249-246 cm^{-1} are known for iridium(III) complexes having chloride, trans phosphines, and hydrides, respectively. The general order of decreasing ν_{Ir-Cl} values according to the nature of the trans ligand has been given as follows:[10] Cl > Br > I ~ CO > CH$_3$ ~ PR$_3$ ~ AsR$_3$ > H. Both IrCl(CN)(SCN)(CO)(PPh$_3$)$_2$ and IrCl(CN)(NCS)(CO)(PPh$_3$)$_2$ show strong absorptions at 310 cm^{-1} in both their infrared and Raman spectra which are assigned as ν_{Ir-Cl}. Structures **6**-**8** can be eliminated for Ir(CN)(SCN)(CO)(PPh$_3$)$_2$ because with Cl trans to triphenylphosphine a ν_{Ir-Cl} at *ca.* 260-280 cm^{-1} would be expected. It is also reasonable to suppose that a CN and an H would have similar effect on a trans Ir-Cl bond, and hence structures **1** and **2** with Cl trans to CN may be eliminated. We are not aware of data for ν_{Ir-Cl} values with chloride trans to *S*-thiocyanate, but do know that at least 20 Ir(III) complexes with chloride trans to carbon monoxide[9-12] exhibit iridium-chlorine stretching frequencies in the narrow 300-310-cm^{-1} range. It seems likely then that the initially isolated *S*-thiocyanate linkage isomer has either the structure **5** or **9**, which corresponds to either a trans or a cis mode of addition, respectively.

The initial product of the reaction of S(CN)$_2$ with the methyldiphenylphosphine complex IrCl(CO)(PMePh$_2$)$_2$, which also is the S-bonded linkage isomer, has mutually trans phosphine groups as deduced from the nmr spectrum which shows a triplet methyl signal that must be a consequence of virtual coupling of two mutually trans phosphorus atoms.

Therefore, IrCl(CN)(SCN)(CO)(PMePh$_2$)$_2$ has either structure **1**, **3**, or **5**. Structure **5** is the preferred structure since the far-infrared spectrum shows a medium-strength band at 315 cm^{-1} which is assumed to be the iridium-chlorine stretching frequency, and this value is consistent as discussed above with Cl being trans to CO, but is less likely for Cl being trans to CN as in structures **1** and **3**. While it does not follow that the triphenylphosphine complexes will necessarily have the same ligand dispositions as the methyldiphenylphosphine complexes, such nevertheless seems more likely and therefore we believe that IrCl(CN)(SCN)(CO)(PPh$_3$)$_2$ also has structure **5**, *i.e.*, a structure derived from a trans addition process.

In summary, it seems likely that S(CN)$_2$ reacts with IrCl(CO)L$_2$ (L = PPh$_3$, PMePh$_2$) *via* a trans mode of oxidative addition to give as the initial products the S isomers and that transformation to the N isomers is facilitated in the recrystallization process when methanol is present. It has been noted previously[8] that trans addition is consistent with orbital symmetry predictions. Finally, the fact that the use of sulfur dicyanide as a thiocyanation reagent in these reactions gives the S-bonded isomers as kinetic products is of some synthetic utility. For example, reaction of Ir(NCS)(CO)(PPh$_3$)$_2$, which contains N-bonded thiocyanate, with S(CN)$_2$ has provided a means of preparing the novel compound Ir(NCS)(SCN)(CN)(CO)(PPh$_3$)$_2$ which contains both N-bonded and S-bonded thiocyanate groups.[13]

Registry No. IrCl(CO)(PPh$_3$)$_2$, 15318-31-7; IrCl(CO)(PMePh$_2$)$_2$, 15318-32-8; S(CN)$_2$, 627-52-1; IrCl(CN)(NCS)(CO)(PPh$_3$)$_2$, 36863-03-3; IrCl(CN)(NCS)(CO)(PMePh$_2$)$_2$, 36863-04-4; IrCl(CN)(SCN)(CO)(PPh$_3$)$_2$, 36863-05-5; IrCl(CN)(SCN)(CO)(PMePh$_2$)$_2$, 36863-06-6.

Acknowledgments. This work was supported by grants from the National Science Foundation.

(11) J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).

(12) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969).

(13) W. H. Baddley and D. S. Hamilton, unpublished work.

