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SYNTHESIS, MOLECULAR STRUCTURES AND PMR SPECTRA OF HETERONUCLEAR NIOBOCENE DERIVATIVES CONTAINING A NIOBIUM–TIN BOND

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Summary

Treatment of niobocene carbonylhydride, $Cp_2Nb(CO)H$ (I), with Ph_nSnCl_{4-n} and Et_2SnCl_2 in THF in the presence of Et_3N leads to the respective heteronuclear complexes $Cp_2Nb(CO)SnR_nCl_{3-n}$ (R = Ph, $n = 3 \div 1$ (II–IV), R = Et, $n = 2$ (V)). Treatment of II with HCl in ether gives $Cp_2Nb(CO)SnCl_3$ (VI). Complex VI and its analog $(MeC_5H_4)_2Nb(CO)SnCl_3$ (VIII) were prepared by an alternative synthesis using direct reaction of I or $(MeC_5H_4)_2Nb(CO)H$ with an equimolar quantity of $SnCl_4$ in THF in the presence of Et_3N. Complex VI is also generated by insertion of $SnCl_2$ into the Nb–Cl bond in $Cp_2Nb(CO)Cl$ (VII). X-Ray analysis of complexes II and VIII was performed: for II, space group $P2_1/n$, $a = 10.1021(21)$, $b = 17.4633(32)$, $c = 14.2473(29)$ Å, $\beta = 95.578(16)°$, $Z = 4$; for VIII, space group. $P2_1/n$, $a = 8.9369(15)$, $b = 13.3589(12)$, $c = 13.9292(20)$ Å, $\beta = 99.490(14)°$, $Z = 4$. The Nb–Sn bond in VIII (2.764(9) Å) is shorter than that in II (2.825(2) Å). In both cases the Nb–Sn bond is significantly shorter than the sum of Nb and Sn covalent radii (1.66 + 1.40 = 3.06 Å). It is probably partly multiple in character owing to an additional interaction of the lone electron pair of the Nb^{III} ion (d^2 configuration) with the antibonding Sn orbitals. The PMR spectra of II–VI exhibit two satellites of the singlet of C_5H_5 protons because of $H–Sn^{117}$ and $H–Sn^{119}$ spin-spin coupling (SSC). The SSC constant correlates with the number of electronegative chlorine atoms on the Sn atom.

Introduction

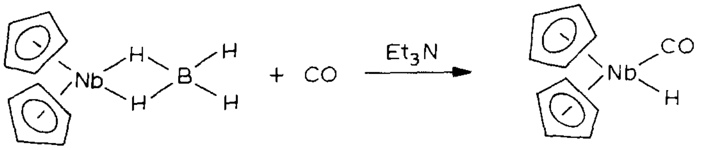
The study of complexes with heteronuclear metal–metal bonds is interesting from two viewpoints.A theoretical approach is directed to understanding coordination of metal-containing ligands compared to bonding of ligands containing the donor atoms traditional in coordination chemistry: O,N,S,P,C etc., [1]. A practical viewpoint is determined first by the specific catalytic action of the heterometallic complexes, owing to the possibility of separating functions between the metallic centers [2], and secondly by the wide use of organometallic compounds as sources of pure metals [3]. The latter fact is most important for the heterometallic complexes, since one may produce highly homogenous powders and films of otherwise hardly combinable metals. This method is particularly promising for obtaining superconducting Nb_3Sn materials [4] from compounds in which the niobium and tin atoms are combined via direct metal–metal bonds. However, here the synthesis of stable covalent Nb–Sn bonds is a problem in itself. Only in a recent patent has the preparation of $CpNb(CO)_3SnR_2$ complexes from the difficult to prepare $CpNb(CO)_3^{2-}$ anion ($Cp = \pi\text{-}C_5H_5$) been reported; no experimental data and characteristics of the complexes were presented [5]. Moreover, the synthesis of complex with a Nb–Sn bond from the also not readily available $Nb(CO)_5PPh_3^-$ anion has been described [6]:

$$\begin{tikzcd}
NbCl_5 + Na + CO \arrow[r, "200\text{ atm}", "\text{diglym}"'] & {[Na(diglym)_2]^+Nb(CO)_6^-} \arrow[d, "h\nu,\ PPh_3"] \\
Ph_3Sn\text{-}Nb(CO)_5PPh_3 & {[Na(diglym)_2]^+Nb(CO)_5PPh_3^-} \arrow[l, "Ph_3SnCl"', "THF"]
\end{tikzcd}$$

Although this complex could be identified readily its X-ray analysis has not yet been performed. Thus, it was interesting to synthesize the compounds with direct niobium–tin bonds and to study their properties.

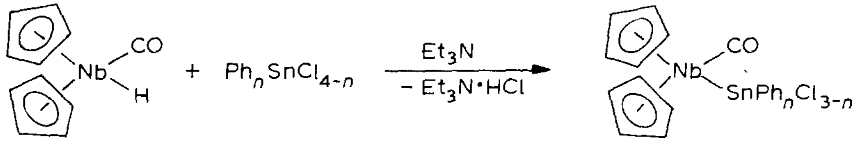
Results

The wedge-like sandwich borohydrideniobium complex Cp_2NbBH_4 [7] was chosen as a relatively readily available starting compound. Treatment with Et_3N under CO atmosphere results in evolution of BH_3 and formation of $Cp_2Nb(CO)H$ (I) [8]:



