

- (15) J. J. Bonnet and Y. Jeannin, *Acta Crystallogr., Sect. B*, **28**, 1079 (1972).
 (16) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
 (17) D. N. Anderson and R. D. Willett, *Inorg. Chim. Acta*, **5**, 41 (1971).
 (18) This band and its assignment have been discussed by numerous authors. One frequently cited paper is that of F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).
 (19) J. Ferguson, *J. Chem. Phys.*, **39**, 116 (1963).
 (20) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).
 (21) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1975.
 (22) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd ed, Wiley, New York, N.Y., 1958.
 (23) J. C. Bailar and C. L. Rollinson, *Inorg. Synth.*, **2**, 222 (1946).

Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Structural and Magnetic Properties of Di- μ -chloro-bis[bis(η^5 -cyclopentadienyl)titanium(III)] and Di- μ -chloro- and Di- μ -bromo-bis[bis(η^5 -methylcyclopentadienyl)titanium(III)]

RUDOLPH JUNGST, DENNIS SEKUTOWSKI, JIMMY DAVIS, MATTHEW LULY, and GALEN STUCKY*

Received December 13, 1976

AIC608946

Single-crystal x-ray diffraction methods have been used to determine the molecular structures of $[(C_5H_5)_2TiCl]_2$ (I), $[(CH_3C_5H_4)_2TiCl]_2$ (II), and $[(CH_3C_5H_4)_2TiBr]_2$ (III). All three compounds crystallize as dimeric molecules whose magnetic properties show antiferromagnetic behavior due to interaction between the unpaired electrons on the titanium atoms. I crystallizes in the space group $P2_1/c$ with six dimers in a unit cell of dimensions $a = 13.422$ (8) Å, $b = 15.666$ (11) Å, $c = 13.083$ (12) Å, and $\beta = 94.21$ (4)°. Refinement has converged at a final weighted R factor of 0.047 based on 3615 independent reflections. II was found to be orthorhombic with space group $Pbca$ and eight molecules per unit cell. Lattice parameters are $a = 16.357$ (9) Å, $b = 19.194$ (13) Å, and $c = 14.232$ (9) Å. The final weighted R factor obtained by least-squares refinement of 3935 reflections is 0.061. III crystallizes in the monoclinic space group $P2_1/c$ with two dimer molecules per unit cell and lattice parameters $a = 6.746$ (6) Å, $b = 10.591$ (10) Å, $c = 17.164$ (20) Å, and $\beta = 112.22$ (6)°. After least-squares refinement of 1459 reflections the weighted R factor is 0.036. Magnetic susceptibility measurements have been made on all three compounds in an attempt to correlate the magnitude of the antiferromagnetic coupling with trends in structural features. Computer fits of the experimental data yield J values of -111, -160, and -138 cm^{-1} for I, II, and III, respectively. The strength of the interaction increases as the metal-metal distance decreases in the case of the chloride-bridged compounds. An anomaly previously observed in the magnetic properties of I has been found to be due to introduction of impurities during sublimation rather than a phase transition in $[(C_5H_5)_2TiCl]_2$.

Introduction

A study of the magnetic properties of the titanium(III) dimers of the formula $[(C_5H_5)_2TiX]_2$, $X = F, Cl, Br, I$, to liquid nitrogen temperatures has been reported,¹ but trends found in the magnitude of the antiferromagnetic coupling observed between the two d^1 centers in this system could not be completely explained due to a lack of any structural data on these compounds. The order of interaction is $F < Cl \sim I < Br$, the iodide seeming out of place. Additional anomalies were found in the magnetic properties of $[(C_5H_5)_2TiCl]_2$ and $[(C_5H_5)_2TiI]_2$ which show scatter in the data near the "turnover" temperature and this has been attributed to a phase transition.² The bromide and fluoride analogues do not exhibit this property.

While preparing bis(methylcyclopentadienyl)titanium halides in order to synthesize mixed-metal complexes containing titanium(III) in our laboratory,^{3,4} it was noted that the magnetic properties were appreciably modified in some cases by introduction of the methyl group on the ring. Since these compounds present an opportunity to study the dependence of magnetic coupling on the geometry of the molecule when the halide is not changed, we felt that insight as to factors influencing coupling in the entire series could be gained by collecting both structural and magnetic susceptibility data. Properties of low-valent titanium dimers would provide a valuable contrast to the much more extensively studied Cu(II) d^9 complexes, due to differences in orbital occupation for the unpaired electron and the greater radial extension of titanium d orbitals. No previous work has involved interpretation of exchange coupling in Ti(III) systems for which detailed crystallographic information was available for all compounds. Of additional interest was the nature of the proposed phase transition and its effect on comparison of the

magnetic properties between compounds. Accordingly, we wish to report x-ray structural results for $[(C_5H_5)_2TiCl]_2$, $[(CH_3C_5H_4)_2TiCl]_2$, and $[(CH_3C_5H_4)_2TiBr]_2$ as well as magnetic susceptibility measurements to liquid helium temperature for these three compounds.

Experimental Section

X-Ray Data. All x-ray intensity data were collected by a θ - 2θ scan method using Mo $K\alpha$ radiation on a Picker four-circle diffractometer equipped with a highly oriented graphite single-crystal monochromator. Stationary-background counts were measured for 10 s before and after each reflection and three standards were collected periodically to monitor crystal and diffractometer stability. A reflection was judged to be observed if the criterion $I_{obsd} > 3\sigma_c(I)$ was met where $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$. Here T_c is the total counts, t_c/t_b is the ratio of time spent counting peak intensity to that counting backgrounds, and B_1 and B_2 are the background counts. Lorentz and polarization corrections and calculation of observed structure factor amplitudes from the data were carried out using the program VANDY.⁵ During early refinement, a data set comprised only of observed reflections was employed, but final refinement in all cases was completed using the entire data set and weights assigned on the basis of counting statistics. At convergence, no significant systematic variation of $w(F_o - F_c)^2$ with respect to $(\sin \theta)/\lambda$ or the magnitude of the structure factors was noted for any of the structures. Cromer and Waber's scattering factors⁶ were used for C, Cl, Br, and Ti, Stewart's scattering factors used for H,⁷ and Cromer and Liberman's anomalous dispersion corrections applied for Cl, Br, and Ti.⁸ Additional programs used in solution, refinement, and interpretation of the data have been previously referenced.⁴

$[(C_5H_5)_2TiCl]_2$. Di- μ -chloro-bis[bis(η^5 -cyclopentadienyl)titanium(III)] was prepared by reduction of $(C_5H_5)_2TiCl_2$ with activated aluminum^{4,9} and sublimed in an evacuated sealed tube at 150 °C to form green crystal chunks of irregular shape. These were mounted in thin-wall glass capillaries using a helium atmosphere drybox. Precession photographs showed monoclinic symmetry and systematic

absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, thus identifying the space group as $P2_1/c$. It should be noted that crystals of this compound can also be obtained by evaporation of benzene solutions in a drybox, but the space group of these could not be determined due to a subtle twinning which generates pseudo-fourfold symmetry which only became apparent in our investigation from scanning reflections on the diffractometer. Comparison of powder patterns with the sublimed material suggests that the distribution of intensities is not the same for the two samples. All further discussion refers to sublimed crystals. A nearly cubic crystal, $0.22 \times 0.19 \times 0.24$ mm, was mounted in a sealed glass capillary for data collection. Least-squares refinement of 14 hand-centered reflections gave the final cell parameters ($T = 23^\circ\text{C}$, $\lambda 0.71069 \text{ \AA}$) $a = 13.422$ (8) \AA , $b = 15.666$ (11) \AA , $c = 13.083$ (12) \AA , and $\beta = 94.21$ (4) $^\circ$. Good agreement was found between the measured density of 1.54 (3) g/cm^3 by flotation in a bromobenzene-1,1,2,2-tetrachloroethane mixture and 1.55 g/cm^3 calculated assuming 6 molecules per unit cell. Typical peak widths at half-height were 0.125° from ω scans. Data were collected using a scan width of 1.7° , a scan rate of $2^\circ/\text{min}$, and a takeoff angle of 1.6° . The three standards measured every 60 reflections showed a systematic and isotropic decrease in intensity during the course of data collection to about 70% of the original values. In order to correct for this, the data were scaled according to the slope of a graph of standard counts vs. reflection number. No absorption correction was applied ($\mu = 11.9 \text{ cm}^{-1}$), the maximum effect on intensities being estimated as $\pm 8\%$. Measurements to $2\theta_{\text{max}} = 45^\circ$ gave 3615 independent reflections of which 2200 were considered observed. Due to the lack of a single heavy atom which would dominate the structure and the fact that 1.5 molecules are present in the asymmetric unit, initial positional coordinates could not be found from a Patterson map and direct methods were used to solve the structure. The program FAME was used to generate a set of 500 normalized structure factors. A set of the top 350 with a minimum value of 1.62 was used in the direct-methods package MULTAN. Eight sets of phases were chosen and generation of an E map from the set with the highest figure of merit allowed determination of coordinates for three titanium atoms and three chlorine atoms. From this point, application of standard Fourier techniques resulted in location of all of the nonhydrogen atoms, and least-squares refinement with isotropic temperature factors and unit weights converged at an $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ of 0.101. Hydrogen atoms were included at their calculated positions (C-H bond distance 0.95 \AA) with each isotropic temperature factor equal to that of the carbon atom to which each hydrogen atom was bonded. Further refinement of all nonhydrogen atoms with anisotropic temperature factors using weights based on counting statistics gave final convergence at an $R_2 = (\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$ of 0.047 (all data). R_1 was 0.085, the estimated standard deviation of an observation of unit weight was 1.18, and a final difference Fourier had no peaks higher than 0.53 e/\AA^3 . Positional parameters and anisotropic temperature factors for all nonhydrogen atoms are given in Tables I and II.

$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2]$. Di- μ -chloro-bis[bis(η^5 -methylcyclopentadienyl)titanium(III)] was prepared as previously described⁴ and crystals were grown by slow evaporation of a benzene solution in an inert atmosphere. These were mounted in thin-wall glass capillaries and sealed off to protect the compound from oxygen. The parallelepiped specimen used for data collection was cleaved from a larger crystal and had dimensions of $0.27 \times 0.42 \times 0.18$ mm. Precession photographs revealed systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, and orthorhombic symmetry, indicating the space group to be $Pbca$. Twenty-five reflections were centered on the diffractometer and least-squares refined to give the lattice parameters $a = 16.357$ (9) \AA , $b = 19.194$ (13) \AA , and $c = 14.232$ (9) \AA . Eight molecules are contained in the unit cell. ω scans showed typical peaks to have a width at half-height of 0.10° and data were collected with a scan rate of $2^\circ/\text{min}$, a scan width of 1.6° , and a takeoff angle of 1.6° . Three standards were measured every 100 reflections and showed no systematic variation in intensity. Data were collected to a limit of $2\theta_{\text{max}} = 50^\circ$ for a total of 3935 reflections, 2195 of which were considered observed. The titanium and chlorine atom positions were determined from a Patterson map and application of standard Fourier techniques resulted in location of all nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters converged at $R_1 = 0.125$ for a data set consisting only of observed reflections. An absorption correction was applied using the program ORABS¹⁰ ($\mu = 9.93 \text{ cm}^{-1}$) giving a range of transmission coefficients from 0.877

Table I. Positional Parameters for Nonhydrogen Atoms in $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$

