chromatography on alumina. An additional product was isolated in ca. 10% yield and tentatively characterized as $[(MeCp)_2Mo_2(SCH_3)_2S_2FeCp][I]$: ^1H NMR ($CDCl_3$) δ 5.44 (m, 2, C_5H_4), 5.29 (m, 4, C_5H_4), 5.07 (m, 2, C_5H_4), 5.01 (s, 5, C_5H_5), 2.67 (s, 3, CH_3), 2.11 (s, 6, CH_3), 1.59 (s, 3, CH_3); mass spectrum, *m/e* 629 (M^+), 614 ($M^+ - CH_3$), 599 ($M^+ - 2CH_3$), 582 ($M^+ - SCH_3$), 567 ($M^+ - S(CH_3)_2$), 535 ($M^+ - 2SCH_3$).

Reaction of III with Potassium Graphite and Acetylene or Ethylene. A suspension of $[(MeCp)_2Mo_2S_4FeCp][I]$ (III) (0.16 g, 0.22 mmol) was prepared in ca. 40 mL of distilled THF and twice freeze–thaw–degassed. Potassium graphite (0.036 g, 0.26 mmol) was added to the solution in a glovebox and stirred under nitrogen for 4 h. The solution was filtered and the solvent removed under vacuum. The brown solid was then dissolved in ca. 3 mL of deuteriochloroform and transferred to two NMR tubes. The solvent in each tube was freeze–thaw–degassed three times and sealed under 1 atm of either acetylene or ethylene. Initially, the ^1H NMR spectra show an intermediate product with the following resonances: δ 6.54 (m), 6.46 (m), 4.42 (s), 2.04 (s), 1.95 (s). This product slowly disappeared with the formation of $[MeCpMo(SC_2H_2S)]_2$[12] and $[MeCpMo(SC_2H_4S)]_2$,[12] respectively.

Synthesis of $[(MeCp)_2Mo_2S_4CoCp][(I)_2]$ (IV). $[MeCpMoS(SH)]_2$ (0.30 g, 0.62 mmol) and $[CpCo(CO)(I)_2]$ (0.25 g, 0.62 mmol) were dissolved in ca. 50 mL of dichloromethane under nitrogen. The solution was stirred at room temperature for ca. 1 h and the solvent removed under vacuum. The solid was redissolved in 20 mL of dichloromethane and filtered in air. A black solid, $[(MeCp)_2Mo_2S_4CoCp][(I)_2]$ (IV), was isolated in 28.6% yield and characterized by the following spectral data: ^1H NMR (CD_3CN) δ 5.92 (m, 4, C_5H_4), 5.85 (m, 4, C_5H_4), 5.78 (s, 5, C_5H_5), 2.25 (s, 6, CH_3); IR (cm^{-1}, Nujol) 1035 (w), 845 (m); mass spectrum, *m/e* 602 ($(MeCp)_2Mo_2S_4Co(C_5H_5)^+$), 570 ($M^+ - S$), 538 ($M^+ - 2S$), 505 ($M^+ - S - C_5H_5$), 473 ($M^+ - 2S - C_5H_5$). Anal. Calcd for $C_{17}H_{19}S_4Mo_2CoI_2$: C, 23.85; H, 2.24; S, 14.98. Found: C, 24.03; H, 2.37; S, 14.95. $E_{1/2}$, V vs. SCE: −0.08, ΔE = 90 mV, i_{pc}/i_{pa} = 1.0; −0.52, ΔE = 80 mV, i_{pc}/i_{pa} = 0.8; −0.76, ΔE = 100 mV, i_{pc}/i_{pa} = 0.4; +0.25, ΔE = 160 mV, i_{pc}/i_{pa} = 0.9; +0.65, ΔE = 135 mV, i_{pc}/i_{pa} = 0.9. Molar conductivity in CH_3CN, Λ_M ($cm^2\ \Omega^{-1}\ mol^{-1}$): 158 ($1 \times 10^{-4}$ M); 116 (5×10^{-4} M).

Acknowledgment. This work was supported by the National Institutes of Health and, in part, by the National Science Foundation. M.R.D. acknowledges support as a Camille and Henry Dreyfus Teacher Scholar (1981–1986) and a John Simon Guggenheim Fellow (1984–1985).

Registry No. I, 85534-08-3; II, 107270-94-0; III, 107246-75-3; IV, 107246-76-4; $[MeCpMoS(SH)]_2$, 75675-65-9; $Fe(CO)_5$, 13463-40-6; $(MeCp)_2Mo_2S_3O$, 107246-77-5; $(MeCp)_2Mo_2S_2O_2$, 107246-78-6; Li_2S_2, 51148-09-5; $CpFe(CO)_2(I)$, 12078-28-3; $[(MeCp)_2Mo_2(SCH_3)_2S_2FeCp][I]$, 107246-79-7; $CpCo(CO)(I)_2$, 12012-77-0; trimethylamine *N*-oxide, 1184-78-7.

Supplementary Material Available: Tables of calculated and observed structure amplitudes for the structures of $[MeCpMoS_2Fe(CO)_3]_2$ (I), $(MeCpMo)_2S_3Fe_2(CO)_6$ (II), and $[(MeCpMo)_2(S_2)(S)_2FeCp][I]$ (III) (45 pages). Ordering information is given on any current masthead page.

Monomeric Bis(pentamethylcyclopentadienyl)titanium(III)[1] Complexes with Halide, Borohydride, Amide, Alkoxide, and Carboxylate Ligands. X-ray Structure of Bis(pentamethylcyclopentadienyl)titanium(III) Chloride

Johannes W. Pattiasina, Hero J. Heeres, Frê van Bolhuis, Auke Meetsma, and Jan H. Teuben*

Department of Inorganic Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

Anthony L. Spek

Department of Structural Chemistry, University of Utrecht, 3508 TB Utrecht, The Netherlands

