

Supplementary Material Available: Listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) For our previous contributions in this area, see ref 2 and 3.
- (2) $(\mu_3\text{-H})_2\text{Ru}_6(\text{CO})_{18}$: M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971).
- (3) $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\text{C}=\text{NMe}_2)$: M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976).
- (4) $\text{HR}_2\text{Mn}(\text{CO})_{14}$: M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).
- (5) $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$: M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
- (6) $[\text{HRe}_3(\text{CO})_{12}]^{2-}$: S. W. Kirtley, H. D. Kaesz, M. R. Churchill, and C. Knobler, in preparation; S. W. Kirtley, Ph.D. Dissertation, UCLA, 1972.
- (7) $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$: H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).
- (8) $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$: M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972).
- (9) $[(\text{C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-H})(\mu\text{-Cl})$: M. R. Churchill and S. W. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).
- (10) $[(\text{C}_5\text{Me}_5)\text{IrCl}]_2(\mu\text{-H})(\mu\text{-Cl})$: M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977).
- (11) $[\text{H}_2\text{W}_2(\text{CO})_2]^{2-}$: M. R. Churchill and S. W. Chang, *Inorg. Chem.*, **13**, 2413 (1974).
- (12) $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
- (13) $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}_2\text{PMe}_2\text{Ph})$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 1141 (1977).
- (14) $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 2397 (1977).
- (15) $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$: M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2697 (1977).
- (16) $(\mu\text{-H})\text{Os}_3(\text{CO})_8[\text{C}(\text{O}-)\text{C}(\text{CHMe}-)\text{CHCHCtEt}]$: M. R. Churchill, R. A. Lashewycz, M. Tachikawa, and J. R. Shapley, *J. Chem. Soc., Chem. Commun.*, 699 (1977).
- (17) $(\mu\text{-H})_2\text{Os}_3\text{Re}_2(\text{CO})_{26}$: J. R. Shapley, G. A. Pearson, M. Tachikawa, G. D. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, **99**, 8064 (1977).
- (18) J. R. Shapley, S. I. Richter, M. R. Churchill, and R. A. Lashewycz, *J. Am. Chem. Soc.*, **99**, 7384 (1977).
- (19) (a) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **98**, 4687 (1976); (b) G. Huttner and H. Lorenz, *Chem. Ber.*, **108**, 973 (1975).
- (20) R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, submitted for publication in *Inorg. Chem.* (We thank Professor R. Bau for providing a copy of this manuscript prior to publication.)
- (21) Reported in footnote 24 of ref 19.
- (22) M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2655 (1977).
- (23) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
- (24) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99-101; (b) pp 149-150.
- (25) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
- (26) Esd's on average values are shown in square brackets.
- (27) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 828 (1972).
- (28) A. Domenicano, A. Vacigo, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 1630 (1975).
- (29) H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).

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Crystal and Molecular Structure of a Tantalum-Alkylidene Complex, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$

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Bis(η^5 -cyclopentadienyl)chloro(neopentylidene)tantalum, $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$, previously prepared by Schrock, has been subjected to a full three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14] with $a = 6.5957$ (8) Å, $b = 15.4418$ (19) Å, $c = 14.3363$ (19) Å, $\beta = 103.023$ (10)°, $V = 1422.6$ (3) Å³, and ρ (calcd) = 1.946 g cm⁻³ for $Z = 4$ and mol wt 416.73. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using Mo $K\alpha$ radiation. The structure was solved via a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 2.7\%$ and $R_{wF} = 2.3\%$ for the 1870 reflections with $4^\circ < 2\theta < 45^\circ$ (no reflections rejected). All atoms, including all hydrogen atoms, were located and refined. The two $\eta^5\text{-C}_5\text{H}_5$ rings subtend an angle of 130.9° at the metal atom; the chloride and neopentylidene ligand occupy equatorial coordination sites, with $d(\text{Ta}-\text{Cl}) = 2.479$ (2) Å and $\text{Cl}-\text{Ta}-\text{C}(1) = 97.63$ (18)°. The tantalum-neopentylidene linkage is 2.030 (6) Å, consistent with its formulation as $\text{Ta}=\text{CHCMe}_3$. A surprising feature of the analysis is the $\text{Ta}=\text{C}(1)-\text{C}(2)$ angle of 150.4 (5)°—some 30° greater than the normal sp^2 -hybridized (trigonal-planar) angle of 120°.

Introduction

Alkylidene and alkylidyne complexes of tantalum have recently been synthesized by Schrock and co-workers;¹⁻⁶ X-ray diffraction studies have previously been reported for the methylene complex $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$ ⁴ and for the neopentylidyne complex $[(\text{Me}_3\text{CCH}_2)_3\text{Ta}=\text{CCMe}_3]\text{Li}(\text{dmp})$.²

We now report the results of a single-crystal X-ray diffraction study of the neopentylidene complex $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$.³ A preliminary account of this work has appeared previously.⁷

Experimental Section

A. Data Collection. Crystals of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ were kindly supplied by Professor R. R. Schrock of the Massachusetts Institute of Technology. The clear yellow columnar crystals are extended along their a axes. The complex is air sensitive, decomposing totally in approximately 24-36 h following initial exposure.

