Journal of Organometallic Chemistry, 162 (1978) 109—120

SYNTHESIS, PROPERTIES AND X-RAY STRUCTURAL DETERMINATION OF CATIONIC FIVE-COORDINATE σ-TRIPHENYLSTANNYLNICKEL (II) COMPLEXES WITH POLY(TERTIARY PHOSPHINES)

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(Received June 7th, 1978)

Summary

Cationic five-coordinate nickel(II) complexes containing a nickel—tin σ-bond with the general formula [Ni(SnPh$_3$)(L)]BPh$_4$ (L = tris(2-diphenylphosphinoethyl)amine, np$_3$; tris(2-diphenylphosphinoethyl)phosphine, pp$_3$) were synthesized by reaction of the five-coordinate complexes [NiCl(L)]BPh$_4$ with LiSnPh$_3$. The structure of the [Ni(SnPh$_3$)(np$_3$)]BPh$_4$ derivative was determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions a 18.88(1), b 38.53(2), c 18.93(1) Å, β 93.3(1)°, D_c1.34 g cm^{-3} for Z = 8. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.088. The structure consists of trigonal bipyramidal [Ni(SnPh$_3$)(np$_3$)]$^+$ cations and BPh$_4^-$ anions, with a Ni—Sn bond distance (av) of 2.556(15) Å.

Introduction

Although a variety of compounds containing a transition metal bonded to a tin atom has been reported, complexes of this type with nickel are rare, and almost always contain carbon monoxide or cyclopentadiene as ancillary ligands [1—4]. However, Uhlig et al. have reported anionic triorganophosphine-cobalt(0) and -nickel(0) complexes having the SnPh$_3$ group coordinated to the metal [5].

We have been studying for a long time the coordinating behavior of tripod poly(tertiary phosphines). These ligands are able to stabilize 3*d* metal five-coordinated complexes with coligands of various types such as X [6,7] (X = halogen or pseudohalogen), SR [8] (R = H, alkyl), H [9], CO [10], NO [11], aryl [12], and alkyl [13]. Now, by treatment of the [NiCl(L)]BPh$_4$] complexes, (L = np$_3$, pp$_3$) with Li(SNPh$_3$) in tetrahydrofuran solution, we have obtained triphenylstannylnickel complexes of the formula [Ni(SnPh$_3$)(L)]BPh$_4$. The compounds have been characterized by standard physical methods and a complete structure determination has been carried out for the complex [Ni(SnPh$_3$)(np$_3$)]BPh$_4$.

Experimental

The tetrahydrofuran was purified by distillation over LiAlH$_4$. The others solvents were of reagent grade quality and were used without further purification. The complexes [NiCl(np$_3$)]BPh$_4$ (np$_3$ = tris(2-diphenylphosphinoethyl)-amine and [NiCl(pp$_3$)]BPh$_4$ (pp$_3$ = tris(2-diphenylphosphinoethyl)phosphine were prepared as previously described [6,7]. The reactions were carried out under nitrogen using deoxygenated solvents.

Preparation of [Ni(SnPh$_3$) (np$_3$)]BPh$_4$

A solution of 1 mmol of LiSnPh$_3$ [14] in 30 ml tetrahydrofuran was added dropwise with stirring to a solution of 1 mmol of [NiCl(np$_3$)]BPh$_4$ cooled to —70° C. During the addition the colour of the solution changed from violet to cherry-red, and green crystals of [NiCl(np$_3$)] complex [15] separated. After 1 h methyl alcohol (5 ml) was added in order to distroy any unreacted lithium salt and the mixture was filtered. Butanol (50 ml) was added to the filtrate, and the resulting solution was concentrated at room temperature. The cherry-red crystals which separated were filtered off, washed with butanol and petroleum ether, and dried under reduced pressure. The complex was recrystallized from butanol/acetone. Anal. Found: C, 72.37; H, 6.14; N, 1.00; Ni, 4.13; Sn, 8.58. $C_{84}H_{77}BNNiP_3Sn$ calcd.: C, 73.02; H, 5.61; N, 1.01; Ni, 4.25; P, 6.72; Sn, 8.59%.

Preparation of [Ni(SnPh$_3$)(pp$_3$)]BPh$_4$.

Brown crystals of the complex were prepared by a method analogous to that described. Anal. Found: C, 71.46; H, 5.59; Ni, 4.50; Sn, 7.91. $C_{84}H_{77}BNiP_4Sn$ calcd.: C, 72.13; H, 5.55; Ni, 4.20; Sn, 8.47%.

Physical measurements

The methods used for the magnetic and molar conductance measurements and the recording of the infrared and UV-visible spectra have been described previously [16].

