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SYNTHESIS AND MOLECULAR STRUCTURE OF NIOBOCENE TRIMETHYLACETATE AND ITS π -COMPLEX WITH DIPHENYLACETYLENE

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Summary

Niobocene trimethylacetate $\text{Cp}_2\text{Nb}(\text{OCCMe}_3)$ (I) does not react with usual n -donors (pyridine and triphenylphosphine), but readily adds a π -acceptor molecule of diphenylacetylene (tolane) in benzene to form $\text{Cp}_2\text{Nb}(\text{OCCMe}_3)(\pi\text{-Ph}_2\text{C}_2) \cdot 0.5 \text{C}_6\text{H}_6$ (II). The structures of the diamagnetic complexes I and II have been determined by an X-ray diffraction study. These molecules represent wedge-like sandwiches with dihedral angles between cyclopentadienyl ligands equal to 44.4 and 50.7°, and average Nb—C distances of 2.39 and 2.44 Å, respectively. The bisector plane of I contains the chelate trimethylacetate group (Nb—O bond lengths 2.23 and 2.24 Å) and that of II contains the coordinated tolane molecule and the oxygen atom of the terminal trimethylacetate ligand (Nb—O 2.16, Nb—C 2.18 and 2.19, C—C 1.29 Å, Ph—C≡C angles 141 and 146°). An unusually large splitting of OCO stretching frequencies is observed in the IR spectrum of I (1652–1305 = 347 cm^{-1}). Structural characteristics of the coordinated C≡C triple bond in II are similar to those found in $\text{Cp}(\pi\text{-Ph}_4\text{C}_4)\text{Nb}(\text{CO})(\pi\text{-Ph}_2\text{C}_2)$ studied earlier. The role played by the Nb^{III} lone pair in I and II is discussed.

Introduction

We have recently reported [1] the isolation of monomeric niobocene trimethylacetate (I) via reaction 1.



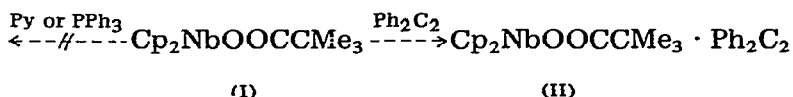
The IR spectrum of I indicates terminal rather than chelate coordination of

the carboxylate group (the difference of asymmetric and symmetric OCO stretching frequencies is $1652-1305 = 347 \text{ cm}^{-1}$ [1]). This feature appeared to be unusual since carboxylate groups act as chelate ligands in similar titanium complexes Cp_2TiOOCR [2] including the case where $\text{R} = \text{CMe}_3$ ($\Delta\nu(\text{OCO}) = 1540-1430 = 110 \text{ cm}^{-1}$) [3]. Therefore it seemed of interest to study the reactivity of I towards typical n - and π -donors.

Results

$\text{Cp}_2\text{Nb}(\text{OCCMe}_3)$ (I) is shown to be unaltered after refluxing in benzene in the presence of pyridine or triphenylphosphine. However, I readily adds one diphenylacetylene (tolane) molecule under the same conditions (Scheme 1).

SCHEME 1



The tolane π -complex of niobocene trimethylacetate (II) is formed as yellow-green elongated prisms, m.p. $196-197^\circ \text{C}$. This complex decomposes slowly in air in the solid state but undergoes rapid oxidation in solution. The compound is soluble in benzene, THF, CHCl_3 and insoluble in heptane. The IR spectrum shows the OCCMe_3 group to be terminal ($\nu_s(\text{OCO}) = 1330 \text{ cm}^{-1}$, $\nu(\text{OCO}) = 1618 \text{ cm}^{-1}$, $\Delta\nu = 288 \text{ cm}^{-1}$) [4], although the value is smaller than as for the initial I. The tolane $\text{C}\equiv\text{C}$ triple bond gives rise to the IR band at 1800 cm^{-1} which is typical for two electron donor non-bridging π -coordination of alkynes in wedge-like sandwiches, e.g. 1775 cm^{-1} in $(\text{MeC}_5\text{H}_4)_2\text{TaH}(\pi\text{-Pr}_2\text{C}_2)$ [5], 1780 cm^{-1} in $\text{Cp}(\pi\text{-Ph}_4\text{C}_4)\text{Nb}(\text{CO})(\text{Ph}_2\text{C}_2)$ [6], $1750-1825 \text{ cm}^{-1}$ in paramagnetic complexes $\text{Cp}_2\text{V}(\text{R}_2\text{C}_2)$ [7]. The mass spectrum of II has no peak of the mole-