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Transition Metal Hydroborate Complexes. V.[1] Crystal Structure of Tetrahydroboratobis(cyclopentadienyl)titanium(III)

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The structure of $(h^5\text{-}C_5H_5)_2Ti(BH_4)$ has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in space group *Fm2m* of the orthorhombic system with $a = 9.336$ (3), $b = 7.991$ (3), $c = 13.467$ (9) Å, and $\rho_{calcd} = 1.27$ g/cm^3 for $Z = 4$. From 249 independent observed reflections collected by diffractometer, the structure was solved by the usual Patterson and Fourier synthesis methods. Least-squares refinement of all atoms except the cyclopentadienyl ring protons converged at values for $R_1 = 0.030$ and $R_2 = 0.038$. The molecule has crystallographically required *m2m* site symmetry with the tetrahydroborate group coordinated to the titanium atom through two bridging hydrogen atoms. The coordination geometry of the titanium atom is quasitetrahedral with an average (ring centroid)-Ti-(ring centroid) angle of 136.7° and a H-Ti-H angle of 60 ± 5°. The refined Ti-H, Ti-B, and average Ti-C distances are 1.75 (8), 2.37 (1), and 2.35 (4) Å, respectively. The carbon atoms of the cyclopentadienyl groups are disordered, the average Ti-(ring centroid) distance being 2.03 Å.

Introduction

The synthesis of tetrahydroboratobis(cyclopentadienyl)titanium(III) was reported by Noth and Hartwimmer,[2] who suggested that the borohydride group contributes two hydrogen atoms to the coordination sphere of the titanium atom. Several discussions[2-5] of the infrared spectrum of this complex revealed the need for definitive structural information. As part of a continuing study of the chemical and geometric

(1) Part IV: S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, **11**, 6 (1972).

(2) R. Noth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).

(3) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1798 (1964).

(4) N. Davies, B. James, and M. G. H. Wallbridge, *J. Chem. Soc. A*, 2601 (1969).

(5) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

properties of metal hydroborate complexes,[1,6-8] the crystal structure of tetrahydroboratobis(cyclopentadienyl)titanium(III) has been investigated. The results, which confirm the geometry originally proposed,[2] are described in this report.

Experimental Procedure

Collection and Reduction of the Data. The compound was prepared as previously reported[2] and crystals were obtained by sublimation of the crude product *in vacuo* at 115°. One of the dark violet, needlelike crystals, of approximate dimension 1.15 × 0.2 × 0.24 mm, was sealed under nitrogen in a glass capillary. The mounting axis, corresponding to the long dimension of the crystal, was parallel to the crystallographic *b* axis. Determination of the space group and unit cell parameters was carried out on the Weissenberg and precession cameras using Ni-filtered Cu $K\bar{\alpha}$ radiation (λ 1.5418 Å). The cell constants and their standard deviations were obtained from a least-squares refinement of the setting angles χ, ϕ, and 2θ for 18 reflections centered on a Picker automated X-ray diffractometer. The results ($\pm 3\sigma$) are $a = 9.336 \pm 0.003$, $b = 7.991 \pm 0.003$, and $c = 13.467 \pm 0.009$ Å. The systematic absences are *hkl*: $h + k \neq 2n$, $k + l \neq 2n$, and $l + h \neq 2n$, consistent with standard space groups *F*222 (No. 22),[9a] *Fmm*2 (No. 42),[9b] or *Fmmm* (No. 69).[9c] Of these three, only *Fmm*2 is compatible with any reasonable site symmetry for the molecule, assuming $Z = 4$ (see below).

Intensity data were obtained using Ni-filtered Cu $K\bar{\alpha}$ radiation at 23° on the diffractometer. A symmetric scan range of 1.40° in 2θ plus the $K\alpha_1$-$K\alpha_2$ difference was used. The takeoff angle was 2.4°, and the symmetrically varying receiving aperture located ∿21 cm from the crystal was set to a 3.0 × 3.0 mm opening. The pulse height analyzer was adjusted to accept 95% of the diffracted intensity. As a check on the crystal and electronic stability, a standard reflection was measured periodically during the run and showed only random statistical fluctuations. A density measurement could not be made owing to the great solubility or chemical sensitivity of the compound in all solvents tried. Assuming 4 molecules per unit cell, the calculated density of 1.27 g/cm³ seems quite reasonable.