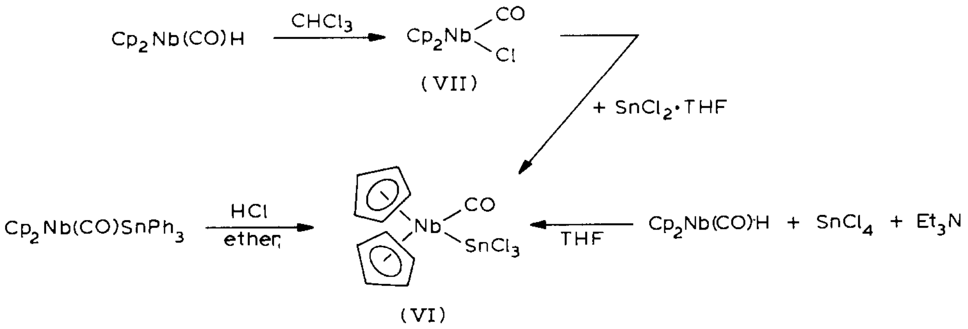
(I)

We found that the covalent Nb–H bond in I is sufficiently labile for the reaction of I with Ph_nSnCl_{4-n} in the presence of Et_3N to result in elimination of HCl and formation of the Nb–Sn bond in the complexes $Cp_2Nb(CO)SnPh_3$ (II), $Cp_2Nb(CO)SnPh_2Cl$ (III) and $Cp_2Nb(CO)SnPhCl_2$ (IV).



(II-IV)

A similar reaction of I with Et_2SnCl_2 yields $Cp_2Nb(CO)SnEt_2Cl$ (V). Complex II was isolated by recrystallization from THF/benzene in the form of cherry-red prisms. The IR spectrum in KBr contains, besides the characteristic C_5H_5 ligand bands (at 800, 1000, 1430 and 3080 cm^{-1}) and those of C_6H_5 groups (at 700, 1500 and 3000 cm^{-1}), the CO stretching mode at 1890 cm^{-1}, confirming its terminal coordination. The PMR spectrum in DMFA-d_7 shows a singlet from C_5H_5 protons (at δ 5.08 ppm) with satellites due to the presence of the Sn atom (C_5H_5 proton splitting on ^{117}Sn and ^{119}Sn nuclei). There is also a multiplet from C_6H_5 protons at δ 7.22 ppm. The ratio of Cp/Ph signal intensities is 10:15. Complex II is stable for some time in air as crystals, but rapidly oxidizes in solutions. Complex II is readily soluble in polar solvents (THF, DMFA, MeCN etc.), moderately soluble in benzene and toluene and practically insoluble in saturated hydrocarbons. Complexes III–V possess analogous properties. Some of their spectral characteristics are shown in Table 1. The Nb–Sn bond in II is stable towards HCl. Thus treatment of II in THF with ethereal HCl results in cleavage of only the Sn–C_6H_5 bond and generation of the new complex $Cp_2Nb(CO)SnCl_3$ (VI):



Crystalline VI precipitates immediately in quantitative yield from the reaction mixture in the form of orange needle-like crystals. Compound VI is also produced in

TABLE 1

PHYSICAL PROPERTIES OF COMPLEXES WITH Nb–Sn BONDS

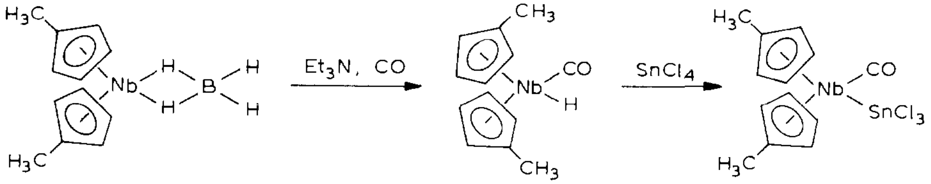
Complex	Color	T dec. (°C)	ν_{CO} (cm^{-1})	$\delta(C_5H_5)$ (ppm)	J(H–Sn) Hz	$\delta(C_6H_5)$ (ppm)
$Cp_2Nb(CO)SnPh_3$ (II)	cherry-red	229–232	1890	5.08	8.8	7.22
$Cp_2Nb(CO)SnPh_2Cl$ (III)	orange-red	177–180	1920	5.29	11.0	7.28
$Cp_2Nb(CO)SnPhCl_2$ (IV)	orange-red	168–171	1929	5.50	14.5	7.41
$Cp_2Nb(CO)SnEt_2Cl$ (V)	orange-red	109–112	1910	5.26	10.0	–
$Cp_2Nb(CO)SnCl_3$ (VI)	orange	106–109	1941	5.64	19.0	–
$(MeC_5H_4)_2Nb(CO)$-$SnCl_3$ (VIII)	orange-red	127–130	1928	5.49 [a]	–	–

[a] Center of C_5H_4 multiplet.

lower yield in the direct reaction of I with $SnCl_4$ in the presence of Et_3N, as well as by insertion of $SnCl_2$ into $Cp_2Nb(CO)Cl$ (VII) [8] (the properties of VI are listed in Table 1).

Attention should be drawn to the increase of CO frequencies, $\delta(C_5H_5)$ and J(H–Sn) upon replacement of phenyl groups at Sn by more electronegative chlorine (Fig. 1). The C_5H_5 chemical shifts and coupling constants for complex $Cp_2Nb(CO)SnCl_3$ (VI) are the same in DMFA and in the nonsolvating solvent CH_2Cl_2. Thus the absence of a linear dependence between $J(^{119/117}Sn-H(C_5H_5))$ and n could not be explained by DMFA coordination with Sn atom as it has been observed previously [9].

It was interesting to elucidate structural features of Nb–SnR_3 bonds for the two limiting cases: when R_3 = Ph_3 or Cl_3. Unfortunately, the poor solubility of VI even in THF hinders preparation of large single crystals of VI. Thus, to increase the solubility of the complex we synthesized the methylcyclopentadienyl analog of complex VI:



(VIII)

Complex VIII is a red crystalline substance, well soluble in polar organic solvents.