(continued on p. 43)

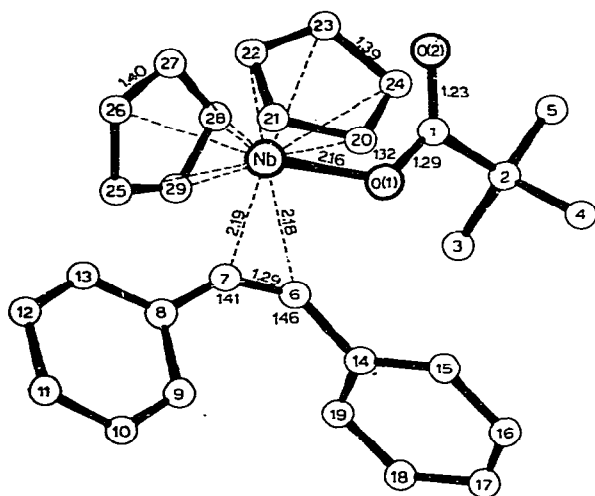


Fig. 1. The molecular structure of II with main bond lengths and angles.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTOR PARAMETERS σ^2 IN STRUCTURE II

X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Nb	1495(1)	507(1)	1865(1)	33.2(3)	43.2(4)	-4.9(2)	-11.8(3)	-6.6(2)
O(1)	440(6)	-1341(4)	44(3)	32(2)	36(3)	-11(2)	-11(2)	-4(2)
O(2)	-222(9)	-1560(6)	124(5)	60(4)	54(4)	-43(3)	-49(4)	7(3)
C(1)	-219(10)	-1947(8)	47(4)	43(5)	44(5)	-2(4)	-26(4)	-11(4)
C(2)	-990(10)	-3192(7)	56(5)	33(4)	47(5)	-24(4)	-16(4)	1(4)
C(3)	-2203(12)	-2909(9)	69(6)	62(6)	59(6)	-19(5)	-12(5)	-8(5)
C(4)	464(11)	-4166(7)	2538(6)	34(4)	63(6)	5(4)	-18(5)	10(4)
C(6)	-1915(13)	-3668(8)	1700(6)	57(5)	68(6)	-53(5)	-39(6)	2(5)
C(6)	1958(9)	-296(7)	3157(5)	39(4)	35(4)	-2(3)	-8(3)	-15(4)
C(7)	2654(9)	826(7)	2920(5)	34(4)	31(4)	-7(3)	-10(3)	-6(3)
C(8)	3468(10)	1666(7)	3214(5)	37(4)	37(4)	-11(3)	-9(4)	-10(4)
C(9)	4167(13)	1191(8)	3966(6)	52(5)	58(6)	-16(5)	-44(5)	-8(4)
C(10)	5072(14)	1965(10)	4248(6)	58(6)	71(7)	-19(6)	-57(6)	-9(5)
C(11)	5292(12)	3241(9)	3793(7)	61(6)	70(7)	12(5)	-29(5)	-20(5)
C(12)	4614(12)	3733(8)	3062(6)	56(5)	68(6)	-21(4)	-32(5)	-16(5)
C(13)	3689(11)	2930(8)	2777(5)	40(4)	52(5)	-15(4)	-15(4)	-11(4)
C(14)	1692(11)	-1469(7)	3844(5)	36(4)	31(4)	-18(4)	-16(4)	-6(4)
C(15)	2832(12)	-2561(9)	3827(6)	49(5)	43(5)	6(5)	-14(5)	4(4)
C(16)	2576(16)	-3692(10)	4447(7)	54(6)	51(6)	-7(6)	-27(6)	3(5)
C(17)	1235(18)	-3739(11)	5077(8)	65(7)	55(7)	-36(7)	-33(7)	-2(6)
C(18)	84(16)	-2688(14)	5102(7)	118(10)	38(6)	-29(8)	11(6)	0(7)
C(19)	313(13)	-1512(10)	4488(6)	82(7)	42(6)	-4(5)	23(5)	0(5)
C(20)	4377(11)	-404(11)	1481(6)	77(7)	30(5)	9(5)	11(4)	-3(5)
C(21)	4377(10)	953(10)	1243(6)	72(6)	56(6)	-11(4)	12(4)	-22(5)
C(22)	3425(11)	1396(9)	599(7)	62(6)	59(6)	-8(4)	8(4)	-3(5)
C(23)	2809(11)	336(13)	436(6)	107(8)	34(5)	-10(5)	-4(4)	-26(5)
C(24)	3414(13)	-782(9)	977(7)	55(6)	59(6)	-18(5)	26(5)	-30(5)
C(25)	-337(13)	2297(10)	2323(8)	48(6)	79(8)	29(5)	-18(5)	-20(5)
C(26)	225(12)	2712(8)	1467(9)	32(5)	95(8)	16(4)	-31(5)	-10(5)
C(27)	-416(15)	1977(13)	1022(7)	72(7)	82(8)	40(5)	-33(6)	-14(6)
C(28)	-1378(13)	1107(11)	1609(12)	59(7)	157(13)	26(5)	-51(7)	-40(8)
C(29)	-1356(13)	1253(11)	2465(9)	52(6)	105(9)	21(4)	-3(6)	-4(6)
C(30)	3607(11)	5879(8)	10170(7)	41(5)	61(6)	-11(4)	-20(5)	-8(4)
C(31)	4669(13)	5332(9)	10757(6)	46(5)	61(6)	-9(4)	-20(5)	-10(4)
C(32)	3954(12)	5463(9)	9404(6)	41(5)	68(6)	-11(4)	-23(5)	-5(4)

