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VIII *. TETRAETHYLAMMONIUM TRICARBONYL-η^5-CYCLOPENTADIENYLTRIPHENYLSTANNYL-NIOBATE(I) $[(C_2H_5)_4N][Nb(\eta^5\text{-}C_5H_5)\{Sn(C_6H_5)_3\}(CO)_3]$

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Summary

The crystal and molecular structure of $[(C_2H_5)_4N][Nb(\eta^5\text{-}C_5H_5)\{Sn(C_6H_5)_3\}(CO)_3]$ have been determined. The compound crystallizes in the space group $P2_1/n$ with a 1383.3(9), b 1520.6(18), c 1791.8(14) pm, and β 97.89(6)°. The Nb–Sn bond length is 282.0(2) pm. The three CO groups and tin span a tetragonal plane parallel to the cyclopentadienyl ring. The Sn atom is in a greatly distorted tetrahedral environment: the angles at Sn are 116.8 (Nb–Sn–Ph) and 101.3° (Ph–Sn–Ph). The compound crystallizes with occluded solvent. Structure parameters are compared with those of other phenyltin derivatives of carbonyl transition metal complexes, and discussed in the context of the consistently high transition metal shielding observed for complexes containing a tin ligand.

Introduction and general

There is increasing interest in structural data on transition metal complexes having at the coordination center metal atoms which are readily accessible to NMR spectroscopic investigations. Niobium (^{93}Nb) is such a nucleus [1], and we have recently shown that, in the series $[Nb(Cp)ER_3(CO)_3]^-$ (Cp = η^5-C_5H_5; E = Ge, Sn, Pb), the tin compound shows the largest niobium shielding [2]. ^{93}Nb is not unique in this respect; corresponding observations have been made for the tin derivatives of complexes of ^{51}V ($[V(Cp)EPh_3(CO)_3]^-$ and $[V(ER_3)(CO)_5]^{2-}$ [3]), ^{55}Mn ($[Mn(ER_3)(CO)_5]$ [4]) and ^{59}Co ($[Co(ER_3)(CO)_4]$ [5]). Unusual bond angles and bond distances, such as those in strained ring systems or in the presence of bulky ligands, lead to extreme conditions for the electronic interactions between the metal and its

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* For Part VII see ref. 29.

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ligand system, and are therefore quite often responsible for extreme values of the shielding of the metal nucleus [6,7].

The structural data which we present here may contribute to a deeper understanding of the rather effective shielding of transition metal nuclei bonded to the triorganyltin group, provided, of course, that the solution structure is closely related to the solid state structure. In our case, this precondition is probably fullfilled: the square-pyramidal arrangement of the $\{Nb(SnPh_3)(CO)_3\}$ moiety found in the crystalline state (vide infra) is, according to theoretical considerations on $[M(Cp)L(CO)_3]$ complexes carried out by Hoffmann and co-workers [8], also preferred in solution. The fact that there are only two $\nu(CO)$ absorptions (1897 and 1790 cm^{-1}) despite the local C_s symmetry is not neccessarily in conflict with the assumption of a tetragonal arrangement, since the low-frequency band (centered at 1790 cm^{-1}) is rather broad and may hide a third absorption. There are many examples in the family of $[M(Cp)(CO)_3L]$ complexes of the accidental degeneracy of the two low-frequency bands; examples are $[W(Cp)H(CO)_3]$ [9] and $[V(Cp)(SnPh_3)(CO)_3]^-$ [10]. On the other hand, strong arguments have been put forward for a trigonal geometry (C_{3v} symmetry) for $[V(Cp)H(CO)_3]^-$ in solution [11].

Experimental

The title compound was prepared as described previously [2] from $Na[Nb(Cp)H(CO)_3]$, $[Ph_3Sn]Cl$ and $[Et_4N]Cl$ in acetonitrile, the work-up including washings with water and recrystallization from THF/heptane. Single crystals were grown from THF/heptane (ca. 1/5) solution at −20°C. The crystals were superficially dried (1 Torr) and manipulated under argon. The crystals thus obtained contain occluded solvent which is essential for maintainance of the crystal structure; crystals dried under high vacuum became crystallographically amorphous.

