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Mono- and Bis(dibenzotetramethyltetraaza[14]annulene) Complexes of Group IV Metals, Including the Structure of the Lithium Derivative of the Macrocyclic Ligand

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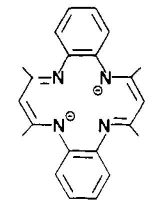
The deprotonation of $tmtaaH_2$ by $LiBu^n$ or LiMe gave a red solid, which upon recrystallization from DME was isolated as crystals suitable for X-ray analysis, $[(tmtaa)_2Li_4(DME)_3]$ (**2**). The lithium derivative was used in situ for the synthesis of [(tmtaa)Ti(Cl)] (**3**), $[(tmtaa)Ti(Cl)_2]\cdot C_6H_6$ (**4**), and $[(tmtaa)M(Cl)_2]\cdot 2THF$ (M = Zr, **5**; M = Hf, **6**). The structure of **2** shows a very pronounced bent cavity derived from the saddle-shape conformation of the ligand where the *cis*-MCl_2 moiety is located. All these complexes should be considered as interesting starting materials for novel early transition metal organometallic chemistry. The reaction of $MCl_4(THF)_2$ with 2 equiv of $[(tmtaa)Li_2]$ and the reaction of $[(tmtaa)M(Cl)_2]$ with $[(tmtaa)Li_2]$ both led to the formation of sandwich complexes $[(tmtaa)_2M]$ (M = Ti, **7**; M = Zr, **8**; M = Hf, **9**), in which the metal achieves a cubic-type octacoordination (through bonding to the eight nitrogen donor atoms, in two staggered N_4 units). The first ^1H NMR study on $[(tmtaa)M]$ diamagnetic complexes is reported. Crystallographic details are as follows: **2**, space group $P\bar{1}$, triclinic, a = 14.433 (2) Å, b = 17.319 (3) Å, c = 11.961 (2) Å, α = 94.76 (2)°, β = 101.24 (2)°, γ = 104.22 (2)°, Z = 2, and R = 0.070 for 7201 independent observed reflections; **3**, space group $C2/m$, monoclinic, a = 34.239 (7) Å, b = 10.101 (2) Å, c = 18.403 (3) Å, $\alpha = \gamma$ = 90°, β = 100.96 (2)°, Z = 8, and R = 0.059 for 1822 independent observed reflections; **5**, space group $P\bar{1}$, triclinic, a = 12.437 (3) Å, b = 15.414 (4) Å, c = 9.337 (2) Å, α = 95.42 (3)°, β = 109.16 (3)°, γ = 111.47 (3)°, Z = 2, and R = 0.044 for 3601 independent observed reflections; **8**, space group $P2_1/n$, monoclinic, a = 11.604 (5) Å, b = 19.073 (3) Å, c = 19.220 (3) Å, $\alpha = \gamma$ = 90°, β = 91.34 (2)°, Z = 4, and R = 0.049 for 3764 independent observed reflections.

Introduction

Dibenzotetramethyltetraaza[14]annulene, $tmtaaH_2$,[1] should be considered as providing an interesting chemical environment for



dibenzotetramethyltetraaza[14]annulene dianion ≡ tmtaa

studying the functionalization and the redox chemistry of early transition metals,[2–4] as an alternative to the classic organic ligand.[5] Such a kind of ligand has been used so far mainly for the synthesis of middle and late transition metal complexes.[6] Studies on the chemical reactivity of the metal center have been limited to a few random cases.[2–4,6,7] A limiting factor in such a chemistry is the synthetic method for preparing a starting material.[2,3] In this perspective, we report here the synthesis of $[(tmtaa)M(Cl)_2]$ (M = Ti, Hf, Zr) by a method leading to a good yield of salt-free crystalline compounds. The cis arrangement of the two chlorides is particularly appropriate for an organometallic functionalization and for reactivity studies in general. Such syntheses have been carried out using the lithium salt of $tmtaaH_2$. It may be a key compound for metal complexation under anhydrous conditions in organic solvents. Its high-yield synthesis and X-ray structure are reported here. The use of a 2:1 $[tmtaa]^{2-}:MCl_4$ ratio led to the formation, for the three metals of group IV, of the unprecedented sandwich-type $[M(tmtaa)_2]$ (M = Ti, Zr, Hf) complexes. The structure of the zirconium derivative has been determined by an X-ray analysis.

Experimental Section

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The syntheses of $MCl_4(THF)_2$[8] (M = Ti, Zr, Hf; THF = tetrahydrofuran) and $tmtaaH_2$[1] were carried out as reported in the literature. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, and ^1H NMR spectra, using a 200-AC Brucker instrument. Elemental analyses were performed on a CHNS-O EA 1108 Carlo Erba instrument at the University of Lausanne.

Preparation of $[(tmtaa)Li_2]$ (2). Method A. $LiBu^n$ (1.68 M in *n*-hexane, 33.2 mL, 55.8 mmol) was added to a benzene (400 mL) solution

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of tmtaaH_2 (9.6 g, 27.9 mmol). A red solid precipitated. The suspension was refluxed overnight, and then the solid was collected and dried in vacuo (6.0 g, 17 mmol). By evaporation of the mother liquor to 200 mL, 1.2 g of the red solid precipitated (7.2 g, 73%). The solid recrystallized from DME gave crystals suitable for X-ray analysis. ^{1}H NMR (C_6D_6, room temperature): δ 6.92 (s, 8 H), 4.65 (s, 2 H), 2.87 (s, 9 H), 2.82 (s, 6 H), 2.19 (s, 12 H).

Method B. MeLi (11 mL, 1.73 M in Et_2O, 19.0 mmol) was added slowly to a THF (100 mL) solution of tmtaaH_2 (3.2 g, 9.3 mmol). The resulting red solution was stirred for 30 min and evaporated to dryness. The residue was dissolved in DME (20 mL) and allowed to stand in the freezer for 2 days, after which time red crystals were collected.

Method C. LiBu^n (17.6 mL, 1.65 M in *n*-hexane, 29.0 mmol) was added to a toluene (100 mL) solution of tmtaaH_2 (5.0 g, 14.5 mmol), resulting in a red suspension which was refluxed overnight. A red crystalline solid was collected and dried in vacuo (58%). Anal. Calcd for $C_{22}H_{22}Li_2N_4$: C, 74.16; H, 6.22; N, 15.72. Found: C, 73.25; H, 6.69; N, 15.42. ^{1}H NMR (C_6D_6, room temperature): δ 6.81–6.67 (m, 8 H), 4.40 (s, 2 H), 1.90 (s, 12 H).

Preparation of [(tmtaa)Ti(Cl)] (3). LiMe (19.2 mL, 1.66 M in Et_2O, 32 mmol) was added dropwise to a benzene (200 mL) solution of tmtaaH_2 (5.46 g, 16 mmol). The red solution was refluxed for 1 h, and then $TiCl_3(THF)_3$ (5.9 g, 16 mmol) was added. The color turned suddenly to green. The suspension was refluxed overnight and then extracted with the mother liquor. A green crystalline product was collected and dried under vacuum (3.5 g, 52%). Anal. Calcd for [(tmtaa)Ti(Cl)], $C_{22}H_{22}ClN_4Ti$: C, 62.06; H, 5.21; N, 13.16. Found: C, 62.08; H, 5.40; N, 12.92.

Preparation of [(tmtaa)Ti(Cl)]·LiCl·2THF (3b). LiMe (55.2 mL, 1.38 M in Et_2O, 76.2 mmol) was added dropwise to a warm THF (200 mL) solution of tmtaaH_2 (13.10 g, 38.1 mmol). The diethyl ether was allowed to evaporate under vacuum. To the red solution obtained, previously heated, was added a THF (150 mL) solution of $TiCl_3(THF)_3$ (14.14 g, 38.1 mmol), resulting in a suspension of a green solid, which was refluxed for 1 h. A green crystalline product was collected, dried under vacuum, and recrystallized from THF (17.95 g, 77%). Anal. Calcd for [(tmtaa)Ti(Cl)]·LiCl·2THF, $C_{30}H_{38}Cl_2LiN_4O_2Ti$: C, 58.82; H, 6.30; Cl, 11.60, N, 9.16. Found: C, 58.17; H, 6.43; Cl, 11.99, N, 8.84. μ_{eff} = 1.76 μ_B at 293 K.