Crystal data and data collection

Crystals suitable for diffraction studies were obtained by crystallization from acetone. The crystal used, of irregular prismatic shape, had dimensions 0.05 × 0.05 × 0.3 mm. The crystals are monoclinic, and belong to space group $P2_1/c$, with 8 molecules of [Ni(SnPh$_3$)(np$_3$)]BPh$_4$ in the unit cell, of dimensions a 18.88(1), b 38.53(2), c 18.93(1) Å, β 93.3 (1)°. Therefore the structure analysis required the determination of the parameters for two individual independent molecules.

Intensity data were collected on an automatic computer-controlled diffractometer Philips PW 1100, equipped with a graphite monochromator, using Mo-K_α radiation. All reflections with $4° \leqslant 2\vartheta \leqslant 40°$ were measured using the ω—2ϑ scan technique with a scan speed of 0.08°/s in a range of 0.8° across the peak. Background times were taken equal to half the scan time on each side of the peak. Because of the large thermal motion of the molecules, reflections having 2ϑ greater than 40°C were in virtually all cases unobservable. Three standard reflections were measured during data collection every 3 h, but no significant trend was noticed.

The intensity data were corrected for Lorentz and polarization effects; the standard deviation $\sigma(I)$ was estimated as described elswhere [17], with an instability factor equal to 0.04. A reflection was considered unobserved if the net intensity I was $<3\ \sigma(I)$. From 3368 total reflections 1919 had intensity $\geqslant 3\ \sigma(I)$. Owing to the small dimensions of the crystal used and to the small value of the linear absorption coefficient, absorption correction was not applied (μ(Mo-K_α) 7.59 cm^{-1}).

Atomic scattering factors were taken from the compilation of Cromer and Waber for all non-hydrogen atoms [18], and those for hydrogen atoms from Stewart et al. [19].

Structure solution and refinement

The positions of the two tin and two nickel atoms in the asymmetric unit were derived from the Patterson function. A first Fourier synthesis revealed the positions of the phosphorus and nitrogen atoms. At this stage the R factor was 36%. Further determination of the structure was not straightforward, owing to disorder in the vicinity of the tin atoms, where some peaks belonging to the phenyl rings were not resolved sufficiently to reveal the positions of all the carbon atoms. Successive delta F Fourier coupled with least-squares led to the assignment of coordinates for all non-hydrogen atoms.

The number of the parameters to be refined was very high (182 non-hydrogen atoms) and the structure refinement was performed by blocking the least-squares matrix (two blocks) and imposing the following constraints on the parameters: (i) the phenyl groups were refined as rigid body (C—H 1.392 Å) with a unique temperature factor associated with each group (ii) all carbon atoms of the ethylenic chains (in each molecule) were constrained to have the same refined temperature factor. In this way the number of parameters to be refined was greatly reduced and refinement of the whole structure was made possible. The function minimized in the least-squares refinement was $\Sigma w(|F_o|-|F_c|)^2$ with $w = 1/\sigma^2(F_o)$. R and R_w are difined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, respectively. The refinement was undertaken * by performing several least-squares cycles with isotropic thermal parameters for all atoms. Then the refinement was continued assuming anisotropic thermal vibrations for Sn, Ni and P atoms. In later stages of refinement the hydrogen atoms were introduced in their calculated positions (C—H 0.95 Å) with thermal parameters equal to those of the carbon atoms to which they were attached increased by 10%. The hydrogen atoms were not refined. The standard devia-

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* The computer programs were obtained from different sources and locally implemented in CII 10070 computer.

tion of unit weight was 1.51. Convergence was reached with R 8.8% and R_w 9.4%, respectively.

Results and Discussion

The complexes here reported are formed by exchange between the $LiSnPh_3$ compound and the five coordinated $[NiCl(L)]BPh_4$ (L = np_3, pp_3) complex according to eq. 1.

$$[NiCl(L)]BPh_4 + LiSnPh_3 \rightarrow [Ni(SnPh_3)(L)]BPh_4 + LiCl \qquad (1)$$

The yield is not quantative owing to the simultaneous reducing effect of the $LiSnPh_3$ on the $[NiCl(L)]^+$ ions. Thus, when L = np_3 the known nickel complex, $[NiClnp_3)]$, is also formed.

The complexes are fairly air stable and behave as 1/1 electrolytes in 1,2-dichloroethane and nitroethane. They are diamagnetic in the solid state. The electronic spectra of the np_3 and pp_3 derivatives, both in the solid state and in solution, show an intense band at 1.96 and 2.22 nm^{-1}, respectively. These spectra can be correlated with those of the corresponding trigonal bipyramidal alkylnickel(II) complexes with the formula $[NiR(L)]BPh_4$, where L = np_3 and R = CH_3, C_2H_5, $CH_2C_6H_5$ [13].