The structure determination was carried out on a Syntex $P2_1$ diffractometer (graphite monochromator, Mo-K_α), following the $\theta/2\theta$ scan method, where $2\theta(max) = 48°$. A total of 5905 reflexions was collected of which 4189 were significant ($F_o > 3\sigma(F_o)$). All non-hydrogen atoms are anisotropic. H atoms were placed in calculated positions. Three solvent atom sites were located; the site occupancy factors are 80% (O(101) and O(102)) and 40% (O(103)). Calculations were carried out with the program system SHELX 76 [12] and MULTAN 80 [13]. The SCHAKAL program [14] was used for the drawing (Fig. 1).

Description of the structure and discussion

The compound crystallizes in the monoclinic space group $P2_1/n$. Crystal data are: a 1383.3(9), b 1520.6(18), c 1791.8(14) pm; β 97.89(6)°. $[(C_2H_5)_4N][Nb(C_5H_5)Sn(C_6H_5)_3(CO)_3]$, $C_{34}H_{40}NNbO_3Sn$; $M = 722.3$ (solvent molecules omitted). $Z = 4$; V 3733.3 10^6 pm^3; D_c 1.28 g cm^{-3}. μ 9.13 cm^{-1}.

Selected bond distances, bond angles and data on molecular planes are given in Table 1, fractional coordinates and equivalenced temperature factors in Table 2 *. Figure 1 is a perspective drawing of the anion; the numbering scheme including the cation and the solvent molecules is depicted in Fig. 2.

The compound crystallizes with three disordered solvent atoms of different site occupancies (see Experimental), amounting to a statistical number of two solvent

TABLE 1

SELECTED STRUCTURAL DATA FOR $[Et_4N][Nb(Cp)(SnPh_3)(CO)_3]\cdot$Solv.

Bond lengths (pm)			
Nb-Sn	282.0(2)	C(1)-O(1)	114.8(20)
Nb-C(1)	212.5(17)	C(2)-O(2)	113.7(17)
Nb-C(2)	209.3(14)	C(3)-O(3)	115.9(16)
Nb-C(3)	204.2(13)	C(11)-C(12)	136.6(23)
Nb-(C(11) to C(15))	av. 241.9	C(12)-C(13)	146.0(24)
Nb-plane 1	211.8	C(13)-C(14)	138.9(24)
Nb-plane 2	119.3	C(14)-C(15)	126.2(23)
Sn-C(21)	217.8(12)	C(15)-C(11)	137.9(25)
Sn-C(31)	218.2(10)	phenyl (C-C)	av. 138.9
Sn-C(41)	217.6(11)		
N-C(51)	151.2(16)	ethyl (C-C)	av. 154.7
N-C(53)	151.4(17)	O(101)-O(102)	286.3
N-C(55)	150.4(17)		
N-C(57)	153.4(17)		

Bond angles (°)		Best planes (deviations in pm)
C(1)-Nb-C(2)	78.1(5)	plane 1:
C(2)-Nb-C(3)	73.2(5)	C(11) C(12) C(13) C(14) C(15)
C(3)-Nb-Sn	69.2(3)	(0.21 −0.15 0.04 0.10 −0.20)
C(1)-Nb-Sn	72.3(4)	plane 2:
Nb-Sn-C(21)	118.1(3)	C(1) C(2) C(3) Sn
Nb-Sn-C(31)	115.4(3)	(0.01 −0.02 0.01 −0.01)
Nb-Sn-C(41)	116.7(3)	plane 3: Nb-C(1)-C(2)
C(21)-Sn-C(31)	103.9(4)	plane 4: Nb-C(3)-Sn
C(21)-Sn-C(41)	100.2(5)	plane 5: Nb-Sn-C(21)
C(31)-Sn-C(41)	99.7(4)	plane 6: C(21)-C(31)-C(41)
O(1-3)-C(1-3)-Nb	av. 177.7	
		Angles between normals of planes
		1/2: 2.7 2/4: 141.2 5/6 90.7
		2/3: 47.0 3/4: 94.6

atoms. There are no contacts within bonding distances between these atoms and either the complex cation or anion. The disordering of the occluded solvent is the main factor responsible for the moderate accuracy of the structure analysis (R 8.0, R_w 6.9%).

