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Crystal Structure of [$Cp_2Ti(THF)_2$][$Co(CO)_4$]: Variation of O–Ti–O Angles in the Same Crystal

JOSEPH S. MEROLA*, KATHRYN S. CAMPO, ROBERT A. GENTILE and M. A. MODRICK

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801 (U.S.A.)

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Abstract

The molecular structure of [$Cp_2Ti(THF)_2$][$Co(CO)_4$] has been determined by X-ray diffraction at –104 °C. The compound crystallizes in the acentric monoclinic space group $P2_1$ with $a = 7.812(4)$, $b = 15.010(4)$, $c = 28.445(9)$ Å, $\beta = 94.10(3)°$, $V = 3327.1$ Å^3 and $Z = 6$. The unique feature of this crystal structure is that there are three independent cation/anion pairs in the unit cell and that the structure of the $Cp_2Ti(THF)_2^+$ fragment is significantly different for each. The most significant difference lies in the O–Ti–O angles which range from 77.2 to 82.9°. This result points out the magnitude of the effect that steric requirements due to crystal packing forces can have in determining structural features.

Introduction

We have been interested in the synthesis and structure of early/late metal carbonyl complexes for some time [1–3]. In a recent paper, we reported on the synthesis of a series of Ti/Co complexes with isocarbonyl bridges between Ti and Co (Ti–O–C–Co) [3]. Along the way to these Ti–O–C–Co compounds, we also isolated a material formulated as the cation/anion pair: [$Cp_2Ti(THF)_2$][$Co(CO)_4$] where THF = tetrahydrofuran. Even though this material does not contain a direct Ti–cobalt carbonyl interaction, we had occasion to determine its crystal structure. This paper describes this structure which shows a significant variation of the structures of three independent $Cp_2Ti(THF)_2^+$ units.

Experimental

Crystal Structure Determination of [$Cp_2Ti(THF)_2$][$Co(CO)_4$]

Crystals of [$Cp_2Ti(THF)_2$][$Co(CO)_4$] suitable for an X-ray study were grown by slow diffusion of hexane into a THF solution of the complex. A green prismatic crystal having approximate dimensions of 0.15 × 0.25 × 0.35 mm was mounted on a

TABLE 1. Crystallographic data for [$Cp_2Ti(THF)_2$][$Co(CO)_4$]

Formula	$C_{22}H_{26}Co_1O_6Ti_1$
Formula weight	643.78
Crystal dimensions	0.15 × 0.25 × 0.35 mm
Radiation	Mo Kα: λ = 0.71073 Å
Temperature	–104 ± 1 °C
Space group	$P2_1$
a	7.812(4) Å
b	15.010(4) Å
c	28.445(9) Å
β	94.10(3)
V	3327(2) Å^3
Z	6
ρ(calculated)	1.53 g/cm^3
μ	4.7 cm^{-1}
Monochromator	graphite crystal, incident beam
Attenuator	Zr foil, factor 20.7
Takeoff angle	2.8°
Detector aperture	2.0 to 2.5 mm horizontal, 4.0 mm vertical
Crystal–detector distance	21 cm
Scan type	ω–2θ
Scan rate	2–20°/min (in ω)
Scan width (°)	0.6 + 0.350 tan θ
Maximum 2θ	55.0°
No. reflections measured	8212 total, 7926 unique
Corrections	Lorentz–polarization; empirical absorption (from 0.92 to 1.00 on I)
Solution	Multan
Hydrogen atoms	not included
Minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
Anomalous dispersion	all non-hydrogen atoms
Reflections included	5367 with $F_o^2 > 3.0\sigma(F_o^2)$
Parameters refined	810
Unweighted/weighted agreement factor	0.0556/0.0707
e.s.d. of obs. of unit weight	1.21
Convergence, largest shift	0.03σ
High peak in final difference map	0.619e/Å^3

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*Author to whom correspondence should be addressed at Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, U.S.A.