A perspective view of the two independent complex cations $[Ni(SnPh_3)(np_3)]^+$ is shown in Fig. 1 and 2. Final positional and thermal parameters are

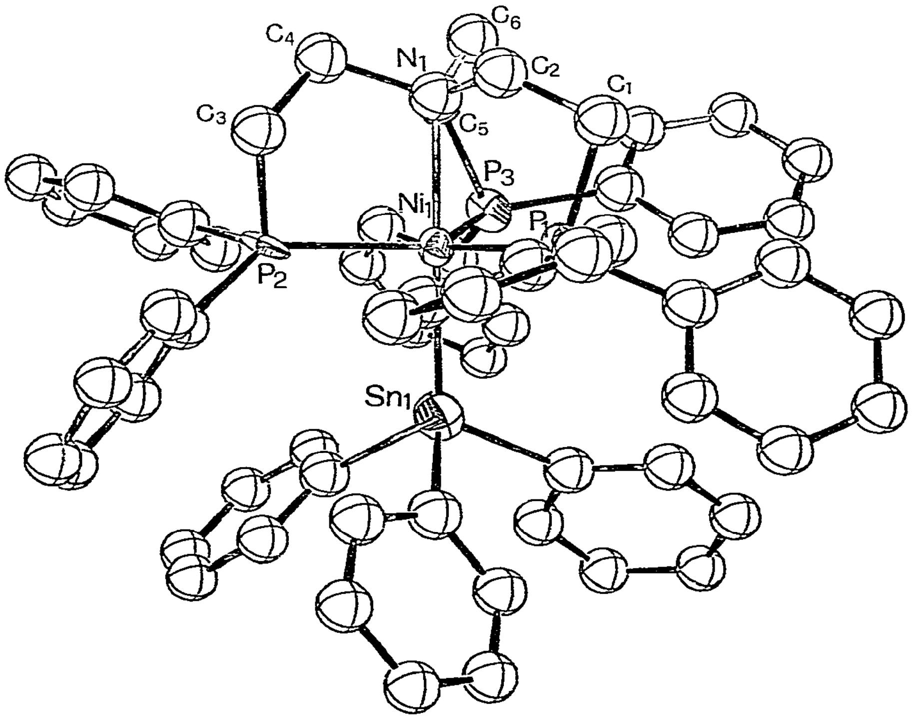

Fig. 1. Perspective view of complex cation A of the asymmetric unit. ORTEP diagram showing 30% probability ellipsoids.

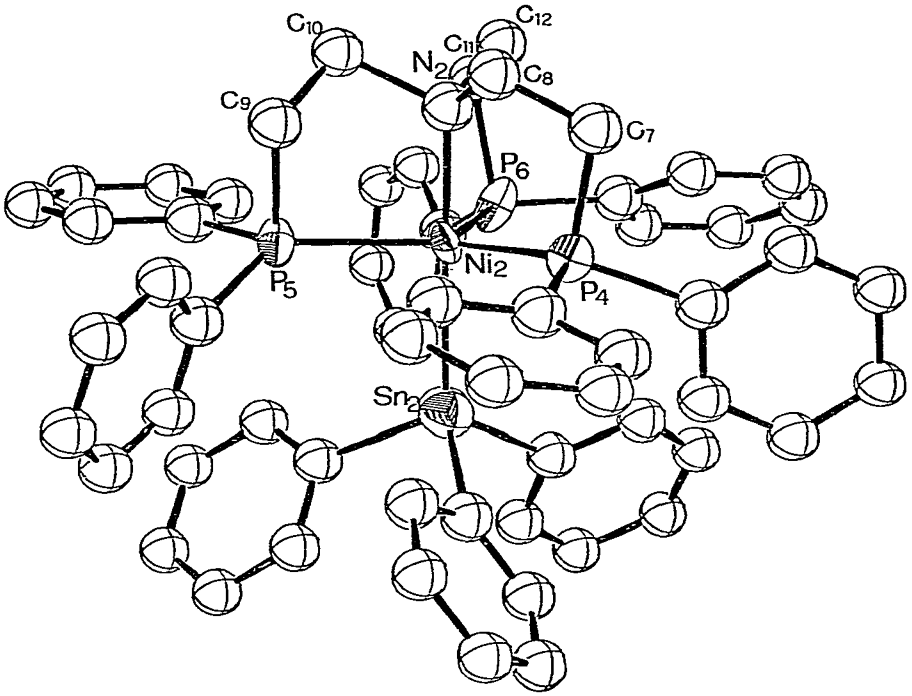

Fig. 2. Perspective view of complex cation B of the asymmetric unit. ORTEP diagram showing 30% probability ellipsoids.

given in Tables 1, 2, 3 and 4. Selected bond lengths and angles are listed in Table 5.

