

behavior of the pyridine ring. The shifts cannot be unambiguously assigned to models at present since the experimental data can be fit by more than one set of geometrical parameters.

Nonetheless, the pyridine ring appears to be positioned such that its symmetry axis makes a roughly 90° angle with respect to the Ln-N⁺ vector, as was found previously.¹⁴ We plan to continue these investigations by studying cations in which the steric bulk in the vicinity of the nitrogen atom varies in a controlled fashion.

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Registry No. (3,5-BUL)₂Er(NO₃)₅, 55723-35-8; (3,5-BUL)₂Yb(NO₃)₅, 55723-36-9; (3,5-BUL)₂Pr(NO₃)₅, 55723-38-1; (3,5-BUL)₂Nd(NO₃)₅, 55723-39-2; (3,5-TMBL)₂Eu(NO₃)₅, 55723-41-6; (3,5-TMBL)₂Sm(NO₃)₅, 55723-43-8; (3,5-TMBL)₂Er(NO₃)₅, 55723-15-4; (3,5-TMBL)₂Yb(NO₃)₅, 55723-17-6; (3,4-TMBL)₂Er(NO₃)₅, 55723-19-8; (3,4-TMBL)₂Tm(NO₃)₅, 55723-21-2; (3,4-TMBL)₂Yb(NO₃)₅, 55723-22-3; (2,6-BUL)₂Nd(NO₃)₅, 55723-25-6; (2,6-BUL)₂Er(NO₃)₅, 55723-26-7; (2,6-BUL)₂Yb(NO₃)₅, 55723-27-8; (2,4-TMBL)₂Er(NO₃)₅, 55723-29-0; (2,4-TMBL)₂Yb(NO₃)₅, 55723-30-3.

References and Notes

- (1) C. C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969).
- (2) U. Huber and C. Pascual, *Helv. Chim. Acta*, **54**, 913 (1971).

- (3) R. E. Davis, M. R. Willcott, III, R. E. Lenkinski, W. von Doering, and L. Birladeanu, *J. Am. Chem. Soc.*, **95**, 6846 (1973).
- (4) R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Am. Chem. Soc.*, **95**, 6046 (1973).
- (5) I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *J. Am. Chem. Soc.*, **96**, 682 (1974).
- (6) H. L. Goering, J. N. Eikenberry, G. S. Koermer, and C. J. Lattimer, *J. Am. Chem. Soc.*, **96**, 1493 (1974).
- (7) (a) C. D. Barry, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *J. Mol. Biol.*, **84**, 471 (1974); (b) C. D. Barry, D. R. Martin, R. J. P. Williams, and A. V. Xavier, *ibid.*, **84**, 491 (1974).
- (8) C.-H. Huang, J. P. Sipe, S. T. Chow, and R. B. Martin, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 359 (1974).
- (9) D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).
- (10) G. N. La Mar, R. H. Fischer, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **6**, 1798 (1967).
- (11) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969); D. R. Eaton, L. Seville, and J. P. Jesson, *ibid.*, **49**, 2751 (1971).
- (12) G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Eds., "Chemical Application of NMR in Paramagnetic Molecules", Academic Press, New York, N.Y., 1974, Chapters 9, 10.
- (13) I. Walker and D. H. Weedon, *Inorg. Chem.*, **12**, 772 (1973), and references contained therein.
- (14) M. S. Quereshi and I. M. Walker, *Inorg. Chem.*, **13**, 2896 (1974).
- (15) W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).
- (16) G. V. Boyd, A. W. Ellis, and M. D. Harms, *J. Chem. Soc. C*, 800 (1970).
- (17) W. Bruegel, *Z. Elektrochem.*, **66**, 159 (1962).
- (18) W. DeW. Horrocks, Jr., *J. Am. Chem. Soc.*, **96**, 3022 (1974).
- (19) Ln = Ce: A. R. Al-Karaghoul and J. S. Wood, *J. Chem. Soc. D*, 135 (1970). Ln = Ho: G. Toogood and C. Chieh, *Can. J. Chem.*, **53**, 831 (1975).
- (20) L. Pauling, "The Nature of the Covalent Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
- (21) N— indicates the pyridine ring.
- (22) Y. Y. Lim and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 84 (1972).

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Synthesis and Structure of Some Bis(cyclopentadienyl)titanium(III) Metal Halides

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A series of air-sensitive Ti(III) complexes of the general formula (Cp₂TiX)₂MX₂ (X = Cl, Br; M = Zn, Be, Mn) have been prepared and characterized. Both solvent and the oxidation potential of the central metal atom are important in the synthesis of these materials. The crystal and molecular structure of (Cp₂Ti-DME)₂(Zn₂Cl₆)·C₆H₆ (I) (DME = dimethoxyethane) and (Cp₂TiCl)₂ZnCl₂·2C₆H₆ (II) have been determined from single-crystal three-dimensional X-ray (Mo Kα) diffraction data collected at room temperature. (Cp₂Ti-DME)₂(Zn₂Cl₆)·C₆H₆ crystallizes in the monoclinic space group *P2₁/n* (nonstandard setting of *P2₁/c*, No. 14) with *a* = 11.810 (4) Å, *b* = 10.201 (5) Å, *c* = 17.284 (7) Å, and β = 93.20 (2)°; *Z* = 4, ρ_{calcd} = 1.527 g cm⁻³, and ρ_{exptl} = 1.49 (3) g cm⁻³. Full-matrix least-squares refinement of 2692 observations gave final agreement factors of *R*₁ = 0.084 and *R*₂ = 0.056. (Cp₂TiCl)₂ZnCl₂·2C₆H₆ crystallizes in the orthorhombic space group *Pbcn* (No. 60) with lattice constants *a* = 18.236 (10) Å, *b* = 15.513 (8) Å, and *c* = 11.237 (6) Å; *Z* = 4 with ρ_{calcd} = 1.503 and ρ_{exptl} = 1.48 (3) g cm⁻³. Least-squares refinement of 2074 observations gave final *R* factors of *R*₁ = 0.071 and *R*₂ = 0.049. Compound I is ionic. The DME coordinates to the titanium(III) atom as a bidentate ligand to form a cation and the zinc trichloride dimerizes to form a dianion with pseudotetrahedral geometry around each zinc atom. Compound II contains an approximately linear Ti-Zn-Ti arrangement with a Ti-Zn-Ti angle of 173.4 (1)°. The geometry around the zinc atom is pseudotetrahedral with chlorine atoms bridging to the titanium atoms. The benzene molecules in both structures reside in the crystal lattice.

Introduction

The reduction of Cp₂TiCl₂ to Cp₂TiCl (Cp = C₅H₅) by zinc was first investigated by Birmingham et al. in 1955^{1a} and by other workers^{1b} in the early 1960's as part of the early studies which were being made on Ziegler-Natta catalysis. The isolation and characterization by Saltzmann² in 1966 of these systems clearly indicated that complex formation had occurred. When this research was initiated, the exact nature of the organometallic complexes formed by titanium with reducing metals and metal complexes was unknown. A single-crystal X-ray study of one of the products formed, (Cp₂TiCl)₂ZnCl₂·2C₆H₆, by us and by Vonk³ independently

with film techniques revealed a trinuclear linear chain configuration.

As part of a broader program to study the structural, electronic, and chemical properties of exchange-coupled low-valent early transition metal complexes and as part of our earlier studies on electronic effects in one-dimensional systems,^{4,5} we wish to report here the synthesis and structural properties of a number of mixed-metal complexes of bis(cyclopentadienyl)titanium(III).

Experimental Section

Syntheses. Starting materials were all commercially available. The solvents were dried and distilled from sodium ketyl and stored under

Table I. Analytical Data^a

Compd	% calcd					% obsd				
	C	H	Ti	X	M	C	H	Ti	X	M
(Cp ₂ TiCl) ₂ ZnCl ₂ ·2C ₆ H ₆	53.40	4.50	13.32	19.75	9.09	53.09	4.67	13.01	19.57	9.03
(Cp ₂ TiBr) ₂ ZnBr ₂ ·2C ₆ H ₆	42.82	3.57	10.66	35.64	7.29	43.20	3.63	10.47	33.87	7.66
[(MeCp) ₂ TiCl] ₂ ZnCl ₂	46.53	4.52	15.48	22.91	10.56	45.70	4.65	14.60	22.46	10.79
(Me ₂ SiCp ₂ TiCl) ₂ ZnCl ₂	42.66	4.15	14.19	21.01	9.68	42.52	4.21	13.43	21.02	10.42
(Cp ₂ TiCl) ₂ BeCl ₂ ·2C ₆ H ₆	57.78	4.81	14.40	21.65	1.35	54.12	4.98	14.71	22.61	
(Cp ₂ TiCl) ₂ MnCl ₂ ·2THF	48.24	5.17	13.75	20.36	7.88	48.08	5.07	13.78	20.00	7.91
(Cp ₂ Ti·2THF) ₂ (Zn ₂ Br ₆)·2THF	37.77	4.86	6.85	37.30	9.35	36.48	4.92	6.88	34.28	9.39
(Cp ₂ Ti·DME) ₂ (Zn ₂ Cl ₆)·C ₆ H ₆	42.62	4.81	10.01	22.22	13.66	43.15	4.93	10.03	22.18	13.61
(Cp ₂ TiCl) ₂ MnCl ₂ ·DME	44.84	4.66	14.90	22.06	8.55	44.14	4.81	14.83	22.59	8.30

^a X = halide, M = metal, THF = tetrahydrofuran, DME = dimethoxyethane.

helium in a Vacuum Atmospheres, Inc., drybox. All preparations of Ti(III) compounds were performed in the drybox while preparation of Ti(IV) compounds were outside the box under a flow (Hg bubbler) of nitrogen or argon.