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glass fiber with its long axis roughly parallel to the phi axis of the goniometer. (Data collection was performed by Molecular Structures Corporation, College Station, TX.) Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $2 < \theta < 14°$, measured by the computer controlled diagonal slit method of centering. Data collection was carried out at −104 °C. Based on the systematic absence of $0k0$, $k = 2n + 1$, the space group was determined to be either $P2_1/m$ or $P2_1$. The structure was solved in the space group $P2_1$ and the non-centrosymmetric nature of the unit cell was verified through comparison of the N(Z) cumulative probability distribution for the observed data versus the theoretically calculated values for acentric, centric, and hypercentric cells. The positions of three cobalt atoms and three titanium atoms were found by application of direct methods to the data (MULTAN, Enraf Nonius). A succession of difference Fourier syntheses alternated with cycles of least-squares calculations revealed the remaining non-hydrogen atoms. Hydrogen atoms were not included in the final refinement. At convergence $R = 0.0570$ and $R_w = 0.0727$. Comparison with a refinement of the structure of the opposite polarity gave $R = 0.0556$ and $R_w = 0.707$, a slight but significant difference. Therefore, the final data is reported for the latter solution. Table 1 lists the experimental details for the structure solution.

Results and Discussion

The X-ray structural determination of $[Cp_2Ti(THF)_2][Co(CO)_4]$ provided no surprises in terms of the identification of the complex and confirmed the cation/anion nature of the material. There are no indications of any cobalt carbonyl oxygen to titanium interactions. The complex crystallizes in the acentric space group $P2_1$ with $Z = 6$ with three independent formula units per unit cell. Figure 1 shows an ORTEP plot of one of the independent $Cp_2Ti(THF)_2$ cations in the unit cell and Fig. 2 shows an ORTEP plot of one of the independent $Co(CO)_4$ anions. Table 2 gives a listing of the atomic positional parameters and isotropic displacement parameters for the molecule.

In all three cases the geometries of the $Co(CO)_4^-$ units were unexceptional. Table 3 gives a listing of select bond lengths and angles for the $Co(CO)_4$ units. However, inspection of the cations, $Cp_2Ti(THF)_2^+$, revealed some significant differences from one unique cation to the next. Table 4 lists several of the structural parameters for each of the independent $Cp_2Ti(THF)_2$ units. The most striking feature is a large variation in THF–Ti–THF bond angles

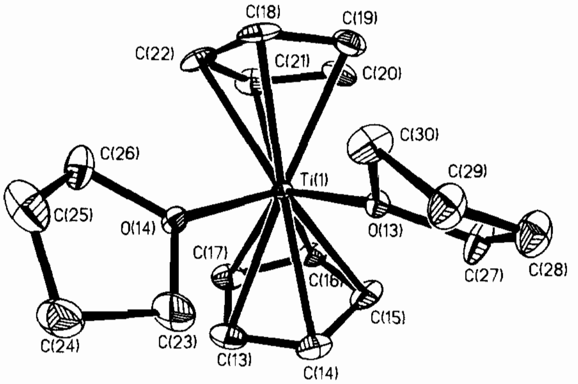

Fig. 1. ORTEP plot of one of the independent $Cp_2Ti(THF)_2^+$ ions in the unit cell.

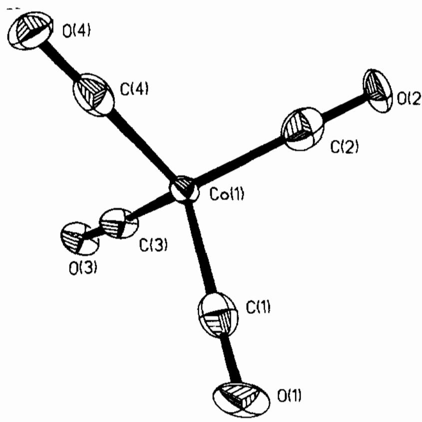

Fig. 2. ORTEP plot of one of the independent $Co(CO)_4^-$ ions in the unit cell.