Two equivalent forms (*hkl* and $\bar{h}kl$) were measured, the collection of data being limited solely by the choice of radiation and instrument design ($\sin\theta < 0.89$). The raw data were corrected for background, use of attenuators, absorption, and Lorentz-polarization effects using a local modification of Prewitt's program ACAC,[10] as described previously,[11] with ϵ set equal to 0.03. The absorption correction ($\mu = 68$ cm^{-1}) was checked against an experimental measure of the change in peak intensity of the (040) reflection ($\chi = 90.0°$) as a function of the angle ϕ; reasonable agreement (to within ±10%) of the corrected intensities was obtained. Transmission factors for the entire data set ranged from 0.175 to 0.365. The corrected data were placed on an approximately absolute scale through a modification of Wilson's method, with a resultant mean *B* of 3.1 Å². Scattering factor tables were obtained from ref 12 with an appropriate correction for anomalous dispersion[13] being included in the contribution of the titanium atom to the calculated structure factors in later computations. Form factors used were for the neutral atoms.

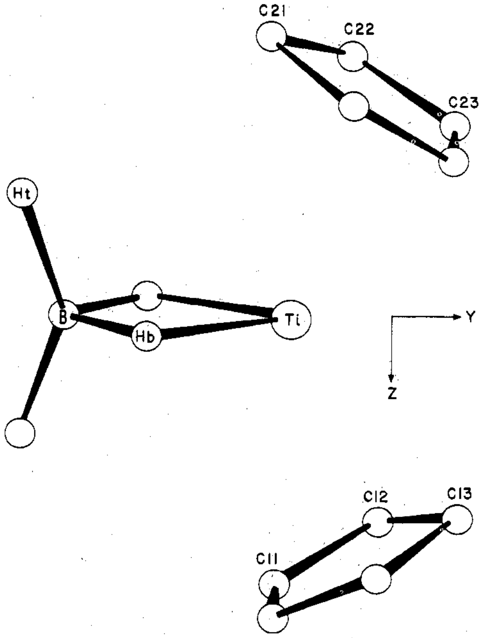

Figure 1. Perspective drawing of the $(C_5H_5)_2Ti(BH_4)$ molecular structure showing the atom-labeling scheme (see footnote *a*, Table I). The thermal ellipsoids have been omitted for clarity (see Figure 2).

At this point the average values of $F^2{}_{hkl}$ and $\sigma(F^2{}_{hkl})$ were computed, where $F^2{}_{hkl} = {}^1/_2(F^2{}_{hkl} + F^2{}_{\bar{h}kl})$ and with $\sigma(F^2{}_{hkl})$ taken as either ${}^1/_2[\sigma(F^2{}_{hkl}) + \sigma(F^2{}_{\bar{h}kl})]$ or ${}^1/_2|F^2{}_{hkl} - F^2{}_{\bar{h}kl}|$, whichever was larger. The agreement factor for the averaging based on F^2 was 0.047, with only a few large discrepencies (±15%) occurring. Of the 256 independent reflections, those for which $I < 3\sigma(I)$[11] were excluded from the refinement. The (200), (111), and (020) reflections were excluded from the final refinement cycles since they appeared to be strongly affected by secondary extinction. All subsequent calculations were performed on the remaining 249 reflections.

Determination of the Structure. Using the corrected data, a Patterson map was computed. Since there are 4 molecules per unit cell, the titanium atom is required to be at the origin (position (4a) of the acentric space group *Fmm*2 (No. 42)),[9a] with site symmetry *mm*2. The other two possible space groups were rejected since, in these, the symmetry of all fourfold special positions is greater than that of the molecule. Ordinarily the Patterson function would have been expected to yield the entire structure. It soon became evident, however, that the cyclopentadienyl rings were disordered. From the Patterson map, only the boron atom and a single carbon atom were definitely located. Since the boron atom was found to be on the *y* axis, the space group was revised to *Fm*2*m* at this stage, in order to be compatible with the initial choice of axes.

Subsequent structure factor calculations and difference Fourier maps yielded trial positional coordinates for the remaining nonhydrogen atoms. The appearance of six carbon atoms (asymmetric unit) in the cyclopentadienyl region confirmed the disorder indicated earlier by the Patterson map. A least-squares refinement, allowing variation only of the multipliers, showed an approximate 50% disorder between the two possible staggered-ring orientations allowed by the *yz* mirror plane (see Figure 1). A difference Fourier map computed at this stage phasing on only one of the two conformations provided further evidence for the disorder.