Using a small (ca. 6-L capacity) specially designed drybox, which permitted examination of the crystals with an externally mounted high-magnification microscope, several samples were cleaved from larger columns and sealed into thin-walled capillaries. All manipulations were carried out in an atmosphere of carefully purified argon. After 24 h, the samples were examined for signs of decomposition. The best crystal was then selected for data collection; it was 0.37 mm \times 0.22 mm \times 0.20 mm and had been mechanically wedged into a 0.2 mm diameter thin-walled capillary. The capillary was inserted into a brass pin with beeswax and mounted in a eucentric goniometer. Preliminary precession and cone-axis photographs provided approximate unit cell parameters, indicated $2/m$ Laue symmetry, and revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14] is strongly indicated. The crystal was transferred to a Syntex $P2_1$ automated diffractometer, its extended (real) a axis being close to coincidence with the spindle axis (ϕ) of the diffractometer. Crystal alignment, determination of orientation matrix and accurate cell

Table I. Experimental Data for the X-ray Diffraction Study of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$

(A) Crystal Parameters ^a at 24 °C	
Crystal system: monoclinic	$\beta = 103.023 (10)^\circ$
Space group: $P2_1/c$	$V = 1422.6 (3) \text{ \AA}^3$
$a = 6.5957 (8) \text{ \AA}$	$Z = 4$
$b = 15.4418 (19) \text{ \AA}$	Mol wt 416.73
$c = 14.3363 (19) \text{ \AA}$	$\rho(\text{calcd}) = 1.946 \text{ g cm}^{-3}$

(B) Measurement of Intensity Data	
Radiation: Mo $K\alpha$ (λ 0.710 730 \AA)	
Monochromator: highly oriented graphite, $2\theta_{\text{mono}} = 12.2^\circ$, equatorial mode	
Reflectns measd: $\cdot +h, +k, \pm l$	
Scan type: coupled θ (cryst)– 2θ (counter)	
2θ range: 4.0–45.0°	
Scan speed: 2.0°/min in 2θ	
Scan width: $[2\theta(\text{Mo } K\alpha_1) - 1.0]^\circ$ to $[2\theta(\text{Mo } K\alpha_2) + 1.0]^\circ$	
Bgd measurement: stationary crystal, stationary counter at beginning and end of each scan, each for one-fourth of the time taken to scan	
Standard reflectns: $40\bar{2}, 0, 10, 0, 0, 0, 10$; these were measured after each 47 reflections; there was a monotonic decrease to 95% of their original intensities	
Reflectns collected: 2059 total, yielding 1870 symmetry-independent data	
Abs coeff: $\mu = 77.6 \text{ cm}^{-1}$	

^a Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo $K\alpha$ components of 24 reflections of the forms $\{149\}$, $\{1, 10, 2\}$, $\{441\}$, $\{227\}$, $\{336\}$, and $\{382\}$, all with 2θ between 25 and 30°.

dimensions, and data collection were all carried out as described previously.⁸ Details specific to the present analysis are listed in Table I.

All crystallographic computations were performed using the Syntex XTL system,⁹ which consists of (i) a Data General NOVA 1200 computer with a 24K 16-bit work memory and with a parallel floating point processor for 32- and 64-bit arithmetic, (ii) a Diablo moving-head disk unit of 1.2 million 16-bit words, (iii) a Versatec electrostatic printer/plotter, and (iv) the XTL conversational crystallographic program package, as modified by our research group at Buffalo.

Data were corrected for absorption ($\mu = 77.6 \text{ cm}^{-1}$) by the following empirical method, using the program TAPER. Several relatively intense and close-to-axial reflections, distributed over the range of 2θ values used in data collection, were measured at 36 positions about their diffraction vectors (from $\psi = 0^\circ$ to $\psi = 350^\circ$, at intervals of 10°). The data from each reflection was used to define a normalized absorption curve vs. ϕ , corrected for ω and χ . The curves bracketing the 2θ value of the primary data reflection under consideration were interpolated in both 2θ and ϕ to derive the transmission factor and thence the absorption correction. Reflections used for the absorption curves, their 2θ values, and their maximum intensity:minimum intensity ratios, were as follows: $2\bar{1}\bar{1}$, 12.63°, 1.234:1; $30\bar{2}$, 18.63°, 1.184:1; $40\bar{2}$, 24.34°, 1.198:1; $5\bar{1}\bar{3}$, 31.35°, 1.183:1.

Analysis of the check reflections showed a steady (monotonic) decrease in intensity over the period of data collection, the final intensities being ~95% of the initial intensity. The three curves of intensity vs. reflection number agreed well (1.5% variance). The decay correction for the primary data set was taken from a mean curve over all three check reflections. (It should be noted that the crystal, which initially was transparent, was found to be opaque upon optical examination immediately following data collection.)

Redundant and equivalent data were averaged [$R_{\text{AV}} = 100 \times \sum |I - I_{\text{AV}}| / \sum I = 2.1\%$] and were converted to unscaled $|F_o|$ values after correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$. The esd's, $\sigma_c(|F_o|)$, were based upon the larger of (i) counting statistics or (ii) the internal esd obtained by averaging symmetry-equivalent reflections.

B. Solution of the Structure. The analytical form^{10a} of the scattering factors for neutral tantalum, chlorine, carbon, and hydrogen were used throughout the analysis; both the real and imaginary components of anomalous dispersion^{10b} were included for all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement. The weight, w , is defined in eq 1; P , the "ignorance factor",

$$w = [\{\sigma_c(|F_o|)\}^2 + \{P|F_o|\}^2]^{-1} \quad (1)$$

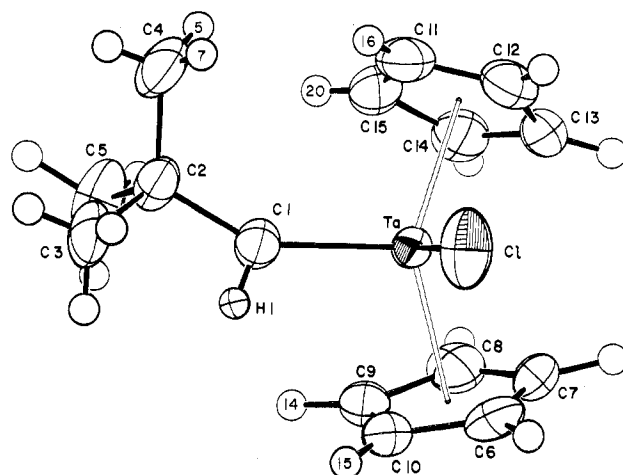


Figure 1. Labeling of nonhydrogen atoms in the $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ molecule (ORTEP diagram; 50% probability ellipsoids, with hydrogen atoms artificially reduced). Hydrogen atoms involved in close intramolecular contacts have been labeled numerically only.

was set at a value of 0.01. Discrepancy indices, R_F and R_{wF} , and the "goodness-of-fit" (GOF) are defined in eq 2–4.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100 (\%) \quad (2)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100 (\%) \quad (3)$$

