

METAL-ORGANIC COMPOUNDS

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A Dinuclear Holmium(III) 'Carbons Apart' Carborane Cluster, $[C_{34}H_{92}B_8Cl_4Ho_2Li_2N_6Si_4] \cdot C_{10}H_8$

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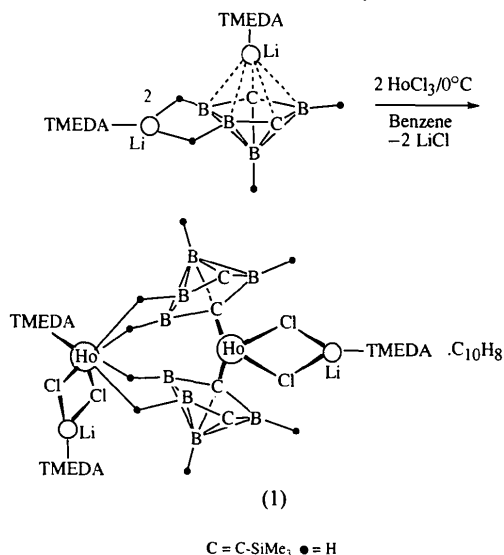
Abstract

The title compound (1), 1-[(μ -Cl) $_2$ Li(TMEDA)]-2,2',4,4'-(SiMe $_3$) $_4$ -5,5',6,6'-[(μ -H) $_4$ Ho(TMEDA)(μ -Cl) $_2$ Li(TMEDA)]-1,1'-*commo*-Ho(2,4-C $_2$ B $_4$ H $_4$) $_2$ ·C $_{10}$ H $_8$ (where TMEDA is tetramethylethylenediamine), bis- $[\mu$ -2 κ^2 H B^5 , H B^6 :3(2,3,4,5,6- η)-2,4-bis(trimethylsilyl)-2,4-dicarbano-*nido*-hexaborate(6)]tetra- μ -chloro-1:2 κ^4 Cl:3:4 κ^4 Cl-tris(*N,N,N',N'*-tetramethyl-1,2-ethanediamine)-1 κ^2 N,N';2 κ^2 N,N';4 κ^2 N,N'-1,4-dilithium-2,3-diholmium naphthalene solvate, crystallizes in the triclinic space group $P\bar{1}$. The cluster consists of an Ho^{III} 'carbons apart' carborane bent-sandwich complex bridging almost symmetrically to an *exo*-polyhedral Li(TMEDA) unit *via* two Cl atoms and, *via* two B—H (terminal) groups of each opposing C $_2$ B $_3$ face, to an *exo*-polyhedral Ho^{III}(TMEDA) unit that is also linked to another *exo*-polyhedral Li(TMEDA) group with two Ho—Cl—Li bridges. The centrally located Ho atom is almost symmetrically bonded to two opposing 'carbons apart' C $_2$ B $_4$ carborane cages with Ho1...Cnt1 2.340, Ho1...Cnt2 2.349 Å, Cnt1...Ho1...Cnt2 130.2, Cnt1...Ho1...Cl1 107.1, Cnt1...Ho1...Cl2 107.1, Cnt2...Ho1...Cl1 109.1 and Cnt2...Ho1...Cl2 109.1°, where Cnt is the centroid of the C $_2$ B $_3$ face of each.

Comment

Our recent work has demonstrated that the reaction of a dilithium-complexed 'carbons adjacent' carborane dianion with a lanthanide chloride in anhydrous thf results in the formation of an unusual trinuclear lanthanacarborane cluster in which three Ln [Ln = Gd (Oki, Zhang & Hosmane, 1992), Tb (Zhang, Oki, Wang, Maguire & Hosmane, 1995)] and six Li atoms form a tricapped trigonal prism with Ln atoms in the capping positions linked to an O atom at the center. Thus, our results have shown that the reactivity of the C $_2$ B $_4$ carborane ligands toward lanthanide metal reagents is quite different from those