In a model containing the cyclopentadienyl rings in the staggered configuration with each carbon atom assigned at half-occupancy, least-squares refinements of the scale factor, atomic positional parameters, and individual isotropic thermal parameters converged at 0.115 and 0.092 for the discrepancy factors $R_1 = \Sigma\| F_o| - |F_c\| / \Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$. Examination of a difference Fourier map revealed several possible hydrogen peaks as well as anisotropic thermal motion for the Ti, the B, and especially the C atoms. Additional refinement was therefore carried out in which nonhydrogen atoms were assigned anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk +$

(6) (a) S. J. Lippard and K. M. Melmed, *J. Amer. Chem. Soc.*, **89**, 3929 (1967); (b) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2773 (1967).

(7) (a) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968); (b) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969); (c) E. R. Bernstein, T. A. Keiderling, S. J. Lippard, and J. J. Mayerle, *J. Amer. Chem. Soc.*, **94**, 2552 (1972).

(8) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, in press.

(9) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969: (a) p 108; (b) p 128; (c) p 159.

(10) Programs for an IBM 360-91 computer used in this work include local versions of MODE-1, the Brookhaven diffractometer setting and cell constant and orientation refinement program, GSET, the Prewitt diffractometer setting program, ACAC-3, a revised version of the Prewitt absorption correction and data reduction program, XDATA, the Brookhaven Wilson plot and scaling program, FORDAP, the Zalkin Fourier program, ORFLS, the Busing-Martin-Levy structure factor calculation and least-squares refinement program, ORFFE, the Busing-Martin-Levy molecular geometry and error function program, ORTEP, the Johnson thermal ellipsoid plotting program, and MEAN PLANE, the Pippy-Ahmed best planes program.

(11) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).

(12) "International Tables for X-Ray Crystallography," Vol. III, 3rd ed, Kynoch Press, Birmingham, England, 1969, pp 202, 204, and 213 ff.

(13) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

Table I. Final Positional and Thermal Parameters of the Atoms[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.0	0.0	0.0	1.03 (1)	1.22 (2)	0.337 (6)	0.0	0.0	0.0
B	0.0	−0.297 (2)	0.0	2.1 (2)	1.2 (2)	0.92 (9)	0.0	0.0	0.0
C11	0.069 (4)	−0.020 (6)	0.168 (1)	0.9 (2)	4 (1)	0.42 (9)	0.2 (4)	0.0 (1)	−0.3 (3)
C12	0.137 (6)	0.115 (9)	0.137 (3)	4.5 (9)	3.3 (5)	0.5 (1)	−1.9 (7)	−0.2 (2)	0.1 (2)
C13	0.0	0.218 (3)	0.117 (1)	4.3 (9)	1.1 (3)	0.3 (1)	0.0	0.0	−0.3 (1)
C21	0.0	−0.034 (3)	0.170 (2)	7 (3)	2.1 (6)	0.15 (9)	0.0	0.0	0.4 (2)
C22	0.122 (3)	0.074 (7)	0.144 (2)	0.9 (2)	3 (1)	0.5 (1)	0.0 (3)	−0.4 (1)	−0.5 (4)
C23	0.078 (2)	0.206 (3)	0.108 (1)	1.5 (3)	3.4 (4)	0.56 (7)	−0.5 (3)	0.0 (1)	−0.7 (1)
H_b	0.094 (8)	−0.19 (1)	0.0	2 (1)					
H_t	0.0	−0.38 (2)	0.097 (7)	5 (2)					

[a] Atoms are labeled as indicated in Figure 1, except that, for clarity, the figure depicts $z = -z$ for H_t and the cyclopentadienyl ring defined by C21, C22, and C23. Standard deviations, in parentheses, occur in the last significant figure for each parameter. [b] β's are defined in the text; values reported here are $\times 10^2$. For hydrogen atoms only, $\beta_{11} = B$, the isotropic thermal parameter, in Å^2, determined during isotropic refinement of all atoms (see text).

$2\beta_{13}hl + 2\beta_{23}kl)$], with due regard given to the anisotropic temperature factor restriction of atoms lying on one or more mirror planes.[14]

Because of the polar nature of the space group, it was decided to refine two possible structures,[15] differing in this case in the sign of the y coordinates for all atoms. Refinement of these two models with only nonhydrogen atoms produced a weighted R factor of 0.038 for the first structure ($y_B < 0$) and 0.044 for the second ($y_B > 0$). The Hamilton R factor test[16] was applied as a hypothesis of one degree of freedom. With the refinement of 55 parameters based on 249 reflections, the ratio of the weighted R factors for the two possible configurations of the structure showed that the second structure could be rejected at the 99.5% confidence level. Further computations were therefore carried out with the first structure, in which the boron atom y parameter is negative.