There are no bonding interactions between the four molecules of the unit cell. The closest through-space intramolecular distances are those between the hydrogen atoms of the phenyl rings Ph(20) and Ph(30) and the carbonyl CO(1): d(H(22)–C(1)) 291, d(H(36)–C(1)) 283, d(H(36)–O(1)) 292 pm.

The $\{Nb(SnPh_3)(CO)_3\}$ moiety of the anion clearly has tetragonal geometry, with the niobium at the top of the pyramid and at 119.3 pm from the center of the almost ideal plane spanned by the four ligands (plane 2). The distance between the

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* A full table of bond lengths and angles and a list of structure factors are available from the authors.

TABLE 2

FRACTIONAL COORDINATES AND EQUIVALENCED ISOTROPIC TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	U_{eq}
Sn	0.31708(6)	0.17719(7)	0.06764(5)	0.0515(9)
Nb	0.37420(8)	0.32595(10)	−0.00956(7)	0.0633(14)
O(1)	0.3562(7)	0.3852(7)	0.1636(6)	0.102(4)
O(2)	0.2282(8)	0.4922(7)	−0.0342(6)	0.115(4)
O(3)	0.1661(7)	0.2581(7)	−0.0887(5)	0.097(4)
C(1)	0.3637(8)	0.3646(9)	0.1030(9)	0.086(4)
C(2)	0.2818(10)	0.4353(9)	−0.0259(8)	0.082(4)
C(3)	0.2415(10)	0.2808(9)	−0.0586(7)	0.071(4)
C(11)	0.4732(11)	0.2559(12)	−0.0932(10)	0.123(4)
C(12)	0.5253(11)	0.2505(10)	−0.0229(10)	0.116(4)
C(13)	0.5519(10)	0.3403(12)	0.0005(10)	0.129(4)
C(14)	0.5111(11)	0.3926(9)	−0.0593(10)	0.115(4)
C(15)	0.4674(12)	0.3443(11)	−0.1105(9)	0.128(4)
C(22)	0.1314(10)	0.2657(10)	0.1193(7)	0.083(4)
C(23)	0.0438(10)	0.2705(11)	0.1507(8)	0.104(4)
C(24)	0.0119(10)	0.1952(14)	0.1861(7)	0.119(4)
C(25)	0.0644(11)	0.1184(12)	0.1920(8)	0.109(4)
C(26)	0.1504(9)	0.1151(10)	0.1581(7)	0.079(4)
C(21)	0.1866(8)	0.1872(10)	0.1226(5)	0.065(4)
C(32)	0.4257(10)	0.0369(9)	0.1759(8)	0.085(4)
C(33)	0.4956(12)	0.0023(11)	0.2297(9)	0.116(4)
C(34)	0.5666(10)	0.0564(10)	0.2672(7)	0.090(4)
C(35)	0.5701(9)	0.1414(9)	0.2488(7)	0.075(4)
C(36)	0.5002(8)	0.1748(9)	0.1921(7)	0.067(4)
C(31)	0.4273(8)	0.1250(8)	0.1552(6)	0.050(4)
C(42)	0.1860(9)	0.0277(9)	−0.0210(7)	0.069(4)
C(43)	0.1654(10)	−0.0423(10)	−0.0674(8)	0.086(4)
C(44)	0.2409(13)	−0.0852(9)	−0.0966(8)	0.098(4)
C(45)	0.3396(11)	−0.0571(10)	−0.0751(9)	0.094(4)
C(46)	0.3553(10)	0.0146(10)	−0.0301(7)	0.075(4)
C(41)	0.2835(8)	0.0586(7)	0.0012(6)	0.053(4)
C(51)	0.3800(11)	0.1801(11)	0.4665(7)	0.116(4)
C(52)	0.4709(11)	0.1153(10)	0.4660(9)	0.141(4)
C(53)	0.3216(10)	0.1455(9)	0.3316(8)	0.105(4)
C(54)	0.2518(12)	0.0759(10)	0.3512(9)	0.128(4)
C(55)	0.2527(10)	0.2670(11)	0.4007(9)	0.125(4)
C(56)	0.2078(10)	0.3177(11)	0.3303(10)	0.142(4)
C(57)	0.4204(10)	0.2765(9)	0.3599(8)	0.103(4)
C(58)	0.4547(10)	0.3522(9)	0.4128(11)	0.148(4)
N	0.3440(7)	0.2178(6)	0.3896(5)	0.064(4)
O(101)	0.2795(5)	0.1692(6)	0.7181(5)	0.058(4)
O(102)	0.1032(6)	0.0753(6)	0.7308(5)	0.057(4)
O(103)	0.2214(13)	0.0993(11)	0.7734(10)	0.084(4)

