Journal of Organometallic Chemistry, 220 (1981) 159—164
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

COMPARISON OF THE MOLECULAR STRUCTURES AND INFRARED SPECTRA OF TITANOCENE AND NIOBOCENE CHELATE TRIMETHYLACETATES

I.L. EREMENKO, Yu.V. SKRIPKIN, A.A. PASYNSKII *, V.T. KALINNIKOV,
N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Leninskii Pr., 31 Moscow V-71 (U.S.S.R.)

Yu.T. STRUCHKOV and G.G. ALEKSANDROV
A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilova St., 28 Moscow V-312 (U.S.S.R.)

(Received May 19th, 1981)

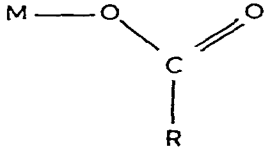
Summary

An X-ray structural study (λ(Mo-K_α), θ—2θ scanning, $2\theta \leqslant 46°$, $T = -120°C$) of $Cp_2TiOOCCMe_3$ (I) has been performed. The cyclopentadienyl ligands form π-bonds with the Ti atom (mean Ti—C_{mean} 2.40(1) Å, mean C—C 1.48(2) Å), the dihedral angle between the rings being 45(1)°. The chelate $OOCCMe_3$ ligand is located in a bisecting plane with equivalent Ti—O bonds equal to 2.13(1) Å (Ti···C_{OCO} 2.51(1) Å, OCO angle 116(1)°). The geometry of I has been compared to the previously investigated structure of $Cp_2NbOOCCMe_3$ (II) which has the carboxylate group farther from the metal atom (Nb—O 2.23(1) Å, Nb···C_{OCO} 2.61(1) Å, OCO angle 118(1)°). The effect of d^1 and d^2 metal electronic configurations on the geometry and IR spectra of I and II is discussed in terms of the nature of the M—OCO bonding.

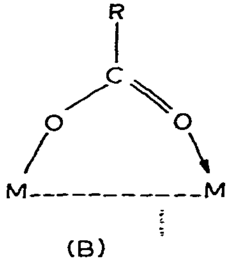
Introduction

The variety of the transition metal carboxylates and their role in industrial and biochemical processes attract attention to the nature of M—OOCR bonding [1] and to the use of infrared spectra in discussing the coordination of the carboxylate group [2]. A common criterion for identifying the M—OOCR coordination type is the frequency difference between the asymmetric and symmetric OCO stretching modes ($\Delta\nu = \nu(OCO)_{as} - \nu(OCO)_s$), which is greater than 200 cm^{-1} for terminal coordination (A) and less than 105 cm^{-1} for chelate coordination

(C) (bridged coordination (B) affords intermediate values) [2,3]:



(A)



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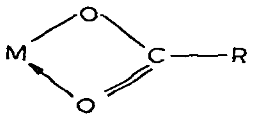

(C)

This criterion is quite acceptable for trimethylacetate transition metal complexes (R = CMe_3). Thus in the tolane adduct $Cp_2NbOOCCMe_3 \cdot Ph_2C_2$ the terminal OOCR coordination (Nb—O 2.26(1) Å) gives $\Delta\nu$ = 1618 — 1330 = 288 cm^{-1} [4]. The bridged OOCR coordination in the numerous dimers having the "chinese lantern"-type structure $LM(OOCCMe_3)_4ML$ [5,6] (L = substituted pyridine or PPh_3) gives $\Delta\nu$ of about 200 cm^{-1}. Finally, for $Cp_2TiOOCCMe_3$ (I) [7], a representative of the family of $Cp_2TiOOCR$ complexes with chelate OOCR coordination [8], the value of $\Delta\nu$ = 1540 — 1430 = 110 cm^{-1} [7].