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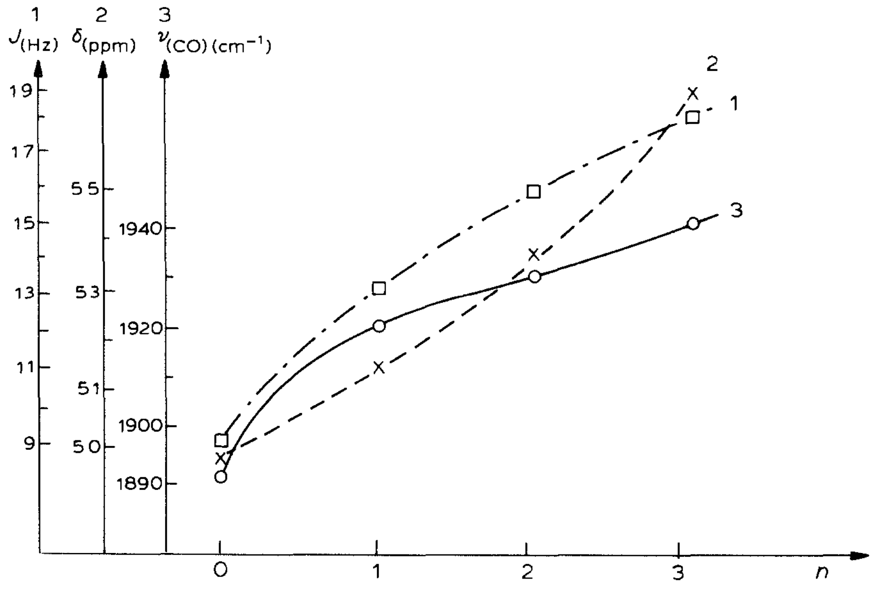

Fig. 1. Spectral characteristics for $Cp_2Nb(CO)SnCl_nPh_{3-n}$.
1. Spin-spin coupling constant $J(^{117/119}Sn-^1H(C_5H_5)$, Hz).
2. C_5H_5 proton chemical shift ($\delta(C_5H_5)$, ppm).
3. CO stretching mode frequency (ν(CO), cm^{-1}).

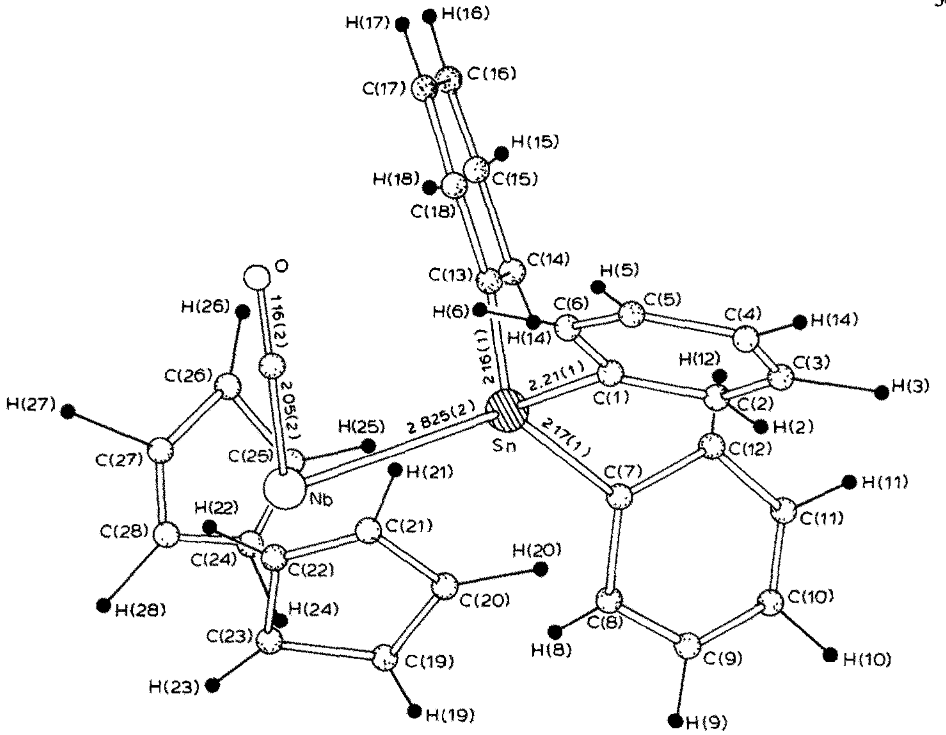

Fig. 2. Molecular structure of $Cp_2Nb(CO)SnPh_3$ (II).

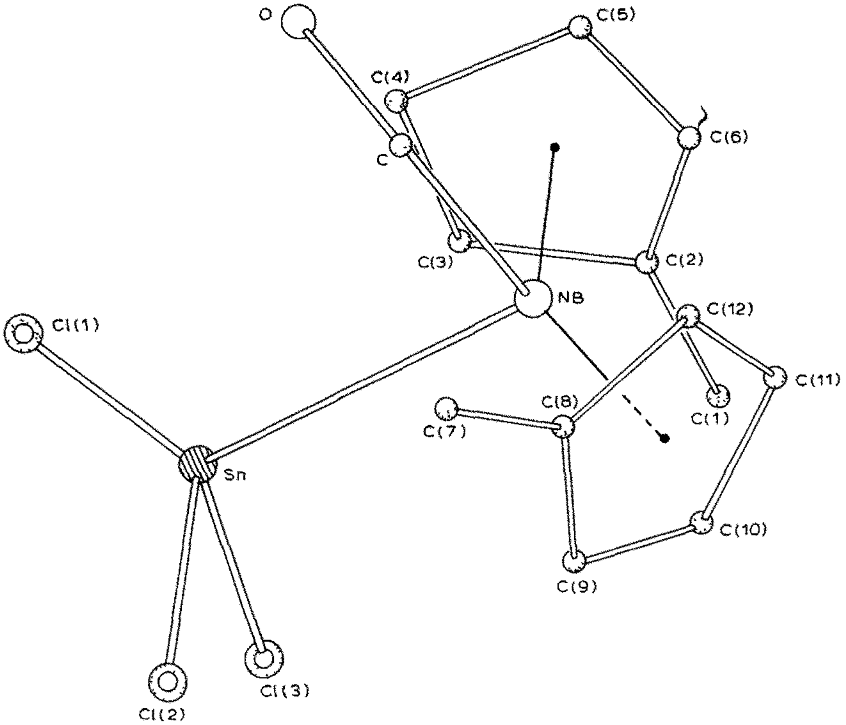

Fig. 3. Molecular structure of $(CH_3C_5H_4)_2Nb(CO)SnCl_3$ (VIII).