TABLE 2. Positional and equivalent isotropic thermal parameters, B_{eq}, for $[Cp_2Ti(THF)_2][Co(CO)_4]$

Atom	x	y	z	B_{eq} (Å^2)
Co(1)	0.5907(2)	0.851	0.58864(4)	2.45(2)
Co(2)	0.8374(2)	0.44408(9)	0.69771(4)	2.37(2)
Co(3)	0.8536(2)	0.03792(9)	0.94596(4)	2.59(2)
Ti(1)	0.6216(2)	0.4224(1)	0.88857(5)	1.47(2)
Ti(2)	0.1001(2)	0.8054(1)	0.80336(5)	1.41(2)
Ti(3)	0.3525(2)	0.1963(1)	0.59581(5)	1.55(2)
C(1)	0.625(1)	0.7336(7)	0.6002(4)	4.6(2)
C(2)	0.558(1)	0.8860(7)	0.6558(4)	5.3(3)
C(3)	0.776(1)	0.9078(1)	0.5795(4)	4.6(2)
C(4)	0.409(1)	0.8759(7)	0.5580(3)	4.6(2)
C(5)	0.682(1)	0.5252(8)	0.7109(4)	5.0(2)
C(6)	0.772(1)	0.3417(8)	0.7181(4)	5.6(3)
C(7)	0.852(1)	0.4406(7)	0.6349(4)	4.9(2)
C(8)	1.043(1)	0.4744(6)	0.7251(4)	4.2(2)
C(9)	0.625(2)	0.0400(7)	0.9295(4)	5.5(3)
C(10)	0.920(1)	−0.0754(7)	0.9529(3)	3.8(2)
C(11)	0.979(2)	0.0873(8)	0.9034(4)	6.4(3)
C(12)	0.893(1)	0.0967(7)	0.9989(4)	5.1(2)

(continued)