of the C $_2$ B $_9$ and C $_2$ B $_{10}$ carborane systems (Manning, Knobler & Hawthorne, 1988; Khattar, Knobler, Johnson & Hawthorne, 1991; Manning, Knobler, Khattar & Hawthorne, 1991; Khattar, Manning, Knobler, Johnson & Hawthorne, 1992). In order to establish a similar pattern of reactivities of the 'carbons apart' C $_2$ B $_4$ carborane ligands in lanthanide chemistry, we have synthesized the title compound in 61% yield by the treatment of a TMEDA-solvated 'carbons apart' dilithiacarborane (Zhang, Wang, Saxena, Oki, Maguire & Hosmane, 1993) with anhydrous HoCl $_3$ in a molar ratio of 1:1 in dry benzene, followed by extraction and recrystallization of the product from a solution containing 50% dry *n*-hexane and 50% dry benzene. This resulted in the isolation of air-sensitive orange-colored plate-shaped crystals of 1-[(μ -Cl) $_2$ Li(TMEDA)]-2,2',4,4'-(SiMe $_3$) $_4$ -5,5',6,6'-[(μ -H) $_4$ Ho(TMEDA)(μ -Cl) $_2$ Li(TMEDA)]-1,1'-*commo*-Ho(2,4-C $_2$ B $_4$ H $_4$) $_2$ ·C $_{10}$ H $_8$, (1).



Although the crystal structures of a number of π -complexes of holmium are known (Schumann, Loebel, van der Helm & Hossain, 1988; Schumann, Esser, Loebel, Dietrich, van der Helm & Ji, 1991; Rogers & Rogers, 1991), there are no structural reports on any of the holmacarborane complexes. Therefore, we have carried out an X-ray diffraction analysis on a single-crystal sample of (1) and report herein the results of this study.

The crystal structure (Fig. 1) shows that (1) is a novel dinuclear holmacarborane bent-sandwich complex in which the central (*commo*) Ho atom is η^5 -bonded to each of the 'carbons apart' C $_2$ B $_3$ faces with Ho...centroid distances of 2.340 and 2.349 Å. These

distances are comparable to the Ho...Cp centroid distances of 2.366 Å in Me₂Ge(C₅Me₄)₂HoCH(SiMe₃)₂ (Schumann, Esser, Loebel, Dietrich, van der Helm & Ji, 1991) and are not much different from the analogous distances in the half-sandwich (*closo*) 'carbons adjacent' trinuclear Gd^{III}- and Tb^{III}-C₂B₄ carborane clusters (2.358–2.399 Å; Oki, Zhang & Hosmane, 1992; Zhang, Oki, Wang, Maguire & Hosmane, 1995). Although the bridging of the sandwiched metal atom (Ho1 in Fig. 1) and the *exo*-polyhedral Li(TMEDA) unit by two Cl atoms [Ho1—Cl1 2.632 (2), Ho1—Cl2 2.654 (2) Å] is similar to that found in Me₂Ge(C₅Me₄)₂SmCl₂Li(thf)₂ (Schumann, Esser, Loebel, Dietrich, van der Helm & Ji, 1991), the linkage of the two B—H(terminal) groups of each opposing C₂B₃ face to an *exo*-polyhedral Ho^{III}(TMEDA) unit and its further bridging to an *exo*-polyhedral Li(TMEDA) group with two Ho—Cl—Li bridges are unusual and unprecedented. Nonetheless, the distorted tetrahedral geometry of the centrally located Ho atom (Ho1...Cnt1 2.340, Ho1...Cnt2 2.349 Å, Cnt1...Ho1...Cnt2 130.2, Cnt1...Ho1...Cl1 107.1, Cnt1...Ho1...Cl2 107.1, Cnt2...Ho1...Cl1 109.1, Cnt2...Ho1...Cl2 109.1°, where Cnt is the centroid of the C₂B₃ face) is essentially identical to those of the *d*⁰ Group IV metallocene, lanthanocene and actinocene derivatives (Rogers & Rogers, 1991; Evans, 1985, 1987; Wilkinson, Stone & Abel, 1982; Wilkinson, Gillard & McCleverty, 1987; Cotton & Wilkinson, 1988) and their carborane analogues known to date (Hosmane & Maguire, 1993; Saxena & Hosmane, 1993). There is no significant influence of the co-crystallized naphthalene molecule on the overall geometry of (1). Although the title compound is the first Ho-carborane complex to be reported, our results do show that the reactivity pattern of the 'carbons apart' C₂B₄ carborane ligand towards a lanthanide-metal reagent is quite different from that observed for the 'carbons adjacent' carborane ligands.