Preparation of [(tmtaa)Ti(Cl)$_2$]·C_6H_6 (4). LiMe (32.4 mL, 1.73 M, 56 mmol) was added dropwise at room temperature and under stirring to a benzene (250 mL) solution of tmtaaH_2 (9.72 g, 28 mmol). A gas was evolved, and the solution color turned to red. When the gas evolution had stopped, $TiCl_4(THF)_2$ (9.34 g, 28 mmol) was added, resulting in formation of a brown suspension which was refluxed for 6 h. The formed brown solid was extracted with the mother liquor for 5 days and then allowed to stand in the refrigerator for 1 day, and the resultant solid was collected (6.9 g, 45%). Anal. Calcd for [(tmtaa)Ti(Cl)$_2$]·C_6H_6, $C_{28}H_{28}Cl_2N_4Ti$: C, 62.35; H, 5.23; N, 10.39. Found: C, 61.77; H, 5.36; N, 10.20. ^{1}H NMR (CD_2Cl_2, room temperature): δ 7.64–7.36 (m, Ph), 5.93 (s, CH), 5.52 (s, CH), 2.66 (s, CH_3), 2.40 (s, CH_3). Intensities of the two peaks for CH and CH_3 are in the 5:1 ratio. ^{1}H NMR (CD_3CN, room temperature): δ 7.60–7.36 (m, Ph), 6.01 (s, CH), 5.64 (s, CH), 2.67 (s, CH_3), 2.43 (s, CH_3). Intensities of the two peaks for CH and CH_3 are in the 4:1 ratio.

Preparation of [(tmtaa)Zr(Cl)$_2$]·2THF (5). LiMe (45 mL, 1.7 M in Et_2O, 75.6 mmol) was added to a THF (300 mL) solution of tmtaaH_2 (13.00 g, 37.8 mmol). The final red solution was stirred for 1 h, and then $ZrCl_4(THF)_2$ (14.3 g, 37.8 mmol) was added. The suspension was refluxed overnight, and then the yellow solid was collected, washed with heptane (3 × 50 mL), and dried under vacuum (20.6 g, 84%). Anal. Calcd for [(tmtaa)Zr(Cl)$_2$]·2THF, $C_{30}H_{38}Cl_2N_4O_2Zr$: C, 55.54; H, 5.90; N, 8.64. Found: C, 55.59; H, 6.35; N, 8.89. ^{1}H NMR (CD_2Cl_2, room temperature): δ 7.60 (bm), 7.24 (bm), 5.71 (s), 5.83 (s), 3.7 (bm), 2.74 (s), 2.52 (s), 1.80 (bm). Intensities of the two peaks for CH and CH_3 are in the 3:1 ratio. ^{1}H NMR (CD_3CN, room temperature): δ 7.73 (bm, 8 H), 5.81 (bs, 2 H), 3.7 (bm, 8 H), 2.5 (bs, 12 H), 1.80 (bm, 8 H). The unsolvated form was obtained by suspending the solid in benzene and then evaporating it to dryness. No trace of solvent was found in the solid by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, room temperature): δ 7.60 (m, Ph), 7.24 (m), 5.83 (s, CH), 5.71 (s, CH), 2.74 (s, CH_3), 2.51 (s, CH_3). Intensities of the two peaks for CH and CH_3 are in the 3:1 ratio. ^{1}H NMR (CD_3CN, room temperature): δ 7.73–7.68 (m, 8 H, Ph), 5.81 (s, 2 H), 2.47 (12 H).

Preparation of [(tmtaa)Hf(Cl)$_2$]·2THF (6). LiMe (42 mL, 1.88 M in Et_2O, 79.0 mmol) was slowly added to a THF (400 mL) solution of tmtaaH_2 (13.6 g, 39.5 mmol). The final red solution was stirred for 1 h, and then $HfCl_4(THF)_2$ (18.5 g, 39.5 mmol) was added. An orange-yellow solid precipitated, which was refluxed overnight, and then collected and dried under vacuum (18.8 g, 65%). Anal. Calcd for [(tmtaa)Hf(Cl)$_2$]·2THF, $C_{30}H_{38}Cl_2HfN_4O_2$: C, 48.95; H, 5.20; N, 7.61. Found: C, 47.48; H, 5.18; N, 7.36. ^{1}H NMR (CD_2Cl_2, room temperature): δ 7.56 (m, 8 H), 5.64 (s, 2 H), 3.67 (m, 8 H), 2.49 (s, 12 H), 1.82 (m, 8 H). ^{1}H NMR (CD_3CN, room temperature): δ 7.68–7.57 (m, 8 H, Ph), 5.74 (s, 2 H, CH), 2.53 (s, 12 H, CH_3). The unsolvated form obtained as reported for **5** gave the same spectra in CD_2Cl_2 and CD_3CN.

Preparation of [(tmtaa)$_2$Ti]·C_6H_6 (7). LiMe (65 mL, 1.7 M, 110 mmol) was added dropwise to a benzene (500 mL) solution of tmtaaH_2 (18.94 g, 55 mmol) at room temperature and under stirring. The green solution color turned to red while gas evolution was observed. When methane evolution stopped, $TiCl_4(THF)_2$ (9.19 g, 27.5 mmol) was added, resulting in a suspension which was refluxed for 12 h. The resulting brick-red solid was extracted with the mother liquor for 5 days and then concentrated to $^1/_4$ of its volume and allowed to stand in the refrigerator (−4 °C) for 1 day to afford the product (12.0 g, 54%). Anal. Calcd for [(tmtaa)$_2$Ti]·C_6H_6, $C_{50}H_{50}N_8Ti$: C, 74.06; H, 6.21; N, 13.82. Found: C, 73.86; H, 6.66; N, 13.54. ^{1}H NMR (CD_3CN, room temperature): δ 7.75–7.09 (m, Ph), 5.45 (s, CH), 4.99 (s, CH), 2.50 (s, CH_3), 2.16 (s, CH_3). Intensities of the two peaks for CH and CH_3 are in a 1:2 ratio.

Preparation of [(tmtaa)$_2$Zr] (8). Method A. LiMe (46 mL, 1.7 M in Et_2O, 78.6 mmol) was added dropwise to a THF (200 mL) solution of tmtaaH_2 (13.5 g, 39.3 mmol). Gas evolution was observed. To the bright red solution obtained was added $ZrCl_4(THF)_2$ (7.41 g, 19.6 mmol), resulting in a suspension which was refluxed overnight, cooled, and concentrated to $^3/_4$ of the initial volume. The resultant powder was collected and dried under vacuum (7.75 g, 51%). Anal. Calcd for [(tmtaa)$_2$Zr], $C_{44}H_{44}N_8Zr$: C, 68.09; H, 5.71; N, 14.44. Found: C, 68.39; H, 6.08; N, 13.89. ^{1}H NMR (C_6D_6, room temperature): δ 7.10 (s, 8 H), 4.20 (s, 2 H), 1.84 (s, 12 H). Suitable crystals have been obtained by recrystallizing **8** from CH_3CN, from which the solvated form [Zr(tmtaa)$_2$]·2CH_3CN was obtained. Anal. Calcd for $C_{48}H_{50}N_{10}Zr$: C, 67.18; H, 5.87; N, 16.32. Found: C, 66.85; H, 5.96; N, 15.79.

Method B. LiMe (9.4 mL, 1.76 M in Et_2O, 16.6 mmol) was added dropwise to a THF (100 mL) solution of tmtaaH_2 (2.86 g, 8.3 mmol). Gas evolution was observed while a red solution formed, to which [(tmtaa)Zr(Cl)$_2$]·2THF (**5**; 5.38 g, 8.3 mmol) was added. The mixture was refluxed for 24 h, concentrated to $^1/_3$ of its volume and allowed to stand in the refrigerator at −4 °C for 1 day. The resultant orange powder was collected and dried under vacuum (4.5 g, 67.5%). Anal. Calcd for [(tmtaa)$_2$Zr], $C_{44}H_{44}N_8Zr$: C, 68.09; H, 5.71; N, 14.44. Found: C, 68.04; H, 6.56; N, 14.06. ^{1}H NMR (C_6D_6, room temperature): δ 7.10 (s, 8 H, CH), 4.20 (s, 2 H, CH), 1.84 (s, 12 H, CH_3).