TABLE 2. *(continued)*

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
C(13)	0.840(1)	0.3371(7)	0.8521(4)	4.6(2)
C(14)	0.849(1)	0.3190(6)	0.8996(4)	4.1(2)
C(15)	0.897(1)	0.3992(7)	0.9233(3)	4.0(2)
C(16)	0.912(1)	0.4667(6)	0.8892(3)	3.4(2)
C(17)	0.870(1)	0.4282(7)	0.8441(3)	4.0(2)
C(18)	0.363(1)	0.5040(6)	0.8854(4)	3.9(2)
C(19)	0.462(1)	0.5324(7)	0.9269(3)	4.2(2)
C(20)	0.608(1)	0.5738(6)	0.9139(3)	3.8(2)
C(21)	0.605(1)	0.5748(6)	0.8644(4)	4.0(2)
C(22)	0.454(1)	0.5312(5)	0.8456(3)	3.7(2)
C(23)	0.484(2)	0.2246(6)	0.8545(4)	5.8(3)
C(24)	0.381(2)	0.1844(8)	0.8118(5)	6.3(3)
C(25)	0.252(1)	0.2519(8)	0.7993(4)	6.2(3)
C(26)	0.344(1)	0.3392(8)	0.8072(4)	5.1(2)
C(27)	0.609(1)	0.3287(8)	0.9915(3)	5.1(2)
C(28)	0.485(1)	0.2754(8)	1.0190(4)	5.2(2)
C(29)	0.341(1)	0.2481(7)	0.9844(3)	4.6(2)
C(30)	0.334(1)	0.3234(7)	0.9491(4)	4.5(2)
C(31)	0.066(1)	0.9946(6)	0.7461(4)	4.7(2)
C(32)	−0.085(1)	1.0535(8)	0.7264(4)	6.5(3)
C(33)	−0.189(1)	1.0628(7)	0.7693(4)	5.6(3)
C(34)	−0.168(1)	0.9714(6)	0.7939(3)	4.1(2)
C(35)	−0.006(1)	0.7981(9)	0.6888(3)	5.4(3)
C(36)	0.085(2)	0.782(1)	0.6467(4)	6.6(3)
C(37)	0.196(1)	0.7007(7)	0.6605(4)	4.9(2)
C(38)	0.259(1)	0.7242(6)	0.7118(3)	3.7(2)
C(39)	0.290(1)	0.9171(7)	0.8378(3)	4.3(2)
C(40)	0.374(1)	0.8721(7)	0.8015(4)	4.4(2)
C(41)	0.399(1)	0.7817(7)	0.8150(3)	3.8(2)
C(42)	0.333(1)	0.7707(7)	0.8588(3)	4.2(2)
C(43)	0.265(1)	0.8558(7)	0.8730(3)	4.1(2)
C(44)	0.020(1)	0.6590(6)	0.8258(3)	3.6(2)
C(45)	−0.033(1)	0.7212(6)	0.8613(3)	3.7(2)
C(46)	−0.160(1)	0.7767(6)	0.8387(3)	3.0(2)
C(47)	−0.1840(9)	0.7495(6)	0.7911(3)	2.8(2)
C(48)	−0.076(1)	0.6774(6)	0.7834(3)	3.4(2)
C(49)	0.120(1)	0.2070(7)	0.6459(3)	3.9(2)
C(50)	0.275(1)	0.2097(7)	0.6736(3)	4.1(2)
C(51)	0.353(1)	0.1235(8)	0.6702(4)	5.0(2)
C(52)	0.252(1)	0.0717(7)	0.6394(4)	4.6(2)
C(53)	0.104(1)	0.1227(8)	0.6234(4)	5.4(2)
C(54)	0.551(1)	0.1120(6)	0.5560(3)	3.3(2)
C(55)	0.548(1)	0.1981(6)	0.5358(3)	3.2(2)
C(56)	0.613(1)	0.2598(6)	0.5691(3)	3.7(2)
C(57)	0.654(1)	0.2107(7)	0.6129(3)	3.9(2)
C(58)	0.617(1)	0.1206(6)	0.6034(3)	3.3(2)
C(59)	0.336(1)	0.3998(6)	0.6290(3)	3.7(2)
C(60)	0.342(1)	0.4923(7)	0.6081(4)	4.7(2)
C(61)	0.388(1)	0.4756(6)	0.5575(3)	4.0(2)
C(62)	0.291(1)	0.3913(6)	0.5445(3)	3.7(2)
C(63)	0.011(1)	0.2310(8)	0.5237(5)	7.4(3)
C(64)	−0.060(1)	0.198(1)	0.4819(4)	9.0(3)
C(65)	0.018(1)	0.1145(8)	0.4688(4)	5.9(3)
C(66)	0.175(1)	0.1061(7)	0.5030(3)	4.1(2)
O(1)	0.640(1)	0.6589(5)	0.6010(4)	6.0(2)
O(2)	0.544(1)	0.9123(6)	0.6944(2)	4.8(2)
O(3)	0.8888(8)	0.9458(5)	0.5662(3)	4.0(2)
O(4)	0.298(1)	0.8919(6)	0.5325(3)	4.6(2)
O(5)	0.580(1)	0.5765(6)	0.7205(3)	5.4(2)
O(6)	0.733(1)	0.2700(6)	0.7333(3)	6.3(2)
O(7)	0.871(1)	0.4358(6)	0.5955(2)	4.5(2)
O(8)	1.1728(8)	0.4943(6)	0.7417(3)	4.3(2)
O(9)	0.484(1)	0.0405(7)	0.9205(4)	7.5(2)
O(10)	0.963(1)	−0.1478(5)	0.9564(2)	3.8(2)
O(11)	1.069(1)	0.1189(6)	0.8766(3)	7.1(2)
O(12)	0.921(1)	0.1350(6)	1.0348(3)	5.6(2)
O(13)	0.5175(7)	0.3418(4)	0.9451(2)	2.1(1)
O(14)	0.4630(8)	0.3215(4)	0.8485(2)	2.5(1)
O(15)	0.1307(7)	0.7856(4)	0.7277(2)	2.0(1)
O(16)	−0.0200(7)	0.9295(4)	0.7747(2)	2.2(1)
O(17)	0.2945(7)	0.3391(4)	0.5876(2)	1.8(1)
O(18)	0.1773(7)	0.1850(4)	0.5325(2)	2.1(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)-$[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)$ $B(1,3) + bc(\cos\alpha)B(2,3)]$.

over the three cations: from a low value of 77.2(2)° to a high of 82.9(2)°. The THF rings in all three conformers are puckered to a larger degree than observed in some other Ti–THF complexes. The THF ligands are neither co-planar with the O–Ti–O planes nor perpendicular to them, but sit at angles ranging from 35 to 50° (using the oxygen and α-carbons of THF to define one plane and using O–Ti–O to define the second and measuring the dihedral angles between the planes). Contrast this with two other group IV transition metal Cp_2M THF complexes. In the case of $[Cp_2Zr(CH_3)(THF)]$-$[BPh_4]$, which is a d^0 Zr(IV) complex, the THF was found to lie perpendicular to the O–Zr–C_{methyl} plane [4]. This was interpreted in terms of significant π-bonding between the THF oxygen and Zr. In the