Atom	x	y	z
Ti(1)	0.24557 (7)	0.10033 (6)	0.05326 (7)
Ti(2)	0.44941 (6)	0.26792 (6)	0.15266 (7)
Ti(3)	-0.09052 (6)	0.08925 (6)	0.43844 (7)
Cl(1)	0.40142 (9)	0.17363 (8)	-0.00159 (10)
Cl(2)	0.29810 (9)	0.18766 (9)	0.21217 (10)
Cl(3)	0.07692 (9)	0.42858 (8)	0.03891 (10)
C(1)	0.2735 (10)	-0.0123 (4)	0.1695 (5)
C(2)	0.2019 (5)	-0.0392 (4)	0.1045 (9)
C(3)	0.2402 (10)	-0.0471 (4)	0.0126 (7)
C(4)	0.3351 (11)	-0.0232 (6)	0.0244 (12)
C(5)	0.3574 (7)	-0.0024 (6)	0.1213 (12)
C(6)	0.1563 (5)	0.1420 (6)	-0.0987 (5)
C(7)	0.0947 (5)	0.0905 (4)	-0.0483 (5)
C(8)	0.0722 (4)	0.1303 (4)	0.0409 (5)
C(9)	0.1196 (5)	0.2068 (5)	0.0423 (6)
C(10)	0.1705 (5)	0.2148 (5)	-0.0412 (8)
C(11)	0.5742 (6)	0.2700 (6)	0.2893 (6)
C(12)	0.5301 (5)	0.1921 (8)	0.2913 (7)
C(13)	0.5518 (6)	0.1516 (4)	0.2011 (8)
C(14)	0.6081 (5)	0.2058 (5)	0.1504 (5)
C(15)	0.6228 (4)	0.2777 (4)	0.2042 (7)
C(16)	0.3712 (7)	0.3715 (4)	0.0379 (6)
C(17)	0.4668 (5)	0.3956 (4)	0.0603 (6)
C(18)	0.4792 (5)	0.4151 (4)	0.1604 (7)
C(19)	0.3890 (7)	0.3998 (4)	0.2038 (5)
C(20)	0.3234 (5)	0.3732 (4)	0.1254 (8)
C(21)	-0.1311 (6)	0.0718 (6)	0.2640 (5)
C(22)	-0.0318 (7)	0.0496 (5)	0.2805 (5)
C(23)	0.0203 (5)	0.1205 (7)	0.3087 (5)
C(24)	-0.0427 (8)	0.1856 (5)	0.3123 (6)
C(25)	-0.1370 (6)	0.1573 (6)	0.2821 (5)
C(26)	-0.1392 (8)	0.1226 (13)	0.6023 (7)
C(27)	-0.2045 (16)	0.0705 (7)	0.5625 (15)
C(28)	-0.2513 (7)	0.1020 (15)	0.4875 (12)
C(29)	-0.2203 (12)	0.1803 (10)	0.4749 (9)
C(30)	-0.1476 (9)	0.1932 (7)	0.5463 (12)

to 0.951. Further refinement with hydrogen atoms at calculated positions as described above and anisotropic temperature factors on all nonhydrogen atoms using the complete data set and statistical weights converged at $R_2 = 0.061$ (all data). Methyl group hydrogen atoms could not be located on a difference Fourier and so were not included in the refinement. A final difference Fourier had a highest peak of 0.65 e/\AA^3 and the estimated standard deviation of an observation of unit weight was 1.37. Tables III and IV give the final positional parameters and anisotropic temperature factors for the nonhydrogen atoms.

$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$. Di- μ -bromo-bis[bis(η^5 -methylcyclopentadienyl)titanium(III)] was prepared by the standard method used for $[(\text{C}_5\text{H}_5)_2\text{TiBr}]_2$ ⁹ and crystals were grown by evaporation of a benzene solution. These were mounted in thin-wall glass capillaries as with the other compounds. A certain amount of twinning was always noted and after examination of a large number of crystals one was chosen with minimal broadening of the peaks. Observation of monoclinic symmetry in precession photographs with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely defined the space group as $P2_1/c$. Fourteen reflections were hand centered on the diffractometer and cell parameters least-squares refined to the values ($T = 23^\circ\text{C}$, $\lambda 0.71069 \text{ \AA}$) $a = 6.746$ (6) \AA , $b = 10.591$ (10) \AA , $c = 17.164$ (20) \AA , and $\beta = 112.22$ (6) $^\circ$. Good agreement was obtained between the measured density of 1.70 (5) g/cm^3 found by flotation in iodobutane-iodomethane compared to the value 1.67 g/cm^3 calculated for 2 molecules per unit cell. Several ω scans showed peak widths at half-height to be less than 0.26° . Collection of data to $2\theta_{\text{max}} = 45^\circ$ was accomplished using a scan rate of $2^\circ/\text{min}$, a scan width of 1.8° , and a takeoff angle of 1.0° . No systematic variation in intensity was noted for the three standards collected every 60 reflections. A total of 1459 independent reflections were measured of which 1095 were considered observed by the criteria given earlier. The crystal used in the data collection had dimensions $0.22 \times 0.11 \times 0.18$ mm with $\mu = 44.6 \text{ cm}^{-1}$. The maximum error introduced into the intensities was estimated on the basis of several diffraction vector scans to be 11% and absorption corrections were not made. The positions of the titanium and bromine atoms were determined from

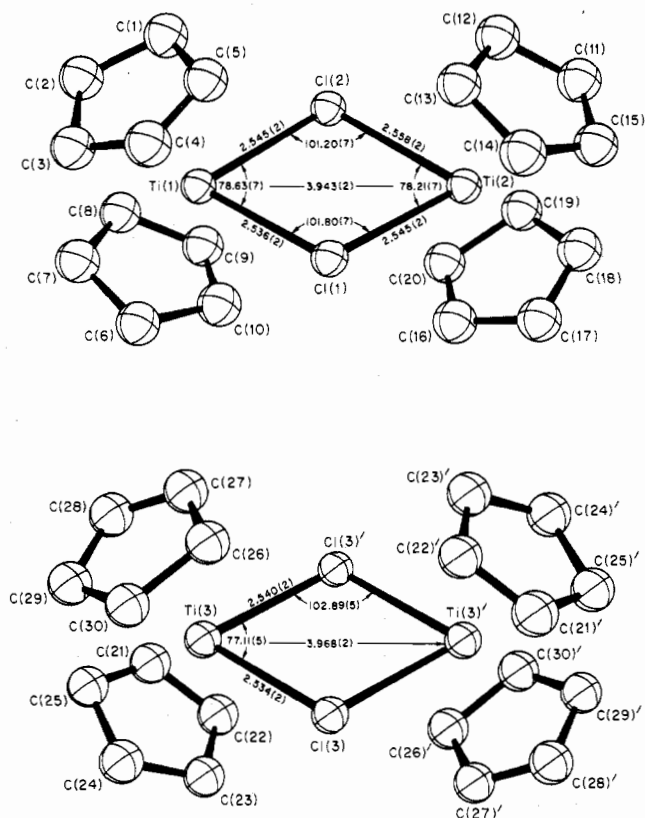


Figure 1. Molecular structure of $[(C_5H_5)_2TiCl]_2$ showing the two independent dimer molecules. Cyclopentadienyl rings are represented with isotropic carbon thermal parameters.

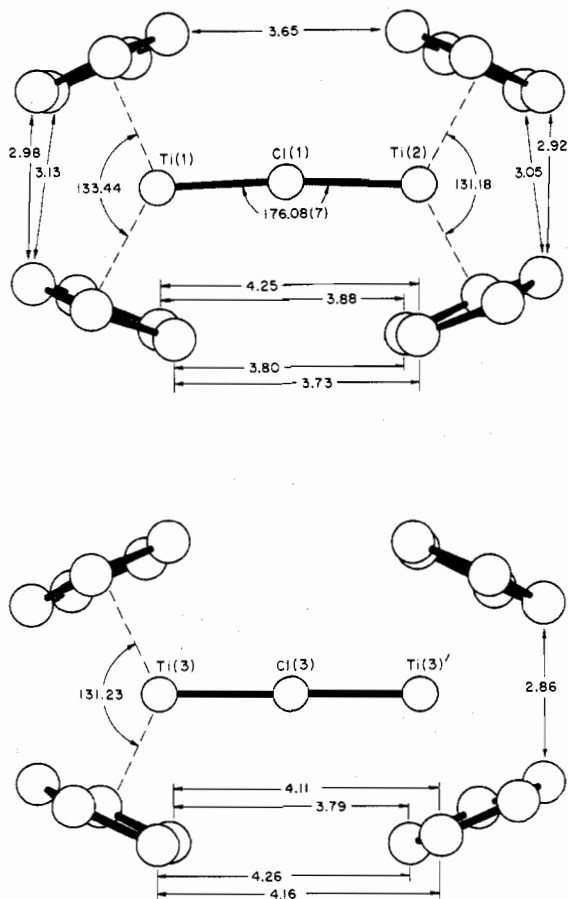


Figure 2. Nonbonded distances between cyclopentadienyl rings in $[(C_5H_5)_2TiCl]_2$.

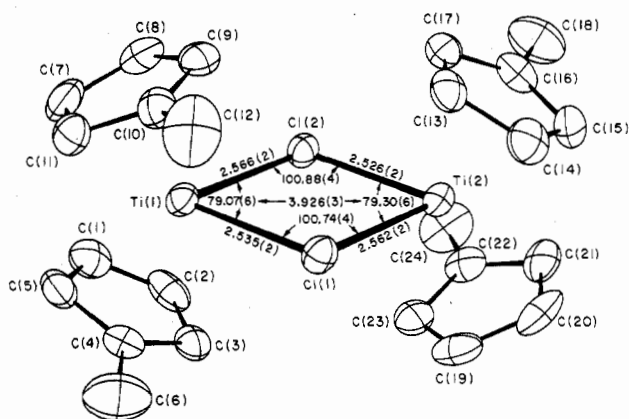


Figure 3. Molecular structure of $[(CH_3C_5H_4)_2TiCl]_2$. Thermal ellipsoids are shown at the 50% probability level.

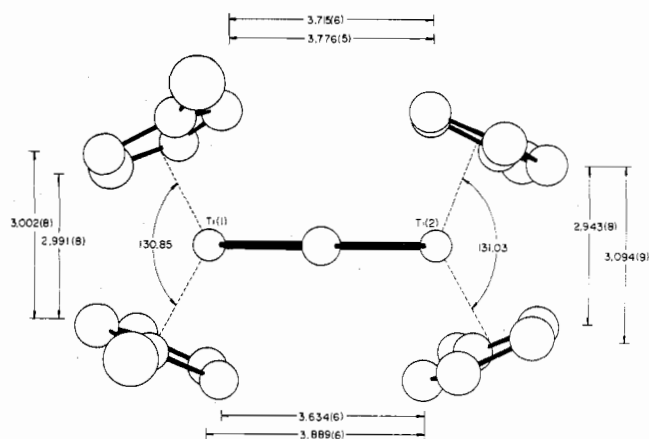


Figure 4. Nonbonded contact distances between methylcyclopentadienyl rings in $[(CH_3C_5H_4)_2TiCl]_2$.

a Patterson map and subsequent Fourier calculations revealed all of the carbon atoms. Least-squares refinement with anisotropic thermal parameters on all nonhydrogen atoms and inclusion of hydrogen atoms at calculated positions using a bond length of 0.95 Å led to the final R factors $R_1 = 0.049$ and $R_2 = 0.036$ using the entire data set and statistical weights. Methyl group hydrogen atoms were positioned in a rotational orientation such that one hydrogen atom is in the plane of the cyclopentadienyl ring, in agreement with the hydrogen atom positions observed on a difference Fourier. The estimated standard deviation of an observation of unit weight was 1.30 and a final difference Fourier had no peaks higher than $0.52 e/\text{Å}^3$. Tables V and VI show the final positional and anisotropic thermal parameters. Listings of the observed and calculated structure factor amplitudes are available for all three structures.¹¹

Physical Measurements. Magnetic susceptibility data were collected on a Princeton Applied Research Model 150A vibrating-sample magnetometer calibrated with $CuSO_4 \cdot 5H_2O$.¹² All experimental data were corrected for diamagnetism using Pascal's constants and computer fit to theoretical expressions using STEPT by J. P. Chandler, Indiana University. Mass spectra were recorded on the CH-5 mass spectrometer of the School of Chemical Sciences, University of Illinois. The compounds were all handled in a Vacuum Atmospheres, Inc., drybox under argon or helium while mounting crystals or loading magnetic susceptibility and mass spectral samples.