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\text{NO} - \text{NP}} \right]^{1/2} \quad (4)$$

Data were placed on an approximate absolute scale by means of a Wilson plot, which also provided the overall isotropic thermal parameter, $B = 2.4 \text{ \AA}^2$. A three-dimensional Patterson map was easily interpreted to yield the positions of the tantalum and chlorine atoms. A difference-Fourier synthesis phased by these two atoms [$R_F = 14.2\%$] revealed unambiguously the locations of all 15 carbon atoms. Full-matrix least-squares refinement of positional and isotropic thermal parameters led, in three cycles, to $R_F = 6.7\%$ and $R_{wF} = 7.1\%$. Continued refinement, now using anisotropic thermal parameters, converged in four cycles with $R_F = 3.3\%$, $R_{wF} = 3.3\%$, and $\text{GOF} = 2.00$. A second difference-Fourier synthesis now revealed the positions of all 20 hydrogen atoms. Continued least-squares refinement, with positional and isotropic thermal parameters of all hydrogen atoms varied, led to $R_F = 2.8\%$, $R_{wF} = 2.4\%$, and $\text{GOF} = 1.46$. A survey of the data set now clearly indicated that a correction for secondary extinction was necessary. (The worst disagreement was for the 002 reflection, for which $|F_o|/|F_c| = 1.06$.) All data were corrected for secondary extinction by applying an empirical correction of the form shown in eq 5, where g was found, graphically, to have a value of 6×10^{-8} .

$$|F_o|_{\text{cor}} = |F_o|_{\text{uncor}}(1.0 + gI_o) \quad (5)$$

Two more cycles of full-matrix least-squares refinement led to final convergence with $R_F = 2.7\%$, $R_{wF} = 2.3\%$, and $\text{GOF} = 1.42$. [NP, the number of parameters varied, was 234; NO, the number of observations, was 1870. No data were rejected.] Each of the final cycles of refinement took about 1.15 h of minicomputer time.

The largest peak on a final difference-Fourier map was of height 0.7 e \AA^{-3} and was close to the tantalum atom. The structure is therefore both correct and complete. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant dependency on $|F_o|$, $(\sin \theta)/\lambda$, sequence number, or identity or parity of Miller indices; the weighting scheme is thus satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles

Table II. Positional Parameters, with Esd's,^a for Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl

Atom	x	y	z	B, Å ²
Ta	0.11647 (3)	0.06201 (1)	0.21238 (2)	
Cl	0.36268 (23)	0.03668 (13)	0.10764 (12)	
C(1)	0.3299 (9)	0.0918 (4)	0.3338 (5)	
C(2)	0.4468 (9)	0.1586 (4)	0.4038 (4)	
C(3)	0.6689 (12)	0.1242 (6)	0.4444 (6)	
C(4)	0.4683 (13)	0.2488 (5)	0.3657 (7)	
C(5)	0.3416 (15)	0.1639 (8)	0.4890 (7)	
C(6)	0.0810 (13)	-0.0928 (4)	0.1727 (6)	
C(7)	-0.1186 (11)	-0.0602 (4)	0.1574 (5)	
C(8)	-0.1488 (12)	-0.0326 (5)	0.2453 (6)	
C(9)	0.0307 (12)	-0.0477 (4)	0.3159 (5)	
C(10)	0.1744 (13)	-0.0837 (4)	0.2721 (5)	
C(11)	0.1188 (13)	0.2132 (4)	0.1739 (5)	
C(12)	0.0262 (11)	0.1731 (5)	0.0882 (5)	
C(13)	-0.1589 (10)	0.1349 (4)	0.0986 (5)	
C(14)	-0.1830 (11)	0.1536 (4)	0.1921 (5)	
C(15)	-0.0108 (11)	0.2020 (4)	0.2378 (6)	
H(1)	0.374 (9)	0.048 (4)	0.364 (4)	3.8 (16)
H(2)	0.677 (12)	0.065 (5)	0.466 (5)	7.0 (21)
H(3)	0.773 (10)	0.119 (4)	0.399 (5)	4.9 (16)
H(4)	0.728 (10)	0.156 (5)	0.491 (5)	5.3 (18)
H(5)	0.327 (11)	0.279 (4)	0.344 (5)	5.6 (17)
H(6)	0.546 (10)	0.275 (4)	0.403 (5)	4.1 (16)
H(7)	0.536 (13)	0.247 (6)	0.307 (6)	9.6 (27)
H(8)	0.202 (13)	0.180 (6)	0.469 (6)	7.9 (24)
H(9)	0.334 (12)	0.106 (6)	0.513 (6)	6.2 (22)
H(10)	0.414 (11)	0.213 (5)	0.539 (5)	7.5 (20)
H(11)	0.158 (9)	-0.118 (4)	0.126 (5)	4.8 (16)
H(12)	-0.217 (13)	-0.059 (5)	0.090 (7)	8.6 (23)
H(13)	-0.257 (9)	-0.008 (4)	0.256 (4)	3.4 (15)
H(14)	0.048 (9)	-0.032 (4)	0.390 (5)	4.4 (14)
H(15)	0.310 (11)	-0.103 (5)	0.296 (5)	5.6 (18)
H(16)	0.229 (9)	0.233 (4)	0.187 (4)	3.4 (16)
H(17)	0.087 (9)	0.174 (4)	0.038 (4)	4.9 (16)
H(18)	-0.270 (12)	0.108 (5)	0.052 (6)	7.7 (22)
H(19)	-0.310 (10)	0.137 (4)	0.213 (4)	4.6 (15)
H(20)	0.018 (11)	0.214 (5)	0.295 (5)	5.4 (20)

^a Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix.

and their esd's are given in Table V. Important least-squares planes (and deviations of atoms therefrom) are presented in Table VI.