$$\sigma^2 = \exp[-1/40(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)].$$

TABLE 2
BOND LENGTHS d (Å) AND BOND ANGLES ω ($^\circ$) IN STRUCTURE II

Bond	d	Bond	d	Angle	ω	Angle	ω
Nb—O(1)	2.16(1)	C(9)—C(10)	1.38(2)	O(1)NbCp(1) ^a	105.2(1)	C(11)C(12)C(13)	118.7(9)
Nb—C(6)	2.18(1)	C(10)—C(11)	1.41(1)	O(1)NbCp(2)	103.8(1)	C(12)C(13)C(8)	121.5(8)
Nb—C(7)	2.19(1)	C(11)—C(12)	1.38(1)	O(1)NbC(ac) ^b	93.9(1)	C(13)C(8)C(9)	118.5(8)
Nb—C(20)	2.44(1)	C(12)—C(13)	1.42(1)	Cp(1)NbCp(2)	129.8(0)	C(13)C(8)C(7)	122.1(7)
Nb—C(21)	2.42(1)	C(13)—C(8)	1.38(1)	Cp(1)NbC(ac)	107.9(0)	C(6)C(14)C(15)	119.3(8)
Nb—C(22)	2.42(1)	C(14)—C(15)	1.40(1)	Cp(2)NbC(ac)	110.0(0)	C(14)C(15)C(16)	120.5(9)
Nb—C(23)	2.42(1)	C(15)—C(17)	1.38(1)	NbO(1)C(1)	132.1(1)	C(15)C(16)C(17)	120.2(11)
Nb—C(24)	2.45(1)	C(16)—C(17)	1.35(2)	O(1)C(1)C(2)	122.6(8)	C(16)C(17)C(18)	120.5(12)
Nb—C(25)	2.44(1)	C(17)—C(18)	1.37(2)	O(1)C(1)C(2)	115.7(7)	C(17)C(18)C(19)	120.9(12)
Nb—C(26)	2.44(1)	C(18)—C(19)	1.42(2)	O(2)C(1)C(2)	121.7(8)	C(18)C(19)C(14)	118.3(10)
Nb—C(27)	2.44(1)	C(19)—C(14)	1.38(1)	C(1)C(2)C(3)	108.8(7)	C(19)C(14)C(6)	121.1(8)
Nb—C(28)	2.42(1)	C(20)—C(21)	1.41(2)	C(1)C(2)C(4)	107.1(7)	C(20)C(21)C(22)	108.0(9)
Nb—C(29)	2.45(1)	C(21)—C(22)	1.38(1)	C(1)C(2)C(6)	108.6(7)	C(21)C(22)C(23)	108.4(9)
C(1)—O(1)	1.29(1)	C(22)—C(23)	1.40(2)	C(3)C(2)C(4)	110.6(7)	C(22)C(23)C(24)	108.0(9)
C(1)—O(2)	1.23(1)	C(23)—C(24)	1.39(2)	C(3)C(2)C(5)	110.1(7)	C(23)C(24)C(20)	108.0(9)
C(1)—C(2)	1.53(1)	C(24)—C(20)	1.39(2)	C(4)C(2)C(6)	111.5(7)	C(24)C(20)C(21)	107.7(9)
C(2)—C(3)	1.51(1)	C(25)—C(26)	1.37(2)	C(6)C(7)C(8)	141.2(7)	C(25)C(26)C(27)	109.2(11)
C(2)—C(4)	1.53(1)	C(26)—C(27)	1.39(2)	C(7)C(6)C(14)	146.4(8)	C(26)C(27)C(28)	107.3(11)
C(2)—C(5)	1.51(1)	C(27)—C(28)	1.37(2)	C(7)C(8)C(9)	119.5(7)	C(27)C(28)C(29)	110.4(11)
C(6)—C(7)	1.29(1)	C(28)—C(29)	1.46(2)	C(8)C(9)C(10)	120.5(9)	C(28)C(29)C(25)	103.1(11)
C(6)—C(14)	1.48(1)	C(29)—C(25)	1.42(2)	C(10)C(11)C(12)	120.7(10)	C(29)C(25)C(26)	110.1(10)
C(7)—C(8)	1.45(1)	C(30)—C(31)	1.38(1)	C(9)C(10)C(11)	120.1(10)	C(30)C(26)C(32)	120.0(9)
C(8)—C(9)	1.41(1)	C(30)—C(32)	1.40(1)				