TABLE 2

ATOMIC COORDINATES OF $Cp_2Nb(CO)SnPh_3$

Atom	X	Y	Z	Atom	X	Y	Z
Nb	0.0396(2)	0.25658(8)	0.3025(1)	C(25)	0.0171(21)	0.1217(9)	0.2777(15)
Sn	0.2559(1)	0.21324(6)	0.19958(7)	C(26)	−0.0755(27)	0.1592(14)	0.2157(14)
O	−0.0808(14)	0.3425(8)	0.1147(10)	C(27)	−0.1680(19)	0.1939(13)	0.2702(28)
C	−0.0330(18)	0.3115(9)	0.1813(14)	C(28)	−0.1179(19)	0.1807(18)	0.3670(28)
C(1)	0.3694(16)	0.3101(7)	0.1509(9)	H(2)	0.555	0.257	0.183
C(2)	0.5041(19)	0.3079(8)	0.1596(10)	H(3)	0.683	0.371	0.146
C(3)	0.5769(16)	0.3728(11)	0.1377(12)	H(4)	0.572	0.487	0.089
C(4)	0.5153(19)	0.4386(9)	0.1067(12)	H(5)	0.331	0.493	0.075
C(5)	0.3802(18)	0.4412(9)	0.0985(10)	H(6)	0.197	0.380	0.115
C(6)	0.3036(15)	0.3772(10)	0.1211(11)	H(8)	0.348	0.155	0.406
C(7)	0.4031(15)	0.1374(8)	0.2673(12)	H(9)	0.507	0.066	0.482
C(8)	0.4142(18)	0.1259(9)	0.3603(12)	H(10)	0.682	0.012	0.395
C(9)	0.5078(23)	0.0778(11)	0.4080(14)	H(11)	0.661	0.023	0.224
C(10)	0.6022(21)	0.0445(10)	0.3597(17)	H(12)	0.497	0.108	0.140
C(11)	0.5925(22)	0.0591(11)	0.2637(17)	H(14)	0.258	0.042	0.121
C(12)	0.4983(18)	0.1004(9)	0.2146(14)	H(15)	0.184	−0.024	−0.036
C(13)	0.1967(14)	0.1535(10)	0.0694(11)	H(16)	0.064	0.098	−0.165
C(14)	0.2139(18)	0.0744(10)	0.0624(12)	H(17)	0.058	0.187	−0.151
C(15)	0.1701(24)	0.0359(12)	−0.0273(14)	H(18)	0.124	0.252	−0.004
C(16)	0.1114(24)	0.0793(16)	−0.0984(15)	H(19)	0.211	0.257	0.494
C(17)	0.0992(20)	0.1545(16)	−0.0917(13)	H(20)	0.317	0.323	0.355
C(18)	0.1388(16)	0.1911(10)	−0.0083(13)	H(21)	0.136	0.418	0.269
C(19)	0.1629(33)	0.2978(12)	0.4454(16)	H(22)	−0.081	0.405	0.357
C(20)	0.2186(22)	0.3318(19)	0.3739(21)	H(23)	−0.035	0.306	0.493
C(21)	0.1228(34)	0.3814(13)	0.3285(17)	H(24)	0.040	0.112	0.428
C(22)	0.0100(25)	0.3747(12)	0.3743(17)	H(25)	0.099	0.088	0.258
C(23)	0.0341(26)	0.3238(14)	0.4450(13)	H(26)	−0.076	0.161	0.141
C(24)	−0.0132(23)	0.1350(11)	0.3664(16)	H(27)	−0.257	0.224	0.245
				H(28)	−0.158	0.204	0.428

TABLE 3

BOND LENGTHS OF $Cp_2Nb(CO)SnPh_3$

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Sn–Nb	2.825(2)	C(7)–C(8)	1.38(2)	C(19)–C(20)	1.35(4)
Sn–C(1)	2.21(1)	C(8)–C(9)	1.37(3)	C(20)–C(21)	1.41(4)
Sn–C(7)	2.17(2)	C(9)–C(10)	1.36(3)	C(21)–C(22)	1.37(4)
Sn–C(13)	2.16(2)	C(10)–C(11)	1.37(4)	C(22)–C(23)	1.35(3)
Nb–C	2.05(2)	C(11)–C(12)	1.39(3)	C(23)–C(19)	1.38(4)
C–O	1.16(2)	C(12)–C(7)	1.43(2)	C(24)–C(25)	1.35(3)
C(1)–C(2)	1.36(3)	C(13)–C(14)	1.40(2)	C(25)–C(26)	1.39(3)
C(1)–C(6)	1.39(2)	C(14)–C(15)	1.47(3)	C(26)–C(27)	1.41(4)
C(2)–C(3)	1.40(2)	C(15)–C(16)	1.36(3)	C(27)–C(28)	1.44(5)
C(3)–C(4)	1.36(2)	C(16)–C(17)	1.32(4)	C(28)–C(24)	1.33(4)
C(4)–C(5)	1.36(3)	C(17)–C(18)	1.37(3)	Nb–C_5H_5(19–23)	2.05
C(5)–C(6)	1.42(2)	C(18)–C(13)	1.37(2)	Nb–C_5H_5(24–28)	2.05

Spectral characteristics of VIII are listed in Table 1. Unfortunately, coupling of signals of the substituted MeC_5H_4 rings did not allow identification of satellites and determination of $J(^{117/119}Sn–H(C_5H_5))$.