The scheme used for numbering nonhydrogen atoms is shown in Figure 1. A stereoview of the molecule can be seen in Figure 2. The molecule consists of a central tantalum atom surrounded by two η^5 -cyclopentadienyl rings, a neopentylidene moiety, and a chloride ligand. The centroids of the η^5 -

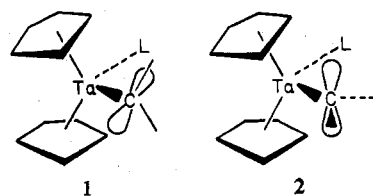
cyclopentadienyl ligands (Cp(1) and Cp(2)) subtend an angle of 130.86° at the metal atom, while the angle between the two equatorial ligands [C(1)-Ta-Cl] is 97.63 (18)°. The remaining interligand angles are fairly regular, with Cp(1)-Ta-Cl = 103.72°, Cp(1)-Ta-C(1) = 106.64°, Cp(2)-Ta-Cl = 105.79°, and Cp(2)-Ta-C(1) = 109.86°. The overall stereochemistry about the metal atom is thus very similar to that found for Ta(η^5 -C₅H₅)₂(CH₂)(CH₃)⁴ and, indeed, for M(η^5 -C₅H₅)₂L₂ complexes in general.¹¹⁻¹³

The tantalum-chlorine distance is 2.479 (2) Å, suggesting that the covalent radius of tantalum in this class of compound is about 1.49 Å (*r*(Cl) is 0.99 Å).¹⁴ [We note here that a similar value may be obtained by subtraction of the radius of sp³-hybridized carbon from the tantalum-methyl distance in Ta(η^5 -C₅H₅)₂(CH₂)(CH₃): i.e., 2.246 (12) - 0.77 Å = ca. 1.48 Å.]

We now turn our attention to the neopentylidene ligand. The tantalum-neopentylidene linkage, Ta-C(1), is 2.030 (6) Å in length and is thus indistinguishable from (but is more accurately determined than) the tantalum-methylene bond length of 2.026 (10) Å in Ta(η^5 -C₅H₅)₂(CH₂)(CH₃).⁴ Each of these tantalum-alkylidene linkages is approximately 0.22 Å shorter than the tantalum-methyl distance of 2.246 (12) Å discussed above. The tantalum-alkylidene linkage is therefore reasonably regarded as being a tantalum-carbon double bond, i.e., Ta=CR₂ (R = H or alkyl). There are two unusual and unexpected features of the tantalum-neopentylidene fragment. These are as follows.

(1) The angle Ta-C(1)-C(2) is extraordinarily obtuse for an angle at a formally sp²-hybridized carbon, having a value of 150.4 (5)°—some 30° greater than the normal trigonal-planar angle of 120°. In keeping with this, the remaining angles at C(1) are reduced from their idealized values, with Ta-C(1)-H(1) = 111 (4)° and C(2)-C(1)-H(1) = 99 (4)°. The atom C(1) appears to be in strictly planar coordination to its surrounding atoms, with H(1) lying 0.09 (6) Å from the plane defined by Ta-C(1)-C(2) [see Table VI].

(2) The dihedral angle between the equatorial Cl-Ta-C(1) plane and the Ta-C(1)-C(2) plane is 79.7°—i.e., the neopentylidene moiety is displaced by ca. 10.3° from the ideal perpendicular geometry (1) toward the parallel geometry (2).

Table III. Anisotropic Thermal Parameters,^a with Esd's,^b for Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ta	2.48 (1)	2.15 (1)	2.64 (1)	-0.03 (1)	0.05 (1)	-0.09 (1)
Cl	3.02 (7)	7.91 (11)	4.21 (8)	-0.13 (7)	0.77 (6)	-1.36 (7)
C(1)	3.34 (28)	3.06 (29)	3.47 (29)	0.32 (23)	-0.03 (22)	-0.45 (25)
C(2)	3.40 (27)	3.31 (28)	3.65 (28)	-0.24 (22)	0.30 (22)	-1.07 (23)
C(3)	4.26 (36)	5.23 (43)	4.25 (37)	-0.59 (31)	-1.15 (30)	-1.17 (34)
C(4)	4.83 (41)	3.73 (35)	6.46 (48)	-0.91 (31)	-1.05 (38)	-1.57 (34)
C(5)	5.77 (48)	7.86 (64)	5.11 (42)	-1.22 (43)	1.37 (35)	-3.10 (46)
C(6)	7.10 (46)	2.00 (26)	5.30 (39)	0.10 (27)	1.04 (35)	-0.79 (26)
C(7)	4.76 (35)	2.83 (27)	4.16 (34)	-1.51 (27)	-0.68 (27)	-0.01 (27)
C(8)	3.94 (35)	3.69 (32)	5.33 (39)	-1.31 (27)	0.68 (31)	0.82 (29)
C(9)	6.32 (41)	2.98 (30)	3.45 (32)	-1.47 (28)	0.28 (30)	0.76 (26)
C(10)	5.49 (40)	2.50 (29)	4.68 (37)	-0.26 (27)	-1.19 (32)	0.35 (26)
C(11)	4.53 (38)	2.93 (31)	5.27 (39)	-0.40 (27)	0.28 (33)	0.90 (27)
C(12)	5.11 (35)	3.82 (32)	4.05 (34)	-0.25 (28)	0.62 (29)	1.44 (28)
C(13)	3.96 (31)	3.23 (29)	3.97 (33)	0.19 (25)	-0.83 (26)	0.47 (25)
C(14)	3.99 (33)	3.50 (31)	5.28 (38)	1.23 (26)	0.38 (29)	-0.09 (28)
C(15)	5.15 (37)	2.81 (32)	4.54 (39)	1.11 (25)	0.09 (31)	-0.64 (29)

^a These enter the expression for the calculated structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}kib^{*}c^{*})]$. ^b See footnote a of Table II.

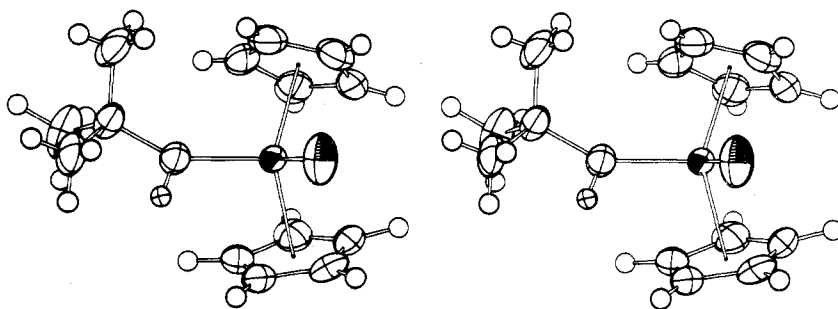


Figure 2. Stereoscopic diagram of the $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ molecule.