The two cations in the asymmetric unit have similar conformations save for some slight differences in the orientations of their phenyl groups. In both of the cations the nickel atom is five coordinated in a trigonal bipyramidal environment, while the tin atom, tetrahedrally coordinated, is bonded to the nickel atom in an apical position trans to the nitrogen atom of the np_3 ligand. The Ni—Sn bond lengths are 2.541(10) and 2.571(10) Å, respectively, in the two cations. At best of our knowledge a Sn—Ni bond value has not previously reported. The averaged value (2.556 Å) is in good agreement with the sum of the covalent radii of nickel and tin atoms (2.56 Å) [20], and can be compared with other *3d* metal—tin bond distances [1,3,4].

The slight displacement of the nickel atom below the equatorial plane toward the Sn atom, with P—Ni—N angles somewhat less than 90°, can be associated with steric hindrance by the bulky $SnPh_3$ moiety. In other cases, owing to the flexibility of the np_3 ligand, the P—M—N angles are very close to 90° [15]. The Ni—P bond distances in both the molecules agree well with those in other d^8 trigonal bipyramidal complexes [21].

Although the parameters are poorly determined (large oscillatory motion and unfavourable data-to-parameters ratio), the deviations from the linearity of the axial Sn—Ni—N array (179.3 and 174.3° angles) can be mainly ascribed to packing effects. This is not novel for five-coordinated metal complexes containing the np_3 ligand [22].

(continued on p. 118)

TABLE 1

ATOMIC[a] PARAMETERS FOR THE STRUCTURE OF [Ni(SnPh$_3$)(np$_3$)]BPh$_4$ (all quantities × 10000)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	−51.90(3)	1763(1)	2106(3)	454(39)	546(43)	694(50)	−22(34)	−38(35)	129(40)
Sn(2)	−300(3)	3392(1)	3344(3)	571(42)	563(45)	953(55)	7(37)	0(39)	184(44)
Ni(1)	−5380(4)	1267(2)	2958(4)	173(55)	429(72)	317(71)	−11(55)	−34(48)	43(64)
Ni(2)	−468(4)	3890(2)	2445(4)	178(59)	429(73)	399(76)	102(57)	−57(52)	35(68)
P(1)	−5091(9)	842(5)	2192(10)	260(149)	689(171)	153(170)	−94(127)	66(125)	−40(151)
P(2)	−6533(9)	1417(4)	3114(9)	377(138)	230(140)	392(147)	−17(109)	113(116)	189(126)
P(3)	−4490(8)	1439(4)	3765(10)	197(130)	338(141)	541(163)	121(108)	77(118)	0(132)
P(4)	−82(9)	4284(5)	3285(10)	408(161)	303(148)	419(166)	−4(115)	−58(125)	−226(144)
P(5)	−1656(9)	3773(5)	2221(10)	306(131)	447(155)	584(166)	−55(118)	−9(117)	−64(144)
P(6)	338(9)	3694(4)	1716(10)	302(126)	456(138)	500(157)	10(133)	−34(117)	−328(158)

F (rel. scale factor) 296808

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[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

TABLE 2

ATOMIC PARAMETERS FOR THE STRUCTURE OF [Ni(SnPh$_3$)(np$_3$)]BPh$_4$ (all quantities X 10000)

Atom	*x*	*y*	*z*	*U* (Å^2)
N(1)	−5534(24)	847(12)	3696(26)	305(156)
N(2)	−630(25)	4302(14)	1833(27)	502(177)
C(1)	−4978(33)	484(16)	2797(39)	609(220)
C(2)	−5487(34)	535(18)	3314(37)	609
C(3)	−6804(31)	1007(16)	3428(33)	609
C(4)	−6253(33)	905(15)	4074(33)	609
C(5)	−4836(30)	1233(17)	4524(31)	609
C(6)	−5045(32)	849(17)	4317(35)	609
C(7)	−86(31)	4687(16)	2721(33)	512(222)
C(8)	−660(31)	4649(17)	2118(33)	512
C(9)	−1897(31)	4208(16)	1812(33)	512
C(10)	−1334(31)	4292(15)	1281(33)	512
C(11)	107(30)	4014(17)	946(33)	512
C(12)	−82(32)	4353(16)	1231(34)	512
B(1)	−5206(47)	4363(21)	2013(46)	905(325)
B(2)	−9487(37)	813(18)	3371(40)	506(271)

TABLE 3

FINAL LEAST SQUARES PARAMETERS FOR [Ni(SnPh$_3$)(np$_3$)]BPh$_4^-$ GROUPS [a]