Discussion

Crystallographic Results. Tables VII–XIV list the final bond distances and angles for the three structures while Figures 1–8 are ORTEP views of the molecules. All form the expected dimeric structure, but there are differences in the metal–metal distances and angles about the core of heavy atoms.

Comparison with Similar d^0 and d^1 Systems. $[(C_5H_5)_2TiCl]_2$ (I) contains two independent dimer molecules and is in fact isomorphous with $[(C_5H_5)_2ScCl]_2$ which has been investigated

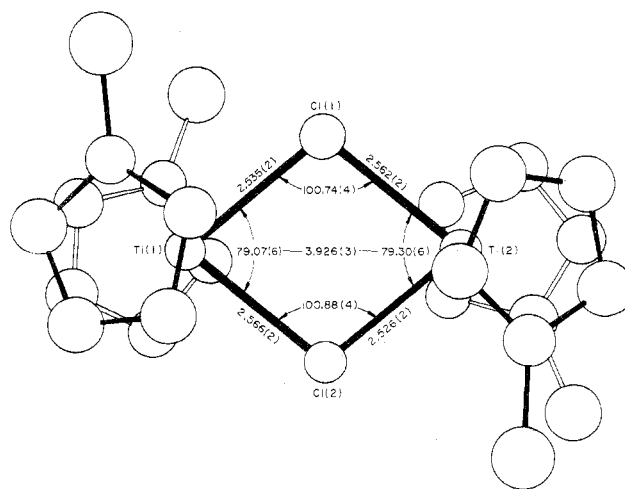
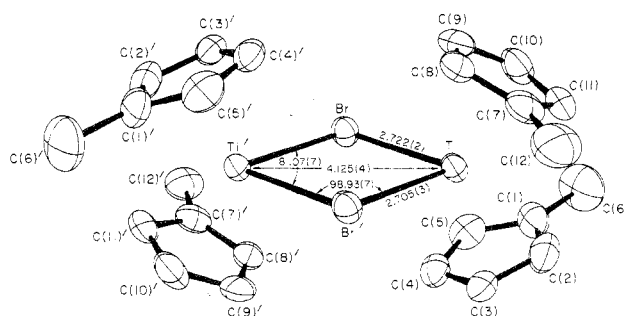
Table II. Anisotropic Thermal Parameters for Nonhydrogen Atoms in $[(C_5H_5)_2TiCl]_2$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0.00435 (6)	0.00309 (5)	0.00551 (7)	0.00013 (4)	0.00039 (5)	-0.00002 (5)
Ti(2)	0.00380 (6)	0.00333 (5)	0.00601 (7)	0.00031 (4)	-0.00020 (5)	-0.00018 (5)
Ti(3)	0.00396 (6)	0.00359 (5)	0.00514 (7)	0.00021 (4)	-0.00032 (5)	-0.00019 (5)
Cl(1)	0.00519 (9)	0.00448 (7)	0.00524 (9)	-0.00044 (6)	0.00125 (7)	-0.00021 (7)
Cl(2)	0.00495 (9)	0.00503 (8)	0.00507 (9)	0.00000 (7)	0.00086 (7)	-0.00058 (7)
Cl(3)	0.00404 (8)	0.00343 (6)	0.00660 (10)	0.00042 (6)	-0.00075 (7)	0.00029 (6)
C(1)	0.0211 (11)	0.0041 (4)	0.0071 (6)	-0.0001 (6)	-0.0030 (7)	0.0018 (4)
C(2)	0.0063 (5)	0.0043 (4)	0.0148 (9)	-0.0003 (3)	0.0017 (6)	0.0016 (5)
C(3)	0.0228 (12)	0.0025 (3)	0.0089 (7)	0.0005 (5)	-0.0045 (8)	-0.0008 (4)
C(4)	0.0178 (13)	0.0037 (5)	0.0267 (16)	0.0036 (7)	0.0150 (13)	0.0029 (8)
C(5)	0.0066 (6)	0.0042 (5)	0.0299 (17)	-0.0005 (4)	-0.0068 (9)	0.0050 (8)
C(6)	0.0069 (5)	0.0087 (5)	0.0063 (5)	-0.0012 (4)	0.0008 (4)	-0.0015 (4)
C(7)	0.0068 (4)	0.0043 (3)	0.0084 (5)	0.0005 (3)	-0.0025 (4)	0.0010 (4)
C(8)	0.0048 (4)	0.0063 (4)	0.0076 (5)	-0.0009 (3)	0.0007 (4)	0.0005 (4)
C(9)	0.0070 (5)	0.0045 (4)	0.0121 (7)	-0.0018 (4)	-0.0046 (5)	0.0028 (4)
C(10)	0.0048 (5)	0.0050 (4)	0.0181 (10)	0.0008 (4)	-0.0028 (5)	-0.0051 (5)
C(11)	0.0075 (6)	0.0102 (6)	0.0072 (6)	0.0035 (5)	-0.0019 (5)	-0.0010 (5)
C(12)	0.0053 (5)	0.0153 (9)	0.0092 (7)	0.0015 (5)	0.0004 (5)	0.0081 (7)
C(13)	0.0073 (6)	0.0030 (3)	0.0186 (10)	-0.0003 (3)	-0.0049 (6)	0.0014 (5)
C(14)	0.0058 (5)	0.0070 (4)	0.0094 (6)	0.0028 (4)	-0.0002 (4)	-0.0014 (5)
C(15)	0.0042 (4)	0.0053 (4)	0.0130 (7)	-0.0002 (3)	-0.0015 (4)	0.0005 (5)
C(16)	0.0106 (7)	0.0035 (3)	0.0122 (7)	0.0003 (4)	-0.0054 (6)	0.0006 (4)
C(17)	0.0086 (6)	0.0041 (3)	0.0113 (7)	-0.0005 (3)	0.0009 (5)	0.0016 (4)
C(18)	0.0072 (5)	0.0032 (3)	0.0155 (8)	-0.0000 (3)	-0.0053 (6)	-0.0011 (4)
C(19)	0.0134 (8)	0.0046 (4)	0.0092 (6)	0.0044 (5)	0.0009 (6)	-0.0007 (4)
C(20)	0.0047 (5)	0.0048 (4)	0.0179 (10)	0.0014 (3)	0.0004 (6)	0.0023 (5)
C(21)	0.0113 (7)	0.0086 (5)	0.0050 (5)	-0.0044 (5)	-0.0023 (5)	0.0004 (4)
C(22)	0.0135 (8)	0.0073 (5)	0.0051 (5)	0.0038 (5)	0.0024 (5)	0.0010 (4)
C(23)	0.0073 (5)	0.0106 (6)	0.0060 (5)	-0.0023 (5)	-0.0001 (4)	0.0020 (5)
C(24)	0.0147 (8)	0.0054 (4)	0.0094 (6)	0.0005 (5)	0.0017 (6)	0.0021 (4)
C(25)	0.0070 (6)	0.0112 (6)	0.0082 (6)	0.0040 (5)	-0.0007 (5)	0.0044 (5)
C(26)	0.0084 (8)	0.0202 (13)	0.0054 (5)	-0.0088 (9)	-0.0004 (6)	0.0015 (8)
C(27)	0.0265 (23)	0.0047 (5)	0.0251 (22)	-0.0019 (9)	0.0213 (16)	-0.0011 (9)
C(28)	0.0042 (5)	0.0223 (18)	0.0195 (18)	0.0045 (9)	0.0043 (8)	0.0144 (14)
C(29)	0.0148 (12)	0.0125 (8)	0.0114 (10)	-0.0108 (8)	0.0032 (8)	-0.0033 (8)
C(30)	0.0096 (8)	0.0060 (5)	0.0171 (12)	0.0031 (5)	0.0067 (7)	0.0061 (6)

^a The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Positional Parameters for the Nonhydrogen Atoms in $[(CH_2C_5H_4)_2TiCl]_2$

Atom	x	y	z
Ti(1)	0.16678 (5)	0.22921 (4)	0.11129 (6)
Ti(2)	0.07188 (6)	0.04848 (4)	0.18046 (6)
Cl(1)	0.10289 (8)	0.12289 (6)	0.03530 (8)
Cl(2)	0.13596 (8)	0.15420 (6)	0.25626 (8)
C(1)	0.3007 (3)	0.2653 (4)	0.1453 (4)
C(2)	0.2998 (3)	0.1938 (4)	0.1566 (4)
C(3)	0.2847 (3)	0.1642 (3)	0.0694 (4)
C(4)	0.2752 (3)	0.2168 (3)	0.0023 (4)
C(5)	0.2869 (3)	0.2799 (3)	0.0509 (4)
C(6)	0.2628 (4)	0.2931 (4)	0.3958 (4)
C(7)	0.1400 (4)	0.3498 (3)	0.1334 (5)
C(8)	0.0907 (4)	0.3130 (3)	0.1945 (4)
C(9)	0.0338 (3)	0.2752 (3)	0.1394 (4)
C(10)	0.0479 (3)	0.2886 (3)	0.0446 (4)
C(11)	0.1149 (4)	0.3343 (3)	0.0430 (4)
C(12)	0.0002 (4)	0.2384 (3)	0.4602 (4)
C(13)	0.4411 (3)	0.0986 (3)	0.3557 (4)
C(14)	0.4386 (4)	0.0272 (3)	0.3749 (4)
C(15)	0.4461 (3)	-0.0072 (3)	0.2892 (4)
C(16)	0.4575 (3)	0.0419 (3)	0.2159 (4)
C(17)	0.4533 (3)	0.1068 (3)	0.2595 (4)
C(18)	0.4657 (4)	0.0271 (4)	0.1103 (4)
C(19)	0.3283 (4)	0.4764 (3)	0.1073 (4)
C(20)	0.3891 (4)	0.4333 (3)	0.1403 (5)
C(21)	0.3881 (4)	0.4372 (3)	0.2398 (4)
C(22)	0.3270 (4)	0.4830 (3)	0.2675 (4)
C(23)	0.2901 (3)	0.5074 (3)	0.1837 (4)
C(24)	0.2996 (4)	0.5012 (4)	0.3689 (4)

Figure 5. Orientation of methyl groups in $[(CH_3C_5H_4)_2TiCl]_2$.Figure 6. Molecular structure of $[(CH_3C_5H_4)_2TiBr]_2$.

crystallographically by Atwood and Smith.¹³ Among the differences between the scandium and titanium structures are Sc-Sc distances of 3.886 (3) and 3.922 (3) Å compared to 3.943 (2) and 3.968 (2) Å in the titanium complex. The

