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Stannylene Complexes of Manganese, Iron, and Platinum

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Abstract—A number of stannylene complexes with different M : Sn ratios were obtained using various metals and substituents at the tin atom. The structures of the complexes were examined. A reaction of $CpMn(CO)_2THF$ with $(Ph_4As)^+(SnCl_3)^-$ gave the ionic complex $[Ph_4As]^+[CpMn(CO)_2SnCl_3]^-$ (**I**). The action of C_6F_5MgBr on the complex $C_5H_5Mn(CO)(NO)SnCl_3$ produced $C_5H_5Mn(CO)(NO)Sn(C_6F_5)_3$ (**II**). Replacement of the Cl ions in the complex $[CpFe(CO)_2]_2SnCl_2$ by phenylacetylenide groups gave rise to the neutral complex $[CpFe(CO)_2]_2Sn(C{\equiv}CPh)_2$ (**III**). A reaction of $(Dppm)PtCl_2$ (Dppm is 1,1-bis(diphenylphosphino)methane) with $SnCl_2 \cdot 2H_2O$ in the presence of diglyme yielded the ionic complex $[\eta^3\text{-}CH_3O(CH_2)_2O(CH_2)_2OCH_3)SnCl]^+[(\eta^2\text{-}Dppm)Pt(SnCl_3)_3]^-$ (**IV**). Transmetalation in a reaction of $[(Dppe)_2CoCl][SnCl_3] \cdot PhBr$ (Dppe is 1,2-bis(diphenylphosphino)ethane) with $(Dcpd)PtCl_2$ (Dcpd is dicyclopentadiene) in the presence of $SnCl_2$ afforded the ionic complex $[Pt(Dppe)_2]_3[Pt(SnCl_3)_5]_2$ (**V**). Structures **I–V** were identified by X-ray diffraction. In these structures, the formally single bonds between the atoms of transition metals M (Mn, Fe, and Pt) and Main Group heavy elements (Sn and P) having vacant *d* orbitals are appreciably shortened. The M–Sn bond length in complexes **II** and **III** are virtually independent of the substituents at the tin atom and the Pt–Sn bond length in complexes **IV** and **V** is virtually independent of the Pt : Sn ratio.

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INTRODUCTION

The facility of M–Sn bond formation producing strong and substantially shortened bonds as well as the possibility of replacing the Cl atoms at tin by various functional groups [1], including other metal atoms, render stannylene complexes (1) attractive objects for chemical bonding research and (2) valuable precursors for the synthesis of catalysts and the preparation of composite inorganic materials by pyrolysis of clusters.

A specific feature of manganese–tin bonding is that the M–Sn bond length only slightly depends on the oxidation state of tin and the ligand environment of manganese. For instance, the Mn–Sn(IV) bond length (2.589 Å) in the ionic complex $[Cp(CO)_2(PPh_3)MnSnCl_3]^+SnCl_5^-$ [2] differs insignificantly from the Mn–Sn(II) bond length (2.518 Å) in $Cp(CO)(NO)Mn{-}SnCl_3$ [3]. Both the bonds are shorter than the sum of the covalent radii of Mn and Sn (2.78 Å) [4], probably because of an extra, reverse $M \rightarrow Sn$ bond involving the lone electron pair of manganese and the vacant *d*-orbitals of tin.

On the other hand, it has been demonstrated with the complex $[CpFe(CO)_2]_2Sn(C{\equiv}CPh)(\mu\text{-}CCPh)Co_2(CO)_6$ as an example that functional phenylacetylenide groups can be coordinated to both the Sn atom and other transition metals (specifically, cobalt carbonyl) without making substantial changes to the geometry of the fragment $[CpFe(CO)_2]_2Sn$ [5]. In addition, according to data obtained by us and French researchers [6] for the ionic complex $[(C_6H_6)Ru(NCPh)_2(SnCl_3)]^+[(C_6H_6)Ru(SnCl_3)_3]^-$, the Ru–Sn bond lengths in the cation (2.598 Å) and the anion (on average, 2.552 Å) differ only slightly.