Table IV. Intramolecular Distances (Å), with Esd's, for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$

(a) Distances from the Tantalum Atom			
Ta-Cl	2.479 (2)	Ta...Cp (1) ^a	2.117
Ta-C(1)	2.030 (6)	Ta...Cp (2) ^a	2.094
Ta-C(6)	2.456 (6)	Ta-C(11)	2.400 (7)
Ta-C(7)	2.457 (6)	Ta-C(12)	2.447 (7)
Ta-C(8)	2.407 (8)	Ta-C(13)	2.427 (7)
Ta-C(9)	2.402 (7)	Ta-C(14)	2.393 (7)
Ta-C(10)	2.406 (6)	Ta-C(15)	2.376 (7)
(b) Distances within Neopentylidene Ligand			
C(1)-C(2)	1.523 (9)	C(3)-H(4)	0.85 (7)
C(1)-H(1)	0.82 (6)	C(4)-H(5)	1.03 (7)
C(2)-C(3)	1.544 (10)	C(4)-H(6)	0.77 (7)
C(2)-C(4)	1.514 (10)	C(4)-H(7)	1.04 (9)
C(2)-C(5)	1.536 (11)	C(5)-H(8)	0.93 (9)
C(3)-H(2)	0.96 (8)	C(5)-H(9)	0.96 (9)
C(3)-H(3)	1.05 (7)	C(5)-H(10)	1.08 (8)
(c) Distances within Cyclopentadienyl Systems			
C(6)-C(7)	1.380 (11)	C(11)-C(12)	1.389 (10)
C(7)-C(8)	1.387 (10)	C(12)-C(13)	1.394 (10)
C(8)-C(9)	1.392 (11)	C(13)-C(14)	1.415 (10)
C(9)-C(10)	1.368 (11)	C(14)-C(15)	1.393 (10)
C(10)-C(6)	1.426 (11)	C(15)-C(11)	1.397 (11)
C(6)-H(11)	1.00 (6)	C(11)-H(16)	0.77 (6)
C(7)-H(12)	1.04 (9)	C(12)-H(17)	0.91 (6)
C(8)-H(13)	0.85 (6)	C(13)-H(18)	0.97 (8)
C(9)-H(14)	1.07 (6)	C(14)-H(19)	0.99 (6)
C(10)-H(15)	0.93 (7)	C(15)-H(20)	0.82 (7)

(d) Intramolecular H(neopentylidene)...H(cyclopentadienyl) Contacts ^b			
H(1)...H(14)	2.57 (9)	H(5)...H(20)	2.24 (10)
H(1)...H(15)	2.51 (9)	H(7)...H(16)	2.36 (11)
H(5)...H(16)	2.32 (9)	H(8)...H(20)	2.57 (11)

^a Cp(1) is the centroid of the carbocyclic ring defined by atoms C(6) through C(10); Cp(2) is the centroid of the C(11) → C(15) system. ^b These distances are based on the "X-ray-determined" positions for the hydrogen atoms and are, on average, systematically greater than their true internuclear values: see M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

In contrast to this, the corresponding dihedral angle between Me-Ta-CH_2 and Ta=CH_2 planes in $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$ is $88(3)^\circ$. This difference is accompanied by a lower barrier to rotation about the Ta-C(alkylidene) bond in the present neopentylidene-chloride complex ($\Delta G_{\text{rot}}^\ddagger = 16.9$ kcal/mol at 323 K) than in the methylene-methyl complex ($\Delta G_{\text{rot}}^\ddagger > 21.4$ kcal/mol at 413 K).⁴ [It is worth mentioning that Lauher and Hoffmann have calculated there to be an energy difference of 1.2 eV (≈ 28 kcal/mol) between configurations 1 and 2 in the "model compound $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{CH}_2$ ".¹³]

The unusual features noted above probably arise principally from steric interaction between the neopentylidene ligand and the cyclopentadienyl systems. As can be clearly seen in the stereoview (Figure 2) there are significant interactions between H(1) and the lower cyclopentadienyl ligand [$\text{H}(1)\cdots\text{H}(14) = 2.57(9)$, $\text{H}(1)\cdots\text{H}(15) = 2.51(9)$ Å] and between hydrogen atoms on C(4) and the upper cyclopentadienyl ligand [H-

Table V. Interatomic Angles (deg), with Esd's, for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$