Preparation of [(tmtaa)$_2$Hf] (9). LiMe (51.7 mL, 1.74 M in Et_2O, 90 mmol) was added dropwise to a THF (400 mL) green solution of tmtaaH_2 (15.5 g, 45 mmol) at room temperature and under stirring. The color turned to red while gas evolution was observed. $HfCl_4(THF)_2$ (10.41 g, 22.5 mmol) was then added, resulting in formation of a suspension which was allowed to reflux for 4 h and then concentrated to $^1/_3$ of the initial volume. A yellow solid precipitated from the red mother liquor. The mixture was allowed to stand at −4 °C for 1 day and then filtered and the resultant solid dried (10.5 g, 54.1%). Anal. Calcd for [(tmtaa)$_2$Hf], $C_{44}H_{44}N_8Hf$: C, 61.21; H, 5.14; N, 12.98. Found: C, 61.23; H, 5.33; N, 12.94. ^{1}H NMR (C_6D_6, room temperature): δ 7.09 (s, 8 H, CH), 4.16 (s, 2 H, CH), 1.83 (s, 12 H, CH_3).

Collection and Reduction of X-ray Data. Suitable single crystals of **2**, **3**, **5**, and **8** were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table I. The reduced cells were obtained with use of TRACER.[9] Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background the three-point technique was used for **3** and **5**. For **2** and **8** individual reflection profiles were analyzed.[10] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[11] The crystal quality of complexes **3**, **5**, and **8** was tested by ψ scans showing that crystal absorption effects could be neglected for **3** and **5**. The intensity data for **2** and **8** were then corrected for absorption using ABSORB[12] for **2** and a semiempirical method[13] for **8**. The function minimized during the least-squares refinement was $\sum w|\Delta F_o|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$ based on counting statistics. Anomalous scattering corrections were included in all structure factor calculations.[14b] Scattering factors for neutral

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds **2**, **3**, **5**, and **8**

compd	2	3	5	8
chem formula	$C_{56}H_{74}Li_4N_8O_6$	$C_{22}H_{22}ClN_4Ti\cdot LiCl(C_4H_8O)_2$	$C_{22}H_{22}Cl_2N_4Zr\cdot 2C_4H_8O$	$C_{44}H_{44}N_8Zr\cdot 2CH_3CN$
a, Å	14.433 (2)	34.239 (7)	12.437 (3)	11.604 (5)
b, Å	17.319 (3)	10.101 (2)	15.414 (4)	19.073 (3)
c, Å	11.961 (2)	18.403 (3)	9.337 (2)	19.220 (3)
α, deg	94.76 (2)	90	95.42 (3)	90
β, deg	101.24 (2)	100.96 (2)	109.16 (3)	91.34 (2)
γ, deg	104.22 (2)	90	111.47 (3)	90
V, Å^3	2816 (8)	6249 (2)	1525.9 (9)	4253 (2)
Z	2	8	2	4
fw	983.0	612.4	648.8	858.2
space group	$P\bar{1}$ (No. 2)	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
T, °C	25	25	25	25
λ, Å	1.541 78	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.160	1.302	1.412	1.340
μ, cm^{-1}	5.59	4.74	5.62	2.98
transm coeff	0.90–1.00	0.96–1.00	0.96–1.00	0.81–1.00
R^a	0.070	0.059	0.044	0.049
$R_w{}^b$	0.082	0.060	0.048	0.055

${}^a R = \sum|\Delta F|/\sum|F_o|$. ${}^b R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$.

Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex **2**

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Li1A	−620 (3)	2484 (3)	1373 (4)	C20A	−2154 (3)	3967 (3)	4336 (3)
Li2A	−2271 (5)	2375 (4)	620 (5)	C21A	−1479 (3)	4112 (2)	3642 (3)
Li1B	2540 (3)	2692 (3)	5739 (4)	C22A	−1315 (2)	3473 (2)	2966 (2)
Li2B	3936 (4)	2395 (4)	6514 (5)	C23A	−2275 (3)	4080 (2)	167 (4)
O1A	−2840 (2)	3268 (1)	92 (2)	C24A	−3754 (3)	3184 (3)	403 (4)
O2A	−3737 (2)	1845 (2)	451 (3)	C25A	−4327 (3)	2347 (3)	95 (4)
O1B	5456 (2)	2866 (2)	6801 (3)	C26A	−4180 (4)	1031 (3)	257 (5)
O2B	4515 (2)	1464 (2)	6973 (3)	C1B	901 (2)	1416 (2)	7679 (3)
O1C	1352 (1)	3005 (1)	5081 (2)	C2B	1639 (2)	1531 (2)	6922 (3)
O2C	618 (1)	2216 (1)	2057 (2)	C3B	1321 (2)	1054 (2)	5827 (3)
N1A	−735 (2)	3530 (1)	2156 (2)	C4B	1811 (2)	1071 (2)	4918 (2)
N2A	−586 (2)	3002 (1)	−93 (2)	C5B	1248 (2)	513 (2)	3810 (3)
N3A	−1603 (2)	1556 (1)	30 (2)	C6B	3256 (2)	1631 (2)	4195 (2)
N4A	−1767 (2)	2077 (1)	2225 (2)	C7B	3417 (2)	969 (2)	3559 (3)
N1B	2507 (2)	2078 (1)	7209 (2)	C8B	4108 (3)	1078 (2)	2894 (3)
N2B	2675 (2)	1592 (1)	5001 (2)	C9B	4677 (3)	1841 (3)	2869 (3)
N3B	3721 (2)	3013 (1)	4930 (2)	C10B	4545 (2)	2511 (2)	3497 (3)
N4B	3530 (2)	3514 (1)	7135 (2)	C11B	3838 (2)	2417 (2)	4154 (2)
C1A	571 (3)	4761 (2)	3147 (3)	C12B	3809 (3)	4057 (2)	3608 (3)
C2A	57 (2)	4117 (2)	2140 (3)	C13B	3768 (2)	3770 (2)	4762 (3)
C3A	499 (2)	4135 (2)	1202 (3)	C14B	3731 (2)	4337 (2)	5649 (3)
C4A	206 (2)	3621 (2)	131 (3)	C15B	3611 (2)	4225 (2)	6769 (3)
C5A	896 (3)	3807 (2)	−685 (3)	C16B	3565 (3)	4962 (2)	7504 (3)
C6A	−991 (2)	2528 (2)	−1146 (2)	C17B	3454 (2)	3347 (2)	8244 (2)
C7A	−1030 (2)	2776 (2)	−2236 (3)	C18B	3951 (2)	3833 (2)	9286 (3)
C8A	−1520 (2)	2251 (2)	−3238 (2)	C19B	3881 (3)	3560 (3)	10341 (3)
C9A	−2019 (2)	1465 (2)	−3171 (2)	C20B	3367 (3)	2783 (3)	10374 (3)
C10A	−2043 (2)	1212 (2)	−2107 (2)	C21B	2888 (2)	2279 (2)	9352 (3)
C11A	−1531 (2)	1724 (2)	−1091 (2)	C22B	2896 (2)	2548 (2)	8283 (2)
C12A	−1402 (3)	168 (2)	−270 (3)	C23B	5952 (3)	3678 (3)	6925 (5)
C13A	−1583 (2)	871 (2)	431 (2)	C24B	6002 (3)	2331 (3)	6903 (4)
C14A	−1689 (2)	764 (2)	1559 (3)	C25B	5410 (3)	1528 (3)	6694 (4)
C15A	−1750 (2)	1340 (2)	2427 (2)	C26B	3896 (4)	684 (3)	6890 (5)
C16A	−1736 (3)	1083 (2)	3610 (3)	C1C	874 (3)	3247 (2)	5924 (3)
C17A	−1870 (2)	2679 (2)	3011 (2)	C2C	705 (2)	2611 (2)	4029 (3)
C18A	−2573 (2)	2562 (2)	3691 (3)	C3C	1258 (2)	2626 (2)	3105 (3)

atoms were taken from ref 14a for non-hydrogen atoms and from ref 15 for H atoms. Among the low-angle reflections no corrections for secondary extinction was deemed necessary.

Solution and Refinement. The structure of **2** was solved by direct methods using SHELX-86.[16] The structures of **3**, **5**, and **8** were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement for all complexes was first isotropically and then anisotropically for non-hydrogen atoms. The hydrogens associated with the complex molecules were located from difference Fourier maps; those associated with the THF molecules in complex **3** were put in calculated positions. They were introduced in calculations prior the last stage of refinement as fixed contributors with isotropic U's fixed at 0.08 Å^2 for **2**, **5**, and **8** and 0.10 Å^2 for **3**. The hydrogen atoms belonging to the THF solvent molecules in complex **5** and to the MeCN solvent molecule in complex **8** were ignored. One of the latter showed the C≡N group statistically distributed over two positions (A and B), which were anisotropically refined with a site occupation factor of 0.5. The final difference maps showed no unusual feature, with no peak having chemical meaning above the general background. All calculations were carried out using SHELX76.[17] Final atomic coordinates are listed in Tables II–V, and bond

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(16) Sheldrick, G. SHELX-86. Program for the solution of crystal structures. University of Göttingen, Germany, 1986.