A difference Fourier map was then calculated, which revealed the BH_4^- protons as the most prominent peaks. The peak heights for these atoms were approximately one-sixth the value of a carbon atom. Owing to the large amount of anisotropic motion of the carbon atoms, it was not possible to locate all the hydrogens of the cyclopentadienyl rings. These atoms were included in later geometric calculations at a C-H distance of 1.06 Å, but not in the refinement. Refinement of positional parameters and first isotropic, followed by anisotropic, thermal parameters for all heavy atoms, and isotropic refinement of the tetrahydroborate thermal parameters, converged at final values of 0.030 and 0.038 for the discrepancy indices of R_1 and R_2, respectively. The thermal parameters of the tetrahydroborate hydrogen atoms converged nicely during isotropic, but not anisotropic, refinements of the carbon temperature factors. The values from the isotropic refinements were therefore used but not varied during subsequent calculations. In the final refinement cycles the parameters of the four noncyclopentadienyl atoms varied by less than 20% of their estimated standard deviations. The carbon atom parameters showed a greater variance, oscillating by as much as $\pm 1\sigma$ about the mean values and having some high (0.6–0.85) correlation coefficients. The thermal parameters of atom C21 tested non-positive-definite at times during the refinement.[17]

Table II[a]

Intramolecular Bond Distances, Å

Ti· · ·B	2.37 (1)	Ti-H_b	1.75 (8)
Ti-C11	2.36 (2)	B-H_b	1.23 (8)
Ti-C12	2.42 (4)	B-H_t	1.4 (1)
Ti-C13	2.35 (2)	C11-C12	1.32 (8)
Ti-C21	2.30 (2)	C12-C13	1.54 (8)
Ti-C22	2.33 (2)	C11-C11′	1.29 (8)
Ti-C23	2.31 (2)	C21-C22	1.47 (6)
Ti-RC1[b]	2.06	C22-C23	1.23 (7)
Ti-RC2	2.00	C23-C23′	1.45 (3)

Intramolecular Bond Angles, Deg

H_b-Ti-H_b′	60 (5)	C11′-C11-C12	119 (4)
Ti-H_b-B	104 (5)	C11-C12-C13	95 (4)
H_b-B-H_b′	91 (7)	C12-C13-C12′	112 (5)
H_b-B-H_t	108 (3)	C23′-C23-C22	110 (2)
H_t-B-H_t′	129 (9)	C21-C22-C23	110 (2)
		C22-C21-C22′	101 (3)

Best Planes Calculations

Best plane through C11, C12, C13, C12′, C11′: $-0.3444Y - 0.9388Z = -2.0629$. Distances (in Å) of atoms from plane: C11 (C11′), −0.01; C12 (C12′), 0.01; C13, −0.02

Best plane through C21, C22, C23, C23′, C22′: $0.4029Y - 0.9152Z = 2.0002$. Distances (in Å) of atoms from plane: C21, −0.01; C22 (C22′), 0.01; C23 (C23′), −0.01

[a] See footnote *a* of Table I; values reported have not been corrected for thermal motion. Primes indicate reflection through the mirror plane at $X = 0$. [b] RC = ring centroid.

Table III. Root-Mean-Square Amplitudes of Vibration (Å) for $(C_5H_5)_2Ti(BH_4)$[a]

Atom	Minimum	Medium	Maximum
Ti	0.176 (2)	0.199 (2)	0.213 (2)
B	0.20 (2)	0.29 (2)	0.31 (2)
C11	0.19 (2)	0.21 (3)	0.38 (5)
C12	0.22 (3)	0.26 (4)	0.49 (5)
C13	0.13 (3)	0.21 (3)	0.44 (5)
C21	0.08 (7)	0.27 (4)	0.57 (12)
C22	0.12 (2)	0.25 (3)	0.34 (9)
C23	0.17 (1)	0.25 (2)	0.37 (2)

[a] Taken along the principal axes of the thermal ellipsoids, the directions of which may be judged for the carbon atoms from Figure 2. The minimum vibrational amplitude for the boron atom is along the Ti-B vector (crystallographic y direction). See footnote *a* of Table I.