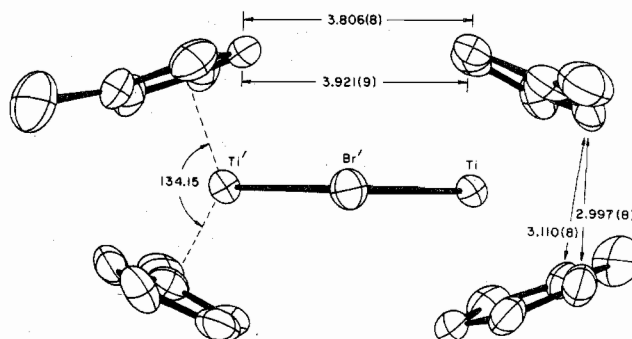
Table IV. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in $[(CH_3C_5H_4)_2TiCl]_2$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0.00229 (4)	0.00157 (3)	0.00401 (5)	0.00007 (3)	-0.00002 (4)	0.00001 (3)
Ti(2)	0.00273 (4)	0.00150 (3)	0.00832 (5)	0.00006 (3)	-0.00010 (4)	-0.00007 (3)
Cl(1)	0.00348 (6)	0.00194 (4)	0.00361 (7)	-0.00008 (4)	-0.00037 (5)	-0.00018 (4)
Cl(2)	0.00302 (5)	0.00188 (4)	0.00356 (7)	-0.00019 (4)	-0.00005 (5)	-0.00024 (4)
C(1)	0.0025 (2)	0.0041 (3)	0.0058 (4)	-0.0010 (2)	0.0002 (2)	-0.0009 (3)
C(2)	0.0024 (2)	0.0041 (2)	0.0048 (4)	-0.0017 (2)	-0.0001 (2)	0.0015 (2)
C(3)	0.0026 (2)	0.0024 (2)	0.0052 (3)	0.0003 (2)	0.0004 (2)	0.0003 (2)
C(4)	0.0024 (2)	0.0029 (2)	0.0044 (3)	0.0001 (2)	0.0004 (2)	0.0003 (2)
C(5)	0.0029 (2)	0.0028 (2)	0.0058 (4)	-0.0002 (2)	0.0008 (2)	0.0007 (2)
C(6)	0.0059 (4)	0.0054 (3)	0.0035 (3)	-0.0011 (3)	0.0003 (3)	-0.0006 (3)
C(7)	0.0044 (3)	0.0016 (2)	0.0016 (2)	-0.0000 (2)	0.0004 (3)	-0.0006 (2)
C(8)	0.0052 (3)	0.0021 (2)	0.0059 (4)	0.0011 (2)	0.0003 (3)	-0.0009 (2)
C(9)	0.0031 (2)	0.0021 (2)	0.0072 (4)	0.0009 (2)	0.0011 (2)	0.0006 (2)
C(10)	0.0032 (3)	0.0019 (2)	0.0066 (4)	0.0005 (2)	0.0004 (2)	0.0012 (2)
C(11)	0.0041 (3)	0.0022 (2)	0.0070 (4)	0.0007 (2)	0.0011 (3)	0.0013 (2)
C(12)	0.0043 (3)	0.0043 (2)	0.0077 (5)	-0.0004 (2)	-0.0030 (3)	-0.0006 (3)
C(13)	0.0025 (2)	0.0028 (2)	0.0060 (4)	-0.0000 (2)	0.0005 (2)	-0.0007 (2)
C(14)	0.0036 (3)	0.0032 (2)	0.0052 (4)	-0.0005 (2)	0.0006 (3)	0.0006 (2)
C(15)	0.0035 (3)	0.0022 (2)	0.0082 (4)	-0.0009 (2)	-0.0003 (3)	0.0005 (2)
C(16)	0.0023 (2)	0.0036 (2)	0.0054 (4)	-0.0005 (2)	-0.0004 (2)	-0.0005 (2)
C(17)	0.0025 (2)	0.0023 (2)	0.0061 (4)	-0.0002 (2)	-0.0004 (2)	0.0005 (2)
C(18)	0.0053 (3)	0.0068 (3)	0.0039 (3)	0.0002 (3)	-0.0004 (3)	-0.0006 (3)
C(19)	0.0054 (3)	0.0028 (2)	0.0048 (4)	-0.0019 (2)	-0.0007 (3)	-0.0002 (2)
C(20)	0.0062 (4)	0.0021 (2)	0.0074 (4)	-0.0014 (2)	0.0018 (3)	-0.0013 (2)
C(21)	0.0046 (3)	0.0018 (2)	0.0073 (4)	-0.0005 (2)	0.0002 (3)	0.0010 (2)
C(22)	0.0042 (3)	0.0021 (2)	0.0048 (4)	-0.0009 (2)	-0.0002 (3)	0.0008 (2)
C(23)	0.0032 (2)	0.0024 (2)	0.0063 (4)	-0.0011 (2)	-0.0002 (3)	0.0003 (2)
C(24)	0.0075 (4)	0.0046 (3)	0.0034 (3)	-0.0010 (3)	0.0021 (3)	0.0003 (2)

^a See footnote *a* of Table II.Table V. Positional Parameters for Nonhydrogen Atoms in $[(CH_3C_5H_4)_2TiBr]_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.26418 (8)	-0.05867 (5)	0.03642 (3)
Ti	0.08320 (14)	0.12244 (8)	0.10076 (5)
C(1)	0.2082 (10)	0.0949 (5)	0.2538 (3)
C(2)	-0.0010 (10)	0.1430 (5)	0.2246 (3)
C(3)	-0.1390 (8)	0.0560 (6)	0.1713 (3)
C(4)	-0.0189 (10)	-0.0454 (5)	0.1642 (3)
C(5)	0.1937 (9)	-0.0224 (6)	0.2148 (3)
C(6)	0.4075 (11)	0.1493 (7)	0.3181 (4)
C(7)	0.0126 (9)	0.3411 (5)	0.0682 (4)
C(8)	0.0726 (10)	0.2909 (5)	0.0045 (3)
C(9)	0.2824 (10)	0.2498 (5)	0.0395 (4)
C(10)	0.3580 (9)	0.2714 (5)	0.1257 (4)
C(11)	0.1937 (9)	0.3303 (5)	0.1435 (4)
C(12)	-0.1937 (10)	0.4007 (5)	0.0587 (4)

Sc-Cl-Sc angles are 97.6 (1), 98.2 (1), and 99.6 (1)°, while the corresponding Ti-Cl-Ti angles are 101.20 (7), 101.80 (7), and 102.89 (5)°. The Cl-Sc-Cl angles of 80.4 (1), 81.8 (1), and 82.3 (1)° are larger than in the titanium analogue where the Cl-Ti-Cl angles are 77.11 (5), 78.21 (7), and 78.63 (7)°. The scandium-cyclopentadienyl ring distances range from 2.17

Figure 7. Nonbonded distances between carbon atoms of methylcyclopentadienyl rings in $[(CH_3C_5H_4)_2TiBr]_2$.

to 2.20 Å, 0.12–0.13 Å longer than in I. Sc-Cl bond lengths were also slightly longer than Ti-Cl bond lengths ranging from 2.559 (4) to 2.585 (4) Å in contrast to 2.534 (2)–2.558 (2) Å in I.

Some of these structural differences can be rationalized. The covalent radius of scandium is 0.12 Å greater than that of titanium which is close to the difference observed in the

Table VI. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in $[(CH_3C_5H_4)_2TiBr]_2$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.01687 (15)	0.00666 (6)	0.00291 (2)	-0.00038 (8)	0.00210 (4)	-0.00039 (3)
Ti	0.01892 (28)	0.00518 (9)	0.00250 (4)	-0.00161 (13)	0.00247 (9)	-0.00031 (5)
C(1)	0.0347 (22)	0.0100 (7)	0.0021 (2)	-0.0034 (10)	0.0021 (6)	-0.0003 (3)
C(2)	0.0372 (22)	0.0084 (7)	0.0030 (3)	0.0013 (10)	0.0050 (7)	-0.0009 (3)
C(3)	0.0250 (17)	0.0114 (7)	0.0030 (3)	-0.0031 (10)	0.0049 (6)	-0.0011 (4)
C(4)	0.0409 (22)	0.0065 (6)	0.0027 (2)	-0.0018 (10)	0.0058 (6)	-0.0001 (3)
C(5)	0.0291 (20)	0.0112 (8)	0.0031 (3)	0.0039 (10)	0.0026 (6)	0.0019 (4)
C(6)	0.0447 (27)	0.0203 (11)	0.0037 (3)	-0.0063 (14)	-0.0008 (8)	-0.0003 (5)
C(7)	0.0243 (18)	0.0044 (5)	0.0049 (3)	-0.0003 (8)	0.0047 (7)	0.0005 (3)
C(8)	0.0359 (22)	0.0054 (5)	0.0037 (3)	-0.0048 (9)	0.0057 (7)	-0.0002 (3)
C(9)	0.0337 (22)	0.0069 (6)	0.0060 (4)	-0.0055 (10)	-0.0095 (10)	-0.0006 (4)
C(10)	0.0236 (18)	0.0082 (7)	0.0053 (4)	-0.0055 (9)	0.0029 (7)	-0.0019 (4)
C(11)	0.0295 (19)	0.0064 (6)	0.0045 (3)	-0.0050 (9)	0.0054 (7)	-0.0020 (3)
C(12)	0.0414 (23)	0.0073 (6)	0.0063 (4)	0.0004 (10)	0.0078 (8)	0.0011 (4)

^a See footnote *a* of Table II.

Table VII. Interatomic Distances, (Å) for $[(C_5H_5)_2TiCl]_2^a$

Ti(1)-Ti(2)	3.943 (2)	Ti(2)-C(11)	2.358 (7)
Ti(1)-Cl(1)	2.536 (2)	Ti(2)-C(12)	2.364 (7)
Ti(1)-Cl(2)	2.545 (2)	Ti(2)-C(13)	2.341 (6)
Ti(2)-Cl(1)	2.545 (2)	Ti(2)-C(14)	2.344 (6)
Ti(2)-Cl(2)	2.558 (2)	Ti(2)-C(15)	2.380 (6)
Ti(3)-Ti(3) ^b	3.968 (2)	Ti(2)-C(16)	2.399 (7)
Ti(3)-Cl(3)	2.534 (2)	Ti(2)-C(17)	2.357 (6)
Ti(3)-Cl(3)'	2.540 (2)	Ti(2)-C(18)	2.342 (7)
Cl(1)-Cl(2)	3.219 (3)	Ti(2)-C(19)	2.336 (6)
Cl(3)-Cl(3)'	3.162 (3)	Ti(2)-C(20)	2.372 (6)
Ti(1)-C(1)	2.341 (7)	Ti(3)-C(21)	2.323 (6)
Ti(1)-C(2)	2.373 (6)	Ti(3)-C(22)	2.348 (6)
Ti(1)-C(3)	2.370 (7)	Ti(3)-C(23)	2.388 (7)
Ti(1)-C(4)	2.324 (8)	Ti(3)-C(24)	2.359 (7)
Ti(1)-C(5)	2.332 (8)	Ti(3)-C(25)	2.350 (6)
Ti(1)-C(6)	2.337 (6)	Ti(3)-C(26)	2.346 (9)
Ti(1)-C(7)	2.344 (5)	Ti(3)-C(27)	2.329 (10)
Ti(1)-C(8)	2.368 (6)	Ti(3)-C(28)	2.305 (9)
Ti(1)-C(9)	2.373 (6)	Ti(3)-C(29)	2.328 (8)
Ti(1)-C(10)	2.361 (6)	Ti(3)-C(30)	2.321 (7)

^a Errors in the lattice parameters are included in the estimated standard deviation. ^b Prime indicates an atomic position generated by a center of inversion at 0, 0, 1/2.