(17) Sheldrick, G. SHELX-76. System of Crystallographic Computer Programs. University of Cambridge, Cambridge, England, 1976.

Table III. Fractional Atomic Coordinates ($\times 10^4$) for [Ti(tmtaa)(Cl)] (3)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Ti	1857.4 (5)	1287.5 (16)	3298.1 (8)	C9	3129 (3)	252 (12)	2537 (6)
Cl1	1646 (1)	1323 (3)	2039 (1)	C10	2847 (3)	−388 (10)	2865 (5)
N1	1591 (3)	2631 (8)	3901 (4)	C11	2610 (3)	316 (9)	3261 (5)
N2	2370 (2)	2371 (7)	3676 (4)	C12	2605 (3)	−2334 (9)	3958 (5)
N3	2277 (2)	−182 (7)	3544 (4)	C13	2260 (3)	−1378 (9)	3853 (4)
N4	1501 (2)	93 (7)	3786 (4)	C14	1931 (3)	−1778 (8)	4122 (5)
C1	1480 (4)	4344 (11)	4808 (6)	C15	1574 (3)	−1110 (10)	4115 (5)
C2	1747 (4)	3618 (10)	4357 (5)	C16	1275 (3)	−1716 (10)	4538 (6)
C3	2138 (4)	3996 (9)	4443 (5)	C17	1137 (3)	809 (10)	3716 (5)
C4	2443 (3)	3412 (9)	4141 (5)	C18	758 (4)	287 (11)	3497 (6)
C5	2857 (3)	3969 (9)	4384 (5)	C19	428 (3)	1162 (19)	3367 (6)
C6	2661 (3)	1735 (8)	3351 (5)	C20	493 (5)	2528 (17)	3425 (8)
C7	2948 (3)	2356 (9)	3016 (5)	C21	864 (4)	3062 (12)	3612 (7)
C8	3182 (3)	1617 (12)	2623 (6)	C22	1190 (3)	2203 (10)	3769 (5)

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for [Zr(tmtaa)(Cl)$_2$] (5)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	3384.5 (4)	1758.9 (3)	4011.6 (6)	C9	164 (6)	−1013 (4)	4270 (8)
Cl1	3137 (1)	2492 (1)	6312 (2)	C10	1441 (5)	−471 (4)	5115 (7)
Cl2	1731 (1)	2218 (1)	2417 (2)	C11	2200 (5)	−45 (3)	4345 (6)
N1	4369 (4)	2221 (3)	2501 (5)	C12	4082 (5)	−456 (4)	6705 (7)
N2	2497 (4)	462 (3)	2128 (5)	C13	4375 (5)	472 (4)	6214 (6)
N3	3495 (4)	600 (3)	5093 (4)	C14	5595 (5)	1180 (4)	6910 (6)
N4	5370 (4)	2339 (3)	5447 (5)	C15	6088 (5)	2065 (4)	6554 (6)
C1	5065 (7)	2430 (5)	326 (8)	C16	7477 (5)	2694 (5)	7428 (8)
C2	4232 (5)	1870 (4)	1061 (6)	C17	5738 (4)	3224 (4)	5054 (6)
C3	3346 (6)	940 (4)	230 (6)	C18	6425 (5)	4120 (4)	6111 (7)
C4	2531 (5)	265 (4)	733 (6)	C19	6604 (6)	4949 (5)	5563 (9)
C5	1733 (6)	−722 (4)	−337 (7)	C20	6061 (7)	4889 (4)	3991 (10)
C6	1668 (5)	−117 (3)	2713 (6)	C21	5339 (6)	4008 (4)	2924 (8)
C7	371 (5)	−643 (4)	1895 (7)	C22	5178 (4)	3167 (4)	3443 (6)
C8	−361 (5)	−1084 (4)	2679 (9)				

Table V. Fractional Atomic Coordinates ($\times 10^4$) for [Zr(tmtaa)$_2$] (8)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	2114.0 (4)	2539.4 (3)	95.3 (3)	C19A	5086 (7)	1243 (4)	1526 (4)
N1A	1946 (4)	2303 (2)	1273 (2)	C20A	4132 (8)	949 (4)	1797 (4)
N2A	541 (4)	3183 (2)	470 (3)	C21A	3057 (6)	1272 (4)	1756 (4)
N3A	2332 (4)	3747 (2)	−27 (2)	C22A	2973 (5)	1936 (3)	1427 (3)
N4A	3730 (4)	2857 (3)	767 (2)	C1B	2320 (6)	2999 (4)	−2334 (3)
N1B	2430 (4)	2778 (2)	−1075 (2)	C2B	1822 (5)	2788 (3)	−1659 (3)
N2B	483 (4)	2142 (2)	−527 (3)	C3B	665 (5)	2560 (4)	−1683 (3)
N3B	1759 (4)	1338 (3)	212 (2)	C4B	69 (5)	2231 (3)	−1172 (3)
N4B	3710 (4)	1961 (2)	−353 (2)	C5B	−1092 (6)	1908 (4)	−1389 (4)
C1A	1327 (8)	2174 (5)	2502 (4)	C6B	−102 (5)	1770 (3)	−4 (3)
C2A	1168 (6)	2413 (3)	1758 (3)	C7B	−1255 (6)	1869 (4)	175 (4)
C3A	187 (6)	2816 (4)	1620 (3)	C8B	−1705 (6)	1529 (4)	743 (4)
C4A	−99 (5)	3202 (3)	1036 (3)	C9B	−1012 (7)	1104 (4)	1150 (4)
C5A	−1121 (7)	3677 (5)	1084 (4)	C10B	142 (6)	1006 (4)	988 (4)
C6A	304 (5)	3617 (3)	−113 (3)	C11B	582 (5)	1331 (3)	406 (3)
C7A	−749 (5)	3699 (3)	−468 (4)	C12B	1880 (7)	46 (3)	364 (5)
C8A	−841 (6)	4082 (4)	−1066 (4)	C13B	2377 (6)	756 (3)	170 (3)
C9A	132 (6)	4408 (3)	−1333 (4)	C14B	3473 (6)	745 (3)	−87 (4)
C10A	1194 (5)	4319 (3)	−1005 (3)	C15B	4085 (5)	1304 (4)	−364 (4)
C11A	1289 (5)	3933 (3)	−380 (3)	C16B	5164 (7)	1118 (4)	−730 (5)
C12A	3013 (6)	4976 (3)	−73 (4)	C17B	4317 (5)	2519 (3)	−666 (3)
C13A	3128 (5)	4224 (3)	131 (3)	C18B	5472 (6)	2693 (4)	−556 (4)
C14A	4105 (5)	4057 (3)	525 (3)	C19B	5899 (6)	3304 (4)	−827 (4)
C15A	4373 (5)	3432 (3)	846 (3)	C20B	5218 (6)	3752 (4)	−1203 (4)
C16A	5390 (6)	3454 (4)	1358 (4)	C21B	4078 (6)	3585 (3)	−1323 (3)
C17A	3965 (6)	2238 (3)	1149 (3)	C22B	3616 (5)	2973 (3)	−1060 (3)
C18A	5013 (6)	1891 (4)	1191 (4)				

distances and angles, in Tables SX–SXIII.[18]

Results

The deprotonation of tmtaaH_2 is usually carried out in THF using LiMe, and the resulting red solution was used in the synthesis of metal complexes. However, when the reaction was carried out in benzene with LiMe or LiBu, it produced in the former case a red solution and in the latter a red solid. This result is not associated with any chemical difference in the product formed from the deprotonation reaction. In the reaction with LiBu^n, butane, a reaction product, led to a solvent mixture in which the lithium salt is unsoluble. The recrystallization of both compounds from DME gave the same solvated form as red crystals **2**.

The ^{1}H NMR spectrum and the analytical data agree with the structure of **2**, which is shown in Figure 1, while the structural parameters are listed in Table VI. Reaction 1 is a good synthetic

(18) See paragraph at the end of paper regarding supplementary material.
(19) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.