Received October 30, 1986

The synthesis and characterization of monomeric Cp^*_2TiX complexes (X = Cl, Br, I, BH_4, $OCMe_3$, O_2CH) are reported. These 15-electron d^1 systems have one unpaired electron and form perfect Curie paramagnetic systems. They are NMR and ESR active. ^1H NMR spectra show broad lines (width 600–5000 Hz) for the Cp* hydrogens between 14.0 and 18.4 ppm. Observation of the protons of the non-Cp* ligands is possible if they are positioned at least β with respect to the metal. The ESR spectra are singlets (g = 1.939–1.978), with for some complexes the expected Ti isotope hyperfine splitting. Hyperfine splittings due to interaction with hydrogen or other nuclei of the ligands are not observed. The structure of Cp^*_2TiCl (1) was determined by X-ray diffraction. 1 crystallizes in the monoclinic space group $P2_1/n$, with a = 9.339 (2) Å, b = 13.632 (1) Å, c = 15.140 (3) Å, β = 99.55 (1)°, and Z = 4. The structure was refined to R = 0.045 and R_w = 0.050 for 290 parameters and 2909 observed reflections (with $F > 3\sigma(F)$). The molecule exhibits an approximate twofold noncrystallographic axis along the Ti–Cl bond. The chlorine ligand is coordinated in the equatorial plane of a bent-sandwich permethyltitanocene fragment (Ti–Cl = 2.363 (1) Å). The Cp* rings coordinate in a true η^5 way to the metal. Methyl–methyl contacts between the staggered Cp* ligands cause a deviation of one of the methyl groups out of the plane of the ring and away from the metal of 0.40 (1) Å.

Introduction

With the exciting chemistry of bis(pentamethylcyclopentadienyl) compounds of group 3[2,3] and the lanthanides,[4,5] Cp^*_2MR, developing rapidly the last few years, it is relevant to study the relations between these classes of

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[1] In this paper the following abbreviations are used: Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5.

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0276-7333/87/2306-1004$01.50/0

compounds and the corresponding group 4 complexes Cp^*_2MR. For M = Zr and Hf no such compounds are available to date. For M = Ti only three complexes Cp^*_2TiR (R = Cl,[6] H,[7] Np[8]) have been mentioned in the literature, but information on synthesis and properties of these paramagnetic complexes is scarce.

We decided to work out a convenient route to titanium compounds Cp^*_2TiR starting from the chloride Cp^*_2TiCl (**1**). In this paper the synthesis and crystal structure of **1** are described together with a number of related complexes Cp^*_2TiX, where X is an anionic ligand, e.g. Br, I, BH_4, NMe_2, $OCMe_3$, or O_2CH, made from **1** by substitution of the chloride ligand.

Experimental Section

General Considerations. All compounds are extremely air sensitive. Manipulations were performed under nitrogen by using glovebox (Braun MB-200) or Schlenk-line techniques.

Solvents (pentane, Et_2O, THF, benzene, toluene-d_8) were purified by destillation from Na/K alloy. Benzene-d_6 was distilled from Na. $TiCl_3(THF)_3$ was prepared from $TiCl_3$ (Ventron) and THF according to a published procedure.[9] Cp*MgCl(THF) was synthesized from Cp*H[10] as described by Marks et al.[11] LiBr, LiI, and $LiNMe_2$ were prepared from *n*-BuLi (Merck) and EtBr (Baker), MeI (Merck) and $HNMe_2$ (Fluka), respectively. $LiBH_4$ (Merck), KO-*t*-Bu (Merck), and NaO_2CH (UCB) were used as purchased. ^1H NMR spectra of the paramagnetic compounds were recorded in benzene-d_6 or toluene-d_8 by using a Nicolet NT 200 spectrometer. Isotropic downfield shifts are positive. IR spectra were recorded from 4000 to 400 cm^{-1} on a Pye Unicam SP3-300 spectrophotometer. Samples were mulled in Nujol between KBr disks. Mass spectra were obtained on an AEI MS-902 instrument operating at 70 eV. A Varian-E4 spectrometer was used to record EPR spectra. Spectra were run from pentane solutions (concentrations ca. 10^{-3} M) at 20 °C, unless otherwise stated. Temperature-dependent magnetic susceptibility measurements were performed on a Faraday-type system (Oxford Instruments) equipped with a Mettler ME 21 electronic vacuum microbalance. Elemental analyses were carried out at the micro-analytical department of our laboratory.

Preparation of Cp^*_2TiCl (1). This compound can be prepared as reported before from $TiCl_3(THF)_3$ and Cp*Li.[6] This route gives a rather low yield and oily byproducts that are difficult to remove. Alternative methods were worked out with Cp*Na and Cp*MgCl(THF). The latter gave the best results and is described below.

A mixture of 18.7 g (50.5 mmol) of $TiCl_3(THF)_3$ and 27.4 g (102.4 mmol) of Cp*MgCl(THF) in 300 mL of THF was stirred for 48 h at room temperature. A dark blue solution formed. The solvent was stripped under vacuum, and the residue was continuously extracted with 300 mL of pentane. The extract was cooled to −80 °C, and dark blue crystals separated. The solvent was decanted and the residue washed with cold (−80 °C) pentane. Yield: 16.0 g (45.2 mmol, 90%) of **1**. IR (cm^{-1}): 2720 (w), 1480 (m), 1375 (s), 1020 (m), 800 (w), 440 (s). MS: M^+ at *m/e* 354. UV-vis (toluene, 340–1600 nm): λ_{max} 560 nm (ϵ 144 $L\cdot mol^{-1}\cdot cm^{-1}$). Magnetic moment: μ_{eff} (100–300 K) = 1.75 μ_B. Anal. Calcd for $C_{20}H_{30}ClTi$: C, 67.96; H, 8.50; Cl, 10.02; Ti, 13.54; mol wt (C_6H_6), 354. Found: C, 68.05; H; 8.73; Cl, 9.93; Ti, 13.49; mol wt (C_6H_6), 360.

Preparation of Cp^*_2TiBr (2). (a) A solution of BBr_3 (0.1 mL, 1.05 mmol) in benzene (10 mL) was added at room temperature to a solution of **1** (0.804 g, 2.27 mmol) in benzene (10 mL). The reaction mixture immediately turned blue-green. After 0.5 h of stirring, the volatiles were removed under vacuum and the residue was extracted with pentane. The extract was concentrated to 10 mL and slowly cooled to −80 °C to give blue-green crystals of **2**. Yield: 0.68 g (1.71 mmol, 75%).

(b) Halide exchange between **1** and LiBr in Et_2O (reaction time of 24 h at room temperature) proved to be a good route to **2**. With a workup similar to a, the yield of **2** was 80%. IR (cm^{-1}): 2720 (w), 1485 (m), 1375 (s), 1025 (m), 445 (s). MS: M^+ at *m/e* 396. Anal. Calcd for $C_{20}H_{30}BrTi$: C, 60.32; H, 7.59; Br, 20.06; Ti, 12.03; mol wt (C_6H_6), 396. Found: C, 60.15; H, 7.53; Br, 20.14; Ti, 11.90; mol wt (C_6H_6), 410.