Table VIII. Interatomic Distances (Å) for Cyclopentadienyl Rings of $[(C_5H_5)_2TiCl]_2^a$

Cp 1		Cp 4	
C(1)-C(2)	1.306 (9)	C(16)-C(17)	1.348 (8)
C(1)-C(5)	1.340 (12)	C(16)-C(20)	1.353 (9)
C(2)-C(3)	1.348 (10)	C(17)-C(18)	1.344 (9)
C(3)-C(4)	1.326 (12)	C(18)-C(19)	1.396 (9)
C(4)-C(5)	1.322 (13)	C(19)-C(20)	1.367 (9)
Cp 2		Cp 5	
C(6)-C(7)	1.360 (8)	C(21)-C(22)	1.378 (9)
C(6)-C(10)	1.373 (9)	C(21)-C(25)	1.364 (10)
C(7)-C(8)	1.375 (8)	C(22)-C(23)	1.349 (9)
C(8)-C(9)	1.357 (8)	C(23)-C(24)	1.328 (9)
C(9)-C(10)	1.336 (9)	C(24)-C(25)	1.372 (10)
Cp 3		Cp 6	
C(11)-C(12)	1.357 (10)	C(26)-C(27)	1.280 (14)
C(11)-C(15)	1.336 (9)	C(26)-C(30)	1.327 (12)
C(12)-C(13)	1.390 (10)	C(27)-C(28)	1.229 (16)
C(13)-C(14)	1.343 (9)	C(28)-C(29)	1.309 (14)
C(14)-C(15)	1.335 (8)	C(29)-C(30)	1.315 (12)

^a Errors in the lattice parameters are included in the estimated standard deviation.

Table IX. Bond Angles (deg) for Nonhydrogen Atoms in $[(C_5H_5)_2TiCl]_2$

Ti(1)-Cl(1)-Ti(2)	101.80 (7)	C(13)-C(14)-C(15)	109.9 (7)
Ti(1)-Cl(2)-Ti(2)	101.20 (7)	C(14)-C(15)-C(11)	107.5 (7)
Cl(1)-Ti(1)-Cl(2)	78.63 (7)	C(15)-C(11)-C(12)	109.8 (8)
Cl(1)-Ti(2)-Cl(2)	78.21 (7)	C(16)-C(17)-C(18)	108.8 (7)
Ti(3)-Cl(3)-Ti(3)'	102.89 (5)	C(17)-C(18)-C(19)	108.0 (6)
Cl(3)-Ti(3)-Cl(3)'	77.11 (5)	C(18)-C(19)-C(20)	106.1 (6)
C(1)-C(2)-C(3)	107.5 (8)	C(19)-C(20)-C(16)	108.7 (7)
C(2)-C(3)-C(4)	107.2 (9)	C(20)-C(16)-C(17)	108.3 (7)
C(3)-C(4)-C(5)	109.3 (10)	C(21)-C(22)-C(23)	108.2 (7)
C(4)-C(5)-C(1)	106.5 (9)	C(22)-C(23)-C(24)	108.8 (7)
C(5)-C(1)-C(2)	109.5 (8)	C(23)-C(24)-C(25)	108.6 (7)
C(6)-C(7)-C(8)	108.8 (6)	C(24)-C(25)-C(21)	107.6 (6)
C(7)-C(8)-C(9)	106.3 (6)	C(25)-C(21)-C(22)	106.7 (6)
C(8)-C(9)-C(10)	109.8 (6)	C(26)-C(27)-C(28)	111.3 (12)
C(9)-C(10)-C(6)	108.2 (6)	C(27)-C(28)-C(29)	109.1 (12)
C(10)-C(6)-C(7)	106.9 (6)	C(28)-C(29)-C(30)	106.3 (10)
C(11)-C(12)-C(13)	106.0 (7)	C(29)-C(30)-C(26)	107.0 (9)
C(12)-C(13)-C(14)	106.9 (7)	C(30)-C(26)-C(27)	106.2 (10)

cyclopentadienyl ring to metal distances. An increase of similar magnitude does not occur in the metal-chlorine distances. This parallels the trends which have been found in studies on $(CH_3C_5H_4)_2MCl_2$,¹⁴ $(C_5H_5)_2M(SC_6H_5)_2$,¹⁵ and

Table X. Interatomic Distances (Å) for $[(CH_3C_5H_4)_2TiCl]_2^a$

Ti(1)-Ti(2)	3.926 (3)	Ti(1)-C(10)	2.447 (5)
Ti(1)-Cl(1)	2.535 (2)	Ti(1)-C(11)	2.394 (5)
Ti(1)-Cl(2)	2.566 (2)	Ti(1)-C(12)	3.527 (6)
Ti(2)-Cl(1)	2.562 (2)	Ti(2)-C(13)	2.401 (5)
Ti(2)-Cl(2)	2.526 (2)	Ti(2)-C(14)	2.353 (6)
Cl(1)-Cl(2)	3.247 (3)	Ti(2)-C(15)	2.358 (6)
Ti(1)-C(1)	2.348 (6)	Ti(2)-C(16)	2.386 (5)
Ti(1)-C(2)	2.368 (6)	Ti(2)-C(17)	2.397 (5)
Ti(1)-C(3)	2.372 (5)	Ti(2)-C(18)	3.472 (6)
Ti(1)-C(4)	2.368 (5)	Ti(2)-C(19)	2.380 (5)
Ti(1)-C(5)	2.355 (5)	Ti(2)-C(20)	2.370 (6)
Ti(1)-C(6)	3.472 (6)	Ti(2)-C(21)	2.387 (5)
Ti(1)-C(7)	2.376 (5)	Ti(2)-C(22)	2.419 (5)
Ti(1)-C(8)	2.353 (5)	Ti(2)-C(23)	2.392 (5)
Ti(1)-C(9)	2.381 (5)	Ti(2)-C(24)	3.526 (6)

^a Errors in the lattice parameters are included in the estimated standard deviation.

Table XI. Interatomic Distances (Å) for Cyclopentadienyl Rings of $[(CH_3C_5H_4)_2TiCl]_2$

Cp 1		Cp 3	
C(1)-C(2)	1.381 (8)	C(13)-C(14)	1.396 (7)
C(1)-C(5)	1.390 (7)	C(13)-C(17)	1.392 (7)
C(2)-C(3)	1.386 (7)	C(14)-C(15)	1.392 (7)
C(3)-C(4)	1.399 (7)	C(14)-C(16)	1.419 (7)
C(4)-C(5)	1.409 (7)	C(16)-C(17)	1.393 (6)
C(4)-C(6)	1.540 (7)	C(16)-C(18)	1.535 (7)
Cp 2		Cp 4	
C(7)-C(8)	1.381 (8)	C(19)-C(20)	1.377 (8)
C(7)-C(11)	1.382 (8)	C(19)-C(23)	1.387 (8)
C(8)-C(9)	1.418 (8)	C(20)-C(21)	1.417 (8)
C(9)-C(10)	1.393 (7)	C(21)-C(22)	1.389 (7)
C(10)-C(11)	1.403 (7)	C(22)-C(23)	1.416 (7)
C(10)-C(12)	1.524 (8)	C(22)-C(24)	1.550 (7)

Table XII. Bond Angles (deg) for Nonhydrogen Atoms in $[(CH_3C_5H_4)_2TiCl]_2$

Ti(1)-Cl(1)-Ti(2)	100.74 (7)	C(9)-C(10)-C(12)	128.0 (6)
Ti(1)-Cl(2)-Ti(2)	100.88 (7)	C(11)-C(10)-C(12)	126.9 (6)
Cl(1)-Ti(1)-Cl(2)	79.07 (6)	C(13)-C(14)-C(15)	106.9 (5)
Cl(1)-Ti(2)-Cl(2)	79.30 (6)	C(14)-C(13)-C(17)	107.9 (5)
C(1)-C(2)-C(3)	107.8 (5)	C(14)-C(15)-C(16)	109.9 (5)
C(2)-C(1)-C(5)	108.2 (5)	C(15)-C(16)-C(17)	105.0 (5)
C(2)-C(3)-C(4)	109.6 (5)	C(13)-C(17)-C(16)	110.2 (5)
C(3)-C(4)-C(5)	105.6 (5)	C(15)-C(16)-C(18)	127.5 (6)
C(3)-C(4)-C(6)	126.8 (5)	C(17)-C(16)-C(18)	127.3 (6)
C(5)-C(4)-C(6)	127.4 (5)	C(19)-C(20)-C(21)	107.5 (6)
C(1)-C(5)-C(4)	108.9 (5)	C(20)-C(19)-C(23)	108.3 (5)
C(7)-C(8)-C(9)	107.2 (5)	C(20)-C(21)-C(22)	109.0 (6)
C(8)-C(7)-C(11)	107.6 (5)	C(21)-C(22)-C(23)	106.0 (5)
C(8)-C(9)-C(10)	109.4 (5)	C(19)-C(23)-C(22)	108.9 (5)
C(9)-C(10)-C(11)	105.1 (5)	C(21)-C(22)-C(24)	128.0 (6)
C(7)-C(11)-C(10)	110.6 (5)	C(23)-C(22)-C(24)	125.9 (6)

Table XIII. Interatomic Distances (Å) for $[(CH_3C_5H_4)_2TiBr]_2^a$

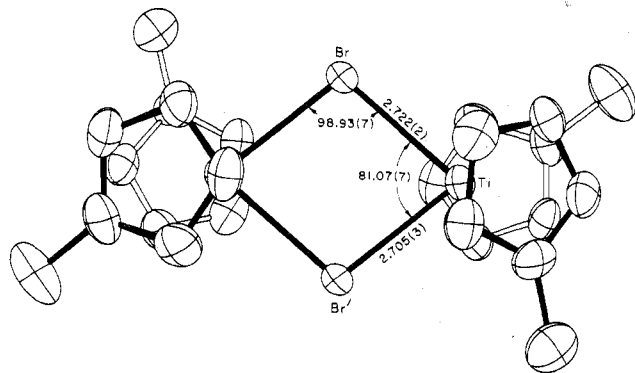
Ti-Ti'	4.125 (4)	Ti-C(11)	2.351 (6)
Ti-Br	2.722 (2)	C(1)-C(2)	1.403 (8)
Ti-Br'	2.705 (3)	C(2)-C(3)	1.382 (7)
Br-Br'	3.527 (3)	C(3)-C(4)	1.378 (7)
Ti-C(1)	2.454 (6)	C(4)-C(5)	1.388 (8)
Ti-C(2)	2.409 (6)	C(5)-C(1)	1.397 (8)
Ti-C(3)	2.363 (5)	C(1)-C(6)	1.495 (8)
Ti-C(4)	2.321 (5)	C(7)-C(8)	1.406 (7)
Ti-C(5)	2.374 (6)	C(8)-C(9)	1.382 (7)
Ti-C(7)	2.387 (6)	C(9)-C(10)	1.390 (8)
Ti-C(8)	2.415 (5)	C(10)-C(11)	1.402 (7)
Ti-C(9)	2.408 (5)	C(11)-C(7)	1.407 (8)
Ti-C(10)	2.347 (6)	C(7)-C(12)	1.480 (8)

^a Errors in the lattice parameters are included in the estimated standard deviation.