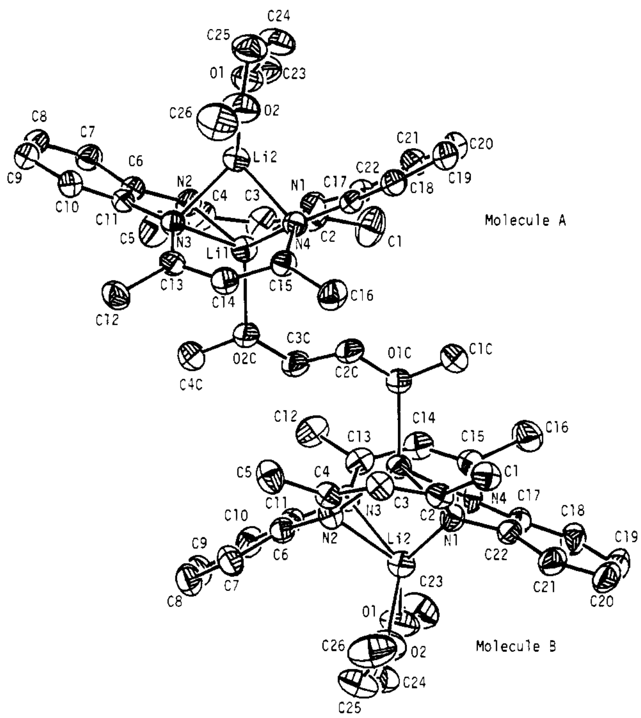

Figure 1. ORTEP[11] drawing for complex **2** (30% probability ellipsoids).

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for Complex **2**

Li1A–Li2A	2.332 (9)	Li1B–Li2B	2.246 (8)
Li1A–O2C	1.994 (6)	Li1B–O1C	1.963 (6)
Li1A–N1A	2.028 (6)	Li1B–N1B	2.131 (6)
Li1A–N2A	2.038 (6)	Li1B–N2B	2.102 (6)
Li1A–N3A	2.177 (5)	Li1B–N3B	2.102 (6)
Li1A–N4A	2.116 (6)	Li1B–N4B	2.129 (5)
Li2A–O1A	2.012 (8)	Li2B–O1B	2.092 (7)
Li2A–O2A	2.051 (8)	Li2B–O2B	2.057 (9)
Li2A–N1A	2.813 (6)	Li2B–N1B	2.331 (7)
Li2A–N2A	2.736 (8)	Li2B–N2B	2.361 (6)
Li2A–N3A	2.052 (9)	Li2B–N3B	2.259 (8)
Li2A–N4A	2.070 (7)	Li2B–N4B	2.267 (8)
N3A–Li1A–N4A	80.6 (3)	N3B–Li1B–N4B	82.6 (2)
N2A–Li1A–N4A	131.9 (3)	N2B–Li1B–N4B	128.0 (3)
N2A–Li1A–N3A	76.3 (2)	N2B–Li1B–N3B	75.4 (2)
N1A–Li1A–N4A	77.9 (3)	N1B–Li1B–N4B	74.5 (2)
N1A–Li1A–N3A	133.5 (3)	N1B–Li1B–N3B	126.8 (3)
N1A–Li1A–N2A	88.4 (3)	N1B–Li1B–N2B	82.1 (2)
N3A–Li2A–N4A	84.7 (3)	N3B–Li2B–N4B	76.2 (3)
O2A–Li2A–N4A	98.1 (4)	N2B–Li2B–N4B	110.5 (3)
O2A–Li2A–N3A	110.1 (4)	N2B–Li2B–N3B	67.5 (2)
O1A–Li2A–N4A	133.5 (4)	N1B–Li2B–N4B	68.2 (2)
O1A–Li2A–N3A	140.2 (4)	N1B–Li2B–N3B	111.1 (3)
O1A–Li2A–O2A	79.5 (3)	N1B–Li2B–N2B	72.6 (2)
		O1B–Li2B–O2B	74.8 (3)

procedure making available the lithium salt of tmtaa in its solvated or unsolvated form (from toluene), which should be considered the parent compound for the synthesis of tmtaa complexes in non-protic conditions.

$$\underset{\mathbf{1}}{\mathrm{tmtaaH_2}} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{LiR,\,-RH}} \xrightarrow{\mathrm{DME}} \underset{\mathbf{2}}{[\mathrm{(tmtaa)_2Li_4(DME)_3}]} \quad (1)$$

$$\mathrm{R = Me, Bu^n}$$

In the asymmetric unit there are two independent [(tmtaa)-Li_2(DME)] units (A and B) linked together by a third DME molecule (C) which behaves as a bridging ligand through the oxygen atoms giving rise to a dimer (Figure 1). In each [(tmtaa)Li_2(DME)] unit the two Li cations are capping on both sides the N_4 core. The environment of the Li1 cations is nearly the same in the two units, lithium being bonded to the four nitrogen atoms of the N_4 core and to the oxygen atom of the bridging DME

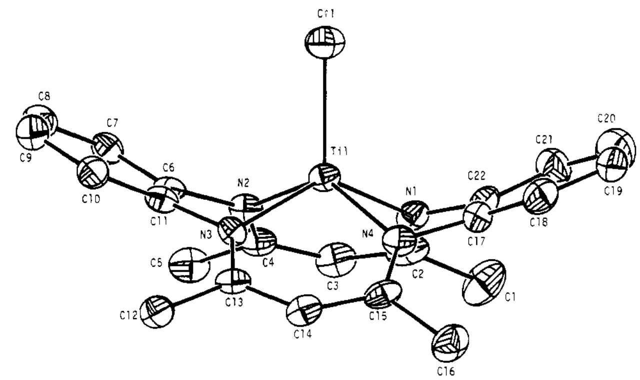

Figure 2. ORTEP[11] drawing for complex **3** (30% probability ellipsoids).

molecule. The resulting coordination polyhedron is a square pyramid. The Li1–N distances are very close ranging from 2.028 (6) to 2.177 (5) Å and from 2.102 (6) to 2.131 (6) Å for A and B, respectively. By contrast the Li2 atoms anchored to the N_4 cores on the opposite sides with respect to Li1 interact with the N_4 core in a different way. In molecule A, Li2 bonded to the N3 and N4 nitrogen atoms [Li2–N3 = 2.052 (9) Å and Li2–N4 = 2.070 (7) Å] and not to N1 and N2 (Table VI), while in molecule B Li2 interacts with the four nitrogen atoms, the Li2–N distances ranging from 2.259 (8) to 2.361 (6) Å. These values are significantly longer than the Li1–N and Li2A–N bond distances. Coordination around Li2 is completed both for A and B by a DME molecule behaving as a chelating ligand through the O1 and O2 oxygen atoms. As a consequence, the coordination polyhedron around Li2 can be described as a tetrahedron in molecule A, while in molecule B the Li2 cation achieves hexacoordination with the oxygen atoms in a cis arrangement. The plane running through Li2B, O1B, and O2B is nearly perpendicular with respect to the N4 core, the dihedral angle they form being 82.7 (3)°.

The saddle-shape conformation of tmtaa is maintained in complex **2**, which represents a rare macrocyclic complex of the lithium cation.[20] The ligand tmtaa displays a binding capability on both sides of the N_4 core, which is rather unique in the chemistry of such a ligand. A comparison of the conformational parameters of the ligand is reported in Table X.