Many complexes obtained by reactions of $PtCl_2$ and $PtCl_4$ with $SnCl_2 \cdot 2H_2O$ have a shortened Pt–Sn bond and the Pt : Sn ratio varying from 1 : 5 to 1 : 3. For instance, the anionic platinum(II) complex $[EtNH_3]_3[Pt(SnCl_3)_5]$ that forms in 3 M HCl in the presence of $[EtNH_3]Cl$ shows a trigonal-bipyramidal environment of the platinum atom [7]. The anion in the complex $[\{Pt(PEt_3)Cl\}_2\mu\text{-}(TPP)][Pt(SnCl_3)_4(PEt_3)]$ (TPP is 2,3,5,6-tetrakis(α-pyridyl)pyrazine) has a similar geometry, the dinuclear cation also containing the platinum atoms [8]. The organometallic anionic complex $(COD)Pt(SnCl_3)_3^-$ (COD is 1,5-cyclooctadiene) has been synthesized [9]. Finally, the intermetallic compound $PtSn_2$ has been reported to have a Pt : Sn ratio of 1 : 2 and a Pt–Sn bond length of 2.78 Å [10], which is close to the sum of their covalent radii.

This work was intended to continue our investigations into the synthesis and structures of new stannylene complexes of transition metals (manganese, iron, and platinum) with varied environment of the metal and tin atoms.

EXPERIMENTAL

All reactions were carried out under argon in dehydrated solvents using standard Schlenk ware. IR spectra were recorded on Specord 82 IR and Specord 75 IR spectrometers (KBr pellets) in the 400–4000 cm^{-1} range. Elemental analysis was performed on a Carlo-Erba CHNS analyzer.

Synthesis of $AsPh_4^+CpMn(CO)_2SnCl_3^-$ (I). A solution of $CpMn(CO)_3$ (0.30 g, 1.47 mmol) in THF (25 mL) was exposed to UV light for 45 min. Then anhydrous $SnCl_2$ (0.14 g, 0.74 mmol) and tetraphenylarsonium chloride (0.30 g, 0.74 mmol) were added. The resulting solution was stirred for 2 h (its color turned from crimson to orange) and evaporated to dryness. Organic materials were extracted from the residue with CH_2Cl_2 (20 mL). The extract was filtered, and then benzene (2 mL) was added. The mixture was concentrated in vacuo until crystallization began. The crystallization at –10°C for 24 h produced yellow crystals. The yield of complex **I** was 0.26 g (46.4%). Single crystals were used for X-ray diffraction.

For $C_{31}H_{25}O_2Cl_3MnAsSn$ (M = 784.46)

anal. calcd., %:	C, 47.46;	H, 3.21.
Found, %:	C, 47.82;	H, 3.24.

IR (KBr, ν, cm^{-1}): 1910 vs, 1840 vs, 1420 m, 1060 m, 730 s, 660 m.

Synthesis of $(CpMn(CO)(NO)Sn(C_6F_5)_3$ (II). An ethereal 1.38 M solution of C_6F_5MgBr (1.9 mL, 2.59 mmol) was added dropwise at room temperature to a solution of $CpMn(CO)(NO)SnCl_3$ (302 mg, 0.75 mmol) in Et_2O (20 mL). The reaction mixture was stirred for 1 h, which resulted in dissolution of the orange crystals of the starting compound and formation of a gray precipitate. The mixture was evaporated to dryness, producing an orange-brown oil. Organic materials were extracted from the oil with CH_2Cl_2 (15 mL). The extract was diluted with hexane (10 mL), concentrated to 15 mL, and kept at –10°C. The resulting large ruby crystals were washed with CH_2Cl_2–C_5H_{12} (1 : 1) (2 × 10 mL) and pentane (10 mL) and dried in vacuo. The yield of complex **II** was 37.8 mg (6.3%).