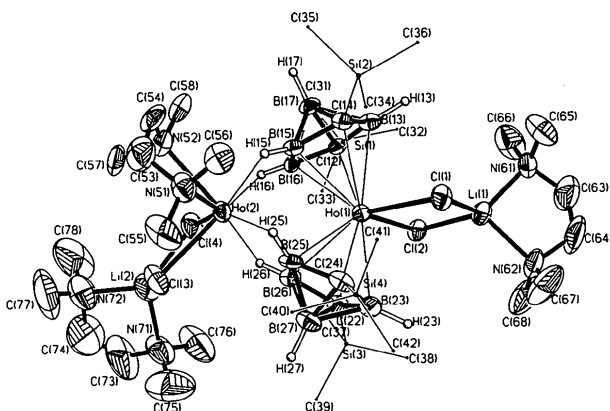


Fig. 1. Displacement ellipsoid plot (40% probability) of the title cluster. H atoms other than those on the carborane cages have been omitted and the atoms of the trimethylsilyl groups have been drawn as small circles of arbitrary radii for clarity.

Experimental

Crystal data

[Ho₂Li₂Cl₄(C₈H₂₂B₄Si₂)₂·(C₆H₁₆N₂)₃].C₁₀H₈

M_r = 1397.68

Triclinic

P $\bar{1}$

a = 11.996 (3) Å

b = 13.048 (3) Å

c = 25.017 (8) Å

α = 98.93 (2)°

β = 90.46 (2)°

γ = 114.00 (2)°

V = 3523 (2) Å³

Z = 2

D_x = 1.318 Mg m⁻³

Data collection

Siemens R3m/V diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan

T_{min} = 0.591, *T_{max}* =

0.919

6937 measured reflections

6544 independent reflections

5258 observed reflections

[*I* > 2 σ (*I*)]

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.0419

wR(*F*²) = 0.1042

S = 1.066

6020 reflections

632 parameters

w = 1/[σ^2 (*F_o*²) + (0.0775*P*)² + 2.5509*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10–15°

μ = 2.481 mm⁻¹

T = 230 (2) K

Plate

0.35 × 0.20 × 0.05 mm

Orange

R_{int} = 0.029

θ_{max} = 20°

h = 0 → 11

k = -12 → 11

l = -24 → 24

3 standard reflections

monitored every 200

reflections

intensity decay: none

(Δ/σ)_{max} = 0.001

$\Delta\rho_{max}$ = 1.146 e Å⁻³

$\Delta\rho_{min}$ = -1.549 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ho1	0.21043 (3)	0.48815 (3)	0.26534 (2)	0.0304 (2)
Ho2	0.34957 (4)	0.30389 (4)	0.17414 (2)	0.0437 (2)
Cl1	0.2659 (2)	0.6522 (2)	0.35002 (10)	0.0527 (7)
Cl2	-0.0105 (2)	0.4889 (2)	0.26550 (9)	0.0430 (6)
Cl3	0.4558 (3)	0.3269 (3)	0.08232 (11)	0.0785 (9)
Cl4	0.1714 (3)	0.1377 (2)	0.10263 (11)	0.0676 (8)
Si1	-0.0841 (2)	0.1749 (2)	0.27099 (12)	0.0481 (7)
Si2	0.3853 (3)	0.4332 (3)	0.39956 (11)	0.0575 (8)
Si3	0.0812 (3)	0.5420 (3)	0.11878 (12)	0.0581 (8)
Si4	0.5455 (3)	0.7682 (3)	0.24861 (14)	0.0681 (9)
C12	0.0770 (7)	0.2767 (6)	0.2846 (3)	0.032 (2)
B13	0.1400 (10)	0.3514 (9)	0.3408 (4)	0.041 (3)
C14	0.2782 (7)	0.3850 (7)	0.3374 (3)	0.037 (2)
B15	0.3079 (9)	0.3407 (8)	0.2806 (4)	0.036 (3)
B16	0.1740 (9)	0.2685 (8)	0.2454 (4)	0.034 (3)
B17	0.1907 (10)	0.2462 (9)	0.3124 (5)	0.043 (3)
C22	0.2012 (8)	0.5469 (7)	0.1667 (4)	0.041 (2)
B23	0.2839 (10)	0.6577 (9)	0.2060 (5)	0.047 (3)