Preparation of Cp^*_2TiI (3). At room temperature LiI (0.193 g, 1.44 mmol) was added to a solution of **1** (0.425 g, 1.20 mmol) in 15 mL of Et_2O. After 20 h of stirring, the solvent was removed under vacuum and the residue was extracted with pentane. The extract was concentrated to 10 mL and slowly cooled to −80 °C to obtain dark green crystals of **3**. Yield: 0.486 g (1.09 mmol, 90%). IR (cm^{-1}): 2720 (w), 1485 (m), 1375 (s), 1025 (m), 435 (s). MS: M^+ at *m/e* 445. Anal. Calcd for $C_{20}H_{30}ITi$: C, 53.95; H, 6.79; I, 28.50; Ti, 10.76; mol wt (C_6H_6), 445. Found: C, 54.04; H, 6.75; I, 28.21; Ti, 10.67; mol wt (C_6H_6), 459.

Preparation of $Cp^*_2TiBH_4$ (4). $LiBH_4$ (0.045 g, 2.07 mmol) was added to a solution of **1** (0.481 g, 1.36 mmol) in THF (15 mL). The reaction mixture was stirred at 50 °C during 7 h, then the solvent was removed, and the residue was extracted with pentane. An analogous workup procedure to that for **3** gave 0.356 g (1.07 mmol, 78%) of **4** as dark purple-blue crystals. IR (cm^{-1}): 2720 (w), 2445 (s), 2410 (s), 2305 (w), 2170 (vw), 2070 (m), 1950 (s, br), 1485 (m), 1375 (s), 1350 (s), 1165 (s), 1025 (s), 440 (s). MS: M^+ at *m/e* 333. Anal. Calcd for $C_{20}H_{34}BTi$: C, 72.09; H, 10.29; Ti, 14.38; mol wt (C_6H_6), 333. Found: C, 71.92; H, 10.28; Ti, 14.20; mol wt (C_6H_6), 318.

Preparation of $Cp^*_2TiNMe_2$ (5). $LiNMe_2$ (0.098 g, 1.91 mmol) was added to a solution of **1** (0.560 g, 1.58 mmol) in 30 mL of Et_2O. The solution immediately turned dark green. After 1.5 h of stirring, the solvent was removed under vacuum. An analogous workup procedure to that for **3** gave 0.399 g (1.10 mmol, 70%) of **5** as dark green crystals. IR (cm^{-1}): 2800 (m), 2770 (m), 2735 (s), 1475 (m, sh), 1375 (s), 1235 (m), 1155 (m), 1115 (w), 1060 (w), 1025 (m), 935 (s), 800 (w), 515 (w). MS: M^+ at *m/e* 362. Anal. Calcd for $C_{22}H_{36}NTi$: C, 72.91; H, 10.01; N, 3.86; Ti, 13.22; mol wt (C_6H_6), 362. Found: C, 72.88; H, 10.05; N, 3.92; Ti, 13.00; mol wt (C_6H_6), 375.

Preparation of $Cp^*_2TiOCMe_3$ (6). $KOCMe_3$ (0.215 g, 1.92 mmol) was added to a solution of **1** (0.473 g, 1.34 mmol) in 30 mL of Et_2O. The solution immediately turned purple. After 3 h of stirring, the solvent was removed under vacuum. An analogous workup procedure to that for **3** gave 0.400 g (1.00 mmol, 74%) of **6** as purple crystals. IR (cm^{-1}): 2720 (w), 1375 (s), 1352 (m), 1210 (w), 1182 (s), 1025 (w), 987 (s), 775 (w), 530 (w). MS: M^+ at *m/e* 401. Anal. Calcd for $C_{24}H_{39}OTi$: C, 73.64; H, 10.04; Ti, 12.24; mol wt (C_6H_6), 401. Found: C, 73.33; H, 10.10; Ti, 12.15; mol wt (C_6H_6), 408.

Preparation of $Cp^*_2TiO_2CH$ (7). NaO_2CH (0.165 g, 2.43 mmol) was added at room temperature to a solution of **1** (0.777 g, 2.20 mmol) in THF (30 mL). After 44 h of stirring under reflux, the solvent was removed under vacuum. The blue residue was extracted with pentane (25 mL). The extract was dried under vacuum. After vacuum sublimation (0.01 mmHg, 100 °C), blue **7** was isolated. Yield: 0.442 g (1.22 mmol, 56%). IR (cm^{-1}): 2720 (w), 1554 (s), 1486 (m), 1378 (s), 1358 (s), 1315 (s), 1162 (w), 1060 (w), 1022 (m), 805 (s), 430 (s). MS: M^+ at *m/e* 363. Anal. Calcd for $C_{21}H_{31}O_2Ti$: C, 69.41; H, 8.60; Ti, 13.18; mol wt (C_6H_6), 363. Found: C, 69.02; H, 8.68; Ti, 13.33; mol wt (C_6H_6), 385.

X-ray Data Collection, Structure Determination, and Refinement for Cp^*_2TiCl (1). Well-shaped blue crystals were obtained from pentane solution and sealed in a Lindemann glass

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Table I. Crystal Data and Details of the Structure Analysis for Cp^*_2TiCl (1)

(a) Crystal Data	
empirical formula	$C_{20}H_{30}ClTi$
mol wt	353.82
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.339 (2)
b, Å	13.632 (1)
c, Å	15.140 (3)
β, deg	99.55 (1)
V, Å^3	1900.7 (6)
Z	4
D(calcd), g·cm^{-3}	1.236
F(000), electrons	756
μ(Cu Kα) cm^{-1}	51.0
cryst size, mm	0.15 × 0.30 × 0.30
min and max applied abs corr factors	0.787 and 1.566
(b) Data Collection	
temp, K	140
radiation, Å	Cu Kα, graphite monochromated, 1.5418
θ_{min}, θ_{max}, deg	1, 70
vert and hor apert, mm	4 and 3.50 + 1.0 tan θ
$\omega/2\theta$-scan width, deg	$\Delta\omega = 0.80 + 0.14 \tan\theta$
data set, h,k,l	$0 \rightarrow 11, 0 \rightarrow 16, -18 \rightarrow 18$
max time/reflcn, s	45
ref reflcn, hkl	240
total data	3592
total unique	3441
obsd data ($F > 3\sigma(F)$)	2911
X-ray exposure time, h	35
(c) Refinement	
no. of parameters varied	290
weighting scheme	$w = 1$
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.045
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2}$	0.050
esd of reflcns with unit weight	$S = 1.17$
min and max density in final diff Fourier map, e Å^{-3}	−0.52 and 0.44
max (shift/σ)	0.35
av (shift σ)	0.02