Mono(dibenzotetramethyltetraaza[14]annulene) Halo Complexes. The lithium salt made from LiMe is normally used in either THF or benzene solution to react with metal chlorides. The choice between the two methods is based on the relative solubility of LiCl–metal complexes in the solvent used. Reactions 2 and 3 summarize the formation of group IV metal complexes.

$$\mathrm{TiCl_3(THF)} + [\mathrm{(tmtaa)Li_2}] \xrightarrow[\mathrm{-LiCl}]{} \underset{\mathbf{3}}{[\mathrm{(tmtaa)Ti(Cl)}]} \quad (2)$$

$$\mathrm{MCl_4(THF)_2} + [\mathrm{(tmtaa)Li_2}] \xrightarrow[\mathrm{-LiCl}]{\mathrm{THF}} [\mathrm{(tmtaa)M(Cl)_2}]\cdot\mathrm{L} \quad (3)$$

$$\mathrm{M = Ti,\ L = C_6H_6},\ \mathbf{4}$$
$$\mathrm{M = Zr,\ L = (THF)_2},\ \mathbf{5}$$
$$\mathrm{M = Hf,\ L = (THF)_2},\ \mathbf{6}$$

Reaction 2 carried out in THF gave **3** cocrystallized with LiCl. The reaction carried out in benzene provided a much better starting material for further reactivity studies. Owing to the crystal quality, the X-ray analysis was carried out on **3** cocrystallized with {[Li(THF)$_2$]$_2$(μ-Cl)$_2$}. The structure reported in Figure 2 and the parameters listed in Table VII show the usual saddle-shape conformation of the ligand. The titanium is five-coordinated in a pseudo-square-pyramidal coordination geometry.[6] The structure is quite similar to that of the analogous vanadium(III) derivative.[4c] The first synthesis and the structure of **4** were published by Goedken.[3b] Our synthesis in benzene allows one to scale the

(20) Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1988; Vol. 3, Chapter 23.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

Ti–Cl1	2.293 (2)		
Ti–N1	2.071 (9)	Ti–N3	2.055 (7)
Ti–N2	2.073 (7)	Ti–N4	2.041 (8)
N1–C2	1.346 (13)	N3–C11	1.432 (13)
N1–C22	1.416 (14)	N3–C13	1.341 (11)
N2–C4	1.349 (12)	N4–C15	1.359 (12)
N2–C6	1.411 (13)	N4–C17	1.425 (12)
N3–Ti–N4	85.8 (3)	N1–Ti–N4	77.9 (3)
N2–Ti–N4	134.7 (3)	N1–Ti–N3	135.7 (3)
N2–Ti–N3	78.2 (3)	N1–Ti–N2	84.6 (3)
Ti–N1–C22	102.7 (6)	Ti–N3–C13	131.2 (6)
Ti–N1–C2	131.0 (9)	Ti–N3–C11	103.8 (5)
C2–N1–C22	126.1 (9)	C11–N3–C13	124.9 (8)
Ti–N2–C6	103.8 (5)	Ti–N4–C17	104.2 (6)
Ti–N2–C4	131.9 (6)	Ti–N4–C15	130.5 (6)
C4–N2–C6	124.3 (8)	C15–N4–C17	125.3 (8)

Table VIII. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

Zr–Cl1	2.493 (2)	N1–C22	1.419 (6)
Zr–Cl2	2.490 (2)	N2–C4	1.327 (8)
Zr–N1	2.163 (5)	N2–C6	1.395 (8)
Zr–N2	2.180 (4)	N3–C11	1.424 (6)
Zr–N3	2.158 (5)	N3–C13	1.333 (7)
Zr–N4	2.163 (4)	N4–C15	1.340 (8)
N1–C2	1.332 (8)	N4–C17	1.397 (8)
N3–Zr–N4	78.5 (2)	Zr–N2–C6	97.6 (3)
N2–Zr–N4	120.4 (2)	Zr–N2–C4	134.1 (4)
N2–Zr–N3	73.2 (2)	C4–N2–C6	127.5 (5)
N1–Zr–N4	73.1 (2)	Zr–N3–C13	136.0 (4)
N1–Zr–N3	121.1 (2)	Zr–N3–C11	97.3 (3)
N1–Zr–N2	78.5 (2)	C11–N3–C13	126.4 (5)
Cl1–Zr–Cl2	85.6 (1)	Zr–N4–C17	98.2 (3)
Zr–N1–C22	96.8 (3)	Zr–N4–C15	134.7 (4)
Zr–N1–C2	135.9 (4)	C15–N4–C17	126.6 (5)
C2–N1–C22	126.7 (5)		

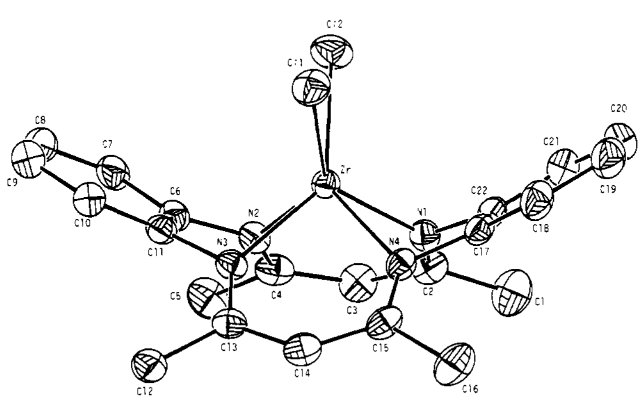

Figure 3. ORTEP[11] drawing for complex **5** (30% probability ellipsoids).

synthesis up and to avoid the presence of R_3NHCl, very often difficult to separate from the complex. The rather poor solubility of **5** and **6** allowed their separation from LiCl, soluble in THF, very easily and in a better yield than **4**. The metal is hexacoordinate with the two Cl's in a cis arrangement. The structure in the solid state has been determined on **4**[3b] and in this work on **5**. Its structure is shown in Figure 3, and the structural parameters are reported in Table VIII.

The structure consists of discrete $[(tmtaa)Zr(Cl)_2]$ molecules and THF solvent molecules in the molar ratio of 1:2. The THF molecules show very high thermal parameters. The two chlorine atoms are bonded to the [Zr(tmtaa)] moiety in a cis arrangement [Cl1-Zr-Cl2 = 85.6 (12)°]. The Cl1-Zr-Cl2 plane is perpendicular to the N_4 core [dihedral angle of 89.9 (1)°], is perpendicular to the N1–N2 and N3–N4 vectors, and is parallel to the N1–N4 and N2–N3 vectors. The cavity where the $ZrCl_2$ is located is quite similar to that defined by two cyclopentadienyl ligands in the $(cp)_2ZrCl_2$ series.[21]

Table IX. Selected Bond Distances (Å) and Angles (deg) for Complex **8**

Zr–N1A	2.321 (4)	Zr–N1B	2.332 (4)
Zr–N2A	2.328 (5)	Zr–N2B	2.341 (5)
Zr–N3A	2.330 (4)	Zr–N3B	2.340 (6)
Zr–N4A	2.332 (5)	Zr–N4B	2.337 (5)
N1A–C2A	1.329 (8)	N1B–C2B	1.312 (7)
N1A–C22A	1.408 (7)	N1B–C22B	1.425 (7)
N2A–C4A	1.332 (8)	N2B–C4B	1.330 (8)
N2A–C6A	1.415 (8)	N2B–C6B	1.416 (8)
N3A–C11A	1.419 (7)	N3B–C11B	1.424 (8)
N3A–C13A	1.327 (7)	N3B–C13B	1.325 (8)
N4A–C15A	1.333 (8)	N4B–C15B	1.327 (8)
N4A–C17A	1.413 (8)	N4B–C17B	1.418 (7)
N3A–Zr–N4A	73.2 (2)	N3B–Zr–N4B	73.5 (1)
N2A–Zr–N4A	108.5 (2)	N2B–Zr–N4B	107.3 (1)
N2A–Zr–N3B	110.2 (2)	N2B–Zr–N3B	65.8 (2)
N1A–Zr–N4B	110.7 (1)	N1B–Zr–N4B	66.0 (1)
N1A–Zr–N3A	107.6 (1)	N1B–Zr–N3B	108.4 (1)
N1A–Zr–N2A	73.5 (2)	N1B–Zr–N2B	73.4 (2)
N3A–Zr–N4B	109.9 (2)	N4A–Zr–N3B	110.0 (2)
N3A–Zr–N2B	110.9 (2)	N4A–Zr–N2B	175.6 (2)
N3A–Zr–N1B	71.9 (1)	N4A–Zr–N1B	109.9 (2)
N1A–Zr–N2B	110.5 (2)	N2A–Zr–N1B	109.7 (2)
N1A–Zr–N4A	66.1 (1)	N2A–Zr–N3A	66.3 (1)
Zr–N1A–C22A	102.2 (3)	Zr–N1B–C22B	101.8 (3)
Zr–N1A–C2A	136.6 (4)	Zr–N1B–C2B	137.3 (4)
C2A–N1A–C22A	121.1 (5)	C2B–N1B–C22B	120.9 (4)
Zr–N2A–C6A	101.7 (3)	Zr–N2B–C6B	101.2 (3)
Zr–N2A–C4A	136.3 (4)	Zr–N2B–C4B	134.8 (4)
C4A–N2A–C6A	121.9 (5)	C4B–N2B–C6B	123.8 (5)
Zr–N3A–C13A	137.0 (4)	Zr–N3B–C13B	135.9 (4)
Zr–N3A–C11A	101.7 (3)	Zr–N3B–C11B	101.9 (4)
C11A–N3A–C13A	121.3 (4)	C11B–N3B–C13B	122.1 (5)
Zr–N4A–C17A	102.3 (3)	Zr–N4B–C17B	102.0 (3)
Zr–N4A–C15A	135.8 (4)	Zr–N4B–C15B	135.6 (4)
C15A–N4A–C17A	121.8 (5)	C15B–N4B–C17B	122.4 (5)

In case of diamagnetic complexes **4** and **5**, the signals for the CH and CH_3 protons appear in the ^1H NMR spectrum as a pair of singlets. Their separation and relative intensity, while depending on the nature of the metal and the solvent (see Experimental Section), is independent of the temperature except for a small change in the relative intensity of the two singlets. Complex **6** showed, under the same conditions, only one singlet.