C24	0.4008 (8)	0.6438 (8)	0.2234 (4)	0.049 (3)	B26—Ho2—B16	77.0 (3)	N62—Li1—N61	90.8 (7)
B25	0.3905 (10)	0.5211 (9)	0.1974 (4)	0.042 (3)	N52—Ho2—B15	89.3 (3)	N62—Li1—C11	116.7 (9)
B26	0.2606 (9)	0.4577 (9)	0.1601 (4)	0.037 (3)	Cl3—Ho2—B15	161.4 (2)	N61—Li1—C11	118.1 (8)
B27	0.3537 (10)	0.6013 (11)	0.1556 (5)	0.051 (3)	B25—Ho2—B15	74.5 (3)	N62—Li1—C12	116.6 (9)
C31	-0.0928 (11)	0.0324 (9)	0.2787 (6)	0.104 (5)	B26—Ho2—B15	86.9 (3)	N61—Li1—C12	117.7 (9)
C32	-0.1857 (9)	0.2144 (10)	0.3174 (4)	0.071 (3)	N52—Ho2—C14	80.8 (3)	Cl1—Li1—C12	98.5 (6)
C33	-0.1375 (9)	0.1672 (10)	0.1995 (4)	0.075 (3)	Cl3—Ho2—C14	78.70 (9)	N71—Li2—N72	87.9 (10)
C34	0.5201 (11)	0.5662 (12)	0.3970 (6)	0.105 (5)	B25—Ho2—C14	127.1 (2)	N71—Li2—C14	121.3 (11)
C35	0.4416 (13)	0.3228 (12)	0.4068 (6)	0.108 (5)	B26—Ho2—C14	91.7 (2)	N72—Li2—C14	120.0 (12)
C36	0.3043 (13)	0.4538 (14)	0.4611 (5)	0.115 (5)	B16—Ho2—C14	85.9 (2)	N71—Li2—C13	115.1 (11)
C37	-0.0426 (10)	0.3974 (10)	0.1028 (4)	0.080 (4)	B15—Ho2—C14	119.9 (2)	N72—Li2—C13	119.8 (12)
C38	0.0115 (11)	0.6407 (11)	0.1476 (5)	0.085 (4)	N52—Ho2—N51	69.5 (3)	Cl4—Li2—C13	95.1 (7)
C39	0.1501 (12)	0.5903 (13)	0.0563 (5)	0.103 (5)	Cl3—Ho2—N51	77.4 (2)		
C40	0.6712 (14)	0.7508 (18)	0.2087 (9)	0.198 (11)				
C41	0.6015 (16)	0.7774 (18)	0.3149 (7)	0.193 (11)				
C42	0.5413 (19)	0.8898 (14)	0.2326 (15)	0.377 (27)				
Li1	0.0645 (16)	0.6348 (15)	0.3434 (7)	0.060 (5)				
Li2	0.2821 (21)	0.1956 (19)	0.0301 (8)	0.086 (6)				
N51	0.5931 (8)	0.3714 (9)	0.2074 (4)	0.070 (3)				
N52	0.3897 (10)	0.1321 (8)	0.1900 (4)	0.077 (3)				
C53	0.6097 (13)	0.2650 (14)	0.2033 (6)	0.102 (5)				
C54	0.5072 (13)	0.1725 (12)	0.2237 (5)	0.089 (4)				
C55	0.6806 (10)	0.4449 (13)	0.1728 (5)	0.106 (5)				
C56	0.6295 (9)	0.4308 (10)	0.2639 (5)	0.075 (3)				
C57	0.3971 (14)	0.0628 (12)	0.1372 (5)	0.105 (5)				
C58	0.2908 (13)	0.0541 (10)	0.2182 (6)	0.092 (4)				
N61	-0.0316 (9)	0.6108 (8)	0.4107 (4)	0.066 (3)				
N62	0.0411 (10)	0.7798 (8)	0.3400 (4)	0.078 (3)				
C63	-0.0842 (17)	0.6933 (15)	0.4129 (7)	0.133 (6)				
C64	-0.0198 (16)	0.7907 (13)	0.3899 (8)	0.127 (6)				
C65	0.0512 (13)	0.6392 (13)	0.4595 (5)	0.109 (5)				
C66	-0.1303 (13)	0.4956 (12)	0.4074 (6)	0.115 (5)				
C67	0.1528 (16)	0.8810 (11)	0.3446 (8)	0.148 (7)				
C68	-0.0412 (19)	0.7621 (14)	0.2937 (7)	0.167 (9)				
N71	0.2190 (13)	0.2569 (15)	-0.0279 (5)	0.113 (4)				
N72	0.2959 (17)	0.0757 (14)	-0.0316 (6)	0.134 (5)				
C73	0.2033 (23)	0.1750 (29)	-0.0749 (7)	0.195 (12)				
C74	0.2462 (35)	0.0990 (25)	-0.0791 (9)	0.228 (15)				
C75	0.2986 (22)	0.3737 (23)	-0.0319 (9)	0.202 (11)				
C76	0.0989 (19)	0.2482 (24)	-0.0145 (7)	0.211 (13)				
C77	0.4218 (24)	0.0944 (23)	-0.0365 (9)	0.220 (13)				
C78	0.2270 (29)	-0.0369 (19)	-0.0254 (9)	0.252 (17)				
C81	0.4691 (14)	-0.0456 (4)	0.4804 (2)	0.159 (9)				
C82	0.4734 (17)	-0.0334 (12)	0.4275 (2)	0.232 (18)				
C83	0.5360 (23)	0.0707 (17)	0.4140 (5)	0.407 (39)				
C84	0.5973 (19)	0.1619 (12)	0.4533 (7)	0.246 (18)				
C85	0.5922 (15)	0.1499 (5)	0.5062 (6)	0.165 (10)				
C91	1.0276 (4)	0.0384 (8)	0.4836 (4)	0.115 (7)				
C92	0.9590 (11)	0.0694 (11)	0.4516 (5)	0.193 (13)				
C93	0.8352 (11)	0.0201 (16)	0.4508 (8)	0.363 (35)				
C94	0.7801 (6)	-0.0579 (16)	0.4830 (8)	0.268 (23)				
C95	0.8486 (6)	-0.0897 (10)	0.5146 (6)	0.200 (13)				