capillary under nitrogen. Data were collected on an Enraf-Nonius CAD4 diffractometer interfaced to a PDP-11/23. Unit cell dimensions were determined from the setting angles of 16 carefully centered reflections, having $16° < \theta < 36°$. The space group was determined as $P2_1/n$ from the observed systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. Data belonging to one quadrant were collected at 140 K in the $\omega/2\theta$ scan mode, using graphite-monochromated Cu Kα radiation. The reference reflection 240, measured every 100 min. showed a slight decay of 10% of the intensity during the data collection. The data were corrected for Lorentz-polarization effects and the observed decay. Absorption correction was applied by using the program DIFABS.[12] Further details of the structure determination are summarized in Table I.

The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least-squares methods. All hydrogen atoms, located in a difference Fourier map, were included in the final refinement, with an overall isotropic temperature factor. All non-hydrogen atoms were assigned anisotropic thermal parameters. The final refinement converged at $R = 0.045$ ($R_w = 0.050$) for 290 parameters and 2909 observed reflections with $F > 3\sigma(F)$. The final positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II.

Two low-order reflections, $30\bar{1}$ and 140, with $F_o < F_c$ were excluded from the final refinement cycle. Neutral scattering factors were taken from ref 13a, corrected for anomalous dispersion.[13b]

Table II. Final Positional and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Cp^*_2TiCl (1)

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ti	0.62393 (6)	0.23121 (4)	0.40542 (4)	0.0136 (1)
Cl	0.6751 (1)	0.16991 (6)	0.55329 (5)	0.0267 (3)
C(1)	0.5829 (3)	0.0958 (2)	0.3057 (2)	0.018 (1)
C(2)	0.6330 (3)	0.1736 (2)	0.2567 (2)	0.017 (1)
C(3)	0.7777 (3)	0.1975 (2)	0.2981 (2)	0.018 (1)
C(4)	0.8172 (3)	0.1320 (2)	0.3712 (2)	0.018 (1)
C(5)	0.6976 (4)	0.0678 (2)	0.3751 (2)	0.018 (1)
C(6)	0.4154 (3)	0.3311 (2)	0.3598 (2)	0.019 (1)
C(7)	0.4404 (3)	0.3283 (2)	0.4549 (2)	0.018 (1)
C(8)	0.5759 (4)	0.3754 (2)	0.4866 (2)	0.020 (1)
C(9)	0.6356 (4)	0.4051 (2)	0.4103 (2)	0.023 (1)
C(10)	0.5339 (4)	0.3809 (2)	0.3321 (2)	0.021 (1)
C(11)	0.4405 (4)	0.0420 (3)	0.2801 (2)	0.025 (1)
C(12)	0.5574 (4)	0.2073 (3)	0.1664 (2)	0.022 (1)
C(13)	0.8789 (4)	0.2701 (3)	0.2665 (2)	0.025 (1)
C(14)	0.9612 (4)	0.1289 (3)	0.4316 (2)	0.026 (1)
C(15)	0.6980 (4)	−0.0188 (2)	0.4354 (2)	0.024 (1)
C(16)	0.2768 (4)	0.2988 (3)	0.3022 (2)	0.029 (1)
C(17)	0.3387 (4)	0.2842 (3)	0.5102 (2)	0.030 (1)
C(18)	0.6380 (4)	0.3987 (3)	0.5814 (2)	0.033 (1)
C(19)	0.7711 (5)	0.4656 (3)	0.4113 (3)	0.044 (1)
C(20)	0.5349 (5)	0.4252 (3)	0.2407 (3)	0.035 (1)

All calculations were carried out on the CYBER 180-855 of the University of Utrecht computer center. Programs used include the XTAL[14] and EUCLID[15] packages.

Results and Discussion

Synthesis. Reaction of $TiCl_3(THF)_3$ in THF with main-group pentamethylcyclopentadienyls Cp^*M (M = Li, Na, MgCl(THF)) gives high yields (70–90%) of blue, crystalline 1 (eq 1). The chloride ligand in 1 is easily replaced by other anionic ligands. Straightforward metathesis reactions afforded a whole series of complexes, Cp^*_2TiX (eq 2). Substitution of Cl in 1 by organic groups R (R = alkyl, allyl, aryl) is readily achieved by treating 1 with appropriate Grignard or lithium reagents. Details on preparation and properties of Cp^*_2TiR will be published elsewhere.[16]

$$2Cp^*M + TiCl_3(THF)_3 \xrightarrow{THF} \underset{1}{Cp^*_2TiCl} + 2\,MCl \qquad (1)$$

$$M = Li,\ Na,\ MgCl(THF)$$

$$\begin{array}{llll} \underset{1}{Cp^*_2TiCl} + XM' \rightarrow & Cp^*_2TiX & + & M'Cl \qquad (2) \\ & 2\text{: } X = Br & & M' = Li,\ BBr_2 \\ & 3\text{: } X = I & & M' = Li \\ & 4\text{: } X = BH_4 & & M' = Li \\ & 5\text{: } X = NMe_2 & & M' = Li \\ & 6\text{: } X = OCMe_3 & & M' = K \\ & 7\text{: } X = O_2CH & & M' = Na \end{array}$$

Characterization. All compounds 1–7 were isolated as crystalline, analytically pure, very air-sensitive com-

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Table III. Magnetic Susceptibility Measurement for $Cp*_2TiCl$ (1) at Various Temperatures

T, K	χ_M(para),[a] 10^{-3} cgs emu	T, K	χ_M(para),[a] 10^{-3} cgs emu
113.3	3.43	218.4	1.72
125.0	3.15	233.1	1.65
139.8	2.79	248.1	1.56
155.7	2.42	263.3	1.48
170.3	2.25	279.9	1.37
184.6	2.04	294.6	1.31
201.9	1.83		

[a] Corrected for diamagnetism: $\chi_M(\text{dia}) = -0.28 \times 10^{-3}$ cgs emu.