Group	*x*′	*y*′	*z*′	θ	ϕ	ψ
GR 1	−0.6216(15)	0.0504(7)	0.1218(13)	0.673(25)	−1.318(49)	−2.474(41)
GR 2	−0.3875(17)	0.0753(7)	0.1138(18)	0.536(25)	3.058(89)	0.540(70)
GR 3	−0.6815(14)	0.1914(7)	0.4293(14)	0.796(25)	−1.478(37)	2.647(27)
GR 4	−0.7681(13)	0.1644(8)	0.2061(13)	0.800(21)	1.812(34)	−1.523(17)
GR 5	−0.4068(12)	0.2163(7)	0.4229(14)	0.943(21)	−0.372(34)	2.057(25)
GR 6	−0.3029(16)	0.1114(6)	0.3712(18)	1.171(25)	3.127(49)	−2.775(30)
GR 7	−0.5898(17)	0.1752(7)	0.0448(18)	1.788(31)	1.850(46)	2.763(50)
GR 8	−0.5802(14)	0.2566(8)	0.2415(16)	2.183(25)	−0.169(49)	1.117(32)
GR 9	−0.3578(19)	0.2007(10)	0.1626(15)	0.599(26)	1.168(63)	1.600(27)
GR 10	−0.1072(16)	0.4531(6)	0.4419(15)	2.000(30)	−0.816(41)	0.042(46)
GR 11	0.1361(19)	0.4258(9)	0.4062(16)	0.732(29)	0.751(60)	−0.479(32)
GR 12	−0.2124(16)	0.3293(7)	0.1018(15)	0.909(27)	−1.254(46)	3.032(55)
GR 13	−0.2812(15)	0.3654(8)	0.3228(14)	0.692(24)	1.966(49)	0.988(29)
GR 14	0.1917(16)	0.3834(8)	0.1943(13)	0.405(24)	−0.555(64)	−2.807(53)
GR 15	0.0427(11)	0.2966(8)	0.0932(16)	1.895(47)	0.849(46)	1.857(30)
GR 16	−0.0713(20)	0.3528(8)	0.5038(23)	1.529(36)	1.906(71)	0.519(38)
GR 17	−0.1270(13)	0.2690(8)	0.3106(19)	1.714(25)	0.046(48)	−0.999(23)
GR 18	0.1396(17)	0.2984(9)	0.3552(12)	2.261(25)	0.085(36)	3.030(49)
GR 19	−0.3727(13)	0.4671(5)	0.1864(14)	1.254(19)	0.144(31)	2.602(21)
GR 20	−0.5472(12)	0.4268(8)	0.3454(15)	0.951(22)	1.529(40)	1.465(17)
GR 21	−0.6088(15)	0.4837(6)	0.1283(16)	1.085(23)	0.528(41)	0.587(27)
GR 22	−0.5258(14)	0.3688(7)	0.1351(12)	0.552(24)	−2.515(49)	−2.048(38)
GR 23	−0.9090(12)	0.0604(6)	0.2004(14)	1.473(29)	1.240(34)	−2.489(24)
GR 24	−1.0628(12)	0.0322(6)	0.3711(14)	1.753(20)	0.233(29)	2.470(20)
GR 25	−0.8340(21)	0.0716(7)	0.4478(14)	2.173(20)	1.315(34)	1.295(18)
GR 26	−0.9965(14)	0.1503(8)	0.3375(12)	0.495(21)	0.092(58)	1.213(46)

[a] x', y', z' (fractional coordinates) define the origin of the working system of the group, the Goldstein definition is used for Euler angles θ, ϕ, ψ (radians) [27].

TABLE 4

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS (all quantities × 10000)