It was thus suprising to find a large value of $\Delta\nu$ = 1652 — 1305 = 347 cm^{-1} for our recently described niobium analog of I, $Cp_2NbOOCCMe_3$ (II), which contains the Nb—O—C(R)=O chelate group [4] (Nb—O 2.23(1) and 2.24(1) Å, other important structural characteristics are listed in Table 4). To elucidate the reasons for this spectral difference between I and II we carried out a complete X-ray analysis of complex I.

Results and discussion

The X-ray study of $Cp_2TiOOCCMe_3$ (I) (Fig. 1) * shows that I is a wedge-like molecule with a chelate-bonded trimethylacetate group. The Ti atom has a pseudotetrahedral environment and is π-bonded to the two cyclopentadienyl ligands (mean Ti—C_{Cp} 2.40(1) Å, mean C—C 1.48(2) Å, C—C—C angle 108°) producing a dihedral angle of 45(1)° (the rings are in the usual eclipsed conformation **). The planar four-membered cycle TiC(1) C(1) O(2) is in a bisecting plane of this angle with Ti—O bonds practically equivalent (2.13(1) and 2.14(1) Å, respectively) and considerably shorter than the 2.23(1) Å in the niobium complex (Table 4). Generally, the molecule is not strained. The O—C bond lengths are 1.17(1) Å. The TiO(1)C(1) and TiO(2)C(2) angles are 91.8(5) and 91.1(5)°, respectively, while the O(1)C(1)O(2) and O(1)TiO(2) angles are 116(1) and 60.9(2)°. All these values are practically equivalent to those found for II, hence the M—O bond length is the principal difference between structures I and II. One cannot explain such a difference by different covalent radii since any

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* Tables 1 and 2 lists the coordinates of the non-hydrogen atoms and anisotropic temperature factors, Table 3 gives the bond length and angles.

** In complex I the Cp ligands have two orientations: C(5)···C(9) (occupancy 0.7) and $C(5)^*\cdots C(9)^*$ (occupancy 0.3).

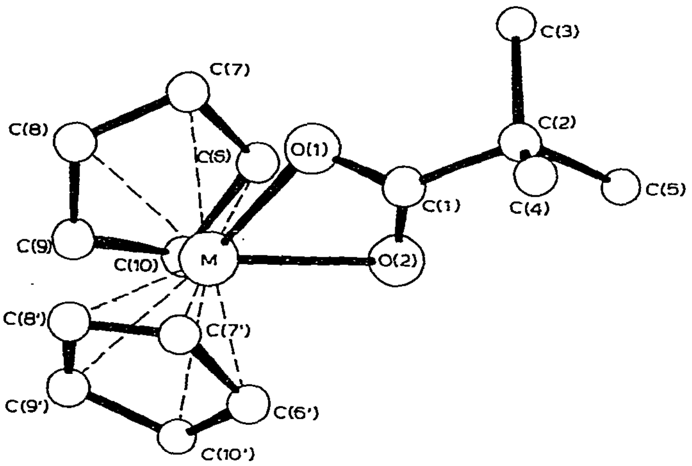


Fig. 1. The molecular structure of $Cp_2MOOCCMe_3$ (M = Ti, Nb). Only one statistical position of the Cp and t-butyl ligands is shown.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$)

Atom [a]	X	Y	Z	
Ti	2006(2)	1238(2)	1/4	—
O(1)	2287(6)	−941(7)	1/4	—
O(2)	3769(7)	466(7)	1/4	—
C(1)	3395(11)	−786(12)	1/4	—
C(2)	4245(10)	−1983(11)	1/4	—
C(3)	5018(7)	−1864(8)	1494(7)	—
C(4)	3112(13)	−3348(12)	1/4	—
C(5)	595(14)	1246(21)	1101(12)	18(3)
C(6)	1695(16)	648(12)	677(9)	14(3)
C(7)	2628(11)	1728(21)	706(11)	20(3)
C(8)	2113(16)	2994(15)	1156(11)	18(3)
C(9)	840(16)	2663(16)	1360(10)	13(3)
C(5)*	1455(39)	2931(31)	1316(23)	16(5)
C(6)*	2443(27)	2435(41)	924(23)	10(6)
C(7)*	2261(28)	1077(36)	657(18)	7(5)
C(8)*	959(38)	901(35)	910(26)	17(8)
C(9)*	634(36)	2001(57)	1240(31)	35(9)