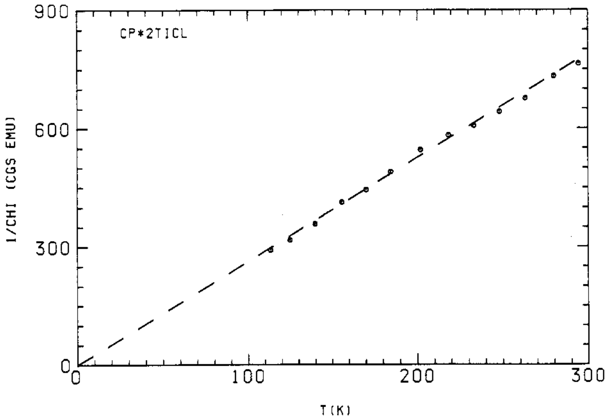

Figure 1. Plot of χ_M^{-1} against T for $Cp*_2TiCl$ (1). The line drawn is the least-squares fit.

pounds. Their thermal stability is high; e.g., 1 can be heated at 250 °C without notable decomposition. The solubility of 1–7 in common organic solvents (pentane, Et_2O, benzene, etc.) is very high and makes purification by crystallization from solution rather difficult.

Mass spectra indicate that the compounds 1–7 are monomers in the gas phase. Molecular weight determinations (cryoscopy in benzene) confirm that they are monomeric in solution too. Monomeric $Cp*_2TiX$ compounds are paramagnetic 15-electron systems with one unpaired electron per titanium. Table III gives magnetic susceptibility data for 1 at various temperatures. The chloride 1 shows perfect Curie paramagnetism (Figure 1) over the temperature range (100–300 K), with $\mu_{eff} = 1.75\ \mu_B$ as expected for a $3d^1$ system (spin only, 1.73 μ_B). There is no indication for antiferromagnetic coupling between the unpaired electrons on neighboring titanium centers. Such coupling is a characteristic property of related, but dimeric complexes $(Cp_2Ti(\mu\text{-}X))_2$ (X = halide).[17] In 1–7 apparently the bulk of the permethylcyclopentadienyl ligands prevents the formation of dimers, although all anionic ligands are well-known for their bridging capacities.

IR Spectra. For paramagnetic compounds, like the series 1–7 under discussion here, NMR is not a very convenient technique for characterization and identification. Also EPR is of relatively little value (vide infra). IR spectroscopy is more important although it also has severe limitations. We have used IR spectroscopy extensively in our studies for diagnostic purposes. All compounds show characteristic Cp* absorptions at about 2720 (w), 1480 (m), 1375 (s), 1020 (m), and 800 (w) cm^{-1}. For the individual compounds characteristic absorptions of the other ligands can be assigned. In 4 terminal B–H stretching vibrations are at 2445 and 2410 cm^{-1} and the bridging hydride stretching modes at 2070 and 1950 cm^{-1}. The bridge deformation mode is at 1350 cm^{-1} and the BH_2 deformation at 1165 cm^{-1}.[18] This borohydride part is virtually identical with that of the analogous $Cp_2Ti(\mu\text{-}H)_2BH_2$ for which the η^2-BH_4 coordination was established by an X-ray structure determination.[19] In the amide 5, strong bands at 1235 and 1155 cm^{-1} are due to deformation modes of the methyl groups of the NMe_2 fragment.[20] Stretching modes of the CNC moiety are located at 1060 (w, ν_{asym}) and 935 (vs, ν_{sym}).[21] The ν_{TiN} is at 515 cm^{-1}. For a NMe_2 group, the characteristic ν_{CH} vibrations are observed at 2800, 2770, and 2735 cm^{-1}.[21] The butoxide 6 has an intense band due to ν_{CO} at 1182 cm^{-1}, and a very strong skeletal vibration of the *tert*-butoxide group is found at 987 cm^{-1}.[20] The Ti–O stretching vibration is at 530 cm^{-1}.[22] The carboxylate 7 shows ν_{sym} (OCO) at 1378 cm^{-1} and ν_{asym} at 1554 cm^{-1}. The separation $\Delta\nu = 176\ cm^{-1}$ is indicative of a symmetric, coordinated carboxylate group.[23] For related compounds Cp_2TiO_2CR much smaller values of $\Delta\nu$ were reported[24a] as characteristic for covalent bidentate carboxylates. In our case $\Delta\nu$ in 7 is intermediate between Cp_2TiO_2CH ($\Delta\nu = 115\ cm^{-1}$ [24a]) and the ionic compound NaO_2CH ($\Delta\nu = 225\ cm^{-1}$ [24b]). This suggests an increase in ionicity of the titanium carboxylate bond going from cyclopentadienyl to pentamethylcyclopentadienyl, an effect that can be rationalized on the basis of inductive effects due to methyl substitution of cyclopentadienyl rings.

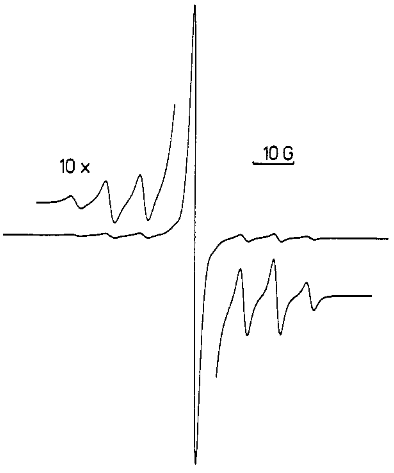

Figure 2. EPR spectrum of $Cp*_2TiOCMe_3$ (pentane, −80 °C).

EPR Spectra. EPR spectra of solutions of 1–7 (ca. 10^{-3} M in pentane) were recorded at various temperatures between +20 °C and −100 °C. Relevant data are summarized in Table IV, and a representative spectrum is given in Figure 2.