^a Cp centre of the cyclopentadienyl ring. ^b C(ac) centre of the triple bond C(6)—C(7).

cular ion but contains the ions $\text{Cp}_2\text{NbOCCMe}_3^+$ (m/e 324) and Ph_2C_2 (m/e 178) and products of their fragmentation, i.e. the main fragmentation path involves a cleavage of the niobium–tolane π -bond. The ^1H NMR spectrum of II (δ (ppm), in THF) contains sharp proton singlets due to CH_3 (0.91) and C_5H_5 (6.03) and a multiplet due to C_6H_5 (7.5) with intensity ratio of 9/10/10.

To determine the structures of I and II unequivocally we carried out their single crystal X-ray study. The results obtained for II (Fig. 1) were consistent with the structure proposed on the basis of the other physical methods. Atomic coordinates and temperature factors are given in Table 1, bond lengths and angles in Table 2. The molecule II represents a wedge-like sandwich with the dihedral angle between two cyclopentadienyl ring planes equal to 50.7° . The carboxylate group is a terminal ligand, and the Nb, O(1) and coordinated triple bond carbon atoms (the $\text{C}=\text{C}$ bond length 1.29 Å) lie in the bisector plane. The dihedral angle between phenyl ring planes of the coordinated tolane molecule is 89.5° . The Nb–C(6) and Nb–C(7) distances are practically identical (2.18 and 2.19 Å, respectively). On the whole the molecule is not sterically strained, although the angles at the acetylenic carbon atoms are somewhat different ($\text{C}(8)\text{—C}(7)\text{—C}(6)$ 141° , $\text{C}(7)\text{—C}(6)\text{—C}(14)$ 146°) probably due to short non-bonded distances $\text{C}(6)\cdots\text{O}(1)$ 2.62 Å, and $\text{C}(7)\cdots\text{C}(25)$ 2.85 Å (there are no such short contacts between carbon atoms of phenyl rings and cyclopentadienyl ligands or t-butyl group). Crystals of II contain one benzene solvent molecule per two molecules of the complex.

TABLE 3

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS IN STRUCTURE I

Atom	x	y	z	$B_{\text{iso}} \times 10$ (Å ²)
Nb	1998(1)	1245(1)	1/4	b
O(1)	2364(7)	−975(8)	1/4	26(2)
O(2)	3833(7)	428(8)	1/4	27(2)
C(1)	3454(10)	−798(12)	1/4	25(2)
C(2)	4350(11)	−1952(13)	1/4	28(2)
C(3)	4969(19)	−2002(21)	1469(17)	27(4)
C(4)	3684(13)	−3321(15)	2717(13)	31(4)
C(5)	5229(19)	−1681(21)	3434(18)	29(5)
C(6)	585(12)	1245(18)	1143(11)	27(3)
C(7)	864(13)	2647(16)	1395(11)	24(3)
C(8)	2112(13)	2930(13)	1140(10)	28(2)
C(9)	2603(11)	1703(17)	697(10)	30(3)
C(10)	1670(12)	653(11)	693(9)	24(2)
C(11)	2223(26)	1099(32)	640(20)	7(4)
C(12)	925(36)	963(35)	955(28)	17(7)
C(13)	690(36)	1993(50)	1237(31)	29(8)
C(14)	1310(39)	2835(38)	1274(32)	28(8)
C(15)	2417(31)	2424(43)	902(28)	20(6)