(a) Angles around the Tantalum Atoms			
Cl-Ta-C(1)	97.63 (18)	Cp(1)-Ta-C(1) ^a	106.64 (...)
Cp(1)-Ta-Cp(2) ^a	130.86 (...)	Cp(2)-Ta-Cl ^a	105.79 (...)
Cp(1)-Ta-Cl ^a	103.72 (...)	Cp(2)-Ta-C(1) ^a	109.86 (...)
(b) Angles within the Neopentylidene Ligand			
Ta-C(1)-C(2)	150.4 (5)	H(3)-C(3)-H(4)	106 (6)
Ta-C(1)-H(1)	111 (4)	C(2)-C(4)-H(5)	112 (4)
C(2)-C(1)-H(1)	99 (4)	C(2)-C(4)-H(6)	110 (5)
C(1)-C(2)-C(3)	108.2 (5)	C(2)-C(4)-H(7)	111 (5)
C(1)-C(2)-C(4)	117.4 (6)	H(5)-C(4)-H(6)	112 (6)
C(1)-C(2)-C(5)	107.9 (6)	H(5)-C(4)-H(7)	108 (6)
C(3)-C(2)-C(4)	107.1 (6)	H(6)-C(4)-H(7)	104 (7)
C(3)-C(2)-C(5)	106.2 (6)	C(2)-C(5)-H(8)	111 (5)
C(4)-C(2)-C(5)	109.5 (6)	C(2)-C(5)-H(9)	108 (5)
C(2)-C(3)-H(2)	115 (5)	C(2)-C(5)-H(10)	111 (4)
C(2)-C(3)-H(3)	120 (4)	H(8)-C(5)-H(9)	103 (7)
C(2)-C(3)-H(4)	109 (5)	H(8)-C(5)-H(10)	106 (7)
H(2)-C(3)-H(3)	98 (6)	H(9)-C(5)-H(10)	118 (6)
H(2)-C(3)-H(4)	109 (7)		
(c) Angles within the Cyclopentadienyl Systems			
C(10)-C(6)-C(7)	107.7 (6)	C(15)-C(11)-C(12)	108.2 (6)
C(6)-C(7)-C(8)	107.1 (6)	C(11)-C(12)-C(13)	108.4 (6)
C(7)-C(8)-C(9)	109.7 (6)	C(12)-C(13)-C(14)	107.6 (6)
C(8)-C(9)-C(10)	107.3 (6)	C(13)-C(14)-C(15)	107.5 (6)
C(9)-C(10)-C(6)	108.1 (6)	C(14)-C(15)-C(11)	108.2 (6)
H(11)-C(6)-C(7)	130 (4)	H(16)-C(11)-C(12)	126 (5)
H(11)-C(6)-C(10)	122 (4)	H(16)-C(11)-C(15)	125 (5)
H(12)-C(7)-C(6)	122 (5)	H(17)-C(12)-C(11)	121 (4)
H(12)-C(7)-C(8)	131 (5)	H(17)-C(12)-C(13)	130 (4)
H(13)-C(8)-C(7)	127 (4)	H(18)-C(13)-C(12)	131 (5)
H(13)-C(8)-C(9)	124 (4)	H(18)-C(13)-C(14)	121 (5)
H(14)-C(9)-C(8)	125 (3)	H(19)-C(14)-C(13)	122 (4)
H(14)-C(9)-C(10)	128 (3)	H(19)-C(14)-C(15)	131 (4)
H(15)-C(10)-C(9)	132 (4)	H(20)-C(15)-C(14)	125 (5)
H(15)-C(10)-C(6)	120 (4)	H(20)-C(15)-C(11)	126 (5)

^a See footnote a of Table IV.

(5)...H(16) = 2.32 (9), H(5)...H(20) = 2.24 (10), H(7)...H(16) = 2.36 (11) Å]. These contacts are far more important than intermolecular contacts (see Table VII). N.B.—all of these contacts are calculated using the "X-ray determined" positions of the hydrogen atoms; the true internuclear separations will be shorter.¹⁵

It is possible that electronic effects may also play some role in causing the large Ta-C(1)-C(2) angle. Thus, it is well-established that the M-C(α)-C(β) angles in perfluoroalkyls (and, sometimes, alkyls) are increased from the ideal sp³ value—in $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\eta^1\text{-C}_3\text{F}_7)$, for example, the Mo-C(α)-C(β) angle is 123.3° .¹⁶

To our knowledge, there have been only two previous X-ray structural studies on metal-alkylidene complexes with which we can compare our results. In $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2)(\text{CH}_3)$, the H-C(methylene)-H angle is reported⁴ as $107(9)^\circ$ and the average Ta-C-H angle is therefore calculable as 126.5° ; however, in the absence of a full account of this structural study it is difficult to assess the statistical significance of this

Table VI. Important Least-Squares Planes for Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl^{a,b}

Atom	Dev, Å	Atom	Dev, Å
I. Ta-C(1)-C(2) Plane			
0.8515X + 0.0461Y - 0.5224Z + 1.4356 = 0			
Ta*	0.000	Cl	2.417 (2)
C(1)*	0.000	C(3)	0.815 (8)
C(2)*	0.000	C(4)	0.569 (9)
H(1)	-0.09 (6)	C(5)	-1.442 (10)
II. Cl-Ta-C(1) Plane			
-0.0019X + 0.9654Y - 0.2607Z - 0.1511 = 0			
Ta*	0.000	H(1)	-0.77 (6)
Cl*	0.000	C(2)	0.740 (6)
C(1)*	0.000		
III. C(6) → C(10) Plane			
0.3826X + 0.9091Y - 0.1645Z + 1.7027 = 0			
C(6)*	-0.005 (7)	H(11)	0.005 (67)
C(7)*	0.002 (6)	H(12)	0.001 (79)
C(8)*	0.002 (7)	H(13)	0.038 (61)
C(9)*	-0.006 (7)	H(14)	-0.004 (61)
C(10)*	0.007 (7)	H(15)	-0.002 (73)
Ta	2.1166 (2)		
IV. C(11) → C(15) Plane			
-0.4242X + 0.8432Y - 0.3301Z - 1.8871 = 0			
C(11)*	-0.007 (7)	H(16)	-0.105 (61)
C(12)*	0.008 (7)	H(17)	0.011 (65)
C(13)*	-0.006 (7)	H(18)	0.100 (83)
C(14)*	0.002 (7)	H(19)	0.072 (63)
C(15)*	0.003 (7)	H(20)	-0.104 (71)
Ta	-2.0938 (2)		
Angles (deg) between Normals to Planes			
I/II	79.69	II/III	23.09
I/III	63.02	II/IV	25.72
I/IV	98.62	III/IV	48.80

^a Equations of planes are expressed in the orthonormal coordinates X, Y, Z, where X = xa + zc cos β, Y = yb, and Z = zc sin β.

^b Atoms marked with an asterisk were used in calculating the plane under consideration.

apparent increase from the ideal sp² angle of 120°. In W(CO)₅(CPh₂),¹⁷ the W-C(α)-C(β) angles within two crystallographically independent molecules range from 120.7 (11) to 126.1 (11)°, averaging 124.0°. There appears, therefore, to be a slight (but not pronounced) tendency for M-C(α)-C(β) angles to be greater than normal in alkylidene complexes—even in the absence of severe steric restraints; further work is clearly necessary before any more definitive generalizations can justifiably be made.