The averaged g values range from $g = 1.939$ (for 3) to $g = 1.978$ (for 4), indicating considerable spin–orbit coupling for the halides and less for the others. The values correspond closely to those found for compounds Cp_2TiR (R = aryl)[25] but are lower than those of the alkyl deriva-

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Table IV. EPR and NMR Data for Cp^*_2TiX

	EPR^a				^{1}H NMR^b			
		ΔH^d						
X (compd)	g^c	+20 °C	−60 °C	a(Ti)	δ(Cp*)	whm^e	δ(X)	whm^e
Cl (**1**)	1.956	60.0	17.5	*f*	14.4	1000		
Br (**2**)	1.953	65.0	*g*	*f*	14.4	880		
I (**3**)	1.939	80.0	*g*	*f*	14.1	620		
BH_4 (**4**)	1.978	10.0	5.4	*f*	18.4	1940	*f*	
NMe_2 (**5**)	1.962	27.0	3.0	11.2	15.3 (s, 30 H)	880	−9.6 (s, 6 H)	650
$OCMe_3$ (**6**)	1.976	3.5	1.6	8.6	14.0 (s, 30 H)	730	0.6 (s, 9 H)	150
O_2CH (**7**)	1.976	13.5	5.3	8.3	16.4^h	5000	*f*	

^{a}In pentane (ca. 10^{-3} M). ^{b}In benzene-d_6 at 18 °C, shifts relative to residual protons in the solvent (δ 7.15), downfield shifts positive. ^{c}Relative to DPPH at g = 2.0036. ^{d}Peak to peak distance (G) measured peak to peak in the first derivative spectrum. ^{e}Widths at half maximum (Hz). ^{f}Not observed. ^{g}Not determined. ^{h}In toluene-d_8 at 21 °C, shift relative to residual protons in the solvent (δ 7.02).

tives Cp_2TiR and $Cp_2TiR{\cdot}L$[26,27] (g varies between 1.980 and 1.999). They are also lower than other di- and monocyclopentadienyl EPR-active titanium species like $(Cp_2TiH)_2(\mu\text{-}H)$ (g = 1.9937)[28] and $Cp_2Ti(\mu\text{-}H)_2AlH_2$ (g = 1.9888)[29] and products obtained from reduction of Cp_2TiR_2 (with either bridged Cp ligands or a bridged R_2 moiety) with g = 1.9811–1.9988.[29,30a,31]

At low gain the spectra show a single-line derivative, and only for compounds **5**–**7** Ti isotope satellites are discerned. The width of the signals depends strongly on the nature of ligand X in Cp^*_2TiX and varies from 3.5 G for the butoxide **6** to over 60 G for the halides **1**–**3**. The lines narrow considerably on cooling, reaching a minimum at about −60 to −80 °C and broadening again at lower temperatures. As a result of this narrowing the spectra give more details with respect to hyperfine interactions at low temperatures. This is clearly the case for the Ti isotope splitting where for compounds **5**–**7** the coupling constants can be determined accurately from the −60 °C spectra (Table IV). Figure 2 shows these satellites due to coupling with the nonzero nuclear spin isotopes ^{47}Ti (I = $^5/_2$, natural abundance 7.28%) and ^{49}Ti (I = $^7/_2$, natural abundance 5.51%). The coupling constant a(Ti) is the same for both isotopes,[32] and the resulting pattern is a superposition of six and eight equidistant and equally intense lines. The intensity distribution of the spectrum is as expected on the basis of relative isotope abundances, and the general features of the spectra agree well with data reported for related compounds like Cp_2TiR,[25,26] $(SiMe_2(C_5H_4)_2TiCl_2)^-$,[31] and $(Cp_2TiCl_2)^-$ [33] and also for monocyclopentadienyl compounds $CpTiR_2$.[30b,34]

Line narrowing at low temperatures is not sufficient to resolve superhyperfine coupling to nuclei of ligand X, and consequently the EPR spectra are rather uninformative with respect to bonding mode of X and spin density distribution in the molecules. As a matter of fact interaction with X is not explicitly observed for any of the compounds, although, with exception of **6** and **7**, all ligands have ligating atoms with nonzero nuclear spin. The width of the signals indicate some small coupling is present, but we were not able to achieve resolution. The EPR spectra discussed here are in sharp contrast with well-resolved spectra reported for dicyclopentadienyltitanium compounds like $Cp_2TiR{\cdot}L$,[27] $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$,[35] $(Cp_2TiH)_2(\mu\text{-}H)$,[28] and those of in situ electrochemically or chemically reduced Cp_2Ti^{IV} compounds of not unequivocally established identity[30a,36,37] and $CpTiR_2$ compounds.[30b] In the spectra of the last mentioned compounds the bonding of the ligands can be inferred from the observed superhyperfine structure. On the other hand, interaction with hydrogen nuclei of the cyclopentadienyl ligands is normally not observed in these compounds and the number of Cp ligands per molecule in the EPR-active species cannot be derived from the EPR data. It must be noted that for these well-resolved spectra the identity of the complexes present and responsible for the EPR spectra has not been confirmed by other physicochemical techniques and their nature is still somewhat mysterious.

It appears that EPR spectroscopy at the moment is still rather disappointing as a technique for the identification of EPR-active organotitanium compounds in solution. The average g values may vary over quite a large range for analogous complexes and overlap with those of other types. Also the titanium isotope coupling constants, $a(^{47,49}Ti)$, are quite variable, and values between 8 and 14 G have been reported. This range, however, seems to be characteristic for mononuclear titanium species.[32]

^{1}H NMR Spectra. The ^{1}H NMR spectra were recorded in benzene-d_6 or toluene-d_8 at room temperature (Table IV). As expected for paramagnetic molecules the resonances are broad and shifted considerably from their usual diamagnetic positions. The pentamethylcyclopentadienyl hydrogen resonances are located in a rather narrow range between δ 14.0 (**5**) and 18.4 (**4**). The widths at half maximum (whm), however, are extremely dependent on the nature of X, varying between 620 Hz for **3** and 5000 Hz for **7**, illustrating the large spread in longitudinal relaxation times T_2. Especially bidentate ligands X (e.g. in **4** and **7**) give extremely broad lines. We do not intend to give a thorough in-depth discussion of the spectra. Moreover, comparison of these data with those of related systems is virtually impossible. The elaborate studies by Koehler et al.[38] on dicyclopentadienylvanadium(III) compounds deal with d^2 systems where the situation is much more complex (e.g. zero-field splitting effects). NMR data on comparable

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Table V. Selected Interatomic Distances (Å) and Angles (deg) for Cp*$_2$TiCl (1)