Results

In Table I are summarized the final atomic positional and thermal parameters for all atoms, together with standard deviations as estimated from the inverse matrix of the final least-squares refinement cycle. Table II contains a summary of the bond distances and angles in the structure. In Table III are listed the root-mean-square components of displacement along the principal axes of the thermal ellipsoids for those atoms that were refined anisotropically. Figure 1 shows the molecular structure and atom-labeling scheme. Figure 2 gives a view perpendicular to the two disordered cyclopentadienyl groups, showing the 50% probability thermal ellipsoids. From Figure 2 it is evident that there is

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(14) W. J. A. M. Peterse and J. H. Palm, *Acta Crystallogr.*, **20**, 147 (1966).

(15) For discussion, see (a) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **20**, 836 (1966); (b) D. W. J. Cruickshank and W. S. McDonald, *ibid.*, **23**, 9 (1967); (c) J. A. Ibers, *ibid.*, **22**, 604 (1967); (d) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

(16) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(17) A list of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-232.

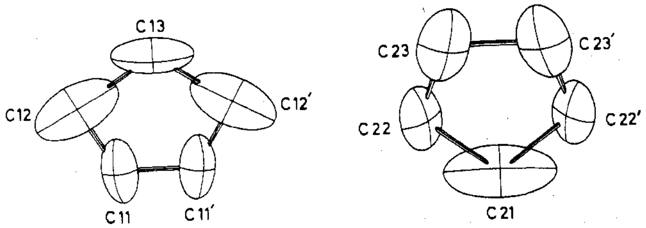

Figure 2. The 50% probability thermal ellipsoids of the disordered cyclopentadienyl rings. The view is normal to the ring planes. The primed atoms are generated from the unprimed atoms (Table I) by reflection through the crystallographic *xz* mirror plane.

not much out-of-plane thermal motion in the cyclopentadienyl groups. Moreover, superposition of the halves of the drawing indicates that the present model results in the almost complete distribution of electron density about the periphery of the ring defined by the 10 disordered carbon atoms.

Discussion

The crystal structure of $(C_5H_5)_2Ti(BH_4)$ consists of monomolecular units, the packing of which in the unit cell resembles that of the isomorphous analog $(C_5H_5)_2ZrF_2$.[18] The closest three intermolecular C - - - C, C - - - H, and H - - - H contacts are 3.49, 2.7, and 2.2 Å, respectively. As shown schematically in Figure 1, the coordination of the BH_4^- group to the titanium atom in tetrahydroboratobis(cyclopentadienyl)titanium(III) is attained through two bridging hydrogen atoms, as was found in $[(C_6H_5)_3P]_2Cu(BH_4)$.[6] The coordination geometry of both the titanium and boron atoms may be described as quasitetrahedral. The average (ring 1 centroid)-Ti-(ring 2 centroid) angle of 136.7° is in agreement with that found in the structure of $(C_5H_5)_2TiS_5$ [19] where this angle has a reported value of 133.7°. This result may also be compared with the ring-metal-ring angle of 127.8° found in the isomorphous structure of $(C_5H_5)_2ZrF_2$.[18] The slightly larger angles observed for the titanium compounds may result from the greater nonbonded steric repulsion between the cyclopentadienyl rings, the M-(ring centroid) distances being 2.03 and 2.21 Å for M = Ti and Zr, respectively.

The observed boron-titanium distance of 2.37 (1) Å is approximately 0.2 Å greater than the metal to boron distance in $[(C_6H_5)_3P]_2Cu(BH_4)$ (see Table IV). This result is consistent with the increase in the single-bond metallic radius from 1.173 Å for the copper atom to 1.324 Å for the titanium atom.[20] The Ti-H bond distances of 1.75 (8) Å (refined; or 1.83 unrefined—see Table IV) may be compared with the value of 1.69 Å calculated from the mean Ti-S bond length (2.43 Å) in $(C_5H_5)_2TiS_5$ [19] and the difference between covalent radii for tetrahedral sulfur[21a] and hydrogen.[21b] A similar calculation using the Ti-Cl bond distance (2.36 Å) in $(C_5H_5)TiCl_2$ [22] results in a computed value of 1.67 Å for the Ti-H bond distance. Although the increase in the observed Ti-H bond length over these calculated values is not statistically significant, it is consistent with the multicenter nature of the Ti-H-B bonds and the lower oxidation state of the titanium atom in $(C_5H_5)_2Ti(BH_4)$.