(Dibenzotetramethyltetraaza[14]annulene)metal Complexes. The reaction of $MCl_4(THF)_2$ with 2 equiv of the lithium derivative of tmtaa was carried out either in benzene (**7**) or in THF solution (**8** and **9**).

$$MCl_4(THF)_2 + [(tmtaa)Li_2] \rightarrow [(tmtaa)_2M] \quad \begin{array}{l} M = Ti,\ \mathbf{7} \\ M = Zr,\ \mathbf{8} \\ M = Hf,\ \mathbf{9} \end{array} \tag{4}$$

The synthesis of complexes **7**–**9** can be achieved in a two-step reaction, as is exemplified for **8**. Complex **5** was reacted with an additional 1 equiv of $[(tmtaa)Li_2]$ to give **8**.

$$\underset{\mathbf{5}}{[(tmtaa)Zr(Cl)_2](THF)_2} + [(tmtaa)Li_2] \xrightarrow{-LiCl} \mathbf{8} \tag{5}$$

The three complexes **7**–**9** have been isolated in a crystalline form. Their separation from LiCl forming in reaction 4 is the major constraint for increasing their yield under the experimental conditions reported. The ^1H NMR spectra of **8** and **9** show sharp singlets for methyne and methyl groups in **8** and **9**, but like for complexes **4** and **5**, in the case of titanium derivative **7**, a pair of singlets for the CH and CH_3 protons appeared. An X-ray analysis was carried out on **8** recrystallized from MeCN to shed light on the structure of the $[(tmtaa)_2M]$ complexes **7**–**9**. The structure consists of discrete $[(tmtaa)_2Zr]$ molecules (Figure 4) and dis-

(21) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, England, 1986.

Table X. Comparison of the Most Relevant Structural Parameters for Complexes **2**, **3**, **5**, and **8**

(a) Dihedral Angles (deg) between Significant Planes[a]

	2		3	5	8	
	mol A	mol B			mol A	mol B
$N_4 \wedge N1,C_3,N2$	157.2 (2)	149.9 (2)	146.7 (3)	147.8 (2)	141.8 (2)	142.7 (2)
$N_4 \wedge N3,C_3,N4$	147.1 (2)	150.7 (2)	149.3 (3)	146.3 (2)	141.3 (2)	141.7 (2)
$N_4 \wedge N1,C_6,N4$	155.3 (1)	157.8 (1)	158.7 (2)	154.5 (1)	164.7 (2)	164.1 (1)
$N_4 \wedge N2,C_6,N3$	157.0 (1)	153.8 (1)	158.7 (2)	154.0 (1)	164.2 (1)	163.7 (1)
$N1,C_6,N4 \wedge N2,C_6,N3$	132.4 (1)	131.6 (1)	137.4 (2)	128.4 (1)	149.0 (1)	147.8 (1)
$N1,C_3,N2 \wedge N3,C_3,N4$	124.2 (2)	120.5 (2)	116.0 (3)	114.1 (2)	103.1 (2)	104.4 (2)
C6...C11 ∧ C17...C22	128.3 (2)	127.0 (2)	131.6 (3)	123.2 (2)	143.9 (2)	142.4 (2)

(b) Out-of-Plane Distances (Å) for the Metal Atoms

	2				3	5	8	
	Li1	Li2	Li1	Li2	Ti	Zr	Zr	
N_4	−0.833 (7)	1.374 (9)	0.937 (7)	−1.307 (8)	0.785 (2)	1.071 (2)	1.368 (1)	1.377 (1)
$N1,C_3,N2$	−1.234 (7)	0.508 (8)	1.460 (6)	−0.444 (8)	0.065 (2)	0.216 (2)	0.296 (1)	0.332 (1)
$N3,C_3,N4$	−1.461 (7)	0.801 (9)	1.444 (7)	−0.549 (8)	0.024 (2)	0.179 (2)	0.271 (1)	0.290 (1)

[a] $N1,C_3,N2$; $N3,C_3,N4$; $N1,C_6,N4$; and $N2,C_6,N3$ define the plane through atoms N1,C2,C3,C4,N2; N3,C13,C14,C15,N4; N4,C17,C18,C19,C20,C21,C22,N1; and N2,C6,C7,C8,C9,C10,C11,N3, respectively. C6...C11 and C17...C22 refer to the planes through the aromatic rings.

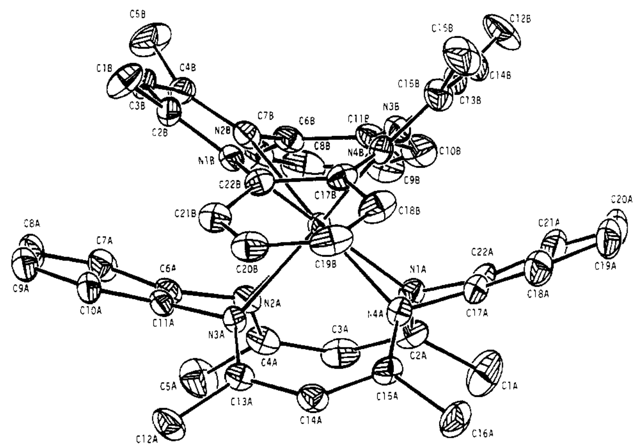

Figure 4. ORTEP[11] drawing for complex **8** (30% probability ellipsoids).

ordered MeCN solvent molecules in a 2:1 molar ratio. The zirconium atom is sandwiched between two tmtaa molecules which are staggered by about 90°. This results in a cubic coordination of nitrogen atoms around the metal (Table IX). The two N_4 cores are parallel, the dihedral angle between them being 0.3 (1)°, and separated by 2.76 Å. The superimposing moieties are not parallel, the corresponding dihedral angles ranging from 19.0 (2) to 20.5 (2)°. The minimum approaching distances between carbon atoms pertaining to different tmtaa molecules are as follows: C7A–C4B, 3.261 (8) Å; C10A–C2B, 3.268 (8) Å; C18A–C15B, 3.346 (11) Å; C21A–C13B, 3.282 (10) Å; C4A–C7B, 3.301 (9) Å; C2A–C10B, 3.275 (10) Å; C13A–C21B, 3.264 (8) Å; C15A–C18B, 3.322 (10) Å. The eight Zr–N distances ranging from 2.321 (4) to 2.341 (5) Å are not significantly different each other and are longer than those observed in complex **3** as a result of the increased coordination number.