Table 2. Selected geometric parameters (Å, °)

Ho1—C11	2.632 (2)	Ho2—N51	2.764 (8)
Ho1—C12	2.654 (2)	Ho2—N52	2.563 (9)
Ho1—C12	2.690 (8)	Ho2—B15	2.718 (10)
Ho1—B13	2.703 (10)	Ho2—B25	2.638 (11)
Ho1—C14	2.709 (8)	Ho2—B26	2.692 (10)
Ho1—B15	2.695 (10)	Ho2—B16	2.712 (10)
Ho1—B16	2.680 (10)	Cl1—Li1	2.34 (2)
Ho1—C22	2.709 (9)	Cl2—Li1	2.38 (2)
Ho1—B23	2.706 (11)	Cl3—Li2	2.31 (2)
Ho1—C24	2.714 (9)	Cl4—Li2	2.30 (2)
Ho1—B25	2.697 (11)	Li1—N61	2.04 (2)
Ho1—B26	2.711 (11)	Li1—N62	2.04 (2)
Ho2—C13	2.635 (3)	Li2—N71	2.04 (2)
Ho2—C14	2.727 (3)	Li2—N72	2.08 (2)
Cl1—Ho1—C12	84.99 (8)	B25—Ho2—N51	86.8 (3)
N52—Ho2—C13	95.8 (2)	B26—Ho2—N51	121.1 (3)
N52—Ho2—B25	152.0 (3)	B16—Ho2—N51	122.1 (3)
Cl3—Ho2—B25	93.3 (2)	B15—Ho2—N51	87.7 (3)
N52—Ho2—B26	168.5 (3)	Cl4—Ho2—N51	139.3 (2)
Cl3—Ho2—B26	91.2 (2)	Li1—Cl1—Ho1	89.0 (5)
N52—Ho2—B16	93.7 (3)	Li1—Cl2—Ho1	87.5 (4)
Cl3—Ho2—B16	160.3 (2)	Li2—Cl3—Ho2	93.7 (5)
B25—Ho2—B16	86.2 (3)	Li2—Cl4—Ho2	91.7 (5)

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses. Full-matrix least-squares refinement was performed. All non-H atoms were refined anisotropically. The centers of two disordered naphthalene solvent molecules are located at $(1, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$. These molecules were elastically restrained and kept 'flat' during the final cycles of refinement. Methyl, methylene and aromatic H atoms were placed using a riding model, while the carborane-cage H atoms were located in ΔF maps.