Atom	*x*	*y*	*z*	*U* (Å^2)
C(1,1)	—5773(23)	640(12)	1599(21)	583(185)
C(2,1)	—5629(23)	325(12)	1277(21)	583(185)
C(3,1)	—6145(23)	166(12)	833(21)	583(186)
C(4,1)	—6806(23)	322(12)	710(21)	583(185)
C(5,1)	—6949(23)	637(12)	1032(21)	583(185)
C(6,1)	—6433(23)	796(12)	1476(21)	583(185)
C(1,2)	—4402(27)	789(14)	1618(31)	910(198)
C(2,2)	—4496(27)	932(14)	943(31)	910(198)
C(3,2)	—3971(27)	895(14)	463(31)	910(198)
C(4,2)	—3349(27)	716(14)	657(31)	910(198)
C(5,2)	—3253(27)	574(14)	1332(31)	910(198)
C(6,2)	—3779(27)	610(14)	1812(31)	910(198)
C(1,3)	—6684(27)	1711(10)	3844(18)	598(91)
C(2,3)	—6184(27)	1959(10)	4064(18)	598(91)
C(3,3)	—6337(27)	2197(10)	4588(18)	598(91)
C(4,3)	—6990(27)	2186(10)	4892(18)	598(91)
C(5,3)	—7490(27)	1937(10)	4673(19)	598(91)
C(6,3)	—7337(27)	1700(10)	4148(18)	598(91)
C(1,4)	—7236(18)	1559(14)	2501(17)	598(154)
C(2,4)	—7353(18)	1909(14)	2354(17)	598(154)
C(3,4)	—7872(18)	2008(14)	1841(17)	598(154)
C(4,4)	—8275(18)	1756(14)	1475(17)	598(154)
C(5,4)	—8158(18)	1406(14)	1622(17)	598(154)
C(6,4)	—7638(18)	1308(14)	2135(17)	598(154)
C(1,5)	—4234(23)	1877(8)	4043(24)	403(156)
C(2,5)	—4527(23)	2023(8)	4632(24)	403(156)
C(3,5)	—4333(23)	2357(8)	4849(24)	403(156)
C(4,5)	—3846(23)	2544(8)	4477(24)	403(156)
C(5,5)	—3553(23)	2398(8)	3888(24)	403(156)
C(6,5)	—3747(23)	2064(8)	3671(24)	403(156)
C(1,6)	—3620(17)	1223(10)	3704(37)	930(116)
C(2,6)	—3228(17)	1185(10)	4344(37)	930(116)
C(3,6)	—2538(17)	1057(10)	4354(37)	930(116)
C(4,6)	—2240(17)	968(10)	3723(37)	930(116)
C(5,6)	—2633(17)	1006(10)	3083(37)	930(116)
C(6,6)	—3323(17)	1134(10)	3073(37)	930(116)
C(1,7)	—5641(32)	1706(12)	1032(21)	929(121)
C(2,7)	—6337(32)	1605(12)	862(21)	929(121)
C(3,7)	—6637(32)	1658(12)	182(21)	929(121)
C(4,7)	—6241(32)	1813(12)	—329(21)	929(121)
C(5,7)	—5544(32)	1915(12)	—160(21)	929(121)
C(6,7)	—5244(32)	1862(12)	520(21)	929(121)
C(1,8)	—5590(27)	2279(9)	2328(33)	829(115)
C(2,8)	—5312(27)	2477(9)	2893(33)	829(115)
C(3,8)	—5560(27)	2812(9)	2994(33)	829(115)
C(4,8)	—6086(27)	2950(9)	2530(33)	829(115)
C(5,8)	—6364(27)	2752(9)	1965(33)	829(115)
C(6,8)	—6116(27)	2416(9)	1864(33)	829(115)
C(1,9)	—4099(25)	1895(21)	1871(25)	1306(143)
C(2,9)	—3165(25)	1670(21)	1586(25)	1306(143)
C(3,9)	—3007(25)	1801(21)	1300(25)	1306(143)
C(4,9)	—2883(25)	2157(21)	1299(25)	1306(143)
C(5,9)	—3367(25)	2382(21)	1583(25)	1306(143)
C(6,9)	—3975(25)	2251(21)	1870(25)	1306(143)
C(1,10)	—671(28)	4429(10)	4000(24)	637(125)
C(2,10)	—409(28)	4566(10)	4643(24)	637(125)
C(3,10)	—877(28)	4686(10)	5131(24)	637(125)
C(4,10)	—1605(28)	4668(10)	4976(24)	637(125)

(Table continued)

TABLE 4 (continued)