$(C_5H_5)_2MS_5$ ¹⁶ complexes where M is Ti or V. In these cases, the V-L bond length is 0.02-0.05 Å longer than Ti-L in the

Table XIV. Bond Angles (deg) for Nonhydrogen Atoms in $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$

Br'-Ti-Br	81.07 (7)	C(5)-C(1)-C(6)	125.3 (6)
Ti'-Br-Ti	98.93 (7)	C(7)-C(8)-C(9)	109.2 (5)
C(1)-C(2)-C(3)	109.2 (5)	C(8)-C(9)-C(10)	108.3 (5)
C(2)-C(3)-C(4)	107.8 (5)	C(9)-C(10)-C(11)	107.6 (5)
C(3)-C(4)-C(5)	108.2 (5)	C(10)-C(11)-C(7)	108.6 (5)
C(4)-C(5)-C(1)	108.9 (5)	C(11)-C(7)-C(8)	106.2 (5)
C(5)-C(1)-C(2)	105.8 (5)	C(11)-C(7)-C(12)	126.1 (5)

Figure 8. Orientation of methyl groups on cyclopentadienyl rings for $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$.

same compound, even though the vanadium-cyclopentadienyl ring distance is 0.076–0.10 Å shorter than the analogous distance from titanium. The L–M–L angle has been found to increase about 6° from 87.1 (1)° in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{VCl}_2$ to 93.2 (1)° in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$. These changes have been attributed to the unpaired electron being in a molecular orbital which is antibonding with respect to the M–L bond and is supported by experimental EPR data and theoretical calculations which also show that the highest occupied molecular orbital is primarily d_z^2 in character with a smaller contribution from $d_x^2 - y^2$ so that the unpaired electron density is oriented in the ML_2 plane and perpendicular to the C_2 axis of the molecule.^{14,17–19} The highest unoccupied molecular orbital in the d^0 compounds is calculated to have a makeup which is very similar to this so that the analysis should be valid for Ti(III) as well as V(IV). Since the change in covalent radius between scandium and titanium is greater than that between titanium and vanadium, the compounds in our study still show a slight decrease in M–L bond length for the d^1 vs. d^0 species, but not nearly so large as the decrease in metal-cyclopentadienyl ring distance. Less change is seen in the Cl–M–Cl angle for the dimers, probably due to the fact that this angle in the scandium compound is already 10° smaller than in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and repulsive interaction between the chlorine atoms resists further decrease. The Cl–Cl separation in $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ is about 0.1 Å less than in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{VCl}_2$. Trends between the two independent molecules are similar in both the titanium and scandium compounds.

Comparison of Structurally Independent $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$

Units. In I, the molecule on the special position is constrained to have inversion symmetry and also shows a significantly longer Ti–Ti distance (3.968 (2) Å) than that of the molecule on the general position (3.943 (2) Å). This increase in the metal–metal separation is achieved by a shift of the atoms so that the angle at the chlorine atom is increased and that at titanium is decreased. The cyclopentadienyl rings are all η^5 bonded to the titanium atoms, but the carbon–carbon distances are scattered somewhat in value because of the relatively large thermal motion in the plane of the rings. Ring–metal distances (2.049 to 2.058 Å) and the angle between rings on a given titanium atom (131.2 to 133.4°) are within the range of values observed in other bis(cyclopentadienyl)titanium(III) structures.²⁰ It should be noted that the molecule on the general

position does not require planarity of the titanium and chlorine atoms and in fact this plane is bent along the Cl–Cl direction by 3.92° away from the shortest contact distance between carbon atoms of cyclopentadienyl rings on opposite ends of the dimer (see Figure 2). The hydrogen atoms on C(5) and C(13) are calculated to be less than 2 Å apart which is close enough for steric repulsion to occur^{21,22} and could be a major factor in determining the direction of the titanium–chlorine plane bend.

$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}]_2$ Structural Results. $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}]_2$ (II) contains only one molecule per asymmetric unit and this is planar (0.24° bend) within the experimental error even though not required to be so. The distance of 3.926 (3) Å between the titanium atoms is further decreased from that of either molecule in I and accompanied by the expected trend in the Cl–Ti–Cl and Ti–Cl–Ti angles. There is a definite anisotropy in the Ti–Cl bond distances, each titanium atom having one distance at the short end of the range observed for I and one distance longer than any found in I. An unexpected feature is the nearly eclipsed conformation of the methyl groups on the cyclopentadienyl rings, which is not due to any obvious packing effect. Nonbonded distances from the methyl group carbon atoms to other carbon atoms on adjacent molecules range from 3.494 to 3.884 Å for the closest interaction. Substitution of the ring does serve to reduce thermal motion of the carbon atoms, but the carbon–carbon nonbonded distances between different cyclopentadienyl rings on the same dimer are similar to those in I. The average C–C ring distance in this compound is 1.396 (13) Å while in the unsubstituted derivative the average C–C distance is 1.34 (3) Å. This difference is only 2σ but is in the direction expected for the larger librational motion of the unsubstituted C_5H_5 ring. Also observed are decreased $(\text{C}_5\text{H}_5)\text{--Ti--}(\text{C}_5\text{H}_5)$ angles of 130.8 and 131.0° as well as somewhat asymmetric Ti– (C_5H_5) distances of 2.043 and 2.074 Å to Ti(1) and 2.059 and 2.071 Å to Ti(2) (see Figure 4).

$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$ Structural Results. $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$ (III) is constrained to have the titanium and bromine atoms coplanar since a center of inversion relates the halves of the molecule. The distance between titanium atoms has increased to 4.125 (4) Å, primarily due to titanium–bromine distances of 2.722 (2) and 2.705 (3) Å, 0.16 Å longer than the titanium–chlorine bond lengths. Decrease of the Ti–Br–Ti angle to 98.93 (7)° and increase in the Br–Ti–Br angle to 81.07 (3)° results in an overall geometry of the core atoms closer to a square than in the chlorine-bridged dimers. This is probably due in part to the larger van der Waals radius of the bromine atom causing increased bromine–bromine repulsion. Another slight change is an increase in the $(\text{C}_5\text{H}_5)\text{--Ti--}(\text{C}_5\text{H}_5)$ angle to 134.2° (Figure 7). The titanium atom–cyclopentadienyl ring distances of 2.062 and 2.068 Å are within the range found for the methylcyclopentadienyl chloride analogue. Nonbonded interactions between carbon atoms on different cyclopentadienyl rings within the dimer are somewhat longer than observed in I and II, the shortest distance between carbons bonded to different titanium atoms being 3.806 (8) Å and that between carbon atoms bonded to the same titanium atom being 2.997 (8) Å, as shown in Figure 7. An orientation of the methyl groups is found which is different from that in II and is close to a trans configuration on each titanium atom. There is no obvious reason why one of the cyclopentadienyl rings on each titanium atom is rotated so that the methyl group moves away from the bromine atom. A calculation of nonbonded interaction distances from C(12) shows 3.630 (8) Å to C(8) in an adjacent molecule while the shortest intermolecular distance from C(6) is 3.974 (10) Å to C(12).

Magnetic Susceptibility Results. All three of these compounds exhibit antiferromagnetic coupling between the two

Table XV. Magnetic Susceptibility Data for $[(C_5H_5)_2TiCl]_2$

Sample A ^a					Sample B ^b				
T, K	$10^3 \chi_M$, cgsu		μ_{eff}/Ti , μ_B		T, K	$10^3 \chi_M$, cgsu		μ_{eff}/Ti , μ_B	
	Obsd	Calcd	Obsd	Calcd		Obsd	Calcd	Obsd	Calcd
266.7	1.69	1.70	1.342	1.348	269.6	2.17	2.11	1.528	1.507
240.4	1.76	1.76	1.302	1.302	248.6	2.30	2.19	1.511	1.474
230.3	1.78	1.78	1.281	1.281	240.3	2.35	2.22	1.502	1.460
220.7	1.80	1.80	1.261	1.260	231.9	2.40	2.25	1.493	1.444
216.0	1.81	1.81	1.251	1.249	216.0	2.45	2.31	1.455	1.411
211.2	1.82	1.81	1.240	1.237	211.2	2.49	2.32	1.449	1.401
206.4	1.83	1.82	1.229	1.225	206.5	2.53	2.34	1.445	1.389
201.5	1.84	1.82	1.218	1.212	201.7	2.57	2.35	1.439	1.378
196.6	1.84	1.83	1.204	1.198	196.9	2.62	2.37	1.435	1.365
191.6	1.83	1.83	1.185	1.183	191.4	2.63	2.38	1.418	1.350
183.9	1.82	1.83	1.156	1.159	185.9	2.49	2.39	1.362	1.334
176.2	1.80	1.82	1.128	1.132	180.5	2.44	2.41	1.328	1.318
165.6	1.79	1.80	1.088	1.093	175.0	2.43	2.42	1.304	1.300
150.3	1.74	1.75	1.022	1.026	169.5	2.43	2.42	1.283	1.281
133.5	1.64	1.65	0.935	0.940	149.2	2.42	2.42	1.203	1.202
94.9	1.19	1.20	0.671	0.676	140.5	2.41	2.41	1.163	1.163
56.9	0.67	0.66	0.390	0.387	120.7	2.35	2.32	1.066	1.058
33.0	0.64	0.63	0.291	0.288	102.7	2.13	2.18	0.936	0.946
20.6	0.62	0.62	0.225	0.225	81.6	1.93	1.96	0.793	0.800
14.3	0.46	0.48	0.162	0.165	70.0	1.86	1.86	0.722	0.722
10.5	0.31	0.31	0.115	0.115	58.1	1.87	1.84	0.659	0.654
7.9	0.16	0.20	0.072	0.080	33.6	2.21	2.22	0.545	0.546
4.2	0.12	0.14	0.045	0.049	20.4	2.35	2.35	0.438	0.438
					15.6	2.09	2.03	0.360	0.355
					9.6	1.32	0.94	0.226	0.190
					7.1	0.68	0.42	0.137	0.110
					4.4	0.13	0.16	0.048	0.053

^a Sublimed at 125 °C (10^{-5} mm) in a conventional sublimator. $J = -111 \text{ cm}^{-1}$, impurity $J = -14.9 \text{ cm}^{-1}$ (4%), $g = 1.85$, $\Theta = 1.0 \text{ K}$. TIP = 1.40×10^{-6} /mol, diamagnetic correction -266.8×10^{-6} . ^b Gradient sublimed at 150 °C (10^{-5} mm); least volatile fraction in 30-in. tube. $J = -107 \text{ cm}^{-1}$, $g = 2.01$, impurity $J = -13.5 \text{ cm}^{-1}$ (13.7%), $\Theta = 1.0$.