Analyses were performed by the Microanalytical Laboratory of the University of Illinois School of Chemical Sciences. The only precaution taken to prevent air oxidation of the samples during this procedure was to weigh the samples under a commercial source of nitrogen. This method proved satisfactory for most of the Ti(III) compounds, although slight decomposition was apparent for the more sensitive samples. Melting points were determined in sealed capillaries filled with helium and were reported as uncorrected. The purity of the Ti(IV) compounds used as starting materials was checked by NMR and mass spectrometry.

Preparation of Ti(IV) Compounds. The method of Reynolds and Wilkinson⁶ was used to prepare (MeCp)₂TiCl₂ with the following modifications. The reaction was run on a much larger scale (0.275 mol based on TiCl₄) and the method of addition was reversed; i.e., NaMeCp was added to a benzene solution of TiCl₄ cooled to 0°. An initial yield of 56.3% was obtained; mp 223–225° (lit. mp 217–218°). Anal. Calcd for (MeCp)₂TiCl₂: C, 52.00; H, 5.06; Ti, 17.30; Cl, 25.64. Found: C, 51.82; H, 5.07; Ti, 17.28; Cl, 25.41.

Me₂Si(C₅H₄)₂TiCl₂ was prepared by the method of Köpf and Kahl;⁷ mp 295–302° dec. Anal. Calcd for Me₂SiCp₂TiCl₂: C, 47.21; H, 4.59; Ti, 15.70; Cl, 23.28. Found: C, 47.55; H, 4.82; Ti, 15.45; Cl, 23.82.

Preparation of Ti(III) Dimers. A number of methods were used to prepare (Cp₂TiCl)₂; however, the best was that by Coutts, Wailes, and Martin.⁸ In all reactions involving Al⁰, the aluminum foil was activated by either I₂ or trialkylaluminum as described in ref 8; yield 87%. Anal. Calcd for Cp₂TiCl: C, 56.24; H, 4.69; Ti, 22.45; Cl, 16.62. Found: C, 56.22; H, 4.78; Ti, 22.23; Cl, 16.62.

The methyl-substituted product was obtained in the same way except that it is soluble in ether but will precipitate before the aluminum etherate does; yield 90%. Anal. Calcd for (MeCp)₂TiCl: C, 59.66; H, 5.80; Ti, 19.85; Cl, 14.69. Found: C, 59.98; H, 5.62; Ti, 19.29; Cl, 14.71.

Neither Me₂Si(C₅H₄)₂TiCl₂ nor (Me₂Cp)₂TiCl₂ could be reduced by Al⁰ even after refluxing for 2 days.

Preparation of Ti(III) Trimers. Only details of the preparation of (Cp₂TiCl)₂ZnCl₂·2C₆H₆ will be given since the other trinuclear metal compounds in Table I were similarly prepared.

Zn dust (0.4 g) was added to 3 g (12 mmol) of Cp₂TiCl₂ in 50 ml of benzene. After being stirred for 25 hr, the solution was filtered, yielding 3.55 g (82% yield) of crude product. Recrystallization from hot benzene gave large, clear green crystals.

Running the reaction in THF leads to large, green crystals of a product containing THF. Precession photographs on a number of these crystals were taken, but all turned out to be twinned. Upon storing, the compound readily loses solvent and the crystals turn chalky. After 1 month, the following analysis was taken, showing that almost complete loss of THF had occurred. Anal. Calcd for (Cp₂TiCl)₂ZnCl₂: C, 42.64; H, 3.55; Cl, 25.17; Ti, 17.00; Zn, 11.60. Found: C, 43.25; H, 4.32; Cl, 23.68; Ti, 16.25; Zn, 11.22.

In an alternative preparation, ZnCl₂ was dried with thionyl chloride by the method of Pray.⁹ The lack of a water peak in the ir spectrum was sufficient proof that the sample was anhydrous. ZnCl₂ (0.32 g, 2.38 mmol) was added to 1 g (4.68 mmol) of Cp₂TiCl in 50 ml of benzene. The reaction turned light green within 1 hr. After stirring the mixture overnight, 1.7 g (100% yield) was filtered off.

Two exceptions were found to the general methods given above:

Cp₂TiCl₂ would not react with Mn⁰ in benzene, although it does in THF; the reaction between Cp₂TiBr₂ and Zn⁰ does not give the expected trinuclear product in THF.

Preparation of (Cp₂Ti·DME)₂(Zn₂Cl₆)·C₆H₆. (Cp₂TiCl)₂ZnCl₂·2C₆H₆ (0.5 g, 0.7 mmol) was dissolved in 20 ml of dioxane. DME was slowly added until precipitation stopped; then 5 extra drops were added and the solution was allowed to sit for 2 hr. A 0.25-g amount was obtained (76% yield). Blue crystals were grown from a benzene–dioxane mixture by slow evaporation.

Zn dust (0.18 g, 12.2 mmol) was added to 3 g (12.1 mmol) of Cp₂TiCl₂ in 100 ml of DME. The reaction turned green within 10 min and blue within 1.5 hr. After 9 hr, the solution was filtered, giving 4.4 g (49.1% yield). Attempts to recrystallize the product only yielded a microcrystalline product. Analysis gave a formula ZnTi_{1.9}Cl_{3.8}C_{28.2}H_{29.5}, which gives an empirical formula close to (Cp₂Ti·DME)₂ZnCl₄.

X-Ray Data. Preliminary precession photographs of [(C₅H₅)₂Ti·DME]₂(Zn₂Cl₆)·C₆H₆ (Mo K α radiation) revealed that the crystals were monoclinic. The observed systematic absences $h0l$, $h+l=2n+1$, and $0k0$, $k=2n+1$, are compatible with the space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14). A triangular prism with sides $0.25 \times 0.20 \times 0.10 \times 0.08$ mm was used for data collection.

Lattice parameters were obtained by a least-squares refinement of 14 reflections, which were carefully hand centered on a Picker four-circle diffractometer ($T = 23^\circ$, $\lambda = 0.71069 \text{ \AA}$). The final values obtained were $a = 11.810$ (4) \AA , $b = 10.201$ (5) \AA , $c = 17.284$ (7) \AA , and $\beta = 93.20$ (2)°. The density calculated on the basis of four molecules per unit cell is 1.527 g cm^{-3} , while the observed value 1.49 (3) g cm^{-3} is obtained by flotation in a 1-bromonaphthalene and *o*-bromotoluene mixture. Several ω scans showed a typical peak width at half-height to be 0.14° , indicating that the mosaicity was acceptably low for data collection.