The structures of complexes II and VIII were established by X-ray analysis. Atomic coordinates, bond lengths and angles for II are shown in Tables 2–4 and for VIII in Tables 5–7. Complex II (Fig. 2) is a wedge-like sandwich compound with the angle between ring planes being 38.9°. The Nb–C(C_5H_5) distances (2.34(5) Å) are normal for the similar niobocene derivatives. The Nb coordination sphere also contains the carbonyl group (Nb–C(CO) 2.05(2) Å, C(CO)–O 1.16(2)Å) and the Sn atom bonded to the Nb atom by the direct Nb–Sn bond (2.825(2) Å), observed for

TABLE 4

BOND ANGLES OF $Cp_2Nb(CO)SnPh_3$

Angle	°	Angle	°
SnNbC	85.2(5)	C(11)C(12)C(7)	117.4(1.5)
NbSnC(1)	114.5(4)	C(14)C(13)C(18)	117.5(1.7)
NbSnC(7)	117.8(4)	C(13)C(14)C(15)	119.0(1.6)
NbSnC(13)	115.2(4)	C(14)C(15)C(16)	117.7(1.9)
C(7)SnC(13)	101.8(6)	C(15)C(16)C(17)	122.6(2)
C(1)SnC(7)	103.7(6)	C(16)C(17)C(18)	120.2(2)
C(1)SnC(13)	101.8(6)	C(17)C(18)C(13)	122.8(1.7)
C(6)C(1)C(2)	119.8(1.5)	C(23)C(19)C(20)	108.3(2)
C(1)C(2)C(3)	120.1(1.5)	C(19)C(20)C(21)	107.4(2.5)
C(2)C(3)C(4)	121.5(1.6)	C(20)C(21)C(22)	107.1(2)
C(3)C(4)C(5)	118.6(1.6)	C(21)C(22)C(23)	108.3(2)
C(4)C(5)C(6)	121.5(1.5)	C(22)C(23)C(19)	108.9(2)
C(5)C(6)C(1)	118.6(1.4)	C(25)C(24)C(28)	111.3(2)
C(8)C(7)C(12)	117.7(1.5)	C(24)C(25)C(26)	108.4(2)
C(7)C(8)C(9)	121.9(1.7)	C(25)C(26)C(27)	107.1(2)
C(9)C(10)C(11)	117.9(2)	C(26)C(27)C(28)	105.6(2)
C(8)C(9)C(10)	121.2(2)	C(27)C(28)C(24)	107.2(2)
C(10)C(11)C(12)	123.5(2)		

TABLE 5

ATOMIC COORDINATES OF $(MeC_5H_4)_2Nb(CO)SnCl_3$

Atom	*X*	*Y*	*Z*
Sn	0.12964(3)	0.21868(4)	0.05534(4)
Nb	−0.07052(11)	0.25593(5)	0.18260(5)
Cl(1)	0.0337(4)	0.1893(2)	−0 1130(2)
Cl(2)	0.3200(4)	0.3381(2)	0.0298(2)
Cl(3)	0.2955(4)	0.0776(2)	0.0757(2)
O	−0.2966(10)	0.3965(6)	0.0234(5)
C(1)	−0.0027(14)	0.0280(7)	0.3132(7)
C(2)	−0.1115(13)	0.0860(6)	0.2365(6)
C(3)	−0.1142(14)	0.0834(6)	0.1333(6)
C(4)	−0.2385	0.1429(7)	0.0832(6)
C(5)	−0.3209(13)	0.1841(8)	0.1601(8)
C(6)	−0.2349(14)	0.1474(6)	0.2530(7)
C(7)	0.0445(15)	0.5104(7)	0.1591(7)
C(8)	0.0404(12)	0.4194(6)	0.2246(6)
C(9)	0.1614(11)	0.3504(6)	0.2513(6)
C(10)	0.1185(14)	0.2860(7)	0.3231(6)
C(11)	−0.0239(11)	0.3157(7)	0.3441(6)
C(12)	−0.0770(12)	0.3997(7)	0.2822(6)
C(CO)	0.1945(13)	0.6527(7)	0.9227(6)

TABLE 6

BOND LENGTHS OF $(MeC_5H_4)_2Nb(CO)SnCl_3$

Bond	(Å)	Bond	(Å)	Bond	(Å)
Nb–Sn	2.764(1)	C(1)–C(2)	1.53(1)	C(7)–C(8)	1.51(1)
Sn–Cl(1)	2.391(2)	C(2)–C(3)	1.45(1)	C(8)–C(9)	1.43(1)
Sn–Cl(2)	2.400(3)	C(2)–C(6)	1.40(1)	C(8)–C(12)	1.44(1)
Sn–Cl(3)	2.339(3)	C(3)–C(4)	1.43(1)	C(9)–C(10)	1.41(1)
Nb–C	2.031(9)	C(4)–C(5)	1.45(1)	C(10)–C(11)	1.41(1)
C–O	1.13(1)	C(5)–C(6)	1.44(1)	C(11)–C(12)	1.44(1)