Table IV. Initial and Refined Geometry of the Metal Tetrahydroborate Linkage in $(C_5H_5)_2Ti(BH_4)$ and $[(C_6H_5)_3P]_2Cu(BH_4)$[a]

Distance	Initial value, Å	Final value, Å
Ti-B	2.36	2.37 (1)
Ti-H_b	1.83	1.75 (8)
B-H_b	1.19	1.23 (8)
B-H_t	1.3	1.4 (1)
Cu-B	2.19	2.18 (1)
Cu-H_b	1.89	2.02 (5)
B-H_b	1.19	1.26 (4)
B-H_t	1.25	1.37 (5)

Angle	Initial value, deg	Final value, deg
H_b-Ti-H_b'	60	60 (5)
Ti-H_b-B	100	104 (5)
H_b-B-H_t	110	108 (3)
H_b-B-H_b'	100	91 (7)
H_t-B-H_t'	114	129 (9)
H_b-Cu-H_b'	66	69 (3)
Cu-H_b-B	87	80 (3)
H_b-B-H_t	110, 113	95 (3), 109 (3)
H_b-B-H_b'	119	132 (5)
H_t-B-H_t'	90	121 (5)

[a] The "initial" heavy-atom positions are those used in the calculation of the Fourier map from which "initial" hydrogen atom positions were located. "Final" values refer to the refined atomic positions of all atoms including hydrogen. Standard deviations, in parentheses, occur in the last significant figure for each parameter. Final values for the copper compound are taken from ref 6.

Table IV shows the comparison of the geometry of the metal tetrahydroborate attachment as originally determined from the difference Fourier maps and after final refinement, for both $[(C_6H_5)_3P]_2Cu(BH_4)$ and $(C_5H_5)_2Ti(BH_4)$. As indicated, the refinement influences both the M-H and B-H bond lengths as well as the interbond angles, and the standard deviations are high. In some instances the initial geometry seems chemically more reasonable than the final one. The value of refinement of the tetrahydroborate hydrogen atom parameters would seem to be uncertain for these structures at the present time. Neutron diffraction studies of related compounds are currently in progress in an attempt to get a more reliable assessment of the geometry of coordinated tetrahydroborate groups.[23]

The titanium-(ring centroid) average distance is 2.03 Å, a value which as indicated by Wheatley[24] is typical for compounds of this type.[25] The individual titanium-carbon distances range from 2.30 to 2.42 Å, with an average value of 2.35 ± 0.04 Å, close to the range and mean values found in other titanium-cyclopentadienyl complexes with a pentahapto coordination mode.[19,25,26] The disorder found in the cyclopentadienyl groups is evidenced by the large carbon atom thermal amplitudes (Table III) which are mainly confined to the C_5H_5 ring planes (Figure 2), as well as by the variation in the interatomic distances and angles (Table II). Similar results have been found in other determinations

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(18) See Figure 2a of M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 2225 (1971). To compare the two structures it is necessary only to interchange the *a* and *b* crystallographic axes in either one.

(19) E. F. Epstein, I. Bernal, and H. Kopf, *J. Organometal. Chem.*, 26, 229 (1971).

(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 256.

(21) (a) See ref 20, p 246; (b) ref 20, p 227.

(22) V. V. Tkachev and L. O. Amovmyan, *Zh. Strukt. Khim.*, 13, 287 (1972).

(23) The first results of the neutron studies (on $U(BH_4)_4$[8]) corroborate the average of all refined and unrefined B-H bond lengths in Table IV, 1.27 Å; the H-B-H angles show less deviation from tetrahedral values, however.

(24) P. J. Wheatley, *Perspect. Struct. Chem.*, 1, 1 (1967).

(25) For more recent data, *cf.* ref 19 and (a) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 93, 3592 (1971); (b) A. C. Skapski and P. G. H. Troughton, *Acta Crystallogr., Sect. B*, 26, 716 (1970).