Intensity data were measured on a fully automated Picker four-circle diffractometer using Mo K α radiation monochromated by a highly oriented graphite crystal. A θ – 2θ scan technique was used with a scan width of 1.6° , a scan rate of $1^\circ/\text{min}$, and a takeoff angle of 1.4° . Background counts, each of 10-sec duration, were taken at both ends of the scan. Copper foil attenuators, whose attenuation factors were known, were automatically inserted in front of the counter whenever the counting rate exceeded 10,000 counts/sec. Three standards were measured every 60 reflections in order to check for crystal and counter stability. These standards showed no significant fluctuations throughout data collection. Two complete quadrants of intensity data ($h\bar{k}l$ and hkl , $h\bar{k}l$ and hkl) were collected to $2\theta = 45^\circ$ and averaged to give 2692 independent reflections. Lorentz–polarization corrections and calculation of the observed structure factor amplitudes from the raw data were carried out using the local program GORDO. Because of the platelike nature of the crystal, an absorption correction was applied with the program ORABS ($\mu = 19.19 \text{ cm}^{-1}$). During the structure solution and early refinement, only the observed reflections from the first form were used. The criteria used for a reflection to be considered observed was $I_{\text{obsd}} > 3\sigma_c(I)$. Here $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$ where T_c is the total counts, t_c/t_b is the ratio of the time counting peak intensity to that spent counting backgrounds, and B_1 and B_2 are the background counts. Final refinement using all of the averaged data set was carried out with weights assigned on the basis of counting statistics. No significant systematic variation of $w(F_o - F_c)^2$ was seen with respect to $(\sin \theta)/\lambda$ or the magnitude of the structure factors. The nonhydrogen scattering factors were taken from the tabulation of Cromer and Waber¹⁰ and the

Table II. Positional Parameters for Nonhydrogen Atoms in $[(C_5H_5)_2Ti \cdot DME]_2 [Zn_2Cl_6] \cdot C_6H_6$

Atom	x	y	z
Zn	-0.06338 (6)	0.39652 (7)	0.44299 (4)
Ti	0.45633 (9)	0.38366 (10)	0.28597 (6)
Cl(1)	0.1222 (1)	0.4075 (2)	0.5000 (1)
Cl(2)	-0.0637 (2)	0.4082 (2)	0.3160 (1)
Cl(3)	-0.1543 (2)	0.2291 (2)	0.4899 (1)
O(1)	-0.3935 (3)	0.2839 (4)	0.2500 (3)
O(2)	-0.5053 (4)	0.4578 (4)	0.1729 (2)
C(11)	-0.3299 (6)	0.1928 (8)	0.2954 (5)
C(12)	-0.3529 (8)	0.3113 (10)	0.1806 (5)
C(13)	-0.4212 (8)	0.3988 (9)	0.1351 (5)
C(14)	-0.5715 (8)	0.5520 (8)	0.1303 (5)
C(1)	-0.0304 (11)	0.0921 (8)	0.1793 (5)
C(2)	-0.0980 (7)	0.0080 (9)	0.1474 (6)
C(3)	-0.0468 (10)	-0.0613 (8)	0.0950 (5)
C(4)	-0.0590 (9)	-0.0148 (14)	0.0964 (6)
C(5)	0.0731 (10)	0.0821 (12)	0.1520 (8)
C(6)	0.3815 (7)	0.1734 (8)	0.2845 (10)
C(7)	0.3243 (10)	0.2398 (14)	0.3372 (5)
C(8)	0.2666 (7)	0.3306 (10)	0.3013 (9)
C(9)	0.2816 (10)	0.3242 (13)	0.2269 (9)
C(10)	0.3533 (11)	0.2255 (14)	0.2136 (7)
C(15)	-0.1127 (7)	0.5025 (9)	0.0162 (6)
C(16)	-0.0446 (9)	0.4044 (8)	0.0447 (5)
C(17)	0.0698 (8)	0.4039 (8)	0.0293 (8)

hydrogen scattering factors were from Stewart et al.¹¹ Anomalous dispersion corrections used for the Zn, Ti, and Cl atoms were those of Cromer and Liberman.¹²

Data collection and reduction for $[(C_5H_5)_2TiCl]_2ZnCl_2 \cdot 2C_6H_6$ were performed in the same way with similar results except for the following differences. Preliminary precession photographs revealed that the crystals were orthorhombic. The observed systematic absences $0kl$, $k = 2n + 1$, $h0l = 2n + 1$, $hk0$, $h + k = 2n + 1$, $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$, are compatible with the space group *Pbcn* (No. 60). A rectangular prism with sides $0.08 \times 0.10 \times 0.25$ mm was used for data collection.

Lattice parameters, from least-squares refinement of 14 hand-centered reflections, were $a = 18.236$ (10) Å, $b = 15.513$ (8) Å, and $c = 11.237$ (6) Å. The density calculated on the basis of four molecules per unit cell is 1.503 g cm⁻³ and the measured density obtained from flotation in a 1-bromonaphthalene and *o*-bromotoluene mixture is 1.48 (3) g cm⁻³. Several ω scans showed a typical peak width at half-height to be 0.12° .

A θ - 2θ scan technique was used with a scan width of 1.5° , a scan rate of 1° /min, and a takeoff angle of 1.5° . Three standards were measured every 100 reflections. One octant of intensity data (hkl)

was measured to 45° in 2θ . A total of 2074 unique reflections were measured, 1396 of which were considered observed. Lorentz polarization corrections and calculation of the observed structure factor amplitudes from the raw data were carried out using the program VANDY. Absorption corrections were made ($\mu = 16.31$ cm⁻¹).

Structure Determination and Refinement. Both structures were solved in a straightforward manner by application of direct methods (FAME and MULTAN) and Fourier techniques.¹³ From the generated *E* maps, both heavy metals and a few of the chlorine atoms could be found. The discrepancy factors used are defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$.

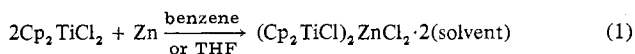
Isotropic refinement of all nonhydrogen atoms in the DME complex, using just the observed reflections from the first form gave $R_1 = 0.121$. The carbon atoms in the cyclopentadienyl rings were not well defined and some had an isotropic temperature factor greater than 9.0, indicating large thermal motion of the rings. After absorption corrections and averaging the data, several cycles of refinement were run before the hydrogen atom positions were calculated from HYGEN. The carbon-hydrogen atom distance was set at 0.95 Å and the hydrogen atoms were given the isotropic temperature factors of the carbon atoms to which they were bonded. Final anisotropic refinement of all nonhydrogen atoms gave a final error of fit equal to 2.241 and $R_1 = 0.084$ and $R_2 = 0.056$. The ratio of shift to error in the final refinement cycle was no greater than 0.11 Å. A final difference Fourier had no peaks higher than 0.90 e/Å.

Isotropic refinement of the trinuclear metal complex using just the observed reflections gave $R_1 = 0.121$. Five of the carbon atoms had isotropic temperature factors of 9 or greater, again indicating the prevalence of ring motion. The hydrogen atoms were calculated the same way, except that their isotropic factors were set at 5.0. Final anisotropic refinement of all nonhydrogen atoms gave a final error of fit equal to 1.596 and $R_1 = 0.071$ and $R_2 = 0.049$. The ratio of shift to error in the final refinement cycle was no greater than 0.12 Å. The highest peak in the final difference Fourier was 0.52 e/Å³.

See Tables II-IX for positional parameters, anisotropic temperature parameters, atomic distances, and bond angles involving nonhydrogen atoms for compounds I and II.

Discussion

The zinc complex $(Cp_2TiCl)_2ZnCl_2 \cdot 2C_6H_6$ can be prepared by the direct reaction of Cp_2TiCl_2 with zinc according to the reaction reported by Saltzmann. Isolation at low temperatures gives an unsolvated product, while at room temperature one obtains the product in reaction 1. If one mixes or switches



solvents in this system, a product is obtained that contains both

Table III. Anisotropic Temperature Parameters for the Nonhydrogen Atoms in $[(C_5H_5)_2Ti \cdot DME]_2 [Zn_2Cl_6] \cdot C_6H_6$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.00691 (7)	0.01188 (10)	0.00331 (4)	-0.00159 (8)	0.00006 (4)	0.00010 (5)
Ti	0.00586 (11)	0.01106 (15)	0.00270 (5)	-0.00027 (11)	0.00007 (6)	-0.00120 (7)
Cl(1)	0.0064 (2)	0.0159 (3)	0.0051 (1)	0.0017 (2)	-0.0001 (1)	-0.0015 (1)
Cl(2)	0.0123 (2)	0.0179 (3)	0.0032 (1)	-0.0009 (2)	0.0002 (1)	0.0009 (1)
Cl(3)	0.0131 (2)	0.0193 (3)	0.0051 (1)	-0.0068 (2)	0.0007 (1)	0.0017 (1)
O(1)	0.0060 (4)	0.0165 (7)	0.0044 (2)	0.0023 (4)	0.0001 (2)	-0.0003 (3)
O(2)	0.0106 (5)	0.0173 (7)	0.0028 (2)	0.0017 (5)	0.0007 (3)	0.0006 (3)
C(11)	0.0087 (8)	0.0155 (11)	0.0075 (5)	0.0033 (8)	-0.0011 (5)	-0.0006 (6)
C(12)	0.0133 (11)	0.0338 (18)	0.0046 (4)	0.0071 (12)	0.0027 (5)	-0.0002 (7)
C(13)	0.0129 (10)	0.0287 (16)	0.0048 (4)	0.0016 (11)	0.0028 (5)	0.0003 (7)
C(14)	0.0159 (11)	0.0168 (12)	0.0058 (5)	-0.0006 (9)	-0.0006 (6)	0.0031 (6)
C(1)	0.0257 (17)	0.0102 (11)	0.0062 (5)	0.0008 (11)	-0.0054 (8)	0.0012 (6)
C(2)	0.01200 (10)	0.0189 (15)	0.0066 (6)	0.0032 (9)	0.0000 (6)	0.0059 (7)
C(3)	0.0204 (14)	0.0216 (14)	0.0034 (4)	0.0019 (12)	-0.0043 (6)	0.0012 (6)
C(4)	0.0120 (12)	0.0525 (30)	0.0056 (6)	0.0097 (15)	0.0042 (7)	0.0133 (10)
C(5)	0.0196 (15)	0.0323 (22)	0.0151 (10)	-0.0207 (16)	-0.0131 (11)	0.0188 (13)
C(6)	0.0079 (9)	0.0115 (10)	0.0176 (11)	-0.0019 (8)	0.0011 (9)	0.0011 (10)
C(7)	0.0138 (14)	0.0334 (25)	0.0057 (5)	-0.0108 (13)	0.0008 (6)	0.0038 (9)
C(8)	0.0068 (9)	0.0203 (16)	0.0120 (8)	-0.0020 (9)	0.0027 (8)	-0.0045 (10)
C(9)	0.0145 (15)	0.0303 (22)	0.0102 (9)	-0.0115 (14)	-0.0071 (8)	0.0061 (11)
C(10)	0.0160 (16)	0.0330 (25)	0.0079 (7)	-0.0159 (15)	0.0065 (8)	-0.0109 (10)
C(15)	0.0115 (10)	0.0201 (14)	0.0078 (6)	0.0056 (10)	0.0007 (6)	0.0006 (6)
C(16)	0.0165 (12)	0.0207 (14)	0.0059 (5)	0.0023 (11)	0.0034 (6)	0.0020 (7)
C(17)	0.0163 (11)	0.0179 (13)	0.0056 (4)	0.0068 (10)	-0.0015 (6)	0.0003 (6)