^a The Cp ligand has two orientations $\text{C}(6)\cdots\text{C}(10)$ (occupancy ~ 0.75) and $\text{C}(11)\cdots\text{C}(15)$ (occupancy ~ 0.25).

^b The t-butyl group $\text{C}(2)\cdots\text{C}(5)$ has also the second orientation related by the mirror plane. Parameters of the anisotropic temperature factor (see Table 1) are:

B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
22.4(4)	25.1(4)	24.2(4)	1.2(5)	0	0

TABLE 4
BOND LENGTHS d (Å) AND BOND ANGLES ω ($^\circ$) IN STRUCTURE I ^a

Bond	d	Angle	ω
Nb—O(1)	2.23(1)	CpNbCp ^b	136(1)
Nb—O(2)	2.24(1)	O(1)NbO(2)	58(1)
Nb—C(1)	2.61(1)	NbO(1)C(1)	93(1)
Nb—C(6)	2.36(1)	NbO(2)C(1)	91(1)
Nb—C(7)	2.35(2)	O(1)C(1)O(2)	118(1)
Nb—C(8)	2.39(1)	O(1)C(1)C(2)	124(1)
Nb—C(9)	2.43(1)	O(2)C(1)C(2)	118(1)
Nb—C(10)	2.40(1)	C(1)C(2)C(3)	110(1)
O(1)—C(1)	1.25(1)	C(1)C(2)C(4)	108(1)
O(2)—C(1)	1.28(1)	C(1)C(2)C(5)	107(1)
C(2)—C(1)	1.53(2)	C(3)C(2)C(4)	111(1)
C(2)—C(3)	1.49(2)	C(3)C(2)C(5)	112(1)
C(2)—C(4)	1.57(2)	C(4)C(2)C(5)	109(1)
C(2)—C(5)	1.58(2)	C(7)C(6)C(10)	106(1)
C(6)—C(7)	1.45(2)	C(6)C(7)C(8)	110(1)
C(7)—C(8)	1.48(2)	C(7)C(8)C(9)	107(1)
C(8)—C(9)	1.45(2)	C(8)C(9)C(10)	108(1)
C(9)—C(10)	1.48(2)	C(6)C(10)C(9)	109(1)
C(10)—C(6)	1.48(2)		

^a For the Cp ligand, values given refer to the position C(6)···C(10) with the greater (~0.75) occupancy.

^b Cp centre of the cyclopentadienyl ring.

Atomic coordinates and temperature factors in the crystal structure of I are given in Table 3, bond lengths and angles in Table 4. The molecule occupies a special position in the mirror plane and is statistically disordered*.

The results of the X-ray study were quite unexpected (Fig. 2). The molecule is also a wedge-like sandwich but contains a chelate carboxylate group, OOCMe₃, rather than the terminal one as was supposed previously [I] on the basis of its IR spectrum. The dihedral angle between the average C₅H₅ ligand planes is equal to 44.4°, the average Nb—C(C₅H₅) and C—C(C₅H₅) bond lengths are 2.39 and 1.47 Å, respectively, the cyclopentadienyl ligands being in an eclipsed conformation with respect to each other. The planar four-membered chelate cycle NbOCO is situated in the crystallographic mirror plane, the Nb—O bond lengths of 2.23 and 2.24 Å are greater than the Nb—O distance to the terminal OOCMe₃ group in II (2.16 Å). Although the Nb—C(1) bond of 2.61 Å is considerably longer than the longest Nb—C(C₅H₅) distance of 2.45 Å, it is rather close to the 2.53 Å length of the Nb—C(μ -CO) bond which doubtlessly exists in the binuclear complex Cp₂Nb(μ -CO)(σ , π -CO)Mo(CO)Cp, studied by us recently [8].