	(a) Bond Distances		
Ti–Cl	2.363 (1)		
Ti–CE(1)[a]	2.06 (1)		
Ti–CE(2)[b]	2.06 (2)		
Ti–C(1)	2.375 (3)	Ti–C(6)	2.383 (3)
Ti–C(2)	2.399 (3)	Ti–C(7)	2.383 (3)
Ti–C(3)	2.385 (3)	Ti–C(8)	2.400 (3)
Ti–C(4)	2.380 (3)	Ti–C(9)	2.374 (3)
Ti–C(5)	2.398 (3)	Ti–C(10)	2.407 (3)
C(1)–C(11)	1.512 (5)	C(6)–C(16)	1.502 (5)
C(2)–C(12)	1.503 (4)	C(7)–C(17)	1.493 (5)
C(3)–C(13)	1.501 (5)	C(8)–C(18)	1.490 (5)
C(4)–C(14)	1.496 (5)	C(9)–C(19)	1.508 (6)
C(5)–C(15)	1.492 (4)	C(10)–C(20)	1.511 (5)
C(1)–C(2)	1.417 (4)	C(6)–C(7)	1.420 (4)
C(2)–C(3)	1.430 (4)	C(7)–C(8)	1.429 (4)
C(3)–C(4)	1.422 (4)	C(8)–C(9)	1.422 (4)
C(4)–C(5)	1.428 (4)	C(9)–C(10)	1.428 (5)
C(5)–C(1)	1.423 (4)	C(10)–C(6)	1.420 (4)
	(b) Bond Angles		
CE(1)–Ti–CE(2)	143.6 (2)		
CE(1)–Ti–Cl	108.7 (3)		
CE(2)–Ti–Cl	108.1 (3)		
C(1)–C(2)–C(3)	108.1 (3)	C(6)–C(7)–C(8)	108.4 (3)
C(2)–C(3)–C(4)	107.6 (2)	C(7)–C(8)–C(9)	107.4 (3)
C(3)–C(4)–C(5)	108.3 (3)	C(8)–C(9)–C(10)	108.1 (3)
C(4)–C(5)–C(1)	107.7 (2)	C(9)–C(10)–C(6)	108.0 (3)
C(5)–C(1)–C(2)	108.3 (2)	C(10)–C(6)–C(7)	107.9 (3)
C(2)–C(1)–C(11)	125.6 (3)	C(7)–C(6)–C(16)	124.2 (3)
C(5)–C(1)–C(11)	125.6 (3)	C(10)–C(6)–C(16)	127.4 (3)
C(1)–C(2)–C(12)	124.0 (3)	C(6)–C(7)–C(17)	124.5 (3)
C(3)–C(2)–C(12)	126.6 (3)	C(8)–C(7)–C(17)	127.1 (3)
C(2)–C(3)–C(13)	127.6 (3)	C(7)–C(8)–C(18)	126.9 (3)
C(4)–C(3)–C(13)	124.5 (3)	C(9)–C(8)–C(18)	125.4 (3)
C(3)–C(4)–C(14)	125.7 (3)	C(8)–C(9)–C(19)	126.1 (3)
C(5)–C(4)–C(14)	126.0 (3)	C(10)–C(9)–C(19)	125.2 (3)
C(4)–C(5)–C(15)	126.0 (3)	C(9)–C(10)–C(20)	124.2 (3)
C(1)–C(5)–C(15)	126.1 (3)	C(6)–C(10)–C(20)	125.8 (3)

[a] CE(1) = [C(1)···C(5)] ring centroid. [b] CE(2) = [C(6)···C(10)] ring centroid.

d^1 systems are scarce. Bercaw[7] reports for Cp*$_2$TiH the resonance of the pentamethylcyclopentadienyl hydrogens at δ 22.2 is very close to the values for our compounds 1–7. The hydride resonance was not located, which is not surprising when compared with our results. We observe clear resonances with correct intensities for protons on the ligand X for 5 and 6. For 4 and 7 these could not be located. This may be due to extremely large shifts but also to extreme broadening of the resonance. It is clear that the shorter the distance of the proton to the metal, the smaller the chance that it can be observed. Apparently for hydrogen atoms in the β-position or farther away from the metal center it may be expected that location is possible without problems. In conclusion it seems that in complexes Cp*$_2$TiX the protons of the rings and ligand X in positions far enough from the paramagnetic center can be located easily and used as a probe in kinetic and reactivity studies.

Structure of Cp*$_2$TiCl (1). Structural data on mononuclear organotitanium(III) compounds are scarce. EPR and NMR spectroscopy are of little use in studying the structure (vide supra), and an X-ray structure determination is essential for obtaining detailed information on bonding aspects. Because 1 is a key compound in our studies on Cp*$_2$Ti^{III} derivatives, we carried out an X-ray diffraction study.

The unit cell contains four discrete monomeric molecules. Bond distances and angles are given in Table V.

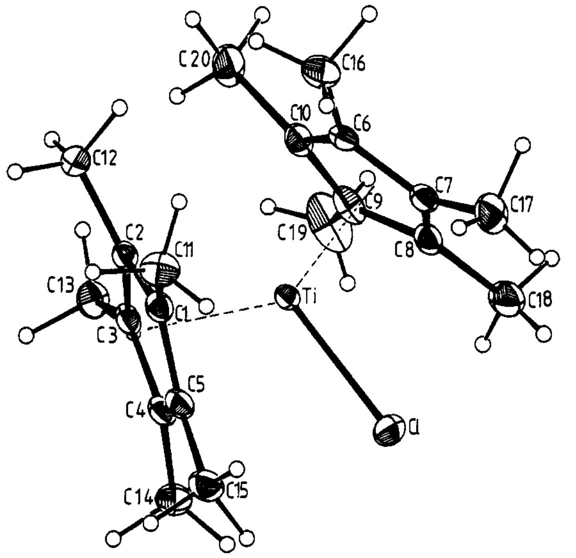

Figure 3. ORTEP drawing (40% level) of Cp*$_2$TiCl (1), with adopted numbering scheme.

Table VI. Structural Comparison of Cp*$_2$Ti Systems

compound	α,[a] deg	Δ_{max},[b] Å	ref
Cp*$_2$Ti(SH)$_2$	135.3	0.26[c]	41a
Cp*$_2$TiS$_3$	136.8	*d*	41b
Cp*$_2$TiCl$_2$	137.4	0.49	41c
Cp*$_2$Ti(η^2-C$_2$H$_4$)	143.6	0.37	41d
Cp*$_2$TiCl	143.6	0.40	this work
(Cp*$_2$Ti)$_2$(μ-N$_2$)	145.7	0.33	41e
Cp*$_2$Ti(CO)$_2$	147.9	*d*	41f

[a] α = CE(1)–Ti–CE(2) in deg. [b] Δ deviation of the Me groups out of the plane of the ring in Å. [c] Average value. [d] not listed.