^a The form of the anisotropic ellipsoids 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 IV. Atomic Distances (Å) for $[(C_5H_5)_2Ti \cdot DME]_2 [Zn_2Cl_6] \cdot C_6H_6$

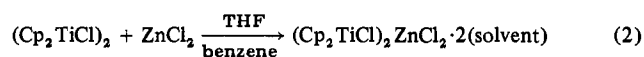
Atoms	Distance ^a	Atoms	Distance
Zn-Zn'	3.303 (2)	Ti-O(1)	2.109 (4)
Zn-Cl(2)	2.199 (2)	Ti-O(2)	2.121 (4)
Zn-Cl(3)	2.151 (2)	Ti-C(1)	2.388 (8)
Zn-Cl(1)	2.455 (2)	Ti-C(2)	2.438 (8)
Zn-Cl(1)'	2.319 (2)	Ti-C(3)	2.436 (8)
Cl(1)-Cl(1)'	3.449 (4)	Ti-C(4)	2.279 (8)
Cl(1)-Cl(2)	3.964 (3)	Ti-C(5)	2.308 (8)
Cl(1)-Cl(3)	3.750 (3)	Ti-C(6)	2.320 (8)
Cl(1)-Cl(2)'	3.727 (3)	Ti-C(7)	2.283 (8)
Cl(1)-Cl(3)'	3.731 (3)	Ti-C(8)	2.305 (8)
Cl(2)-Cl(1)'	3.727 (3)	Ti-C(9)	2.430 (9)
Cl(2)-Cl(3)	3.627 (3)	Ti-C(10)	2.412 (8)
Cl(3)-Cl(1)'	3.731 (3)		
		Cp 1	
	DME	C(1)-C(2)	1.314 (11)
O(1)-C(11)	1.452 (8)	C(2)-C(3)	1.274 (11)
O(1)-C(12)	1.297 (8)	C(3)-C(4)	1.338 (13)
C(12)-C(13)	1.461 (11)	C(4)-C(5)	1.395 (16)
C(13)-O(2)	1.305 (8)	C(5)-C(1)	1.289 (15)
O(2)-C(14)	1.464 (9)		
		Cp 2	
	Benzene	C(6)-C(7)	1.295 (12)
C(17)-C(15)	1.319 (10)	C(7)-C(8)	1.324 (12)
C(15)-C(16)	1.391 (10)	C(8)-C(9)	1.291 (13)
C(16)-C(17)	1.362 (11)	C(9)-C(10)	1.328 (14)
		C(10)-C(6)	1.394 (14)

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

Table V. Bond Angles (deg) for the Nonhydrogen Atoms in $[(C_5H_5)_2Ti \cdot DME]_2 [Zn_2Cl_6] \cdot C_6H_6$

Atoms	Angle	Atoms	Angle
Cl(1)-Zn-Cl(1)'	92.5 (1)		
Cl(2)-Zn-Cl(3)	113.0 (1)		
Cl(2)-Zn-Cl(1)	116.7 (1)		
Cl(2)-Zn-Cl(1)'	111.1 (8)		
Cl(3)-Zn-Cl(1)	108.8 (1)		
Cl(3)-Zn-Cl(1)'	113.1 (1)		
Zn-Cl(1)-Zn'	87.5 (1)		
		Cp 1	
		C(5)-C(1)-C(2)	112.3 (10)
		C(1)-C(2)-C(3)	112.7 (9)
		C(2)-C(3)-C(4)	101.4 (9)
		C(3)-C(4)-C(5)	114.3 (9)
		C(4)-C(5)-C(1)	99.3 (7)
		Cp 2	
	DME	C(10)-C(6)-C(7)	106.1 (9)
C(14)-O(2)-C(13)	117.7 (6)	C(6)-C(7)-C(8)	107.4 (10)
C(11)-O(1)-C(12)	117.5 (6)	C(7)-C(8)-C(9)	112.7 (10)
O(2)-C(13)-C(12)	116.1 (7)	C(8)-C(9)-C(10)	105.1 (10)
O(1)-C(12)-C(13)	116.3 (7)	C(9)-C(10)-C(6)	108.6 (8)
O(1)-Ti-O(2)	76.6 (2)		
		Benzene	
		C(15)-C(16)-C(17)	121.4 (7)
		C(15)-C(17)-C(16)	117.2 (8)
		C(17)-C(16)-C(15)	121.3 (8)

solvents in the crystal lattice. This caused much frustration and irreproducibility in the initial attempts to characterize these compounds. All of the compounds are more conveniently synthesized by the direct reaction of the divalent metal halide with $(Cp_2TiCl)_2$



The use of metallic Cu, Ni, Pt, Pd, Cd, Fe, and Hg gave no reaction. Excess metallic magnesium reduces Cp_2TiCl_2 to titanocene.

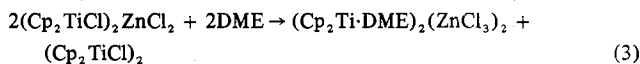
Beryllium is similar to zinc in its ability to give tetrahedrally coordinated halide species and has a similar redox potential. $(Cp_2TiCl)_2BeCl_2 \cdot 2C_6H_6$ is, however, considerably more air sensitive than the zinc derivative. Mn falls between Be and Zn in the oxidation series. It did not react in benzene by (1) but did so in THF to give $(Cp_2TiCl)_2MnCl_2 \cdot 2THF$. Preliminary structural studies show that the THF molecules are coordinated to the Mn atom in the complex. Reaction 2 gave only Cp_2TiCl_2 with MCl_2 ($M = Ni, Pd, Cd$), indicating that stronger reducing metals are required. $CrCl_2$, VCl_2 , and $TiCl_2$ should react according to (2); however, the insolubility of these

Table VI. Positional Parameters for the Nonhydrogen Atoms in $[(C_5H_5)_2TiCl]_2ZnCl_2 \cdot 2C_6H_6$

Atom	x	y	z
Zn	0.5000	0.34874 (5)	0.2500
Ti	0.31672 (5)	0.36149 (5)	0.18801 (8)
Cl(1)	0.43817 (7)	0.42448 (8)	0.11132 (11)
Cl(2)	0.40463 (7)	0.27238 (9)	0.32064 (14)
C(1)	0.2628 (8)	-0.0227 (8)	0.2144 (9)
C(2)	0.2173 (5)	0.4152 (9)	0.2953 (15)
C(3)	0.2716 (8)	0.4076 (5)	0.3706 (8)
C(4)	0.3256 (4)	0.4636 (6)	0.3405 (8)
C(5)	0.3026 (6)	0.5062 (4)	0.2430 (10)
C(6)	0.2381 (8)	0.3298 (6)	0.0295 (12)
C(7)	0.3076 (6)	0.3161 (6)	-0.0093 (6)
C(8)	0.3364 (4)	0.2528 (5)	0.0501 (7)
C(9)	0.2885 (6)	0.2210 (4)	0.1269 (6)
C(10)	0.2278 (4)	0.2655 (8)	0.1161 (10)
C(11)	0.0000	0.1474 (6)	0.2500
C(12)	0.0204 (4)	0.1874 (7)	0.1574 (7)
C(13)	0.0211 (5)	0.2712 (8)	0.1540 (9)
C(14)	0.0000	0.3157 (7)	0.2500
C(15)	0.4485 (4)	0.0315 (5)	0.4247 (7)
C(16)	0.4301 (3)	0.0276 (5)	0.0065 (7)
C(17)	0.4820 (5)	0.0598 (4)	0.0812 (6)

metal chlorides has prevented this route of synthesis.