Discussion

The metalation of the tmtaaH_2 ligand led to the formation of some useful starting materials: (i) The lithium derivative **2** acts as parent compound for the synthesis of tmtaa complexes of transition metals in organic solvents. (ii) Complexes **4–6** show very interesting structural features as the coordination compound equivalents of the $(cp)_2MCl_2$ complexes.[5] The organometallic chemistry derived from them is at an early stage.[4] The essential characteristics of those compounds is in having, unlike many other macrocyclic or polydentate ligands, the cis arrangement of the two functionalizable M–Cl bonds, or in general, the two cis coordination sites are available for reactivity at the metal. The trans arrangements in the large part of transition metal macrocyclic complexes are by far much less useful, since many of the organometallic reactions driven by metals require two active sites in a cis arrangement. (iii) Compounds **7–9** are so far uniquely reported having a sandwich-type structure with two tmtaa ligands. Coordination number 8,[22a] though quite possible for Zr and Hf, is a very rare occurrence in titanium chemistry.[22b]

Table XI

compd	cn	d^n config	M–N_4, Å	ref
[Pd(tmtaa)]	4	d^8	0	6e
[Fe(tmtaa)Na(THF)$_3$]	4	d^7	0.086 (2)	7
[Fe(tmtaa)]	4	d^6	0.114	6f
[Co(tmtaa)I]	5	d^6	0.234	6g
[Fe(tmtaa)CO]	5	d^6	0.29	6h
[Fe(tmtaa)Cl]	5	d^5	0.600	6g
[Fe(tmtaa)$_2$(μ-O)]	5	d^5	0.698 (2)	6g
[Fe(tmtaa)$_2$(μ-S)]	5	d^5	0.698 (2)	23
[Fe(tmtaa)NO]	5	d^5	0.386 (1)*	24
[Mn(tmtaa)(NEt$_3$)]	5	d^5	0.730*	6g
[V(tmtaa)(Ph)]	5	d^2	0.570 (1)	5
[V(tmtaa)(Mes)]	5	d^2	0.626 (2)	5
[V(tmtaa)Cl]	5	d^2	0.644 (2)	5
[V(tmtaa)O]	5	d^1	0.680 (2)	2e
[Ti(tmtaa)Cl]	5	d^1	0.785 (2)	this work
[Ti(tmtaa)(C$_5$H$_5$)]	5	d^1	0.889 (1)	4a
[Nb(tmtaa)(Cl)$_2$]	6	d^1	0.970 (1)	2d
[Ti(tmtaa)O]	5	d^0	0.754	3e
[Ti(tmtaa)(Cl)$_2$]	6	d^0	0.91	3b
[Zr(tmtaa)(CH$_2$Ph)$_2$]	6	d^0	1.019 (2)	4b
[Zr(tmtaa)(Cl)$_2$]	6	d^0	1.071 (2)	this work
[Zr(tmtaa)$_2$]	8	d^0	1.373 (1)	this work

The question arising at this point, due to the importance played by the saddle-shape conformation of the ligand, the out of N_4 plane of the metal and the cis arrangement of the two chlorines, concerns the factors responsible for the overall coordination geometry around the metal. A comparison of the most relevant structural parameters defining the tmtaa conformation, for the complexes in this paper, are reported in Table X.

All the M(tmtaa) units show the already observed saddle-shape conformation,[6] the differences depending mainly on the metal ion radius and its oxidation state. In complex **2** the small size of the Li cations allows two ions to be accommodated into the cavities formed by the bending of the aromatic rings (defined by the dihedral angle between N1, C6, and N4 and N2, C6, and N3)

(22) (a) Fay, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1988; Vol. 3, Chapter 32. (b) McAuliffe, C. A. *Ibid.*, Chapter 31.

(23) Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 551.

(24) Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1988**, 1409.

and by the bending of the N2 and C3 moieties (defined by the dihedral angle between N1, C6, and N2 and N3, C3, and N4). In complexes **3**, **5**, and **8** the metal atom is accommodated in the cavity supplied by the aromatic rings, the $M-N_4$ distances (Table X) showing the expected trend. The most relevant differences concern complex **8** where the presence of two coordinated tmtaa molecules produces a significant flattening of the aromatic rings and longer $Zr-N_4$ out-of-plane distances (Table X).

Considering the tmtaa-derived complexes so far structurally characterized, the out-of-N_4-plane of the metal seems to depend on the d configuration of the metal. Electron-rich metals are almost in the plane, and the saddle-shape conformation almost disappears. A significant comparison should be restricted however to metals having the same oxidation state or coordination number but different d configuration (Table XI). The d^0 and d^1 metals are those having the most pronounced out-of-plane and saddle-shape conformation.

The out-of-plane of the metal seems to increase with its coordination number for the same d^n configuration or the same oxidation state (Table XI) although much less data are available for such a comparison.

NMR spectroscopy could give, eventually, information on the structure of tmtaa complexes in solution. This notwithstanding, very rarely have NMR spectra been reported and discussed for tmtaa. The CH and CH_3 protons should be considered as a spectroscopic probe for the structure of tmtaa in solution. In ^1H NMR spectra of **6** a singlet for CH and a singlet for the $-CH_3$ groups were found, independently of the solvent used. For complexes **4**, independently of the solvent (CD_2Cl_2 or CD_3CN), pairs of singlets appeared for the CH and CH_3 groups, and the intensity ratio changes as a function of the solvent as well as their separation. The temperature seems not to affect such parameters. Complex **5** showed in the ^1H NMR spectrum a pair of singlets for both CH and CH_3 groups in CD_2Cl_2 and one singlet for both CH and CH_3 in CD_3CN. Such factors give rise to some hypotheses concerning the existence in some cases of one form, or in other cases of two forms, of the complex.

The existence of two forms from the ^1H NMR spectrum should not be related to any solvation equilibrium because both in the case of **4** and **5**, two forms are observed in noncoordinating solvents and in the absence of any even weak ligand. In addition, methylene chloride solutions of **5** to which RNC or R′CN have been added did not show any binding to the metal, as seen from the IR spectrum. We never observed Lewis acid adducts of $[(tmtaa)M(Cl)_2]$ complexes during our reactivity studies. The present hypothesis is that the two forms observed in the ^1H NMR spectrum are two saddle-shape conformations of the ligand with a different out-of-N_4-plane distance of the metal in a slow equilibrium determined by the nature of the metal and of the solvent, independently of its binding ability. This equilibrium is not very much affected by the temperature, a small change in the intensity being observed, in the range we explored for **5** in CD_2Cl_2, that is from 233 to 290 K in CD_2Cl_2. In the case of $[M(tmtaa)_2]$ complexes, again the separation of the CH and CH_3 signals in pairs of singlets was observed for titanium complex **7** and disappears in the case of **8** and **9**, which show a singlet for both kinds of protons independently of the solvent. In case of **7** we should invoke either the previous hypothesis, or the nonsymmetric binding of the eight nitrogen atoms derived from two tmtaa's, due to the small size of the titanium atoms.[22b]

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Supplementary Material Available: Experimental details for data collection and refinement of the structures (Table SI) and listings of unrefined hydrogen coordinates (Tables SII–SV), anisotropic thermal parameters (Tables SVI–SIX), and bond distances and angles (Tables SX–SXIII) (18 pages); listings of observed and calculated structure factors (98 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie der Universität, W-3000 Hannover 1, FRG

Synthesis and Properties of Chloryl Chloride, $ClClO_2$

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Halogen exchange between $FClO_2$ and $AlCl_3$, BCl_3, or HCl afforded chloryl chloride, $ClClO_2$, identified by IR and UV spectroscopy in noble gas matrices and in the gas phase. All six fundamental vibrations, as well as some over and combination tones of 12 isotopomers were detected for the novel chlorine oxide having C_s symmetry. Use of the product rule in the symmetry class A″ with vibrational frequencies of four independent isotopomers, in conjunction with experimental and ab initio results of related compounds, allowed the geometric parameters to be estimated ($r(ClCl) = 222 \pm 6$ pm, $r(ClO) = 144.0 \pm 0.5$ pm, $\angle(ClClO) = 103.5 \pm 1°$, $\angle(OClO) = 116.0 \pm 0.5°$) and a force field to be calculated. The UV spectrum shows two maxima at 231 and 296 nm with $\sigma = 1.3 \times 10^{-17}$ and 1.5×10^{-17} cm^2 $molecule^{-1}$, respectively. Photolysis of matrix-isolated $ClClO_2$ resulted in the isomers ClOClO and ClOOCl. In the gas phase $ClClO_2$ decomposes into ClO_2 and chlorine, but it can also be formed by reacting Cl atoms with ClO_2. At room temperature and partial and total pressure of 1 and 4 mbar, respectively, the half-life of $ClClO_2$ is 1 min. The role of $ClClO_2$ in stratospheric chemistry is discussed in relation to possible reaction schemes.

Introduction

Chlorine-containing compounds play an important role in stratospheric chemistry.[1,2] In particular, high concentrations of ClO and ClO_2 have been measured in the polar region during early spring.[2,3] Thus it was suggested that strong ozone depletion occurring after sunrise could be caused by a catalytic cycle in which dimerization of ClO and by photolysis of the products are the main steps[4] (Scheme I). Kinetic investigations[5] together with

Scheme I

$$2(Cl + O_3 \rightarrow ClO + O_2)$$
$$2ClO + M \rightarrow ClOOCl + M$$
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$
$$ClOO + M \rightarrow Cl + O_2 + M$$
$$\text{net:} \quad 2O_3 + h\nu \rightarrow 3O_2$$

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