IR (ν, cm^{-1}): 2010 s, 2000 s, 1780 s, 1755 s, 1625 w, 1535 w, 1500 s, 1550 vs, 1355 m, 1260 w, 1160 w, 1060 s, 950 s, 835 vw, 770 vw, 600 w.

^{19}F NMR (282 MHz; 300 K), δ (ppm): –121.2 (d, 2F, *ortho*, J = 17.6 Hz); –149.8 (t, 1F, *para*, J = 19.0 Hz); –159.4 (m, 2F, *meta*).

^{1}H NMR (300 MHz; 300 K), δ (ppm): 5.10 (s, Cp).

Synthesis of $[CpFe(CO)_2]_2Sn(C\equiv CPh)_2$ (III). A 1.6 M solution of n-LiC_4H_9 (1.4 mL, 2.3 mmol) in hexane was added to a solution of phenylacetylene (0.218 mL, 2.3 mmol) in hexane (10 mL), producing a white jellylike precipitate. The reaction mixture was stirred with a magnetic stirring bar for 20 min. Then an orange-red solution of $[CpFe(CO)_2]_2SnCl_2$ (0.296 g, 1.70 mmol) in benzene (25 mL) was added. The resulting orange solution was stirred for 15 min and evaporated to dryness. Organic materials were extracted from the residue with cyclohexane (22 mL). The extract was concentrated by half and kept at 5°C for 48 h. The yield of complex **III** was 0.082 g (19.6%), dark red crystals suitable for X-ray diffraction. Elemental analysis of complex **III** was not done because of its instability.

IR (KBr, ν, cm^{-1}): 2110 w, 1980 vs, 1960 vs, 1930 vs, 1910 vs, 1680 w, 820 m, 755 m, 630 m, 570 s.

Synthesis of $[(CH_3O(CH_2)_2O(CH_2)_2OCH_3)SnCl(Dppm)]$ $[Pt(SnCl_3)_3]$ (IV). An excess of $SnCl_2 \cdot 2H_2O$ was added to a suspension of $(Dppm)PtCl_2$ (0.5 g) in a mixture of CH_2Cl_2 (15 mL), EtOH (15 mL), and diglyme (15 mL). The reaction mixture was left quiet for 1 h and then stirred. Diethyl ether (55 mL) was added, and the resulting mixture was kept overnight in a refrigerator at –40°C. The red-orange precipitate that formed was separated. The solution was diluted with CH_2Cl_2 (20 mL) and decanted promptly with care (under no circumstances should filtration be used). The red-orange solution was left in air, producing in 12 h red-orange crystals suitable for X-ray diffraction.

For $C_{31}H_{36}Cl_{10}O_3P_2Sn_4Pt$ (M = 1543)

anal. calcd., %:	C, 24.13;	H, 2.35.
Found, %:	C, 24.08;	H, 2.55.

IR (KBr, ν, cm^{-1}): 1437 w, 1351 w, 1308 w, 1243 w, 1097 w, 1083 w, 1041 m, 999 m, 864 m, 828 m, 742 s, 772 m, 689 s, 540 s, 501 s, 479 m, 437 w, 426 w.

Synthesis of $[Pt(Dppe)_2]_3[Pt(SnCl_3)_5]_2$ (V). Tetrahydrofuran (40 mL) was added to a mixture of $[(Dppe)_2CoCl^+][SnCl_3^-] \cdot C_6H_5Br$ (0.22 g, 0.172 mmol), $SnCl_2 \cdot 2H_2O$ (0.156 g, 0.691 mmol), and $(Dcpd)PtCl_2$ (0.115 g, 0.289 mmol) in a molar ratio of 3 : 12 : 5. A red precipitate formed immediately. After 1 h, the blue supernatant was decanted. The precipitate was washed with THF (20 mL), dried, and left with acetonitrile (20 mL) for 12 h. The resulting single crystals were suitable for X-ray diffraction. An additional crop of the product was obtained by concentration of the super-