As indicated, the reaction products are solvent dependent. Compound II is reasonably stable; however, $ZnCl_2$ can be removed by complete removal of all benzene and recrystallization from ether to give $(Cp_2TiCl)_2$.¹⁴ Addition of diethyl ether to a saturated benzene solution does not remove the $ZnCl_2$; however, the addition of dimethoxyethane (DME) leads to the isolation of a product with the stoichiometry $Cp_2TiZnCl_3 \cdot DME$. This compound had limited solubility in organic solvents indicating that it is ionic. The crystallographic study of this material (below) confirmed this with the formulation



Similar reactions with phosphorus and nitrogen bidentate ligands led to dark blue or black solutions from which only tars could be isolated.

Early electrochemical work under N_2 and in oxygen solvents such as THF, DME, and ether on bis(cyclopentadienyl)titanium species led to blue solutions of Ti(III) complexes. Since the products were expected to be green, the blue color was attributed to the formation of titanium-nitrogen species.¹⁵ Later work, however, under argon atmosphere has also led to blue solutions, indicating that the product is not interacting with N_2 , but with the solvent or electrolyte instead.^{16,17} The isolation of solvent-coordinated low-valent Ti species such as $(Cp_2Ti \cdot DME)_2(Zn_2Cl_6)$ supports this theory.

Trimetallic bromide as well as chloride derivatives can be prepared by (1) in benzene, but not in THF. The use of THF leads to a product in which the THF is apparently coordinated to the Ti and a product which readily loses THF with a change in color from a lustrous blue to black. The presence of THF vapor reversibly changes the color back to blue. A number of other anions were tried. Cp_2TiF_2 did not react with either Zn^0 or Mn^0 in THF or benzene even under reflux for 5 hr. $Cp_2Ti(SeMe)_2$, $Cp_2Ti(SCN)_2$, $Cp_2Ti(C_6H_5)_2$, and $Cp_2Ti(NR_2)_2$ also did not react with Zn^0 . Cp_2VCl_2 does react with Zn^0 , but instead of forming a trimetallic compound it yields Cp_2VCl and $ZnCl_2$.

Substitution on the cyclopentadienyl rings can have both inductive and steric effects. If a methyl group is used to give the monomethylcyclopentadienyls, the trinuclear zinc complex is obtained without molecules of solvation. Tying back the Cp rings with a $Me_2Si<$ group does not affect the course of reaction 1. Both $Me_2Si(C_5H_4)_2TiCl_2$ and $(Me_2C_5H_3)_2TiCl_2$

Table VII. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in $[(C_5H_5)_2TiCl_2]_2ZnCl_2 \cdot 2C_6H_6$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.00277 (3)	0.00543 (5)	0.01080 (10)	0.00000	-0.00070 (4)	0.00000
Ti	0.00273 (3)	0.00392 (4)	0.00875 (9)	0.00018 (3)	-0.00033 (5)	0.00006 (5)
Cl(1)	0.00361 (5)	0.00555 (7)	0.00935 (13)	-0.00053 (5)	-0.00012 (7)	0.00156 (8)
Cl(2)	0.00365 (5)	0.00643 (8)	0.01275 (17)	-0.00039 (5)	-0.00108 (8)	0.00373 (10)
C(1)	0.0092 (7)	0.0125 (8)	0.0202 (13)	-0.0083 (6)	0.0025 (8)	-0.0016 (8)
C(2)	0.0034 (3)	0.0167 (11)	0.0379 (26)	0.0009 (5)	0.0021 (8)	-0.0135 (13)
C(3)	0.0117 (6)	0.0061 (4)	0.0153 (10)	0.0006 (4)	0.0089 (7)	0.0012 (5)
C(4)	0.0667 (4)	0.0087 (5)	0.0126 (8)	0.0021 (4)	-0.0017 (5)	-0.0044 (5)
C(5)	0.0069 (4)	0.0046 (3)	0.0213 (13)	0.0011 (3)	0.0043 (6)	-0.0003 (5)
C(6)	0.0101 (6)	0.0087 (6)	0.0318 (19)	0.0050 (5)	-0.0144 (10)	-0.0066 (8)
C(7)	0.0111 (5)	0.0069 (4)	0.0084 (7)	-0.0028 (4)	-0.0036 (5)	0.0006 (4)
C(8)	0.0055 (3)	0.0057 (3)	0.0129 (8)	-0.0004 (3)	-0.0003 (4)	-0.0032 (4)
C(9)	0.0085 (4)	0.0050 (3)	0.0151 (9)	-0.0037 (3)	-0.0011 (5)	0.0003 (4)
C(10)	0.0027 (3)	0.0153 (9)	0.0319 (18)	-0.0017 (4)	0.0000 (6)	-0.0118 (10)
C(11)	0.0054 (5)	0.0058 (5)	0.0282 (23)	0.0000	0.0020 (9)	0.0000
C(12)	0.0050 (4)	0.0165 (8)	0.0123 (10)	0.0000 (6)	0.0006 (5)	-0.0075 (8)
C(13)	0.0049 (4)	0.0176 (10)	0.0202 (16)	-0.0014 (7)	-0.0012 (6)	0.0134 (11)
C(14)	0.0048 (6)	0.0035 (5)	0.0553 (49)	0.0000	-0.0042 (15)	0.0000
C(15)	0.0054 (3)	0.0072 (4)	0.0142 (9)	0.0006 (3)	-0.0031 (4)	-0.0006 (5)
C(16)	0.0040 (3)	0.0084 (5)	0.0141 (8)	0.0011 (3)	0.0007 (4)	0.0024 (5)
C(17)	0.0074 (4)	0.0060 (3)	0.0106 (7)	0.0016 (3)	0.0001 (5)	-0.0002 (4)

^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 VIII. Atomic Distances (Å) for $[(C_5H_5)_2TiCl_2]_2ZnCl_2 \cdot 2C_6H_6$

Atoms	Distance ^a		Atoms	Distance	
	This work	Ref 3		This work	Ref 3
Zn-Ti	3.420 (2)		Ti-C(3)	2.323 (7)	
Zn-Cl(1)	2.254 (2)	2.266 (5)	Ti-C(4)	2.338 (6)	
Zn-Cl(2)	2.249 (2)	2.264 (5)	Ti-C(5)	2.343 (6)	
Ti-Cl(1)	2.570 (2)	2.599 (5)	Ti-C(6)	2.339 (8)	
Ti-Cl(2)	2.589 (2)	2.611 (6)	Ti-C(7)	2.332 (7)	
Ti-Ti'	6.828 (4)		Ti-C(8)	2.318 (6)	
Cl(1)-Cl(2)	3.387 (2)		Ti-C(9)	2.342 (6)	
Ti-C(1)	2.328 (7)		Ti-C(10)	2.345 (7)	
Ti-C(2)	2.331 (9)				
	Cp 1			Cp 2	
C(1)-C(2)	1.374 (14)	1.53 (4)	C(6)-C(7)	1.357 (12)	1.36 (4)
C(2)-C(3)	1.308 (13)	1.39 (4)	C(7)-C(8)	1.297 (9)	1.33 (4)
C(3)-C(4)	1.356 (10)	1.31 (3)	C(8)-C(9)	1.323 (9)	1.41 (4)
C(4)-C(5)	1.347 (10)	1.40 (3)	C(9)-C(10)	1.311 (10)	1.41 (3)
C(5)-C(1)	1.313 (12)	1.36 (4)	C(10)-C(6)	1.407 (13)	1.41 (4)
	Benzene 1			Benzene 2	
C(11)-C(12)	1.268 (11)	1.34 (3)	C(15)-C(16)	1.342 (9)	1.40 (3)
C(12)-C(13)	1.299 (11)	1.32 (4)	C(16)-C(17)	1.343 (9)	1.38 (3)
C(13)-C(14)	1.338 (12)	1.40 (4)	C(17)-C(15)	1.360 (9)	1.43 (3)

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

Table IX. Bond Angles (deg) for the Nonhydrogen Atoms in $[(C_5H_5)_2TiCl_2]_2ZnCl_2 \cdot 2C_6H_6$