Table XVI. Magnetic Susceptibility Data for $[(CH_3C_5H_4)_2TiX]_2$, X = Cl, Br

$[(CH_3C_5H_4)_2TiCl]_2$ ^a					$[(CH_3C_5H_4)_2TiBr]_2$ ^b				
T, K	$10^3 \chi_M$, cgsu		μ_{eff}/Ti , μ_B		T, K	$10^3 \chi_M$, cgsu		μ_{eff}/Ti , μ_B	
	Obsd	Calcd	Obsd	Calcd		Obsd	Calcd	Obsd	Calcd
295.1	1.58	1.58	1.367	1.367	266.7	1.75	1.76	1.367	1.369
231.0	1.54	1.53	1.192	1.188	240.4	1.76	1.76	1.300	1.302
222.4	1.50	1.50	1.156	1.156	225.4	1.75	1.75	1.256	1.257
205.1	1.45	1.44	1.089	1.086	216.0	1.74	1.74	1.226	1.226
196.5	1.39	1.40	1.044	1.048	203.9	1.72	1.71	1.183	1.182
160.8	1.15	1.15	0.859	0.859	194.1	1.69	1.68	1.146	1.142
120.2	0.61	0.71	0.541	0.582	183.9	1.64	1.64	1.098	1.098
73.0	0.15	0.22	0.209	0.255	170.9	1.57	1.56	1.036	1.034
4.3	0.08	0.14	0.036	0.049	150.3	1.39	1.40	0.913	0.917
					133.5	1.20	1.21	0.799	0.804
					94.9	0.61	0.64	0.480	0.492
					62.4	0.23	0.23	0.240	0.240
					42.7	0.14	0.15	0.155	0.158
					20.6	0.14	0.14	0.108	0.107
					4.2	0.22	0.14	0.061	0.048

^a $J = -160 \text{ cm}^{-1}$, $g = 2.09$, $\Theta = 1.13 \text{ K}$, TIP = 140×10^{-6} /mol, diamagnetic correction -326×10^{-6} . ^b $J = -138 \text{ cm}^{-1}$, $g = 2.06$, $\Theta = 1.06 \text{ K}$, TIP = 140×10^{-6} /mol, diamagnetic correction -348.4×10^{-6} .

unpaired electrons on each Ti(III) dimer. Experimental magnetic susceptibility results have been simulated by adjusting parameters in the following expression for the molar susceptibility per dimer molecule

$$\chi_M = \frac{2g^2\beta^2N}{3k(T-\Theta)} [1 + 1/3 \exp(-2J/kT)]^{-1} + N\alpha$$

The usual procedure was to vary J , g , and Θ until the best fit to the data was obtained. In this formulation, the singlet-triplet separation is equal to $-2J$. $N\alpha$, which represents the temperature-independent paramagnetism, was held constant at 140×10^{-6} cgsu/mol, a value obtained from the experimental susceptibility data at very low temperatures. Since antiferromagnetic coupling in these compounds is strong

enough to attenuate the paramagnetism well above 4.2 K, an experimental estimate of the TIP is possible, although small amounts of paramagnetic impurity may raise the experimental values slightly so that this should be treated as an upper limit. Little or no upturn in the χ_M data points at temperatures below 10 K indicates that only negligible amounts of impurity are actually present. Figure 9 shows an example of the type of temperature dependence observed for the magnetic susceptibility data and Tables XV and XVI contain a listing of the best fit parameters and comparison of experimental and calculated results for each compound.

Coutts, Martin, and Wailes have measured the magnetic susceptibility of $[(C_5H_5)_2TiBr]_2$ to liquid nitrogen temperatures and calculated a J of -138 cm^{-1} , identical with our value for $[(CH_3C_5H_4)_2TiBr]_2$. In contrast, the coupling parameters for

Table XVII. Comparison of Geometries for Titanium(III) Halide Dimers

Compd	Ti-Ti, Å	Ti-Cp, Å	Ti-X, Å	Ti-X-Ti, deg	X-Ti-X, deg	Cp-Ti-Cp, deg
$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$ ($J = -138 \text{ cm}^{-1}$)	4.125 (4)	X = Br	2.722 (2)	98.93 (7)	81.07 (7)	134.2
		2.062 2.068	2.705 (3)			
$[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ ($J = -111 \text{ cm}^{-1}$)	3.968 (2) 3.943 (2)	X = Cl	2.534 (2)	102.89 (5) 101.80 (7) 101.20 (7)	77.11 (5) 78.63 (7) 78.21 (7)	131.2 133.4 131.2
		2.050 2.049	2.540 (2)			
		2.058	2.536 (2)			
		2.053	2.545 (2)			
		2.057	2.545 (2)			
		2.056	2.558 (2)			
$[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}]_2$ ($J = -160 \text{ cm}^{-1}$)	3.926 (3)	2.043	2.535 (2)	100.74 (4) 100.88 (4)	79.07 (6) 79.30 (6)	130.8 131.0
		2.074	2.566 (2)			
		2.059	2.562 (2)			
		2.071	2.526 (2)			

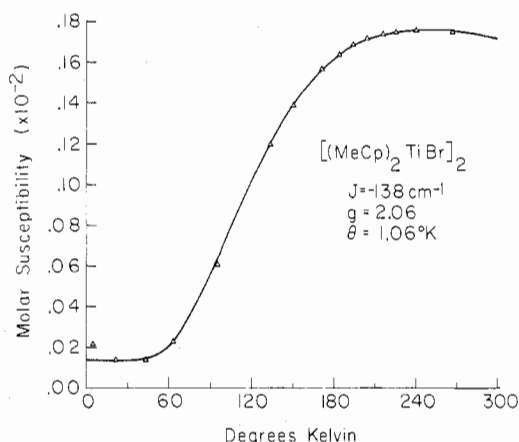


Figure 9. Temperature dependence of the magnetic susceptibility of $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$. Experimental points are shown as triangles and the solid line is generated from the theoretical equation in the text using the appropriate parameters as given in Table XVI.

$[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ and $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}]_2$ are -111 and -160 cm^{-1} , respectively. Table XVII, which compares the bond lengths and angles found in the plane of heavy atoms for the three molecules, suggests some correlations to the trend in coupling from magnetic susceptibility. As the metal-metal distance decreases in the chlorine dimers, the amount of coupling increases, which is consistent with an exchange pathway involving direct overlap of metal orbitals. Superexchange through the bridging chlorine atoms is also possible and the theory of superexchange predicts that as the bridgehead angle decreases toward 90° , the interaction of electrons through metal-bridge bonds should become less antiferromagnetic and change to ferromagnetic at 90° . A trend similar to this has been found by Hatfield in a series of copper dimers,²³ opposite to the correlation observed here. We propose direct overlap of the metal orbitals is a large factor in determining the extent of the antiferromagnetic coupling. The intermediate value of J of -138 cm^{-1} for $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{TiBr}]_2$ partially results from the more than $0.15\text{-}\text{\AA}$ increase in the metal-metal distance in this compound which should cause direct overlap of metal orbitals to be less favorable. Bromine is usually more effective in superexchange pathways as the bridgehead atom than chlorine,²⁴ but if both direct overlap and superexchange are possible, the magnitude of the coupling depends on the overall effectiveness of all pathways. Our previous results on $[(\text{C}_5\text{H}_5)_2\text{TiX}]_2\text{ZnX}_2$, $\text{X} = \text{Cl}, \text{Br}$, systems³ show that a greater interaction between the titanium(III) centers is present in the bromide-bridged compound than in the chloride analogue. In these trimetallic systems, the titanium atoms are too far apart for any direct overlap of d orbitals and substitution of Be for Zn as the

central atom does not affect the magnitude of the interaction significantly, indicating that d orbitals on the central metal are not required in the exchange pathway. This suggests that the bromide-bridged dimer discussed in the present work would be expected to show a larger degree of coupling than the chlorides if the interaction were solely due to a superexchange mechanism and a reduction in the effectiveness of another pathway could account for the overall drop in the J for III compared to that for II.

Several other dibridged titanium(III) dimers have been synthesized which should have an overall structure similar to that of the halides. $[(\text{C}_5\text{H}_5)_2\text{TiN}(\text{CH}_3)_2]_2$,²⁵ $[(\text{C}_5\text{H}_5)_2\text{TiPR}_2]_2$, $\text{R} = \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$,²⁶ and $[(\text{C}_5\text{H}_5)_2\text{TiSPh}]_2$ ²⁷ are reported to be diamagnetic while $[(\text{C}_5\text{H}_5)_2\text{TiOR}]_2$, $\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$,²⁷ are weakly paramagnetic at room temperature. Again, a combination of factors is undoubtedly affecting the overall magnetic properties, but the dimers containing nitrogen and oxygen as bridgehead atoms are estimated to have metal-metal separations at least 0.6 \AA shorter than those observed in the chlorides and those of the compounds containing sulfur and phosphorus should be similar to the chloride values. These numbers were computed assuming the following bridgehead bond lengths and angles: Ti-O and Ti-N, 2.1 \AA ; Ti-S and Ti-P, 2.6 \AA ; Ti-X-Ti, 100° for $\text{X} = \text{O}, \text{S}, \text{P}$ and 90° for $\text{X} = \text{N}$. More structural work is needed to interpret results fully for these materials.

Anomalies in $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ Magnetic Susceptibility. A final question which we have investigated is the postulated phase transition and detailed magnetic susceptibility of $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$. Reproducible scatter in the χ_M data for this compound around 200 K was noted by Coutts, Wailes, and Martin¹ and Martin and Winter.² Our sublimed samples (conventional cold-finger sublimator, 125°C , 10^{-5} mm) show varying amounts of this anomaly which is accompanied by a plateau at temperatures below 30 K as shown in Figure 10. The intensities of these two features rise and fall together relative to the main part of the curve depending on sublimation conditions but could never be entirely eliminated, even by gradient sublimation. Unsublimed $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ does not show any anomaly at 200°C in its magnetic susceptibility vs. temperature curve. This suggests that decomposition to other products having non-Curie law magnetic behavior occurs during sublimation and the anomalies are not an intrinsic property of this compound. In all cases, the starting material for sublimations was analytically pure $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ prepared as described in ref 4. Mass spectral data indicate that $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ is present in the less pure sublimed material, but no other impurities could be conclusively identified.

A gradient sublimation (150°C , 10^{-5} mm , 30-in. tube) revealed two fractions, the more volatile of which contains some $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and also has many more intense lines at low mass number in the mass spectrum, indicating that

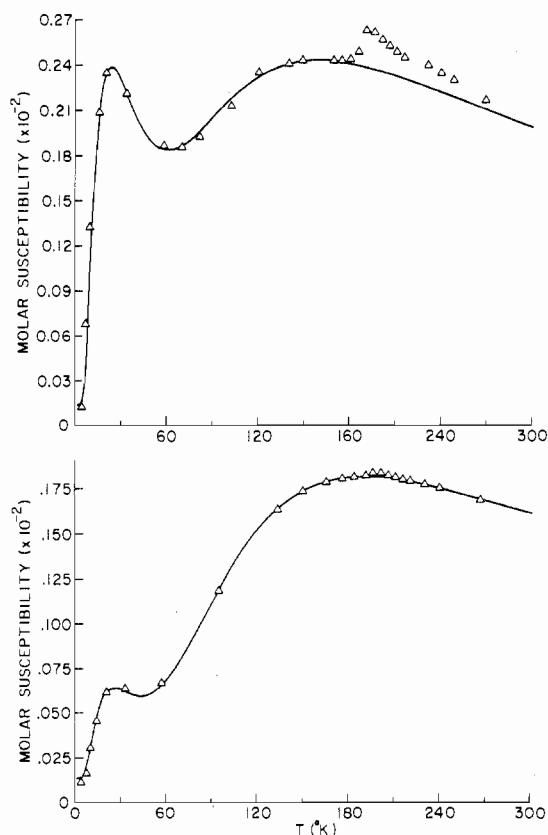


Figure 10. Temperature dependence of the magnetic susceptibility for samples of $[(C_5H_5)_2TiCl]_2$ showing effects of paramagnetic impurities. Solid theoretical curves were generated from the parameters given in Table XV. The upper trace is of the least volatile material from a gradient sublimation at $150^\circ C$ (10^{-5} mm) while the lower curve is of a sample from a conventional cold finger sublimator at $125^\circ C$ (10^{-5} mm).