Data collection: *R3m/V* diffractometer control software. Cell refinement: *R3m/V* diffractometer control software. Data reduction: *R3m/V* diffractometer control software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: SZ1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic *cis*-Dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV)

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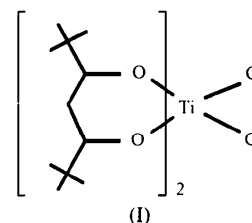
Abstract

The title compound, [Ti(C₁₁H₁₉O₂)₂Cl₂], has a *cis* configuration. The racemic compound crystallizes in space group *P2₁/c* with two molecules in the asymmetric unit: the mean Ti—Cl distance is 2.266 (5) Å and the mean Ti—O distances are (*trans* to O) 1.919 (7) and (*trans* to Cl) 1.999 (9) Å.

Comment

Pentane-2,4-dione (CH₃COCH₂COCH₃, Hacac) reacts with both titanium(IV) chloride and titanium(IV) alkoxides to yield neutral products [Ti(acac)₂X₂], where X = Cl (Dilthey, 1904) or X = OR (Yamamoto & Kambara, 1957). NMR studies suggest that, in solution, these products and the analogous complexes derived from other 1,3-diketones are all octahedral, containing bidentate *O,O'*-chelating diketonate ligands with a *cis* arrangement of the two ligands X (Fay & Lowry, 1967; Serpone & Fay, 1967; Bradley & Hollaway, 1969). Structure analyses of the alkoxide complexes [Ti(acac)₂{OC₆H₃(CHMe₂)₂}]₂ (Bird, Fraser & Lau, 1973), [Ti(PhCOCHCOCF₃)₂(OEt)₂] (Wang, Miao, Fan, Feng & Wang, 1990) and

[Ti(PhCOCHCOCH₃)₂(OCMe₃)₂] (Schubert, Buhler & Hirle, 1992) have shown unambiguously that these complexes all adopt *cis* configurations in the solid state. However, no X-ray structure analysis of any complex of type [Ti(1,3-diketonate)₂Cl₂] has been reported; an attempted structure analysis of [Ti(acac)₂Cl₂] was thwarted by hydrolysis, and the compound actually studied was [Ti(acac)₂Cl]₂O (Watenpaugh & Caughlin, 1967), where the chloride and bridging oxide ligands occupy *cis* sites. The title compound [Ti(Me₃CCOCHCOCHMe₃)₂Cl₂], (I), is much less susceptible to hydrolysis than [Ti(acac)₂Cl₂] and is thus more amenable to X-ray structure analysis. Moreover, the structure of (I) is of considerable interest since the analogous niobium(IV) complex [Nb(Me₃CCOCHCOCHMe₃)₂Cl₂] was found to adopt the *trans* configuration (Cotton, Diebold & Roth, 1985).



Compound (I) crystallizes in the monoclinic space group *P2₁/c*, with two molecules in the asymmetric unit (Fig. 1). The Ti atoms are octahedrally coordinated forming the chromophore TiCl₂O₄ with the two Cl ligands *cis*, so that the molecules are chiral; the centrosymmetric space group accommodates the equal numbers of L and D enantiomers expected in a racemic product, and the asymmetric unit has been chosen to contain one complex of L and one complex of D helicity.

The bond angles around the Ti atom (Table 2) indicate significant distortion from the ideal octahedral geometry: in particular the *trans* O—Ti—O angles are 164.05 (13) and 163.44 (12)° in the two independent molecules, while the corresponding Cl—Ti—Cl angles are 96.97 (9) and 95.50 (6)°; the intraligand O—Ti—O angles range from 82.60 (12) to 83.03 (11)°, associated with O···O 'bites' in the range 2.588 (4)–2.597 (4) Å. The Ti—Cl distances all lie between the mean and lower quartile values for such bonds involving six-coordinate Ti^{IV} (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989), although they are longer than the bonds in TiCl₄ [2.170 (2) Å] (Morino & Uehara, 1966). However, the Ti—O bonds show significant differences between those *trans* to oxygen [mean value 1.919 (7) Å] and those *trans* to chlorine [mean value 1.999 (9) Å]; the bonds *trans* to oxygen are much shorter than the lower quartile value of 1.941 Å (Orpen *et al.*, 1989). A comparable difference was observed in the alkoxide complex [Ti(PhCOCHCOCH₃)₂(OCMe₃)₂] (Schubert *et al.*, 1992) where the Ti—O distances involving the