Nb atom and the center of the capping Cp (plane 1) is 211.8 pm, which is comparable to that in [Nb(Cp)(CO)$_4$] [15]. There are no obvious anomalies in the {Nb(CO)$_3$} system; average bond lengths *d*(Nb–CO) are 208.1 pm (compare [Nb(Cp)(CO)$_4$] 209.6 [15] and [Nb(CO)$_6$]$^-$ 208.9 pm [16]). The cyclopentadienyl ring is practically parallel to plane 2. There is a significantly shorter *d*(C–C) for the

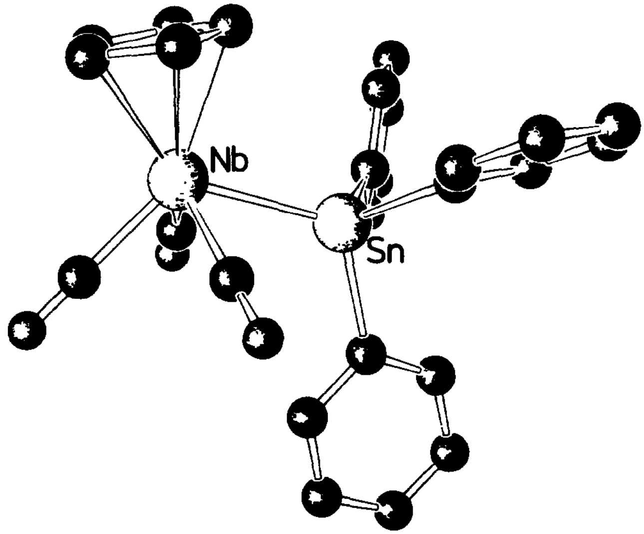

Fig. 1. SCHAKAL drawing for the anion $[Nb(\eta^5\text{-}C_5H_5)\{Sn(C_6H_5)_3\}(CO)_3]^-$; hydrogen atoms omitted for clarity. See Fig. 2 for the numbering of atoms.

ring carbons which are opposite (C(14) and C(15)) than for those which are adjacent (C(12) and C(13)) to Ph(40), the latter being greater than the former by 18 pm.

Probably the most interesting structural feature is the deviation of the angles at tin from tetrahedral values: the phenyl groups are bent towards the outer sphere, producing a mean carbon–tin–carbon angle of only 101.3°, while the niobium–tin–carbon angles are widened to 116.8° such behaviour has also been observed though with smaller deviations, with other phenyltin derivatives of transition metal carbonyls (Table 3), and is in contrast to that of triphenyltin chloride [17].

It has been shown by ^{119}Sn Mössbauer spectroscopy of various $R_3Sn\{M\}$ complexes that the carbonylmetal moiety $\{M\}$ gives rise to especially high $\sigma(s)$ character in the M–Sn bond [26], a view supported by ^{55}Mn NMR investigations on