Atom	x	y	z	U (Å^2)
C(5,10)	—1867(28)	4531(10)	4333(24)	637(125)
C(6,10)	—1400(28)	4411(10)	3845(24)	637(125)
C(1,11)	787(24)	4293(19)	3774(28)	1106(151)
C(2,11)	919(24)	4017(19)	4238(28)	1106(151)
C(3,11)	1589(24)	3975(19)	4574(28)	1106(151)
C(4,11)	2127(24)	4211(19)	4446(28)	1106(151)
C(5,11)	1995(24)	4487(19)	3983(28)	1106(151)
C(6,11)	1325(24)	4528(19)	3647(28)	1106(151)
C(1,12)	—1941(35)	3483(10)	1492(19)	759(109)
C(2,12)	—1440(35)	3345(10)	1058(19)	759(109)
C(3,12)	—1654(35)	3123(10)	506(19)	759(109)
C(4,12)	—2368(35)	3040(10)	387(19)	759(109)
C(5,12)	—2868(35)	3177(10)	820(19)	759(109)
C(6,12)	—2655(35)	3399(10)	1372(19)	759(109)
C(1,13)	—2328(19)	3682(17)	2853(22)	755(108)
C(2,13)	—2796(19)	3957(17)	2923(22)	755(108)
C(3,13)	—3360(19)	3925(17)	3361(22)	755(108)
C(4,13)	—3456(19)	3617(17)	3728(22)	755(108)
C(5,13)	—2988(19)	3342(17)	3658(22)	755(108)
C(6,13)	—2424(19)	3374(17)	3220(22)	755(108)
C(1,14)	1302(18)	3778(16)	1812(21)	879(118)
C(2,14)	1802(18)	3526(16)	1675(21)	879(118)
C(3,14)	2521(18)	3590(16)	1828(21)	879(118)
C(4,14)	2737(118)	3907(16)	2118(21)	879(118)
C(5,14)	2236(18)	4160(16)	2255(21)	879(118)
C(6,14)	1518(18)	4095(16)	2102(21)	879(118)
C(1,15)	389(19)	3286(13)	1269(27)	798(106)
C(2,15)	362(19)	3268(13)	533(27)	798(106)
C(3,15)	400(19)	2948(13)	197(27)	798(106)
C(4,15)	465(19)	2645(13)	596(27)	798(106)
C(5,15)	492(19)	2663(13)	1331(27)	798(106)
C(6,15)	454(19)	2983(13)	1668(27)	798(106)
C(1,16)	—555(47)	3489(17)	4443(29)	1557(157)
C(2,16)	—116(47)	3361(17)	5000(29)	1557(157)
C(3,16)	—300(47)	3408(17)	5695(29)	1557(157)
C(4,16)	—924(47)	3582(17)	5833(29)	1557(157)
C(5,16)	—1363(47)	3709(17)	5275(29)	1557(157)
C(6,16)	—1179(47)	3662(17)	4581(29)	1557(157)
C(1,17)	—930(19)	2952(9)	3134(40)	969(115)
C(2,17)	—1183(19)	2811(9)	3748(40)	969(115)
C(3,17)	—1579(19)	2506(9)	3715(40)	969(115)
C(4,17)	—1723(19)	2342(9)	3068(40)	969(115)
C(5,17)	—1470(19)	2482(9)	2454(40)	969(115)
C(6,17)	—1073(19)	2787(9)	2487(40)	969(115)
C(1,18)	749(25)	3158(17)	3499(23)	1038(125)
C(2,18)	1377(25)	3338(17)	3403(23)	1038(125)
C(3,18)	2023(25)	3163(17)	3456(23)	1038(125)
C(4,18)	2042(25)	2809(17)	3505(23)	1038(125)
C(5,18)	1415(25)	2630(17)	3701(23)	1038(125)
C(6,18)	768(25)	2804(17)	3648(23)	1038(125)
C(1,19)	—4273(15)	4525(8)	1950(25)	348(91)
C(2,19)	—3967(15)	4504(8)	1300(25)	348(91)
C(3,19)	—3330(15)	4674(8)	1200(25)	348(91)
C(4,19)	—2999(15)	4865(8)	1750(25)	348(91)
C(5,19)	—3306(15)	4886(8)	2400(25)	348(91)
C(6,19)	—3943(15)	4716(8)	2500(25)	348(91)
C(1,20)	—5143(17)	4313(16)	2942(17)	769(105)
C(2,20)	—5239(17)	3978(16)	3197(17)	769(105)
C(3,20)	—5623(17)	3926(16)	3795(17)	769(105)

(Table continued)

TABLE 4 (Continued)

Atom	x	y	z	U (Å²)
C(4,20)	—5910(17)	4208(16)	4137(17)	769(105)
C(5,20)	—5813(17)	4543(16)	3882(17)	769(105)
C(6,20)	—5430(17)	4595(16)	3285(17)	769(105)
C(1,21)	—5698(24)	4629(9)	1564(28)	662(104)
C(2,21)	—6308(24)	4732(9)	1887(28)	662(104)
C(3,21)	—6762(24)	4975(9)	1559(28)	662(104)
C(4,21)	—6607(24)	5114(9)	907(28)	662(104)
C(5,21)	—5998(24)	5011(9)	584(28)	662(104)
C(6,21)	—5544(24)	4768(9)	913(28)	662(104)
C(1,22)	—5203(27)	3982(8)	1545(22)	604(97)
C(2,22)	—5814(27)	3874(8)	1160(22)	604(97)
C(3,22)	—5878(27)	3531(8)	935(22)	604(97)
C(4,22)	—5332(27)	3296(8)	1093(22)	604(97)
C(5,22)	—4720(27)	3404(8)	1477(22)	604(97)
C(6,22)	—4656(27)	3747(8)	1703(22)	604(97)
C(1,23)	—9183(22)	688(10)	2598(16)	404(83)
C(2,23)	—9633(22)	810(10)	2045(16)	404(83)
C(3,23)	—9524(22)	713(10)	1352(16)	404(83)
C(4,23)	—8966(22)	492(10)	1212(16)	404(83)
C(5,23)	—8516(22)	369(10)	1765(16)	404(83)
C(6,23)	—8625(22)	467(10)	2458(16)	404(83)
C(1,24)	—10171(17)	520(8)	3568(24)	413(83)
C(2,24)	—10658(17)	403(8)	3041(24)	413(83)
C(3,24)	—11191(17)	172(8)	3208(24)	413(83)
C(4,24)	—11237(17)	59(8)	3902(24)	413(83)
C(5,24)	—10750(17)	176(8)	4429(24)	413(83)
C(6,24)	—10217(17)	406(8)	4262(24)	413(83)
C(1,25)	—8746(17)	745(13)	3974(17)	496(93)
C(2,25)	—8581(17)	1031(13)	4402(17)	496(93)
C(3,25)	—8108(17)	997(13)	4989(17)	496(93)
C(4,25)	—7799(17)	677(13)	5149(17)	496(93)
C(5,25)	—7963(17)	390(13)	4722(17)	496(93)
C(6,25)	—8437(17)	425(13)	4135(17)	496(93)
C(1,26)	—9791(28)P	1205(9)	3402(23)	701(102)
C(2,26)	—9365(28)	1448(9)	3085(23)	701(102)
C(3,26)	—9568(28)	1795(9)	3053(23)	701(102)
C(4,26)	—10197(28)	1899(9)	3338(23)	701(102)
C(5,26)	—10622(28)	1657(9)	3656(23)	701(102)
C(6,26)	—10419(28)	1310(9)	3688(23)	701(102)

