1309 (19)	80 (7)
F(21)	-1297 (8)	-1375 (9)	2106 (10)	89 (4)
F(22)	-2137 (8)	-1948 (9)	220 (11)	99 (4)
F(23)	-2960 (9)	-1970 (11)	1802 (13)	119 (5)
C(14')	-4762 (20)	2758 (29)	1488 (26)	118 (11)
F(41)	-5292 (14)	3642 (22)	824 (21)	218 (12)
F(42)	-5498 (14)	1796 (19)	1560 (26)	218 (14)
F(43)	-4588 (13)	3284 (31)	2637 (17)	248 (15)
C(16')	-1436 (14)	3522 (16)	-274 (15)	69 (6)
F(61)	-457 (8)	3649 (10)	524 (10)	87 (4)
F(62)	-1254 (8)	3097 (10)	-1382 (8)	89 (4)
F(63)	-1799 (11)	4837 (10)	-438 (12)	111 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

on a Perkin-Elmer Spectrograph 735 B instrument. Mass spectra were obtained with a Varian CH-5 MAT instrument. Elemental analyses were done by the analytical laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

1,3,5-Tris(trifluoromethyl)benzene[7,8] and $(Me_3Si)_2O_2$[9] were prepared according to literature methods.

2,4,6-Tris(trifluoromethyl)phenol (4). $(Me_3Si)_2O_2$ (10 g, 56 mmol) was added dropwise at -78 °C to a solution of $C_6H_2(CF_3)_3Li$ prepared from $C_6H_3(CF_3)_3$ (15.8 g, 56 mmol) and *n*-BuLi (36.4 mL, 1.6 M in hexane) in Et_2O. After the addition was complete, the mixture was stirred at room temperature for another 24 h. The contents were treated at 0 °C with dry HCl and stirred at room temperature for an additional 24 h. The white precipitate was filtered off, and the solvent was removed by distillation. The residue, a yellow oil, was distilled at 4 mbar. The pure product **4**, a colorless oil, boiled at 36 °C; yield 10.5 g (63%). Anal. Calcd for $C_9H_3F_9O$: C, 36.3; H, 1.0. Found: C, 36.8; H, 1.3. ^{1}H NMR ($CDCl_3$, TMS external reference): δ 6.4 (m, -OH), 8.0 (s, CH_{ar}). ^{19}F-{^{1}H} NMR ($CDCl_3$, $CFCl_3$ external reference): δ -62.3 (s, *o*-CF_3), -63.2 (s, *p*-CF_3). FI/MS: *m/z* 298 (M, 100%). IR: 3620 m, 1630 s, 1500 m, 1390 w, 1280 s, 1190 s, 1140 s, 920 w, 840 w, 790 w, 690 w, 660 m cm^{-1}.

All manipulations with Tl compounds should be carried out with the greatest care because of their high toxicity.

Thallium 2,4,6-Tris(trifluoromethyl)phenoxide (6). $C_6H_2(CF_3)_3OH$ (2.4 g, 8 mmol) in 20 mL of THF was added dropwise at room temperature to a solution of $TlOC_2H_5$ (2 g, 8 mmol) in 40 mL of THF. After it was stirred for 12 h, the mixture was filtered through Celite and the solvent was evaporated. The residue, a light yellow solid, was washed three times with 10 mL of *n*-hexane. The pure product, a colorless solid, was identified as **6**: yield 3.2 g (80%); mp 164 °C dec. Anal. Calcd for $C_9H_2F_9OTl$: C, 21.5; H, 0.4. Found: C, 21.5; H, 0.7. ^{1}H NMR (CD_3CN, TMS external reference): δ 7.82 (s, CH_{ar}). ^{19}F{^{1}H} NMR (CD_3CN, $CFCl_3$ external reference): δ -59.9 (s, *p*-CF_3), -60.8 (s, *o*-CF_3). IR (Nujol): 1630 m, 1580 w, 1320 s, 1270 s, 1200 m, 1150 m, 1125 s, 1090 s, 920 w, 835 w, 790 w cm^{-1}. FI/MS: *m/z* 502 (M, 100%).

X-ray analysis: $[C_6H_2(CF_3)_3OTl]_2$, monoclinic, $P2_1/c$, a = 1257.5 (7) pm, b = 946.1 (7) pm, c = 1060.9 (5) pm, β = 101.41 (4)°, Z = 2, d_{calcd} = 2.69 g/cm^3, $\mu_{Mo\,K\alpha}$ = 13.3 mm^{-1}. A total of 1712 reflections were measured on a Stoe four-circle diffractometer in the profile-fitting mode ($2\theta_{max}$ = 45°). Absorption corrections by azimuthal scans (crystal size 0.2 × 0.2 × 0.4 mm^3, transmission 0.18–0.59, agreement within scans before and after correction 0.17 and 0.06). A total of 1589 reflections were unique, of which 1424 with $F_o > 3\sigma(F_o)$ were used in the refinement (SHELX): R = 0.056, R_w = 0.064, $w^{-1} = \sigma^2(F_o) + 0.0004(F_o^2)$.

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Registry No. 4, 122489-60-5; **5**, 122489-61-6; **6** (coordination compound entry), 122489-62-7; **6** (salt entry), 122489-63-8; $(Me_3Si)_2O_2$, 5796-98-5; $C_6H_2(CF_3)_3Li$, 444-40-6.

Supplementary Material Available: Listings of crystal data and intensity measurement and refinement parameters, bond lengths, bond angles, anisotropic displacement parameters, H atom coordinates and isotropic displacement parameters, and torsion angles (4 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page. Complete crystal data are deposited at Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG.

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