fragmentation of the cyclopentadienyl ring may be involved in the decomposition. The less volatile gradient-sublimed product does not show any $(C_5H_5)_2TiCl_2$ in the mass spectrum, which is identical with that of the unsublimed material, but the magnetic susceptibility data still exhibit impurity features at 200 and 25 K (see Figure 10). Coutts, Wailes, and Martin¹ noted that the high-temperature anomaly in the magnetic susceptibility of $[(C_5H_5)_2TiCl]_2$ occurred at a point close to that at which $\alpha-TiCl_3$ undergoes a phase transition and becomes nearly diamagnetic. Contamination of the sublimed product with a small amount of $TiCl_3$ formed by scrambling of cyclopentadienyl groups and chlorides could produce the scatter around 200 K. An antiferromagnetic impurity with a J of approximately -13 to -15 cm^{-1} will fit the region near 25 K and was used in simulating the data in Figure 10 assuming an impurity molecular weight similar to that of $[(C_5H_5)_2TiCl]_2$. The identity of this substance is not clear, but one possibility is a form of $(C_5H_5)TiCl_2$, which has been prepared by pyrolysis of $(C_5H_5)_3TiCl_2(THF)$.²⁸ This pyrolysis product shows a nearly constant magnetic moment down to liquid nitrogen temperature, the limit of investigation of its magnetic properties. Coutts, Martin, and Wailes have suggested that the magnetic moment might increase at lower temperatures since it is already increasing at 107 K for the bromide analogue.²⁷

Several facts oppose the postulation of these two materials as those responsible for the impurity features in the magnetic susceptibility data. The elemental analysis of the least volatile gradient-sublimed material is good. Anal. Calcd for $C_{10}H_{10}TiCl$: C, 56.25; H, 4.72; Ti, 22.43; Cl, 16.60. Found: C, 56.46; H, 4.84; Ti, 22.27; Cl, 17.02. The value for chlorine

is slightly high due to a small amount of $(C_5H_5)_2TiCl_2$. If $(C_5H_5)TiCl_2$ and $TiCl_3$ are present, some other material such as $(C_5H_5)_3Ti$ must be included to lower the chlorine and raise the carbon and hydrogen percentages. This would be a logical component if cyclopentadienyl ring-chlorine interchange is occurring and would be volatile enough to register in the mass spectrum. Müller has reported the mass spectrum of $(C_5H_5)_3Ti$ includes a parent peak,²⁹ but no evidence was seen for it in any of our samples. The magnetic susceptibility data show that all of the material in our sublimed samples has an antiferromagnetic temperature dependence and this also seems inconsistent with the presence of $(C_5H_5)_3Ti$ whose structure is monomeric and which has been found to have a constant magnetic moment down to 121 K.³⁰ Furthermore, $(C_5H_5)_2TiCl$ and $TiCl_3$ are known to be relatively nonvolatile, and while the magnetic susceptibility anomaly at about 200 K has a shape similar to that of the $\alpha-TiCl_3$ magnetic susceptibility curve, the sharp decrease in magnitude occurs at a temperature about 25 K lower than that found for the $\alpha-TiCl_3$ phase transition. The variation of the relative intensity of both the 200- and 25-K features with respect to the main part of the curve still implies they arise from a separate species, and it may be that another crystal form of $[(C_5H_5)_2TiCl]_2$ which does undergo a phase transition is involved.

In sublimed $[(C_5H_5)_2TiCl]_2$, our crystallographic determination has shown that two independent dimers are present which differ in metal-metal separation by an amount similar to the change in comparison to $[(CH_3C_5H_4)_2TiCl]_2$. Since J is 48 cm^{-1} larger for the methylcyclopentadienyl compound, treatment of the magnetic susceptibility of $[(C_5H_5)_2TiCl]_2$ itself by a single interaction parameter may not be valid. Accordingly, an attempt was made to fit the experimental data with the expression

$$\chi_M = \frac{2g^2\beta^2N}{3k(T-\Theta)} \{^{1/3}[1 + ^{1/3}\exp(-2J_1/kT)]^{-1} + ^{2/3}[1 + ^{1/3}\exp(-2J_2/kT)]^{-1}\} + N\alpha$$

Trial simulations show that, for J_1 and J_2 in the vicinity of -100 cm^{-1} , they must differ by more than 30 cm^{-1} in order that this equation do a noticeably better job of fitting the data than one with a single J whose value is a weighted average of J_1 and J_2 . The presence of impurity features which distort the curve shape means that it would be difficult to reach this level of sensitivity for the magnetic susceptibility measurements we have made on $[(C_5H_5)_2TiCl]_2$. It appears in this case that the magnitudes of the interactions are too close to be differentiated and it is not possible to determine a J value for each of the independent molecules in the unit cell.

Acknowledgment. This research was supported by the National Science Foundation under Grants NSF DMR-7203026 and NSF MPS 74-23000. We are also grateful to Professor D. N. Hendrickson and members of his group for assistance in collecting low-temperature magnetic susceptibility data.

Registry No. I, 62415-21-8; II, 62415-22-9; III, 62415-23-0.

Supplementary Material Available: Listings of structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.

References and Notes

- R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Aust J. Chem.*, **26**, 2101 (1973).
- R. L. Martin and G. Winter, *J. Chem. Soc.*, 4709 (1965).
- R. Jungst, D. Sekutowski, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 8108 (1974).
- D. G. Sekutowski and G. D. Stucky, *Inorg. Chem.*, **14**, 2192 (1975).
- P. G. Lenhart, *J. Appl. Crystallogr.*, **8**, 568 (1975).
- D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

- (8) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
 (9) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organomet. Chem.*, **47**, 375 (1973).
 (10) D. J. Wehe, W. R. Busing, and H. A. Levy, USAEC Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
 (11) Supplementary material.
 (12) For a more detailed description of the techniques used in the magnetic measurements, see D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973).
 (13) J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2488 (1973).
 (14) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6422 (1975).
 (15) E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, **111**, 73 (1976).
 (16) E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organomet. Chem.*, **111**, 91 (1976).
 (17) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 2248 (1974).
 (18) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6416 (1975).
 (19) J. L. Petersen, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6433 (1975).
 (20) D. G. Sekutowski and G. D. Stucky, *J. Am. Chem. Soc.*, **98**, 1376 (1976).
 (21) A. I. Kitaigorodsky in "Physical Chemistry," Vol. 29, E. M. Loebl, Ed., Academic Press, New York, N.Y., 1973, p 387.
 (22) T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, **102**, 457 (1975).
 (23) K. J. McGregor, N. J. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, **9**, 423 (1973).
 (24) R. L. Martin, *New Pathways Inorg. Chem.*, 175 (1968).
 (25) M. F. Lappert and A. R. Sanger, *J. Chem. Soc., A*, 874 (1971).
 (26) K. Issleib and H. Häckert, *Z. Naturforsch., B*, **21**, 519 (1966).
 (27) M. F. Lappert and A. R. Sanger, *J. Chem. Soc. A*, 1314 (1971).
 (28) R. S. P. Coutts, R. L. Martin, and P. C. Wailes, *Aust. J. Chem.*, **24**, 2533 (1971).
 (29) J. Müller, *Chem. Ber.*, **102**, 152 (1969).
 (30) A. J. Canty, R. S. P. Coutts, and P. C. Wailes, *Aust. J. Chem.*, **21**, 807 (1968).

Contribution from the Departments of Chemistry, University of Wollongong, Wollongong, New South Wales 2500, Australia, and University of Virginia, Charlottesville, Virginia 22901

Five- and Six-Coordinated Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes of the Pentadentate Schiff Base Ligands

N,N'-Bis[(2-hydroxy-5-Y-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine (Y = Chloro or Methyl) and *N,N'*-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine

EDWARD M. BOGE,^{1a} DEREK P. FREYBERG,^{1b} ERNEST KOKOT,^{1a} GARRY M. MOCKLER,^{*1a} and EKK SINN^{1b}

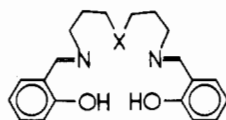
Received August 17, 1976

AIC605971

Zinc(II), copper(II), nickel(II), and cobalt(II) complexes of the potentially pentadentate ligands H₂cbpN, H₂mbpN, and H₂cbpS and some Lewis base adducts (with pyridine (py) and 2-, 3-, and 4-methylpyridine (2-Mepy, 3-Mepy, 4-Mepy)) have been isolated and their spectral and magnetic properties investigated. The ligands are formed from the Schiff base condensation of 2-hydroxy-5-Y-benzophenone (Y = chloro, methyl) with 4-azaheptane-1,7-diamine (H₂cbpN and H₂mbpN) and 5-chloro-2-hydroxybenzophenone with 4-thiaheptane-1,7-diamine (H₂cbpS). These data indicate that the complexes ML (L = cbpN, mbpN, cbpS) are all five-coordinate. Previous x-ray structural data had shown that Ni(mbpN), Cu(mbpN), Zn(mbpN)·H₂O, and Zn(cbN)·H₂O were five-coordinate. Spectral data indicate that the adducts with heterocyclic Lewis bases, ML·base (M = Co(II), Ni(II)), are octahedral with the Schiff base ligands acting as pentadentates. The postulated structures of the cbpX complexes differ unexpectedly from those previously postulated for the analogous salicylaldimines.

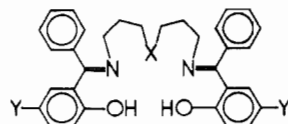
Introduction

Potentially pentadentate ligands salXH₂ (**1**) have been



1, salXH₂ (X = NH, NC₆H₅, S, O, PCH₃)

prepared by the Schiff base condensation of salicylaldehyde with tridentate amines. We have synthesized a series of ligands



2, H₂cbpN (X = NH, Y = Cl), H₂mbpN (X = NH, Y = CH₃), H₂cbpS (X = S, Y = Cl)

2 based on substituted *o*-hydroxybenzophenones and amines containing central "NH" and thioether groups. These complexes of cbpX and mbpX invariably have greater solubility and are more suitable for the growth of crystals for x-ray crystallography than their salicylaldehyde analogues and were synthesized to take advantage of these properties. In this series of complexes the mbpN compounds are more soluble than their cbpN analogues.

Single-crystal x-ray diffraction studies on two nickel complexes^{2,3} with salX ligands (X = NH, NCH₃) have shown the metal environments to be intermediate between square-pyramidal and trigonal-bipyramidal geometries, while other studies^{4,5} have shown that Zn(cbN)·H₂O, Zn(mbpN)·H₂O, Ni(mbpN), and Cu(mbpN) are all five-coordinate with the central donor atom coordinated to the metal atom. The water molecules in the two zinc complexes are not coordinated to the metal atom. The zinc complexes have trigonal-bipyramidal geometry, while the copper and nickel complexes have a distorted square-pyramidal geometry. In the copper complex the copper(II) to central nitrogen bond (2.37 Å) is significantly longer than in the corresponding nickel(II) (2.04 Å) or zinc(II) (2.16, 2.19 Å) complexes.

On the basis of spectral and magnetic data, Niswander et al.⁶ have concluded that for salX complexes where X = NH, NCH₃, NC₆H₅, PCH₃ the cobalt(II) complexes are five-coordinate and where X = S, O the central donor atom remains uncoordinated and the complexes are tetrahedral. From a spectroscopic study⁷ of similar copper(II) complexes, it was concluded that assignment of even gross stereochemical features is very difficult from electronic spectral data.

It was concluded that, in general, M-X bonds did not form, especially when M = Cu, Co and X = S, though a weak M-X interaction was considered possible.⁶ The structures of the complexes ML were therefore presumed to be tetrahedral for M = Co(II) and planar for M = Cu(II). For M = Ni(II),