(26) (a) S. F. Watkins and L. F. Dahl, unpublished results quoted in ref 19; (b) V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 1340 (1971); (c) G. R. Davies and B. T. Kilbourn, *J. Chem. Soc. A*, 87 (1971).

involving cyclopentadienyl rings bonded to transition metals.[25b,27] An appropriate method of handling this particular problem is to treat the rings as hindered rotors, the X-ray scattering by such groups having been given by King and Lipscomb.[28] In the determination of the structure of $(C_5H_5FeS)_4$, Schunn, Fritchie, and Prewitt felt that the Lipscomb-King hindered-rotor scattering expression would describe the thermal motion more accurately than a model based on refinement of individual ellipsoidal atoms. Their resultant average C-C bond distance of 1.43 ± 0.01 Å was in good agreement with the average C-C bond length of 1.43 Å found by Hardgrove and Templeton[29] in ruthenocene (where the molecular packing does not allow libration of the cyclopentadienyl groups) or the average value of 1.419 Å found in the recent survey of cyclopentadienyl complexes of the transition metals.[24] In the present instance, the main concern is with the interaction of the tetrahydroborate ion with the titanium atom. Since in this and other cases individual atom anisotropic refinement does give a satisfactory description of the electron density distribution of the cyclopentadienyl carbon atoms for purposes of structural determination (although a poor description of the geometry of the C_5H_5 rings), the use of the hindered-rotor model was felt to be unnecessary. It may be noted that the individual atom anisotropic refinement model used does result in the carbon atoms of the cyclopentadienyl rings being close to planar (Table II) and a relatively low value for the discrepancy index.

The disorder itself may be thought of in terms of individual molecules containing cyclopentadienyl rings which are in a staggered configuration with respect to each other across the *xy* mirror plane (Figures 1 and 2). Preservation of mirror symmetry for this plane in the lattice is then achieved by alternation of this configuration to the image obtained by a C_2 rotation about the *y* axis. In both forms the mirror symmetry of the individual cyclopentadienyl rings imposed by the crystallographic *yz* mirror plane is maintained, thus giving a $^1/_2$-$^1/_2$ distribution of carbon positions as found experimentally. The average carbon-carbon bond distances for rings 1 and 2 are 1.40 ± 0.13 and 1.37 ± 0.13 Å, respectively, compared to an expected value of 1.43 Å (*vide supra*). The average bond angle found for both rings, 108 ± 10°, is in agreement with the expected value for a planar (Table II) five-membered ring.

Registry No. $(h^5\text{-}C_5H_5)_2Ti(BH_4)$, 12772-20-2.

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(27) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

(28) M. V. King and W. N. Lipscomb, *Acta Crystallogr.*, **3**, 155 (1950).

(29) G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, **12**, 28 (1959).

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Electron-Transfer Reactions of Cobalt(III) and Ruthenium(III) Ammines with Europium(II), Ytterbium(II), and Samarium(II) in Aqueous Solutions

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Kinetic measurements, using the pulse radiolysis technique, have been made on the reaction of Sm(II), Yb(II), and Eu(II) with pentaammine complexes of Co(III) and Ru(III). It has been found that the order of reactivity is Sm(II) > Yb(II) > Eu(II). This order is correlated with the electrode potential E° of the divalent ions. The resulting reactivity patterns are examined with the view of providing a possible kinetic basis for distinguishing between inner- and outer-sphere electron-transfer mechanisms. The reactions of the three divalent lanthanide ions with the hexaammine- and the ethylenediaminecobalt(III) complexes were too slow to be followed by this technique. With the exception of a possible significant contribution of an outer-sphere mechanism to the reduction of the cobalt(III) aquo complex with Sm(II), the reactions of the three Ln(II) ions with the other cobalt pentaammine complexes take place predominantly by an inner-sphere mechanism. Reactivities of corresponding Ru(III) and Co(III) complexes are compared. The electron-exchange rate constants for the Ln(II)-Ln(III) couples were calculated using Marcus' theory of electron-transfer reactions.

Introduction

Previous studies[1] led to the conclusion that the reduction of the cobalt(III) ammine complexes of the type $\mathrm{Co(NH_3)_5X^{3-n}}$ (where X^{n-} is one of the ligands NH_3, H_2O, OH^-, F^-, Cl^-, Br^-, I^-, CN^-, NCS^-, N_3^-, etc.) proceeds either by outer-sphere (OS) or inner-sphere (IS) mechanisms.[1] The X^{n-} acts as an inner-sphere bridge for the electron transfer in the latter case.

Several factors, based on kinetic evidence, have been suggested to differentiate between inner-sphere and outer-sphere reducing agents.[2-7] The specific rate of reaction of a series

(1) For review see: (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1950); (b) J. Halpern, *Quart. Rev., Chem. Soc.*, **15**, 207 (1961); (c) N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119 (1966); (d) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1968).

(2) A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

(3) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

(4) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(5) D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 2272 (1968).

(6) D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80**, 1091 (1958).

(7) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).