* The cyclopentadienyl ring has two orientations C(6)···C(10) and C(11)···C(15) with occupancy factors of ca. 0.75 and 0.25 respectively. These two positions are rotated with respect to each other by 26° around the ring 5-fold axis. The t-butyl group also has two orientations related by the mirror plane and differing by rotation around the C—CMe₃ bond by ca. 16° and naturally having equal occupancies.

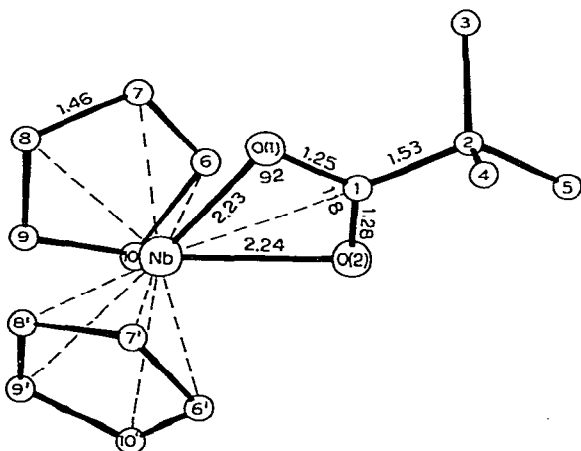


Fig. 2. The molecular structure of I with main geometrical parameters. Only one statistical position of Cp and t-butyl ligands is shown.

Discussion

The results of the present study reveal a close relationship between structures and reactivities of compounds I and II. In particular, the chelate type trimethylacetate group coordination in I results in a rare gas electronic configuration for the Nb atom, which explains the inertness of I towards strong n -donors. On the other hand, the presence of a lone pair on the Nb^{III} ion (d^2 -configuration) makes possible a reaction of I with such ligands as tolane, having a strong π -acceptor ability.

A similar tendency of addition of only those ligands which are strong π -acceptors was earlier observed for Cp_2V (coordination with CO, CS_2 , dipyriddy, diethyl-maleate and -fumarate, inertness towards pyridine, phosphines and olefins containing no strong electron acceptor groups [9]) and for Cp_2VX ($\text{X} = \text{I}$, R, or SR) [10] and Cp_2NbCl [11] which both readily add CO. This tendency was discussed recently [12,13].

The existence of the niobium—tolane π -interaction in II seemed to follow from the similarity of the geometrical and IR spectral parameters of a tolane molecule in II and in the wedge-like sandwich complex $\text{Cp}(\pi\text{-Ph}_4\text{C}_4)\text{Nb}(\text{CO})(\pi\text{-Ph}_2\text{C}_2)$, studied by us earlier [14–16] (Table 5). In fact, we explained the decrease in the $\text{Ph-C}\equiv\text{C}$ angles from 180 to 140° on coordination of a tolane molecule to Nb [17,18] by an electron density shift to the triple bond anti-bonding orbitals, i.e. by a contribution from a dative $\text{M} \rightarrow \text{R}_2\text{C}_2$ bond, by analogy with calculations by Blizzard and Santry [19]. The decrease in angle is responsible for the lowering of the $\nu(\text{C}\equiv\text{C})$ frequency to $1700\text{--}1800\text{ cm}^{-1}$ [20]. On the other hand, a decrease of electron density on the $\text{C}\equiv\text{C}$ bonding orbitals (i.e. a strengthening of $\text{R}_2\text{C}_2 \rightarrow \text{M}$ donor-acceptor interaction) would weakly affect the alkyne geometry, only slightly elongating the $\text{C}\equiv\text{C}$ bond [19] (from 1.26 to 1.29 Å on going from Nb^{I} to Nb^{III} complex in the present case).

Low sensitivity of I to air oxidation in the solid state distinguishes it from $\text{Cp}_2\text{Nb}(\text{OCCMe}_3)_2$ [1], and particularly $\text{Cp}_2\text{Ti}(\text{OCCMe}_3)$ [3]. Another inter-

TABLE 5
COMPARISON OF STRUCTURAL PARAMETERS OF NIOBIUM WEDGE-LIKE SANDWICHES

Parameter	Cp ₂ Nb(OOCCMe ₃)(π-Ph ₂ C ₂)	Cp(π-Ph ₄ C ₄)Nb(CO)(π-Ph ₂ C ₂)
ν(C≡C) (cm ⁻¹)	1800	1780
C≡C (Å)	1.29	1.26
Ph-C≡C (°)	143.5 (av.)	142 (av.)
Nb-C(Ph ₂ C ₂) (Å)	2.18, 2.19	2.20, 2.24
Nb-X (Å)	2.16 (X = OOCCMe ₃)	2.06 (X = CO)
τ ^a (°)	50.7	51.0
Nb-C ^b (Å)	2.44	2.42 (Cp) 2.38 (Ph ₄ C ₄)