TABLE 7

BOND ANGLES OF $(MeC_5H_4)_2Nb(CO)SnCl_3$

Angle	°	Angle	°
NbSnCl(1)	119.54(7)	C(2)C(3)C(4)	107.1(8)
NbSnCl(2)	121.61(7)	C(3)C(4)C(5)	111.6(9)
NbSnCl(3)	121.40(8)	C(4)C(5)C(6)	102.6(9)
Cl(1)SnCl(3)	95.3(1)	C(5)C(6)C(2)	111.5(9)
Cl(1)SnCl(2)	96.5(1)	C(7)C(8)C(9)	125.3(8)
Cl(2)SnCl(3)	95.5(1)	C(7)C(8)C(12)	124.9(8)
SnNbC	88.8(2)	C(9)C(8)C(12)	103.5(8)
NbCO	176.3(8)	C(8)C(9)C(10)	107.6(8)
C(1)C(2)C(3)	125.5(9)	C(9)C(10)C(11)	109.5(8)
C(1)C(2)C(6)	127.2(9)	C(10)C(11)C(12)	108.8(9)
C(6)C(2)C(3)	107.3(8)	C(11)C(12)C(8)	106.2(8)

the first time. The tin atoms in II possess a distorted tetrahedron environment of phenyl groups and Nb atoms (mean Sn-C(Ph) distance 2.14 Å, C(Ph)-Sn-C(Ph) angles 101.7-103.7(5)°, Nb-Sn-C(Ph) 114.5-117.8(4)°). The Sn-Nb-C(CO) angle is equal to 85.2(5)°. In general, the molecule II, even in the presence of bulky phenyl substituents on the Sn atom, is not sterically strained. On the other hand, substitution of the phenyl groups on the Sn atom by the smaller but more electronegative Cl atoms causes an significant distortion of the structure of complex VIII. Its structure is generally similar to that of II. However, the Nb-Sn is shorter (2.764(1) Å), the angle between MeCp ligands is increased to 42.2°, the Nb-C(MeCp) distance is elongated to 2.40 Å, and the Sn-Nb-C(CO) angle is increased to 88.8(2)°. The Nb-C(CO) distance is the same (2.03(1) Å), the C(CO)-O distance shorter (1.13(1) Å). The tin polyhedron becomes close to a trigonal pyramid (Nb-Sn-Cl angles are 119.54(7), 121.40(7) and 121.6(7)°, and Cl-Sn-Cl angles are 95.5(1), 95.3(1) and 96.5(1)°. The Sn-Cl distances are 2.391(2), 2.400(4) and 2.339(3) Å. The molecule of VIII as well as those of II are not sterically strained.

Discussion

Formation of the direct Nb-Sn bond in the reactions of $Cp_2Nb(CO)H$ (I) with Ph_nSnCl_{4-n} in the presence of Et_3N may occur via a preliminary bridged coordination of a hydride atom with tin ($\mathrm{Nb{-}H{\cap}Sn}$), analogously to that in $Cp_2Nb(CO)H \cdot ML$ complexes ($ML = Zn(BH_4)_2$ [10], $Ni(CO)_3$, 1/2 $Mo(CO)_4$ [11], $Fe(CO)_4$ [12]). Such two-electron three-center interaction facilitates the transformation of the hydride ion into a proton. The latter is accepted by triethylamine and is removed in the form of $Et_3NH^+Cl^-$ producing the Nb-Sn bond. It is also generated by insertion of $SnCl_2$ carbenoid in the Nb-Cl bond in $Cp_2Nb(CO)Cl$ (VII) (with chloride ion coordinating to the lowest vacant orbital in $SnCl_2$). Along with generation of a Nb-Sn bond the Nb^{III} ion retains its lone electron pair in a plane between the rings. In the starting complexes I and VII this was employed for interaction with the antibonding CO orbitals, resulting in a normal partial double bonding $\mathrm{Nb}\overset{\frown}{-}\mathrm{C}$ with the weaker triple bonding $\mathrm{C}\overset{\frown}{\equiv}\mathrm{O}$. Thus, for I the Nb-C and C-O distances are 2.039(7) and 1.15(1) Å, respectively [13]. In complexes II and VIII this lone electron pair also interacts with the antibonding $SnCl_3$ orbitals resulting in partial $\mathrm{Nb}\overset{\frown}{-}\mathrm{Sn}$ double bonding and simultaneous weakening of the SnCl bonds. This is pronounced in complex $(MeCp)_2Nb(CO)SnCl_3$ (VIII). Here the Nb-Sn bond (2.764(1) Å) is significantly shorter (by 0.3 Å) than the sum of covalent radii of Nb and Sn (1.66 [14] + 1.40 [15] = 3.06 Å), whereas the Sn-Cl bonds (2.336(3), 2.391(2) and 2.400(4) Å) are more elongated than those in $SnCl_4$ (2.31 Å) [16]. Compared to VIII, $Cp_2Nb(CO)SnPh_3$ (II), containing the less electronegative $SnPh_3$ group, has a reduced degree of $\mathrm{Nb}\overset{\frown}{-}\mathrm{Sn}$ double bonding (the bond is elongated to 2.825(2) Å). This in turn reduces the repulsion between SnX_3, CO and cyclopentadienyl ligands, thus decreasing the Sn-Nb-C(CO) angle (from 88.8 to 85.8°), the angle between Cp ring planes (from 42.2 to 38.9°) and the Nb-C(Cp) distances (as an average from 2.40 to 2.34 Å). One may assume that the structural characteristics of $Cp_2Nb(CO)SnCl_3$ (VI) are similar to those observed for VIII and that intermediate values should be observed for complexes III-V containing $SnPh_2Cl$, $SnPhCl_2$, $SnEt_2Cl$, respectively. This is in agreement with the variation of the spectral characteristics of II-IV with the increase in the number of chlorine atoms on Sn (Table 1). In particular, the value of the $^{117/119}$Sn–C–H spin-spin coupling constant is known [17] to depend linearly on the *s* character of tin hybrid orbitals. Bent's rehybridization theory [18] assumes that *s* electron density is concentrated mainly over the bonds with the least electronegative ligands (in this case with $Cp_2Nb(CO)$ fragment). Thus the $J(^{117/119}Sn–^{1}H(C_5H_5))$ constant should increase with the number of electronegative chlorine atoms on Sn, which is actually observed.