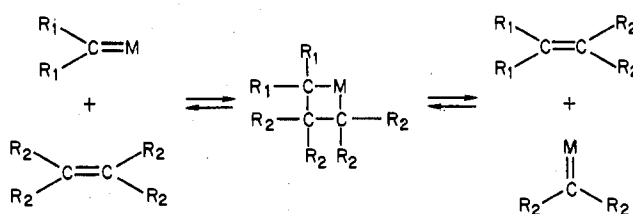
Other distances and angles within the neopentylidene ligand appear to fall within the normal ranges. The C(1)-C(2) distance of 1.523 (9) Å is close to the accepted C(sp²)-C(sp³) single bond distance of 1.510 ± 0.005 Å;¹⁸ the C(2)-Me bond lengths range from 1.514 (10) to 1.544 (10) Å, averaging 1.533 Å, as compared to the accepted C(sp³)-C(sp³) distance of 1.537 ± 0.005 Å;¹⁸ and the C-H distances within the neopentylidene ligand range from 0.77 (7) to 1.08 (8) Å, averaging 0.95 Å, in good agreement with the expected "X-ray determined" distance of 0.95 Å.¹⁵

The η^5 -cyclopentadienyl ligands each have D_{5h} symmetry within the limits of experimental error. The lower ring, defined by atoms C(6) through C(10), has a root-mean-square deviation from planarity of 0.005 Å and is associated with C-C distances of 1.380 (11)-1.426 (11) Å, C-H distances of 0.85 (6)-1.07 (6) Å, C-C-C angles of 107.1 (6)-109.7 (6)°, and H-C-C angles of 120 (4)-132 (4)°. The upper pentaatomic carbocyclic ring, defined by carbon atoms C(11) through C(15), has a root-mean-square deviation from planarity of 0.006 Å, C-C distances of 1.389 (10)-1.415 (10) Å, C-H distances of 0.77 (6)-0.99 (6) Å, C-C-C angles of 107.5 (6)-108.4 (6)°, and H-C-C angles of 121 (5)-131 (5)°. The

Table VII. Intermolecular Contacts, to 3.0 Å, Based upon "X-ray-Determined" Positions^a

Atoms	Trans ^b	Dist, Å	Atoms	Trans	Dist, Å
Cl···H(12)	3000	2.80	H(11)···H(6)	21-10	2.66
Cl···H(13)	1100	2.98	H(11)···H(11)	21-10	2.91
Cl···H(18)	1100	2.93	H(11)···H(17)	3000	2.68
Cl···H(19)	1100	2.81	H(11)···H(18)	3000	2.82
C(7)···H(5)	20-10	2.83	H(12)···Cl	3000	2.80
H(2)···H(9)	3101	2.67	H(12)···H(5)	20-10	2.81
H(2)···H(14)	3101	2.47	H(12)···H(17)	3000	2.81
H(3)···H(8)	1100	2.94	H(13)···Cl	1-100	2.98
H(3)···H(13)	1100	2.81	H(13)···H(3)	1-100	2.81
H(3)···H(14)	1100	2.98	H(14)···H(2)	3101	2.47
H(3)···H(19)	1100	2.61	H(14)···H(3)	1-100	2.98
H(3)···H(20)	1100	2.85	H(14)···H(4)	3101	2.77
H(4)···H(14)	3101	2.77	H(16)···H(10)	4010	2.80
H(5)···C(7)	2000	2.83	H(17)···H(8)	4010	2.64
H(5)···H(12)	2000	2.81	H(17)···H(10)	4010	2.77
H(6)···H(11)	2100	2.66	H(17)···H(11)	3000	2.68
H(6)···H(18)	4111	2.85	H(17)···H(12)	3000	2.81
H(7)···H(11)	2111	2.91	H(18)···Cl	1-100	2.93
H(7)···H(19)	1100	2.52	H(18)···H(6)	4-110	2.85
H(8)···H(3)	1-100	2.94	H(18)···H(11)	3000	2.82
H(8)···H(17)	4011	2.64	H(19)···Cl	1-100	2.81
H(9)···H(2)	3101	2.67	H(19)···H(3)	1-100	2.61
H(10)···H(16)	4011	2.80	H(19)···H(7)	1-100	2.52
H(10)···H(17)	4011	2.77	H(20)···H(3)	1-100	2.85

^a These contacts are based upon the "X-ray-determined" positions of the hydrogen atoms and are systematically foreshortened from the true internuclear separations by up to ~0.2 Å—see M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973). ^b The transformation of the second atom is given by a four-digit code. The first represents the equipoint (see below) while the second through fourth represent the addition (+1) or subtraction (-1) of unit cell vectors a, b, and c. Transformation code: 1, x, y, z; 2, -x, 1/2 + y, 1/2 - z; 3, -x, -y, -z; 4, x, -1/2 - y, -1/2 + z.

Scheme I

tantalum atom lies 2.117 Å above the lower plane and 2.094 Å below the upper plane.

Finally, we point out that the observed Ta-C(1)-C(2) angle of 150.4 (5)° suggests that the M-C(α)-C(β) backbones of metal-alkylidene complexes may, in certain cases, rather easily be deformed. This may possibly be relevant to detailed topological considerations of the mechanism of the olefin metathesis reaction, which is believed to proceed via the reaction of an olefin with a metal-alkylidene complex to yield a metallacyclobutane complex. (See Scheme I.)

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Registry No. Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl, 57483-58-6.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

- R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974).
- L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975).
- R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).
- L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975).
- R. R. Schrock, *J. Am. Chem. Soc.*, **98**, 5399 (1976).