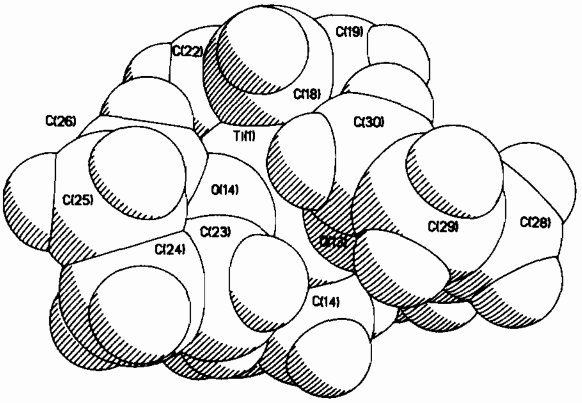

Fig. 3. Space-filling model of one of the independent $Cp_2Ti(THF)_2^+$ ions in the unit cell.

TABLE 3. Comparison of key structural features of the $Co(CO)_4$ anions

Parameter	Anion 1	Anion 2	Anion 3
C–Co–C ∠ (av.)	109.5	109.5	109.5
O–C–Co ∠ (av.)	177.6	177.5	177.9
Co–C1	1.787(11)	1.779(11)	1.817(12)
Co–C2	1.743(12)	1.733(13)	1.784(10)
Co–C3	1.794(11)	1.799(12)	1.771(13)
Co–C4	1.804(12)	1.792(10)	1.754(12)

TABLE 4. Comparison of key structural features of the $Cp_2Ti(THF)_2$ cations

Parameter	Cation 1	Cation 2	Cation 3
THF–Ti–THF ∠	77.2(2)	80.0(2)	82.9(2)
Cp–Ti–Cp ∠	131.30(8)	132.02(7)	134.16(8)
Ti–O1	2.213(5)	2.202(5)	2.201(5)
Ti–O2	2.219(6)	2.215(5)	2.190(5)
Ti–Cp1	2.051(1)	2.055(1)	2.064(1)
Ti–Cp2	2.052(2)	2.054(1)	2.047(1)

Cp angles and distances measured from the ring centroid.

case of $Cp_2Ti(THF)OCMo(CO)_2Cp$, the THF is much closer to planarity with the O–Ti–O plane (dihedral angle = 17°) [1]. Since the latter is a Ti(III) complex with an electron in the metal d orbital which would be used for π-bonding to the THF, we would expect less π-bonding than in the d^0 case and THF–Cp ring interactions would be expected to dominate in determining the THF orientation. $Cp_2Ti(THF)_2^+$ is also a d^1 Ti(III) complex. However, in this case THF–THF interactions dominate, forcing the THF rings into these intermediate conformations. Figure 3 shows a space-filling plot of one of the $Cp_2Ti(THF)_2^+$ ions in the structure which clearly illustrates the unfavorable THF–THF interactions.

Over the years a widely accepted picture has emerged to explain the L–M–L angles in Cp_2ML_2 complexes as a combination of electronic effects (which depend on the d^n count of the metal) and on the steric constraints of the ligands [5]. So while the 6° range seen in the O–Ti–O angles may seem a small perturbation, the values spanned have in the past been used to explain differences in d^n configurations. The angles reported in this study are smaller than those usually observed for d^1 complexes and more in line with the angles found for d^2 compounds [5a]. Our structural results for $[Cp_2Ti(THF)_2][Co(CO)_4]$ clearly underscores the magnitude the steric effect can have. All three conformers have the same electronic configuration: d^1, Ti(III), so the structural differences can only be attributed to steric effects associated with crystal packing. In many cases this may serve as a caution that when ascribing such structural differences to electronic effects, differences of the magnitude seen in this study can be explained by steric effects alone.

Supplementary Material

ORTEP plots of each of the independent cation/anion pairs in the unit cell (3 pages); Tables of anisotropic displacement parameters, bond distances and bond angles (18 pages); and a Table of calculated and observed structure factors (30 pages) are available upon request from the principal author.

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