Experimental

The synthesis and isolation of complexes I–VIII were performed under argon atmosphere in pure solvents saturated with argon. Cp_2NbBH_4 was prepared by a reported method [7]. $(MeC_5H_4)_2NbBH_4$ was obtained analogously. Commercial Ph_nSnCl_{4-n} ($n = 0–3$), $SnCl_4$ and Et_2SnCl_2 reagents were crystallized or distilled before use. Triethylamine was distilled over sodium.

The IR spectra were recorded in KBr pellets on a Specord 75 IR instrument. The PMR spectra were recorded on a pulsed Bruker WP 80 spectrometer at 30°C with internal stabilization over deuterium. Chemical shifts are given on the δ scale to an accuracy of 0.01 ppm, spin-spin coupling constants are to an accuracy of 0.5 Hz. DMFA-d_7 was used as solvent with hexamethyldisiloxane as internal standard ($\delta = 0.05$ ppm from Me_4Si). To avoid hydrolysis and oxidation of compounds the samples were measured in sealed ampoules inserted in a standard ampoule.

X-Ray study of crystals II and VIII was performed on an automatic Syntex P2$_1$ diffractometer with graphite monochromator, $\theta/2\theta$ scanning ($2\theta_{max} = 55°$). The structures were decoded by heavy atom techniques using Patterson and Fourier syntheses and full-matrix least squares refinement methods in isotropic and anisotropic approximations with the XTL program complex on a NOVA-1200 computer. The hydrogen atomic coordinates were evaluated with the HPOSN program starting with the standard C–H bond lengths of 1.07 Å and angles for sp^2 hybridized carbon atoms. The crystals of complex II are monoclinic (space group $P2_1/n$) with cell parameters $a = 10.102(2)$, $b = 17.463(3)$, $c = 14.247(2)$ Å, $\beta = 95.58(1)°$, $V = 2501.50(8)$ Å^3, $Z = 4.2407$ independent reflections with $J \geqslant 1.96\ \sigma$ were obtained. The crystals of complex VIII are monoclinic (space group $P2_1/n$). The cell parameters are $a = 8.367(1)$, $b = 13.359(1)$, $c = 13.929(3)$ Å, $\beta = 99.49(1)°$, $Z = 4$, $V = 1640.18(4)$ Å^3. 4008 independent reflections with $J \geqslant 2\sigma$ were obtained. The final values of R factors are 0.062 and 0.056 for II and VIII, respectively.

I. $Cp_2Nb(CO)H$ [8]

1 ml of Et_3N was added in a CO stream to a dark-green solution of 1.05 g (4.41 mmol) of Cp_2NbBH_4 in 40 ml of THF; the solution became red-brown. The reaction mixture was refluxed for 3 h under a CO stream; the solution changed color to cherry-violet. The filtered solution was concentrated in the presence of 5 ml of heptane to 10 ml and cooled to −5°C. The red-brown crystals precipitated were separated from the solution, washed with benzene/heptane (1/1) mixture and dried under vacuum: yield 0.9 g (86%). IR spectrum (cm^{-1}): 430w, 470(sh), 555m, 686m, 764s, 815s, 987m 1045m, 1083m, 1670w, 1890vs, 3045m.

II. $Cp_2Nb(CO)SnPh_3$

A solution of 1.01 g (2.10 mmol) of Ph_3SnCl in 20 ml of THF was added dropwise to a violet-red solution of $Cp_2Nb(CO)H$ (prepared by method I from 0.5 g (2.10 mmol) of Cp_2NbBH_4) in 25 ml of THF under refluxing. The dark-red solution was evaporated to one half volume, filtered from the precipitated $Et_3N \cdot HCl$, concentrated to 5 ml and cooled to -5°C. The cherry-red crystals precipitated were separated from the solution, washed with THF/heptane (2/1) and recrystallized from benzene/THF: yield 1.0 g (84%). IR spectrum (cm^{-1}): 432m, 447(sh), 476w, 585w, 685s, 712s, 802m, 893w, 980m, 1000w, 1049m, 1160w, 1243w, 1286w, 1412m, 1463m, 1615m, 1890vs, 2920m, 3047m. Found: C, 57.35; H, 4.15; Nb, 15.65; Sn, 20.00. $C_{29}H_{25}NbSnO$ calcd: C, 57.90; H, 4.15; Nb, 15.50;Sn, 19.81%.

Complexes III–V were prepared by procedure II.

III. $Cp_2Nb(CO)SnPh_2Cl$

From 1.2 g (4.92 mmol) Cp_2NbBH_4 and 1.45 g (4.33 mmol) of Ph_2SnCl_2. Yield of orange-red crystals 1.86 g (71%). IR spectrum: (cm^{-1}); 435m, 445(sh), 479w, 679s, 707s, 800s, 885w, 972m, 1000w, 1042m, 1087w, 1150w, 1240w, 1279w, 1392m, 1448m, 1615m, 1920vs, 2990m, 3070m. Found: C, 48.79; H, 4.14; Cl, 6.43; Nb, 16.28; Sn 20.80. $C_{23}H_{20}NbSnClO$ calcd.: C, 49.32; H, 3.57; Cl, 6.43; Nb, 16.60; Sn, 21.28%.