Atoms	Angle		Atoms	Angle	
	This work	Ref 3		This work	Ref 3
Cl(1)-Zn-Cl(2)	97.57 (6)	97.3 (2)	Zn-Cl(1)-Ti	90.06 (6)	90.4 (2)
Cl(1)-Zn-Cl(1)'	117.16 (8)	117.6 (2)	Zn-Cl(2)-Ti	89.68 (6)	90.1 (2)
Cl(1)-Zn-Cl(2)'	114.67 (6)	114.5 (2)	Ti-Zn-Ti	173.4 (1)	
Cl(1)-Ti-Cl(2)	82.09 (6)	81.6 (2)			
	Cp 1			Cp 2	
C(5)-C(1)-C(2)	108.6 (10)	107 (1)	C(10)-C(6)-C(7)	103.7 (7)	109 (1)
C(1)-C(2)-C(3)	106.8 (10)	105 (1)	C(6)-C(7)-C(8)	109.3 (8)	109 (1)
C(2)-C(3)-C(4)	109.4 (9)	108 (1)	C(7)-C(8)-C(9)	110.6 (7)	110 (1)
C(3)-C(4)-C(5)	106.9 (8)	115 (1)	C(8)-C(9)-C(10)	107.9 (8)	106 (1)
C(4)-C(5)-C(1)	108.3 (8)	105 (1)	C(9)-C(10)-C(6)	108.9 (9)	106 (1)
	Benzene 1			Benzene 2	
C(12)'-C(11)-C(12)	121.5 (12)	122 (3)	C(17)'-C(15)-C(16)	119.9 (6)	120 (2)
C(11)-C(12)-C(13)	121.1 (9)	121 (3)	C(15)-C(16)-C(17)	120.5 (6)	121 (2)
C(12)-C(13)-C(14)	119.3 (10)	118 (3)	C(16)-C(17)-C(15)'	119.6 (6)	118 (2)
C(13)-C(14)-C(13)'	117.8 (12)	119 (3)			

could not be reduced to the monochlorides by conventional methods, however. This suggests that the π - and σ -Cp re-arrangement of (4) might be operative in this reduction. Such

a mechanism has been proposed for a number of cyclopentadienyl organometallic compounds. Because of increased steric effects on the intermediate, the activation energy may

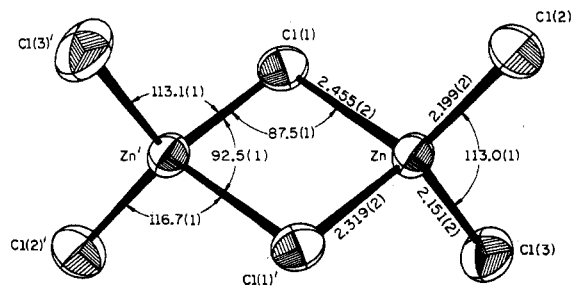


Figure 1. Molecular geometry of the dimeric anion in $(\text{Cp}_2\text{Ti-DME})_2(\text{Zn}_2\text{Cl}_6)\cdot\text{C}_6\text{H}_6$. Thermal ellipsoids are shown at the 42% probability level.

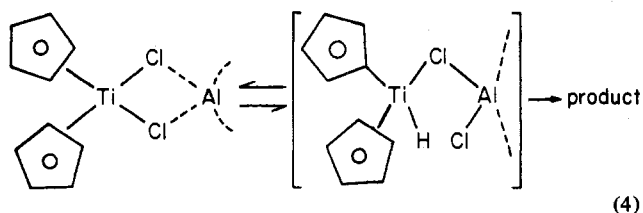


Figure 2. Perspective view of the cation in $(\text{Cp}_2\text{Ti-DME})_2(\text{Zn}_2\text{Cl}_6)\cdot 2\text{C}_6\text{H}_6$. Thermal ellipsoids are shown at the 42% probability level for the DME ligand and titanium and with isotropic thermal parameters for the cyclopentadienyl rings.

be high enough to prohibit such a pathway for reduction in these particular compounds. This is also supported by the deuterium-exchange experiment with $\text{Cp}_2\text{Ti}(\text{allyl})$ ¹⁸ and also by the fact that zinc reduction of these compounds to form trimetallic complexes (without needing such an intermediate) occurs very readily. Additional work in this area is in progress.

Physical Properties. The magnetic properties of these compounds are their most interesting physical feature. All the trimetallic compounds exhibit 1–3 antiferromagnetic exchange.^{19,20} Details on this aspect of the compounds will be given in a later paper.

The ir spectrum of all compounds were taken between 4000 and 600 cm^{-1} . The results again indicate that the oxidation state of Ti and halide substitution exert no influence on the absorption of the cyclopentadienyl ligand.⁹

Attempts to obtain mass spectra of the compounds were unsuccessful. Even at 10 eV the molecules easily fall apart giving Cp_2TiX^+ as the highest mass peak. This is in contrast to $(\text{Cp}_2\text{Ti})_2\text{SO}_4$, which has the same general structure and is purified by sublimation.²¹ Melting points on all of the trimetallic complexes at 1 atm lead first to a gradual color change, mainly being due to loss of solvent, and then to gradual decomposition over a large temperature range. Since the results are not reproducible, they have not been reported.

$(\text{Cp}_2\text{Ti-DME})_2\text{Zn}_2\text{Cl}_6\cdot\text{C}_6\text{H}_6$. The molecular structure of $(\text{Cp}_2\text{Ti-DME})_2\text{Zn}_2\text{Cl}_6$ is shown in Figures 1 and 2 and consists of $(\text{Cp}_2\text{Ti-DME})^+$ cations with $(\text{Zn}_2\text{Cl}_6)^{2-}$ anions. The only indication of the $(\text{Zn}_2\text{Cl}_6)^{2-}$ species in the literature when this research was initiated was from the infrared studies of Coates and Ridley²² for $(\text{bipyBPh}_2)\text{ZnCl}_3$. Ir peaks at 238, 225 and 334, 301 cm^{-1} were assigned to bridging and terminal $\nu(\text{Zn-Cl})$ in $(\text{Zn}_2\text{Cl}_6)^{2-}$. It is apparent from these two examples that a large cation is necessary to stabilize the Zn and Cd dimers. The $(\text{Zn}_2\text{Cl}_6)^{2-}$ dimer has also been crystallographically observed in $(\text{C}_6\text{H}_{11})\text{Ni}(\text{PPh}_3)_2\text{ZnCl}_3$.²³ A similar effect is seen for CuCl_3 where small cations lead to distorted octahedral bonding around the Cu atom and large cations to isolated dimeric $(\text{Cu}_2\text{Cl}_6)^{2-}$ anions.²⁴

The Zn dimer is required by space group symmetry to have an inversion center (Figure 1) with the symmetry around each Zn atom being that of a distorted tetrahedron. The terminal Cl distances 2.199 (2) and 2.151 (2) Å are significantly shorter than the bridging Cl distances of 2.455 (2) and 2.319 (2) Å. The bridging Cl's also are considerably distorted, with a 0.13-Å difference between the metal-bridge Cl distances.

Ross and Stucky²⁵ have proposed the theory that intra-ring chlorine-chlorine repulsions are primarily responsible for

halogen-bridged four-member ring geometries. Using this assumption, they have shown that a plot of the metal-bridge distances vs. the secant of half the bridge angle does give a straight line for 17 chlorine-bridged dimers, according to the equation $\text{MB} = \text{BB}/[2 \sec(\alpha/2)]$, where MB is the metal-bridge chlorine distance and α is the metal-bridge chlorine-metal angle. They obtained two straight lines, one for symmetric dimers and one for "asymmetric" bridged systems which have unequal bridge distances as seen for $(\text{Zn}_2\text{Cl}_6)^{2-}$. From these data, an average $\text{Cl}_{\text{bridge}}\text{-Cl}_{\text{bridge}}$ ($\text{Cl}_{\text{b}}\text{-Cl}_{\text{b}}$) distance of 3.17 ± 0.12 Å was obtained. The bridging angles of the compounds could be predicted to within 2° by a least-squares analysis, except for $(\text{GaCl}_3)_2$, which has a $\text{Cl}_{\text{b}}\text{-Cl}_{\text{b}}$ distance of 3.35 Å. $(\text{ZnCl}_3)_2^{2-}$, which is isoelectronic with $(\text{GaCl}_3)_2$, also has an anomalously long $\text{Cl}_{\text{b}}\text{-Cl}_{\text{b}}$ distance of 3.449 (4) Å so that Cl-Cl repulsion does not appear to be the determining factor in the geometries of either of these two groups.