^a Dihedral angle between two cyclic ligands. ^b Distances to carbons of cyclic ligands.

esting feature of the solid I is an inexplicably large difference between asymmetric and symmetric OCO stretching frequencies ($\Delta\nu$ 347 cm⁻¹) when compared with an analogous compound Cp₂Ti(OOCCMe₃) ($\Delta\nu$ 110 cm⁻¹). It seems that one cannot exclude the possibility of an interaction of the Nb lone pair with vacant orbitals of the carboxylate group C(1) atom at the distance of 2.61 Å, by analogy with the Nb-C (μ -CO) interaction at a distance of 2.53 Å in the aforementioned complex Cp₂Nb(μ -CO)(σ , π -CO)Mo(CO)Cp [8]. However, the possibility of such interactions and of their effect on OCO stretching frequencies needs further detailed consideration.

Experimental

All operations were carried out under pure argon in absolute solvents saturated with argon. Cp₂Nb(OOCCMe₃) was prepared according to the literature method [1]. The IR spectra were recorded in KBr pellets with an UR-20 instrument (400 to 3500 cm⁻¹). The ¹H NMR spectrum was obtained with a Perkin-Elmer instrument (60 MHz), the mass spectrum with an AEI MS 30 instrument equipped with a DS-50 data processing system. The direct inlet temperature was 100°C and the ionisation electron energy 70 eV.

The X-ray data were collected with a Syntex P2₁ automatic diffractometer (λ (Mo-K α), $\theta/2\theta$ scan). 1068 reflections with $F^2 \geq 2\sigma$ were measured for Cp₂-NbOOCCMe₃.

The structure was solved by the heavy atom method and refined by the least squares procedure in isotropic approximation for all atoms except niobium (anisotropic) to R 0.05, R_w 0.06. Crystals are orthorhombic, a 11.383(2), b 9.816(2), c 12.708(2) Å, Z = 4, D_c 1.69, D_m 1.65 g cm⁻³, space group $Pnam$. For CpNb(OOCCMe₃)(π-Ph₂C₂) · 0.5 C₆H₆, 3681 reflections with $F^2 > 2\sigma$ were measured. The heavy atom method was applied. The structure was refined by the least squares method in the full matrix anisotropic approximation to R 0.065 and R_w 0.053. Crystals are triclinic, a 8.104(3), b 10.695(3), c 16.422(4) Å, α 76.15(2), β 78.99(2), γ 82.71(2)°, Z = 2, D_c 1.20, D_m 1.19 g cm⁻³, space group PI .

Preparation of Cp₂NbOOCCMe₃(π-Ph₂C₂) · 0.5 C₆H₆

A solution of toluene (0.49 g, 2.78 mmol) in 10 ml of benzene was added to a

brown solution of $\text{Cp}_2\text{NbOCCMe}_3$ (0.90 g, 2.78 mmol) in 30 ml of benzene. after refluxing for 1 h, 15 ml of heptane was added to the mixture, the solution was evaporated to half its volume under vacuum and cooled to 0°C . Yellow-green crystals which precipitated were separated by decantation, washed with benzene/heptane 1/4 and dried under a high vacuum at 20°C . Yield 0.66 g (47%), m.p. $196\text{--}197^\circ\text{C}$ (dec.). (Found: C, 70.63; H, 5.78; Nb, 16.84. $\text{C}_{32}\text{H}_{32}\text{NbO}_2$ calcd.: C, 70.96; H, 5.96; Nb, 17.15%.)

IR spectrum (cm^{-1}): 400 m, 427 w, 565 m, 585 m, 612 m, 636 s, 695 s, 765 s, 788 m, 813 s, 833 m, 850 m, 1012 w, 1026 w, 1070 w, 1219 s, 1260 w, 1330 s, 1360 w, 1392 m, 1443 m, 1480 s, 1578 s, 1598 s, 1618 s, 1800 m, 2870 m, 2900 m, 2925 m, 2950 m, 3090 m.

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