[a] The Cp ligand has two orientation C(5) . . . C(9) (occupancy 0.7) and C(5)* . . . C(9)* (occupancy 0.3)

TABLE 2

TEMPERATURE FACTORS FOR Ti AND THE $OOCCMe_3$ GROUP IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}kha^{*}\,{}^{*})]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	1.09(8)	1.22(8)	1.15(8)	0.27(11)	0	0
O(1)	1.14(44)	1.03(37)	2.36(37)	0.14(28)	0	0
O(2)	1.52(39)	0.89(36)	2.66(41)	−0.23(31)	0	0
C(1)	1.31(54)	1.88(58)	1.30(52)	−0.21(41)	0	0
C(2)	1.50(52)	1.44(49)	1.34(49)	1.15(46)	0	0
C(3)	2.09(40)	2.97(41)	2.05(41)	0.18(35)	0.66(34)	0.04(33)
C(4)	5.14(78)	1.54(64)	4.33(78)	1.41(56)	0	0

TABLE 3

BOND LENGTHS AND BOND ANGLES IN THE STRUCTURE $Cp_2TiOOCCMe_3$

Bond	d(Å)	Angle	(°)
Ti—O(1)	2.13(1)	CpTi Cp [a]	135(1)
Ti—O(2)	2.14(1)	O(1)TiO(2)	60.9(2)
Ti—C(1)	2.51(1)	TiO(1)C(1)	91.8(5)
Ti—C(5)	2.38(2)	TiO(2)C(1)	91.1(5)
Ti—C(6)	2.40(1)	O(1)C(1)O(2)	116(1)
Ti—C(7)	2.42(1)	O(1)C(1)C(2)	123(1)
Ti—C(8)	2.40(1)	O(2)C(1)C(2)	121(1)
Ti—C(9)	2.40(1)	C(1)C(2)C(3)	108(1)
O(1)—C(1)	1.27(1)	C(1)C(2)C(4)	112(1)
O(2)—C(1)	1.28(1)	C(3)C(2)C(4)	110(1)
C(2)—C(1)	1.51(2)	C(5)C(6)C(7)	109(1)
C(2)—C(3)	1.55(1)	C(6)C(7)C(8)	108(1)
C(2)—C(4)	1.50(2)	C(7)C(8)C(9)	106(1)
C(5)—C(6)	1.48(2)	C(8)C(9)C(5)	111(1)
C(6)—C(7)	1.49(2)	C(9)C(5)C(6)	107(1)
C(7)—C(8)	1.47(2)		
C(8)—C(9)	1.50(3)		
C(9)—C(5)	1.43(3)		

[a] Cp centre of the cyclopentadienyl ring. For the Cp ligand, values given refer to the position of C(5) . . . C(9) with the greater (0.7) occupancy.

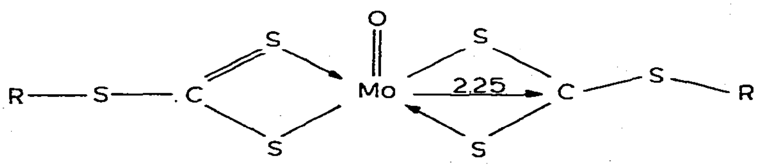
TABLE 4

COMPARISON OF THE MAIN STRUCTURAL DATA FOR $Cp_2MOOCCMe_3$ (M = Ti, Nb) (Å, °)