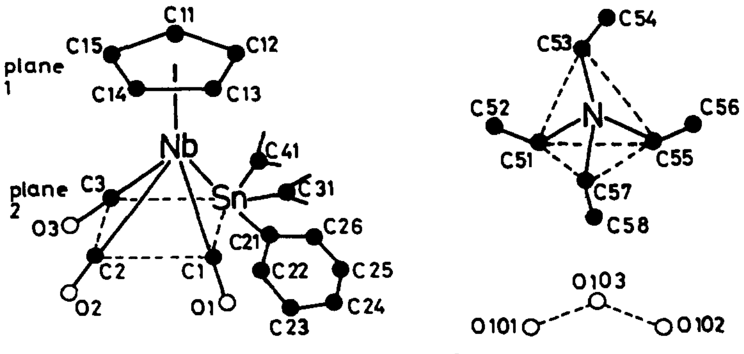

Fig. 2. Numbering scheme for $[(C_2H_5)_4N][Nb(\eta^5\text{-}C_5H_5)\{Sn(C_6H_5)_3\}(CO)_3]\cdot H_2O$. For the phenyl rings Ph(30) and Ph(40) only the carbon atoms directly attached to Sn are indicated. Dashed lines are non-bonding. Site occupancies for the occluded solvent molecule atoms are O(101)(100%)–O(103)(0%)–O(102)(100%)/O(101)(0%)–O(103)(100%)–O(102)(0%) = 2/1.

TABLE 3

SOME STRUCTURE DATA FOR SELECTED PHENYLTIN COMPLEXES [a]

Complex	Ref.	d(M–Sn)	∢(M–Sn–Ph) [b]	∢(Ph–Sn–Ph)
Ph_3SnCl	21		106.4	112.3
$[Ph_3SnNb(Cp)(CO)_3]^-$	[c]	282.0	116.8	101.3
$[Ph_3SnFe(Cp)(CO)_2]$	18	253.3, 254.0	113.5	105.3
$[Ph_2Sn\{Mo(Cp)(CO)_3\}_2]$	19	287	116	[d]
$[Ph_2Sn\{W(Cp)(CO)_3\}_2]$	19	281	121	[d]
$[Ph_3SnMn(CO)_5]$	20	267.2–267.8	112.7	106.0
$[Me_3SnMn(CO)_5]$	22	[d]	111.6	107.3
$[Ph_3SnMn(CO)_4PPh_3]$	23	262.7	114.3	104.7
$[Ph_2Sn\{Mn(CO)_5\}_2]$	24	270	117	100
$[Ph_2SnCo(CO)_4\{Mn(CO)_5\}]$	25	266 and 273	114	107.5
$[(Ph_3Sn)_2V(CO)_5]^-$	17	275.7, 278.5	115.7	102.6
$[Ph_3SnNb(Cp)_2CO]$	30	282.5	[d]	[d]

[a] Bond distances d in pm, bond angles in deg. Mean values if not indicated otherwise. [b] ∢(M–Sn–M) in the case of the Ph_2Sn complexes. [c] This work. [d] Not reported.

$R_3SnMn(CO)_5$ [4,27]. Although, as shown by the IR spectroscopic ν(CO) and ν(Sn–M) frequencies of $R_3Sn\{M\}$ complexes [28], M–Sn π-interaction also plays a significant role, the strong $\sigma(s)$ interaction must be the dominant factor responsible for the high shielding of the transition metal nucleus in transition metal tin compounds. This high shielding is only exceeded in the corresponding hydrido complexes, H{M} [3], where σ-type overlap is the only possible bonding interaction. Further, it has been demonstrated (again from consideration of the Mössbauer central isomer shifts) that the extent of distortion from tetrahedral geometry around tin is a measure of the differences of the s character of the Sn–L bonds (L = halogen, R, {M}) [26] and thus if, as in our cases (Table 3), R is always the phenyl group, is a measure of the contribution of {M} to the s character. This contribution is highest in our triphenyltinniobium compound which shows the greatest deviation from tetrahedral angles.

It should be noted, however, that in the niobium complex π-interaction will have a greater impact on the electronic situation governing the metal shielding than, e.g., in carbonylmanganese(I)-tin complexes. The fact that the phenyl groups on tin are bent away from the Nb–Sn fragment may thus also be a consequence of increased engagement of Sn-5$d(\pi)$ orbitals in Nb → Sn π-delocalization. Finally, the enlarged Nb–Sn–C angles may also reflect effects primarily steric in nature, such as mutual hindrance between the $\{Nb(Cp)(CO)_3\}$ and $\{SnPh_3\}$ moieties. Electronic factors as those discussed above are then secondary effects resulting from steric crowding.

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