Several bonding schemes have been proposed to rationalize four-center ring geometries.²⁶⁻²⁸ The large asymmetry in the $(\text{Zn}_2\text{Cl}_6)^{2-}$ anion with a difference in Zn-Cl_b distances of 0.13 Å suggests that a simple rationalization may not be possible in terms of symmetry and simple molecular orbital arguments.

The cation $(\text{Cp}_2\text{Ti-DME})^+$ is the first structural example of a monomeric low-valent organometallic Ti cation and the first with Ti(III) oxygen coordination. The ring-Ti-ring angle is a normal 133.5° and Figure 2 clearly indicates that the rings are staggered. The O-Ti-O angle of 76.6 (2)° is acute due to the "bite" size of the bidentate ligand. In Cp_2TiCl_2 , where the Cl atoms are unrestricted, the Cl-Ti-Cl angle is 94.5°. The only Ti structure with a smaller angle is $\text{Cp}_2\text{Ti}(\text{bipy})$: 76.1°.²⁹ This indicates that in Cp_2TiX_2 complexes, the ring-Ti-ring angle is independent of the X-Ti-X angle. A question of interest is whether the converse is true: i.e., as one decreases the ring-Ti-ring angle in compounds like $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ or $\text{H}_2\text{C}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$, will the TiCl_2 angle remain the same? The fact that $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2]\text{ZnCl}_2$ can be easily made, where both angles are strained, suggests that this is probably the case.

$(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2\cdot 2\text{C}_6\text{H}_6$. The dipole measurements of Saltzmann² on $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ indicated a noncentrosymmetric structure for this complex in solution, and there is some evidence of this in the structure observed in the solid state, as shown in Figure 3. The Ti-Zn-Ti angle is 173.4 (1)°. A rough calculation suggests that this deviation is not enough to account for the dipole moment of 4.9 D measured by Saltzmann in dioxane and either dissociation of the trimer or coordination of the solvent may be responsible for the nonzero dipole moment observed by him.

A number of organometallic mixed-metal trinuclear compounds have been found to be diamagnetic. In $[\text{Cp}_2\text{Mo}(\text{SMe})_2]_2\text{M}^{2+}$ (M = Ni, Pd, Pt), the central metal atom is thought to be square-planar d^8 , while in $[\text{Cp}_2\text{Nb}(\text{SMe})_2]_2\text{M}^{2+}$ (M = Ni, Pd, Pt), the central metal atom is tetrahedral d^{10} .³⁰ The structure of $[\text{Cp}_2\text{Nb}(\text{SMe})_2]_2\text{Ni}$

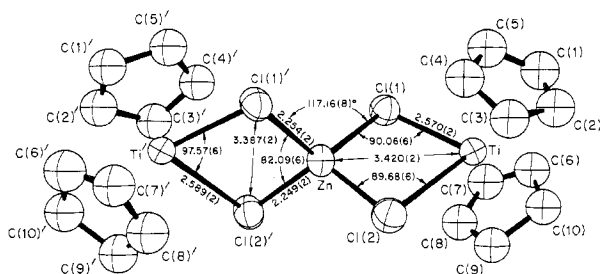


Figure 3. Molecular structure of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$. Thermal ellipsoids are shown at the 42% probability level for the heavy atoms and with isotropic thermal parameters for the cyclopentadienyl rings.

$(\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ indicates that the diamagnetism occurs because of metal-metal bonding.³¹ The bridgehead angle is small (Ni-S-Nb average angle 72.3° (0.3°)), while the average angles around the metal are large ($\text{S-Ni-S} = 117.2^\circ$, $\text{S-Nb-S} = 98.2^\circ$). Similar criteria have been used to indicate M-M bonding in $\text{Cp}_2\text{Ti}(\text{SR})_2\text{Mo}(\text{CO})_4$.³² Little or no metal-metal bonding is suggested in $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$, with $\text{Cl}(1)\text{-Zn-Cl}(2) = 97.57(6)^\circ$, $\text{Cl}(1)\text{-Ti-Cl}(2) = 82.09(6)^\circ$, $\text{Zn-Cl}(1)\text{-Ti} = 90.06(6)^\circ$, and $\text{Zn-Cl}(2)\text{-Ti} = 89.68(6)^\circ$. The molar susceptibility at room temperature agrees with the spin-only value for two unpaired electrons per molecule and also indicates the weakness of a metal-metal interaction. The compound can be considered as a $d^1\text{-}d^{10}\text{-}d^1$ system.

A comparison of the two bridged ZnCl structures shows expected trends. In $(\text{Zn}_2\text{Cl}_6)^{2-}$, with the bridging chlorine atoms shared equally between two zinc atoms, the Zn-Cl_b distances (2.45, 2.32 Å) are larger than in $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$ (2.25 Å), where the bridging chlorine atoms are bonded more tightly to Zn than to Ti. The Ti-Cl_b distances of 2.57–2.59 Å are longer than in TiCl_3 (2.45–2.46 Å in all four forms) but are the same length as in $[(\text{MeCp})_2\text{TiCl}]_2$ (2.57, 2.52, 2.53, 2.57 Å) and Cp_2TiCl_2 (2.55 Å average).³³ The cyclopentadienyl rings are almost eclipsed and are packed intermolecularly in a plane perpendicular to the *a* axis. The closest approach of carbon atoms between molecules is 3.67 Å, which is larger than the van der Waals π carbon- π carbon contact. The nearest approach between metals ($\text{Zn-Zn}'$ distance) is 7.321 (3) Å. The benzene molecules are packed between the trimetallic molecules in the *ab* plane, in both the *a* and *b* directions. However, there are no benzene molecules between molecules along the direction of closest approach.

The thermal motion of the cyclopentadienyl rings and the benzene molecules in the two structures has already been mentioned. Unsuccessful attempts were made during refinement to superimpose rigid groups in different orientations for the cyclopentadienyl rings. The C-C distances in the rings from Tables IV and VIII vary from 1.274 (11) to 1.395 (16) Å in structure I and from 1.297 (9) to 1.407 (13) Å in structure II. The average C-C distances are shorter than normal, as one would expect from librational motion in the ring plane. The largest deviations of carbon atoms from the best planes calculated for the rings are 0.016 (13) and 0.011 (12) Å for structures I and II, respectively. C-C distances in π -cyclopentadienyltitanium complexes have varied considerably in other structures; e.g., in Cp_2TiS ³⁴ the variance is from 1.305 (10) to 1.405 (7) Å. X-Ray and neutron diffraction studies have been performed on trimethylene-bridged ring compounds where the ring motion is restricted.^{35–37} In these complexes, the average C-C ring distance has increased toward the “true” value, but, nevertheless, there still is some variance; e.g., in $(\text{CH}_2)_3(\text{C}_5\text{H}_4)_2\text{HfCl}_2$,³⁷ the C-C ring distances vary from 1.387 (17) to 1.438 (12) Å. The benzene molecules in both structures I and II are located on special positions and only

half of each molecule is unique. Since the compounds are efflorescent and readily lose benzene of solvation, it is not surprising that the molecules are disordered. A discussion of some of the problems typically associated with the structural refining of cyclopentadienyl ring carbon atom position has been given a number of times previously and will not be repeated here.³⁸

While this work was in progress, a preliminary account was published of the structural properties of $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$ as determined by 350 X-ray data measured by film techniques.³ The structure was converged at $R = 0.117$, and because of the limited accuracy of the intensity data, absorption corrections and application of anisotropic temperature factors to the carbon atoms were deemed unjustified. A comparison of bond distances and angles from the two independent determinations is given in Tables VIII and IX. Although the structural parameters are expected to be less accurate when determined from a limited number of film data, the trends within the structure are the same. Both show thermal problems within the cyclopentadienyl rings and benzene molecules; e.g., C-C ring distances in Vonk's determination vary from 1.53 (4) to 1.31 (4) Å, a 0.22-Å difference as compared to this work where 1.297 (9) to 1.407 (13) Å is a 0.11-Å difference. The disorder in the benzene molecules is also similar as the longest C-C distances in both benzene molecules are the same for both determinations. The trends in the geometry around the Ti^0 , Zn^0 , and Cl^0 atoms are also the same and the differences in the distances and angles are within 3σ of Vonk's final values.

Summary

Trimetallic Ti(III) complexes can easily be prepared by two general methods: reduction of Ti(IV) species by free metal or simple addition of Ti(III) species to the metal halide. The complexes are weakly held together. If the oxidation potential of the central metal is not high enough, one cannot reduce the Ti atom to an oxidation state of III and a $\text{Ti}^{\text{IV}}\text{-M}^0\text{-Ti}^{\text{IV}}$ complex does not appear to be stable. Even changes in the basicity of the solvent can cause dissociation of the trinuclear compound. For instance, an ionic complex is formed in DME, while Cp_2TiCl is obtained in diethyl ether.