Bonds and angles	$Cp_2TiOOCCMe_3$	$Cp_2NbOOCCMe_3$
M — O(1)	2.13(1)	2.23(1)
M — O(2)	2.14(1)	2.24(1)
M — C_{OCO}	2.51(1)	2.61(1)
M — C_{Cp}	2.40(1)	2.39(1)
O(1)—C(1)	1.27(1)	1.25(1)
O(2)—C(2)	1.28(1)	1.28(1)
CpMCp	135(1)	136(1)
O(1)MO(2)	60.9(2)	58.0(1)
O(1)C(1)O(2)	116(1)	118(1)

difference would affect the M—C_{Cp} distances [9], which are almost the same in I and II.

Most evident is the difference between the electronic configuration of the central atom in complexes I and II: d^1 for Ti^{III} in I and d^2 for Nb^{III} in II. The effect of such a difference on the M—OCO bonding may be dual: either enhancing or weakening this interaction. Thus the Nb^{III} lone electron pair could be bound more efficiently to the carbon atom of OCO when the latter has a vacant orbital of appropriate symmetry and energy. In particular, such bonding has been observed in oxo-bis(isopropyl thioxanthato)Mo^{IV}, which has a lone electron pair on the metal:



$R = i\text{-}C_3H_7$

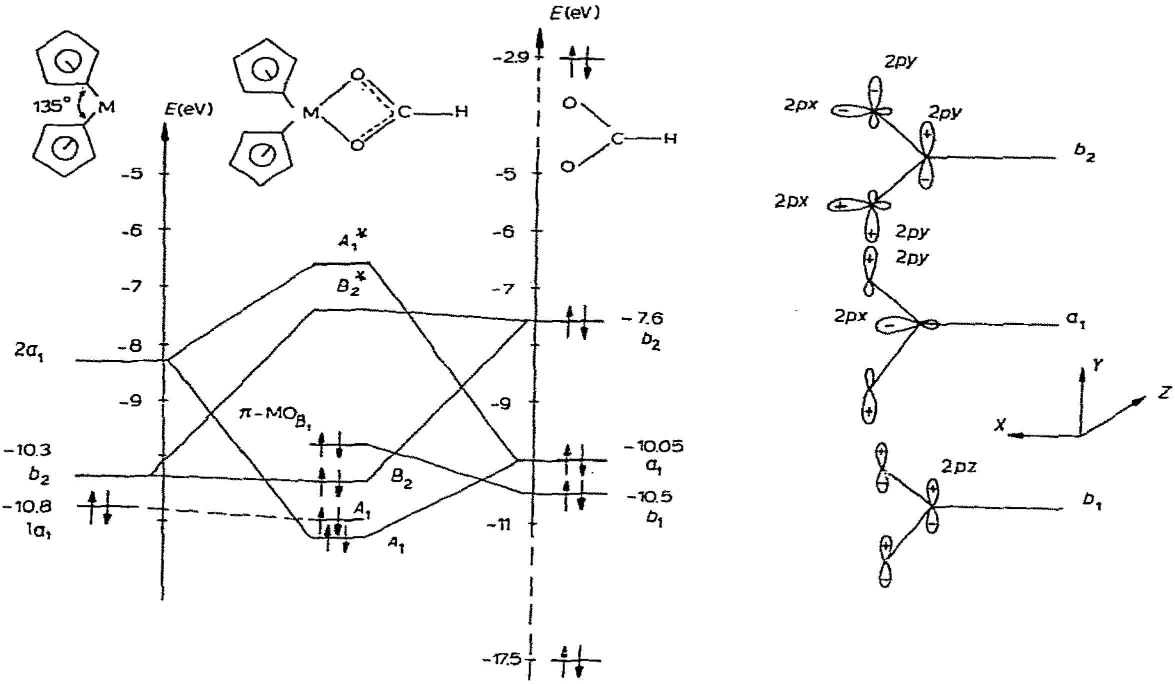


Fig. 2. MO correlation diagram for the model complexes Cp_2MOOCH (the vacant orbital energies of the $HCOO^-$ anion are +15.77, +16.29, +22.24, +23.70 eV).