In Figure 3 an ORTEP[39] drawing of the molecule is given with the adopted numbering scheme. The molecule exhibits an approximate twofold noncrystallographic axis along the Ti–Cl bond. The chlorine ligand coordinates in the equatorial plane of a bent-sandwich decamethyltitanocene fragment. The distortion from an idealized trigonal coordination, as measured by the ring centroid–Ti–ring centroid angle α (= CE(1)—Ti—CE(2)) of 143.6 (2)°, is close to that found in other Cp*$_2$Ti derivatives (Table VI). The CE(1)–Ti–Cl and CE(2)–Ti–Cl angles are 108.7 (3)° and 108.1 (3)°, respectively. The three angles add up to 360° and illustrate the planar-triangular coordination. The rather large value of α may be attributed to steric crowding due to the bulky Cp* ligands. Angle α increases with increasing bulk of the substituents directly attached to the metal (Table VI). The Ti–CE distances of 2.06 (2) Å are a little shorter than found for Cp*$_2$TiCl$_2$ (Ti–CE = 2.127 (4) and 2.128 (4) Å, respectively)[40c] and are within the range of values observed in other bis(cyclopentadienyl)titanium structures.[40]

The cyclopentadienyl rings are close to planar.[41] The C(ring)–C(ring), C(ring)–C(methyl), and even the Ti–C-

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[41] See supplementary material for least-squares planes.

(ring) distances vary over a very small range (1.417 (4)–1.430 (4), 1.490 (5)–1.512 (5), and 2.375 (3)–2.400 (3) Å, respectively). So the pentamethylcyclopentadienyl rings coordinate in a true η^5 way to the metal.

An interesting feature is the deviation (Δ) of the methyl groups out of the plane of the ring and away from titanium, which varies from 0.01 (2) to a maximum of 0.40 (1) Å.[41] Especially the large values of Δ for the methyl groups that contain atoms C_{12} and C_{20} of 0.31 (1) and 0.40 (1) Å, respectively, are noticed here. It is evident that they are caused by the methyl–methyl contacts between the staggered Cp* ligands. These large deviations correspond with the shortest nonbonded intramolecular C–C distances of 3.196 (6) Å. It is interesting to note that in $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ α and Δ_{max} are almost the same.[40d]

The important contribution of steric crowding is also reflected in the rather long Ti–Cl distance of 2.363 (1) Å that does not differ much from those found in $Cp^*_2TiCl_2$ (Ti–Cl = 2.352 (1) and 2.346 (1) Å respectively) and is also comparable with that in $(CH_2)_3(C_5H_4)_2TiCl_2$ (Ti–Cl = 2.368 (4) Å),[42] $CpCp^*TiCl_2$ (Ti–Cl = 2.3518 (9) Å),[43] or Cp_2TiCl_2 (Ti–Cl = 2.364 (2) Å).[44] On the other hand a significant difference is observed, when the Ti–Cl distance is compared with the range of 2.526–2.566 Å observed in the dimeric analogues of 1, $(Cp_2Ti(\mu\text{-}Cl))_2$ and $(Cp'_2Ti(\mu\text{-}Cl))_2$.[17] In 1 the shortest Ti–Ti distance between the monomeric units is 7.496 (8) Å; this also makes it clear why antiferromagnetic coupling is not observed in 1 (vide supra): the d^1 centers are too far apart. Finally all hydrogen atoms could be located. Their positions and bond angles are comparable with those of normal sp^3-hybridized carbon atoms. The shortest nonbonded intermolecular distance is between Cl and H(63) (2.82 (4) Å) and is similar to that found in $Cp^*_2TiCl_2$.

Acknowledgment. We thank Dr. L. C. ten Cate for performing the magnetic measurements. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 73348-99-9; 2, 107495-35-2; 3, 107495-36-3; 4, 96289-67-7; 5, 107495-37-4; 6, 107495-38-5; 7, 107495-39-6; $TiCl_3(THF)_3$, 18039-90-2; Cp*MgCl(THF), 107495-40-9.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, least-squares planes and deviations therefrom, and additional bond distances and angles and PLUTO and ORTEP drawings of Cp^*_2TiCl (1) (7 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Structures and Rearrangement Mechanisms for Some Bicyclo[6.1.0]nona-2,4,6-triene Complexes of Chromium, Molybdenum, and Tungsten

Frank J. Liotta, Jr., Gregory Van Duyne, and Barry K. Carpenter*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received August 22, 1986

The structures of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum and (*endo*-9-bromobicyclo[3.1.0]nona-2,4,6-triene)tricarbonylmolybdenum have been investigated by X-ray crystallography. The first crystallized in the orthorhombic space group *Pnma*: $a = 14.185$, $b = 10.417$, $c = 7.230$ Å; $Z = 4$; 1143 reflections were measured, of which 756 were considered observed; the final structure had $R = 0.115$ and $R_w = 0.137$. The second complex crystallized in monoclinic space group $P2_1/m$: $a = 8.740$, $b = 10.038$, $c = 13.742$ Å; $\beta = 85.9°$; $Z = 4$; 1736 reflections were measured, of which 1494 were considered observed; $R = 0.068$ and $R_w = 0.077$. Both are shown to have geometries in which the cyclopropane ring is syn to the metal. In the 9-bromo complex only two of the three C=C bond are coordinated to the metal; the third coordination site is occupied by the halogen. The mechanism of thermal rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum has been investigated by deuterium-labeling and kinetic studies. A new, degenerate rearrangement of the starting complex has been discovered in the course of this investigation. Similar processes are shown to occur for the corresponding chromium and tungsten complexes. It is concluded that both types of rearrangement are sigmatropic processes in which the metal does not directly participate in cleavage of the C–C bond. The difference in thermal chemistry of the complexed and uncomplexed hydrocarbon is proposed to be due to selective inhibition of certain reaction pathways by the metal.

Introduction

The thermal rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum, characterized by Grimme[1] as shown in Scheme I, is an intriguing reaction. It is a rearrangement that does not occur for the uncomplexed hydrocarbon,[2,3] which, instead, undergoes only epimerization and rearrangement to *cis*- and *trans*-8,9-dihydroindenes. The chromium[4] and tungsten[5] com-

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