The crystalline compounds are solvated, though very efflorescent; however, substitution onto the cyclopentadienyl rings allows crystallization without solvent in the lattice. Attempts to prepare the trinuclear complexes with bridging groups other than halides have so far not been successful.

The fact that zinc reduction is fairly easy in tied-back and disubstituted bis(cyclopentadienyl)titanium(IV) systems while it does not occur under more extreme conditions with activated aluminum (which has a higher oxidation potential) indicates that kinetic and possibly steric effects of the cyclopentadienyl rings may play a very important role in low-valent titanium chemistry.

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Registry No. $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$, 54040-41-4; $(\text{Cp}_2\text{TiBr})_2\text{ZnBr}_2$, 54004-69-2; $[(\text{MeCp})_2\text{TiCl}]_2\text{ZnCl}_2$, 54064-96-9; $(\text{Me}_2\text{SiCp}_2\text{TiCl})_2\text{ZnCl}_2$, 55800-01-6; $(\text{Cp}_2\text{TiCl})_2\text{BeCl}_2$, 54004-68-1; $(\text{Cp}_2\text{TiCl})\text{MnCl}_2 \cdot 2\text{THF}$, 55799-99-0; $(\text{Cp}_2\text{Ti} \cdot 2\text{THF})_2(\text{Zn}_2\text{Br}_6)$, 55701-46-7; $(\text{Cp}_2\text{Ti} \cdot \text{DME})_2(\text{Zn}_2\text{Cl}_6) \cdot \text{C}_6\text{H}_6$, 55701-49-0; $(\text{Cp}_2\text{TiCl})_2\text{MnCl}_2 \cdot \text{DME}$, 55800-00-5; $(\text{Cp}_2\text{Ti} \cdot \text{DME})_2\text{ZnCl}_4$, 55701-50-3; Cp_2TiCl_2 , 1271-19-8; Zn, 7440-66-6; ZnCl_2 , 7646-85-7; Cp_2TiCl , 31781-62-1.

Supplementary Material Available. Tables of structure factors and hydrogen atom positional parameters for compounds I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American

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References and Notes

- (1) (a) J. M. Birmingham, A. K. Fischer, and G. Wilkinson, *Naturwissenschaften*, **42**, 96 (1955); (b) G. Hamprecht and L. Taglinger, German Patent 1,153,749 (1963).
- (2) von J. J. Saltzmann, *Helv. Chim. Acta*, **51**, 526 (1968).
- (3) C. G. Vonk, *J. Cryst. Mol. Struct.*, **3**, 201 (1973).
- (4) R. A. Craven, M. B. Salamon, G. DePasquali, R. M. Herman, A. Schultz, and G. D. Stucky, *Phys. Rev. Lett.*, **82**, 769 (1974).
- (5) G. L. McPherson, R. C. Koch, and G. D. Stucky, *J. Chem. Phys.*, **60**, 1424 (1974), and included references.
- (6) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959).
- (7) H. Köpf and W. Kahl, *J. Organomet. Chem.*, **64**, C37 (1974).
- (8) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organomet. Chem.*, **47**, 375 (1973).
- (9) A. R. Pray, *Inorg. Synth.*, **5**, 153 (1957).
- (10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- (11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (13) A set of computer programs from Picker Nuclear, Inc., was utilized for automatic operation of the diffractometer. The general plane Fourier mapping program, JIMDAP, modified by J. Ibers and F. Ross from the original version FORDAP by H. Zalkin and D. H. Templeton, was used to calculate Fourier maps. The least-squares program used was a local version of ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy. Standard deviations were calculated using ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy. ORTEP by C. K. Johnson was used to plot the molecular structures and theoretical hydrogen atom positions were calculated from known atomic positions and hybridizations using HYGEM by F. K. Ross.
- (14) M. L. H. Green and C. R. Lucas, *J. Chem. Soc., Dalton Trans.*, 1000 (1972).
- (15) R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 5112 (1966).
- (16) T. Chivers and E. D. Ibrahim, *Can. J. Chem.*, **51**, 815 (1973).
- (17) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94**, 1219 (1972).
- (18) H. A. Martin, M. van Gerkom, and R. O. de Jongh, *J. Organomet. Chem.*, **36**, 93 (1972).
- (19) R. Jungst, D. Sekutowski, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 8108 (1974).
- (20) D. Sekutowski, R. Jungst, and G. D. Stucky, ACS Symposium Series, No. 5, L. V. Interrante, Ed., American Chemical Society, Washington, D.C., 1974, Chapter 11.
- (21) R. S. P. Coutts and P. C. Wailes, *Aust. J. Chem.*, **21**, 1181 (1968).
- (22) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
- (23) M. Zocchi and A. Albinati, *J. Organometal. Chem.*, **77**, C40 (1974).
- (24) E. M. Texter, E. Dubler, and H. R. Oswald, *Inorg. Chem.*, **13**, 1361 (1974).
- (25) F. K. Ross and G. D. Stucky, *J. Am. Chem. Soc.*, **92**, 4538 (1970).
- (26) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, **50**, 53 (1973).
- (27) L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1953 (1969).
- (28) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.*, **70**, 413 (1974).
- (29) A. M. McPherson, Thesis, University of Illinois.
- (30) A. R. Dias and M. L. H. Green, *Chem. Commun.*, 962 (1969); *J. Chem. Soc. A*, 1951 (1971).
- (31) W. E. Douglas, M. L. H. Green, C. K. Prout, and G. V. Rees, *Chem. Commun.*, 896 (1971).
- (32) T. S. Cameron, C. K. Prout, G. V. Rees, M. L. H. Green, K. K. Joshi, G. R. Davics, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *Chem. Commun.*, 14 (1971).
- (33) D. Sekutowski, R. Jungst, J. Davis, and G. D. Stucky, to be submitted for publication.
- (34) E. F. Epstein, I. Bernal, and H. Kopf, *J. Organomet. Chem.*, **26**, 229 (1971).
- (35) B. R. Davis and I. Bernal, *J. Organomet. Chem.*, **30**, 75 (1971).
- (36) E. F. Epstein and I. Bernal, *Inorg. Chim. Acta*, **7**, 211 (1973).
- (37) C. H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, *Inorg. Chem.*, **13**, 2880 (1974).
- (38) For example, see K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, **12**, 232 (1973).

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Yttrium Phosphate-Yttrium Vanadate Solid Solutions and Vegard's Law

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Previously reported deviations from Vegard's law for the YVO₄-YPO₄ system have now been demonstrated to be due to side reactions occurring during the preparation of the solid solution. Several methods of preparation were investigated and their solid solution yields were evaluated. An aqueous coprecipitation method offers a 100% yield. Using precipitated YPO₄ as a source of phosphate results in good yields of solid solution; the poorest yields are obtained by using (NH₄)₂HPO₄ as the source of phosphate, the method used by prior investigators. The yields are affected by the formation of polyphosphates and polyvanadates. The produced solid solution particles are pseudomorphs of the original YPO₄ particles.

Introduction

The rare earths form a homologous series of phosphates, arsenates, chromates, and vanadates, as has been shown by Feigelson,¹ Stubican and Roy,² and notably by Schwarz.³ These compounds crystallize either in the tetragonal xenotime or monoclinic monazite structures, depending upon the lanthanide involved. A more detailed discussion has appeared recently, in regard to the dimorphism of LaVO₄.⁴

These isomorphous compounds should form complete solid solutions and the lattice parameters should be subject to Vegard's law. However, it appears to be accepted that solid solutions of Y(PO₄)_{1-x}(VO₄)_x deviate appreciably from Vegard's law.⁵ This conclusion may also be culled from the X-ray data of Aia.⁶ (It is significant, however, that both of these authors employed (NH₄)₂HPO₄ as a reactant in solid

solution formation.) His graphical representation of the lattice parameters a_0 and c_0 of the tetragonal unit cell for these solid solutions indicate that at the 50% mole fraction of vanadate, both a_0 and c_0 suffer a sizable decrease from the values deduced from Vegard's law.⁶ In view of the fact that the size of the tetrahedral vanadate anion is only some 8% larger than that for the phosphate anion,⁴ a value well within the 15% limit that usually bounds Vegard's law, it was decided to reinvestigate the Y(PO₄)_{1-x}(VO₄)_x system of solid solutions.

Early in this work it was suspected that deviations from Vegard's law were only apparent and were due to the presence of a small amount of an additional phase in the solid solutions, the new phase being caused by a side reaction during the firing process. A number of methods of preparation of Y(PO₄)_{1-x}(VO₄)_x solid solutions were examined. Fortunately, one method, that of coprecipitation, was found to yield solid solutions that adhered strictly to Vegard's law. This relationship formed a basis for the analyses of the products re-

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