This results in a rotation of the S_2CS plane about the Mo—C axis by 22.3° and formation of a short Mo—C bond (2.25 Å) [10]. If such rotation were impossible then the two electrons (instead of one) at the metal would hinder the M—OCO bonding.

A theoretical computation was performed for molecules I and II using an MO diagram for the interaction of the wedge-like fragments Cp_2M and the formate anion $OOCH^-$ located in the bisecting plane of the ring angle *. To estimate the shape and energy of the Cp_2M fragment orbitals the data of Lauher and Hoffmann [11] were used with the Cp—M—Cp angle equal to 135° and close to that found experimentally for I and II. The electronic structure of the $OOCH^-$ anion was computed by the INDO method [12], the qualitative MO pattern was estimated from MO expansion over AO. The correlation diagram obtained is shown in Fig. 2. First of all, it may been seen that the vacant orbitals of the $HCOO^-$ anion are very high in energy (above +15 eV) and incapable of efficient overlap with the occupied M orbital in the Cp_2M fragment (its energy is about —10.8 eV). Among the $HCOO^-$ orbitals only the two occupied a_1 and b_2 orbitals (with energies of —10.05 and —7.6 eV, respectively) may overlap with the vacant $2a_1$ and b_2 orbitals of the Cp_2M fragment. On the other hand, the $1a_1$ orbital of the Cp_2M fragment occupied in the case of Nb^{III} (d^2 configuration) is nonbonding. However, in the Ti^{III} complex (d^1 configuration) this orbital is half filled and

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* The authors thank Prof. Yu.A. Ustynyuk (Moscow State University) for this computation carried out in his laboratory.

may overlap with the a_1 MO responsible for M—O bonding. Such overlap may reduce the energy of the new bonding MO and thus strengthen the Ti—O bond with respect to the Nb—O bond as is observed experimentally. Obviously a still greater strengthening of the M—O bond should be expected for a Ti^{IV} complex (d^0 configuration). An analogous trend would be expected upon oxidation of II and other chelate-bonded carboxylate derivatives containing the Cp_2M fragment. Such a investigation would be of interest.

The dependence of Δ(OCO) on the strength of the M—O bond is not surprising since the frequencies of the chelate-bonded OCO group are determined by vibrations of the entire MOCO metallocycle. Unfortunately, at present one cannot relate ν(OCO) to the M—O bond length because of the undetermined force constants of M—O and O—C.

It may be noted that recently [2] it has been assumed that the abnormally large frequency difference $\Delta\nu$(OCO) of 347 cm^{-1} for complex II may be explained by partial hydrolysis or by Br^- ions entering the niobium coordination sphere on pressing the KBr pellets. Since in Nujol the spectra are repeatedly reproducible and unchanged our explanation seems to be more reasonable.

Experimental

The dark-blue $Cp_2TiOOCCMe_3$ prisms were prepared by a reported method [7]. Owing to the high sensitivity to the atmospheric oxygen the crystals were sealed in a capillary. Experimental X-ray data were obtained on a Syntex P21 autodiffractometer (λ(Mo-K_α), θ—2θ scan, $2\theta \leqslant 46°$, $T = -120°$). 834 reflections had $I > \sigma$, from which 607 reflections $\geqslant 2\sigma$ were used for the full-matrix iteration (anisotropic for Ti, O and C ($CCMe_3$) atoms, isotropic for C(Cp)). Cell parameters: a 11.343(3) Å, b 9.646(2) Å, c 12.619(2) Å, space group *Pnam*, $V = 1380.7(1)$ Å^3, $R_1 = 0.051$, $R_w = 0.054$.

The IR spectra were recorded on a UR-20 instrument as KBr pellets or in Nujol protected against oxygen and atmospheric moisture.

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