The mean of the six Sn—C bond lengths is in agreement with the sum of covalent radii (2.18 Å), and agrees very well with other Sn—C bond lengths reported [23]. While C—Sn—C angles are lower than the idealized tetrahedral value, the C—Sn—Ni angles are some larger. This feature, which can be explained in terms of packing forces and of the large residual of *p* character in the tin orbitals pointing to the carbon ligands, has been noticed before [24—26].

The appreciable stability of these stannyl complexes is surprisingly high compared with that of other transition metal—tin derivatives previously reported. This fact can be ascribed to the geometry of the polydentate ligand used, which forms a "nest" around the nickel atom, preventing the approach to the metal atom of other reagents.

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

Ni(1)—Sn(1)	2.541(10)	Ni(2)—Sn(2)	2.571(10)
Ni(1)—P(1)	2.274(21)	Ni(2)—P(4)	2.286(20)
Ni(1)—P(2)	2.289(18)	Ni(2)—P(5)	2.303(18)
Ni(1)—P(3)	2.302(18)	Ni(2)—P(6)	2.245(20)
Ni(1)—N(1)	2.169(49)	Ni(2)—N(2)	1.978(52)
Sn(1)—C(1,7)	2.169(42)	Sn(2)—C(1,16)	2.194(59)
Sn(1)—C(1,8)	2.173(39)	Sn(2)—C(1,17)	2.097(37)
Sn(1)—C(1,9)	2.192(50)	Sn(2)—C(1,18)	2.181(51)
Sn(1)—Ni(1)—P(1)	95.1(6)	Sn(2)—Ni(2)—P(4)	90.8(5)
Sn(1)—Ni(1)—P(2)	93.5(5)	Sn(2)—Ni(2)—P(5)	93.3(5)
Sn(1)—Ni(1)—P(3)	94.6(5)	Sn(2)—Ni(2)—P(6)	95.3(5)
Sn(1)—Ni(1)—N(1)	179.3(1.3)	Sn(2)—Ni(2)—N(2)	174.3(1.6)
P(1)—Ni(1)—P(2)	122.0(7)	P(4)—Ni(2)—P(5)	121.7(7)
P(1)—Ni(1)—P(3)	116.0(7)	P(4)—Ni(2)—P(6)	116.8(7)
P(1)—Ni(1)—NI(1)	85.4(1.4)	P(4)—Ni(2)—N(2)	84.7(1.6)
P(2)—Ni(1)—P(3)	120.3(7)	P(5)—Ni(2)—P(6)	120.5(7)
P(2)—Ni(1)—N(1)	86.6(1.3)	P(5)—Ni(2)—N(2)	86.2(1.5)
P(3)—Ni(1)—N(1)	84.7(1.3)	P(6)—Ni(2)—N(2)	89.8(1.6)
Ni(1)—Sn(1)—C(1,7)	117.2(1.3)	Ni(2)—Sn(2)—C(1,16)	118.4(1.7)
Ni(1)—Sn(1)—C(1,8)	120.1(1.6)	Ni(2)—Sn(2)—C(1,17)	115.6(1.7)
Ni(1)—Sn(1)—C(1,9)	118.1(1.7)	Ni(2)—Sn(2)—C(1,18)	118.3(1.4)
C(1,7)—Sn(1)—C(1,8)	98.8(2.0)	C(1.16)—Sn(2)—C(1,17)	99.4(2.8)
C(1,7)—Sn(1)—C(1,9)	99.0(2.0)	C(1,16)—Sn(2)—C(1,18)	100.9(2.4)
C(1,8)—Sn(1)—C(1,9)	99.7(2.4)	C(1,17)—Sn(2)—C(1,18)	101.0(1.9)

Acknowledgement

Thanks are expressed to Mr. F. Cecconi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

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