- (6) S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977).
 (7) M. R. Churchill, F. J. Hollander, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 647 (1978).
 (8) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
 (9) "Syntex XTL Operations Manual", 2nd ed, Syntex Analytical Instruments, Cupertino, Calif., 1976.
 (10) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99-101; (b) pp 149-150.
 (11) See, for example, J. L. Atwood, W. E. Hunter, D. C. Hrncoir, E. Samuel, H. Alt, and M. D. Rausch, *Inorg. Chem.*, **14**, 1757 (1975), and references contained therein.
 (12) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6416 (1975).
 (13) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).
 (14) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y. 1960, p 224.
 (15) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
 (16) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).
 (17) C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977).
 (18) *Chem. Soc., Spec. Publ.*, No. 18, S14s-S15s (1965).
 (19) T. J. Katz and J. L. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975).
 (20) R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Am. Chem. Soc.*, **97**, 3265 (1975).
 (21) T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **98**, 2519 (1976).
 (22) R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *J. Am. Chem. Soc.*, **98**, 3478 (1976).

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Synthesis and Crystal Structure of a Neodymium Isopropoxide Chloride, $\text{Nd}_6[\text{OCH}(\text{CH}_3)_2]_{17}\text{Cl}^1$

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Neodymium(III) chloride reacts with sodium isopropoxide in isopropyl alcohol to produce a complex which has been characterized by an X-ray crystal structure determination to be hexaisopropoxynona- μ -isopropoxy-di- μ_3 -isopropoxy- μ_6 -chloro-hexaneodymium, $\text{Nd}_6[\text{OCH}(\text{CH}_3)_2]_{17}\text{Cl}$. The pale blue crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a = 24.52$ (2) Å, $b = 22.60$ (2) Å, $c = 14.22$ (1) Å, and $\beta = 101.05$ (5)°; for four molecules in the unit cell the calculated density is 1.636 g/cm³. The structure was refined by full-matrix least squares to a conventional R factor of 0.076 for 2327 data with $I > 2\sigma$. The six neodymium atoms form a trigonal prism centered about the chlorine atom. Six isopropoxide groups are terminal, nine are edge bridging, and two are bridging a trigonal face of the prism yielding six two-coordinate, nine three-coordinate, and two four-coordinate oxygen atoms, respectively. The average Nd-Cl distance is 3.05 (1) Å. The average Nd-O distances for oxygen atoms which are bonded to one, two, and three Nd atoms are 2.05 (2), 2.36 (4), and 2.45 (5) Å, respectively.

Introduction

Neodymium triisopropoxide, prepared from neodymium trichloride and sodium isopropoxide in refluxing isopropyl alcohol, is said to be monomeric in benzene solution (ebullioscopically) as is the praseodymium analogue.^{2,3} In contrast, gadolinium and erbium isopropoxides are tetrameric in benzene.⁴ The samarium⁵ and ytterbium⁶ compounds are also known though their solution molecular weights have not been reported. Mass spectrometric examination of $\text{M}(\text{O}-i\text{-Pr})_3$ [$\text{M} = \text{Nd, Er, Tb, Lu}$], prepared from the metal and alcohol, shows tetrameric ions in the gas phase.⁷

It has been said that preparation of isopropoxides of the lanthanide elements from sodium isopropoxide and metal chloride results in materials that are contaminated by chloride though nothing was known about their constitution.^{7,8} We have carried out a single-crystal X-ray analysis of the chloride-containing material and have shown it to be $\text{Nd}_6(\text{O}-i\text{-Pr})_{17}\text{Cl}$.

Experimental Section

Microanalysis was performed by Analytical Laboratories, University of California, Berkeley, Calif. Isopropyl alcohol was dried by refluxing over and distilling from magnesium isopropoxide. Neodymium trichloride was dried by refluxing with thionyl chloride. The magnetic susceptibility was measured with a PAR Model 155 vibrating-sample magnetometer and was calibrated with $\text{HgCo}(\text{CNS})_4$.⁹ Temperature was measured with a calibrated GaAs diode.

Heptadecaisopropoxychlorohexaneodymium(III). Sodium isopropoxide was prepared from sodium (1.3 g, 0.055 mol), isopropyl alcohol (20 mL), and benzene (40 mL); it was then added to a gently refluxing solution of neodymium trichloride (4.6 g, 0.018 mol) in isopropyl alcohol (40 mL). The suspension was refluxed for 12 h and then centrifuged. The light blue mother liquor was filtered, and the residue was washed with benzene (2 × 25 mL). The combined extracts were evaporated to dryness in vacuo. The blue solid was crystallized

from toluene (-15 °C) as light blue needles. The yield was 6.2 g. The compound did not melt nor decompose when heated in a sealed capillary to 300 °C. Anal. Calcd. for $\text{C}_{51}\text{H}_{119}\text{ClNd}_6\text{O}_{17}$: C, 32.2; H, 6.25; Cl, 1.86. Found: C, 31.8; H, 6.04; Cl, 1.80.

X-ray Diffraction. The pale blue crystals were transferred to quartz capillaries inside an argon-filled drybox and sealed with vacuum grease. The capillaries were fire-sealed immediately upon removal from the box. Weissenberg photography showed the material to be monoclinic, and rough cell dimensions were obtained. A crystal was mounted on a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. The cell dimensions were obtained by a least-squares procedure from the angular settings of 12 manually centered reflections for which the 2θ values were between 29 and 32°. The space group and cell dimensions are given in Table I with some other details of the experiment. ω scans of several low-angle reflections showed widths at half-peak height of about 0.25°. Using the θ - 2θ scan technique, a total of 10397 scans, including standards, were measured and later averaged to give a set of 4920 unique data of which 2137 had $F^2 > 2\sigma$. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. A decay of about 15% was observed in the intensities of all three standard reflections, and the data were adjusted accordingly.

No absorption correction was made because the crystal faces were too indistinct to measure. Azimuthal scans of a few reflections indicated variations in intensities of about 10% from the average. The data were processed, averaged, and given estimated standard deviations using formulas available as supplementary material. The factor $p = 0.06$ was used in the calculation of $\sigma(F^2)$.

The full-matrix least-squares program used minimizes the function $\sum w(\Delta F)^2 / \sum wF_o^2$. Scattering factors for Nd were taken from Cromer and Waber¹⁰ and those for Cl, C, and O from Doyle and Turner;¹¹ dispersion corrections used were from Cromer and Liberman.¹²

Structure Determination. The positions of the six Nd atoms, at the corners of a regular trigonal prism, were deduced from a three-dimensional Patterson function calculation. A least-squares