IV. $Cp_2Nb(CO)SnPhCl_2$

From 1.2 g (4.92 mmol) of Cp_2NbBH_4 and 1.25 g (4.13 mmol) of $PhSnCl_3$. Yield of orange-red crystals was 1.36 g (61%). IR spectrum (cm^{-1}): 428w, 468w, 685m, 711m, 801s, 824(sh), 982m, 1042w, 1083w, 1364s, 1400(sh), 1622m, 1929vs, 2902m, 3071m. Found: C, 39.41; H, 3.06; Cl, 13.80; Nb, 17.80; Sn, 22.70. $C_{17}H_{15}NbSnOCl_2$ calcd: C, 39.38; H, 2.89; Cl, 13.70; Nb, 17.95; Sn, 22.78%.

V. $Cp_2Nb(CO)SnEt_2Cl$

From 0.53 g (2.19 mmol) of Cp_2NbBH_4 and 0.4 g (2.21 mmol) of Et_2SnCl_2. Yield 0.48 g (64%) of orange-red crystals. IR spectrum (cm^{-1}): 432m, 449w, 479m, 618w, 658w, 800s, 821(sh), 981m, 1002m, 1043w, 1098m, 1153w, 1337m, 1398s, 1410(sh), 1445m, 1624m, 1910vs, 2841m, 2884m, 3054m. Found: C, 39.05; H, 4.52; Cl, 11.18; Nb, 19.78; Sn, 25.27. $C_{15}H_{20}NbSnClO$ calcd: C, 38.83; H, 4.30; Cl, 7.77; Nb, 20.02; Sn, 25.67%.

VI. $Cp_2Nb(CO)SnCl_3$

a) 0.057 g (1.58 mmol) of a HCl solution in diethyl ether was added dropwise to a dark-red solution of 0.3 g (0.51 mmol) of $Cp_2Nb(CO)SnPh_3$ (II). The solution was cooled to -5°C. The precipitated orange crystals were separated from the solution, washed with THF/heptane (1/5), then with pure pentane and dried under vacuum. Yield is 0.17 g (74%). IR spectrum (cm^{-1}): 435m, 474m, 583w, 812s, 925w, 982s, 1044m, 1098w, 1148w, 1326w, 1400s, 1617m, 1941vs, 3081m. Found: C, 27.54; H, 2.34; Cl, 22.16; Nb, 19.64; Sn, 25.31. $C_{11}H_{10}ONbSnCl_3$ calcd: C, 27.70; H, 2.10; Cl, 22.35; Nb, 19.51; Sn, 24.97%.

b) A solution of 1.19 g (4.53 mmol) of $SnCl_4$ in 15 ml of THF was added dropwise to a violet-red solution of $Cp_2Nb(CO)H$ (I) (prepared by method I from 1.15 g (4.75 mmol) of Cp_2NbBH_4) in 35 ml THF under refuxing in the presence of 1 ml of Et_3N. The orange-red solution was evaporated to one-half volume; 2 ml of heptane were added and the mixture concentrated to 5 ml. The solution was cooled to -5°C. The orange crystals precipitated were separated from the solution and washed with THF/heptane (1 : 5), pure pentane and dried under vacuum. Yield is 1.14 g (54%).

c) A solution of 0.86 g (4.54 mmol) of $SnCl_2$ in 15 ml of THF was added dropwise to a violet-brown solution of $Cp_2Nb(CO)Cl$ (VII) (prepared by method VII from 1.05 g (4.17 mmol) of Cp_2NbBH_4) in 40 ml of THF. The mixture was refluxed for 1 h. The orange solution was filtered, evaporated to one-half; volume 2 ml of heptane were added and the solution concentrated to 5 ml the solution was cooled to -5°C. The orange crystals precipitated were separated from the solution, washed with THF/heptane (1/5), then with pure pentane and dried under vacuum. Yield is 1.73 g (89%).

VII. $Cp_2Nb(CO)Cl$ [8]

$CHCl_3$ 0.7 g (5.88 mmol) was added dropwise to a violet-red solution of $Cp_2Nb(CO)H$ (prepared by method I from 1.2 g (4.92 mmol) of Cp_2NbBH_4) in 35 ml of THF. The reaction mixture was stirred at room temperature for 1 h, the solution was evaporated to one-half volume, 1 ml of heptane was added, and the mixture was concentrated to 3 ml and cooled to -5°C. The precipitated violet-brown crystals were separated from the solution, washed with benzene/heptane (1/5) and pure pentane, and dried under vacuum. Yield 1.19 g (91%). IR spectrum (cm^{-1}): 441m, 482w, 601w, 800s, 820s, 911w, 987m, 1017m, 1073m, 1361w, 1409m, 1427m, 1625w, 1915vs, 3054m, 3420(br).

VIII. $(MeC_5H_4)_2Nb(CO)SnCl_3$

A solution of 1.42 g (5.45 mmol) of $SnCl_4$ in 35 ml of THF was added dropwise in a CO stream to a violet-red solution of $(MeC_5H_4)_2Nb(CO)H$ (prepared analogously to I from 1.6 g (5.70 mmol) of $(MeC_5H_4)_2NbBH_4$ in 50 ml of THF at room temperature). After the addition, the reaction mixture became red-brown. The solution was evaporated to dryness, the residual oil was extracted with 25 ml of toluene and concentrated to 15 ml. After cooling to -5°C black (identified as $(MeC_5H_4)_2NbCl_2$) and orange-red crystals precipitated. They were separated by fraction crystallization and washed with a toluene-heptane mixture. The crystals were dried under vacuum. Yield 0.6 g (43%) of orange-red crystals. IR spectrum (cm^{-1}): 452w, 481m, 815s, 911w, 1022s, 1117w, 1358m, 1441m, 1619m, 1928vs, 2898m, 3098m. Found: C, 31.05; H, 2.75; Cl, 19.26; Nb, 18.34; Sn, 23.46. $C_{13}H_{14}NbSnOCl_3$ calcd: C, 30.92; H, 2.77; Cl, 21.10; Nb, 18.48; Sn, 23.58%.

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