Crystallographic parameters and the data collection and refinement statistics for structures **I–V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
M	823.46	797.92	759.01	1542.96	2808.10
Diffractometer	Bruker APEX II CCD			Oxford Diffraction Gemini Ultra	Bruker APEX II CCD
Radiation (λ, Å)	MoK_{α} (0.71073)				
Temperature, K	296(2)	296(2)	150(2)	123(2)	296(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$C2/c$	$P2_1/c$	$C2/c$
a, Å	18.3759(9)	10.548(4)	27.823(3)	13.3951(1)	56.30(3)
b, Å	15.5817(8)	10.862(4)	7.6556(7)	16.8117(2)	13.762(6)
c, Å	23.0296(12)	11.497(4)	16.9124(16)	20.9786(2)	28.903(13)
α, deg	90	78.813(5)	90	90	90
β, deg	90	85.536(5)	116.355(2)	92.899(1)	119.292(6)
γ, deg	90	81.112(5)	90	90	90
V, Å^3	6594.0(6)	1275.2(8)	3227.9(5)	4718.22(8)	19529(15)
Z	8	2	4	4	8
ρ_{calcd}, g/cm^{-3}	1.659	2.078	1.562	2.172	1.910
μ, mm^{-1}	2.409	1.610	1.692	5.707	5.371
F(000)	3256	764	1528	2896	10640
θ scan range, deg	1.77–28.35	1.81–29.19	2.45–30.00	3.05–36.51	1.62–26.00
Scan mode	ω				
Number of unique reflections (N_1)	8234 (R_{int} = 0.0347)	6797 (R_{int} = 0.0238)	4658 (R_{int} = 0.0191)	23046 (R_{int} = 0.0465)	19181 (R_{int} = 0.2043)
Number of reflections with $I > 2\sigma(I)$ (N_2)	6740	5782	4127	5256	8292
Number of parameters refined	379	397	195	462	961
GOOF (F^2)	1.063	0.995	1.056	1.033	0.924
R_1 for N_2	0.0269	0.0289	0.0219	0.0276	0.0664
wR_2 for N_1	0.0791	0.0780	0.0580	0.0582	0.1872
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.500/–0.358	0.449/–0.324	1.010/–0.306	1.517—1.051	1.961/–2.582

natant and crystallization from THF. The yield of complex **V** was 0.265 g (87.5%).

For $C_{156}H_{144}P_{12}Cl_{30}Sn_{10}Pt_5$ (M = 5616)

anal. calcd., %:	C, 33.36;	H, 2.58.
Found, %:	C, 33.47;	H, 2.75.

IR (KBr, ν, cm^{-1}): 2920 w, 1438 m, 1434 m, 1401 w, 1307 w, 1238 w, 1189 w, 1161 w, 1102 m, 999 m, 879 m, 825 w, 818 w, 706 m, 689 s, 668 m, 534 s, 511 w, 480 m, 445 w, 431 w.

X-ray diffraction study. The crystallographic parameters and the data collection and refinement statistics for structures **I–V** are given in table. Absorption correction was applied by multiple measurements of equivalent reflections with the SADABS programs [10]. Structures **I–V** were solved by the direct methods and refined anisotropically for the non-hydrogen atoms by the least-squares method on F^2 with the SHELXTL program package [11]. The hydrogen atoms were located geometrically. Selected bond lengths and bond angles in structures **I–V** are given in the captions to Figs. 1–5.

Atomic coordinates and other parameters for structures **I–V** have been deposited with the Cambridge Crystallographic Data Centre (nos. 953659 (**I**), 953335 (**II**), 953334 (**III**), 947794 (**IV**), and 947123 (**V**)); http://www.ccdc.cam.ac.uk/data_request/cif).

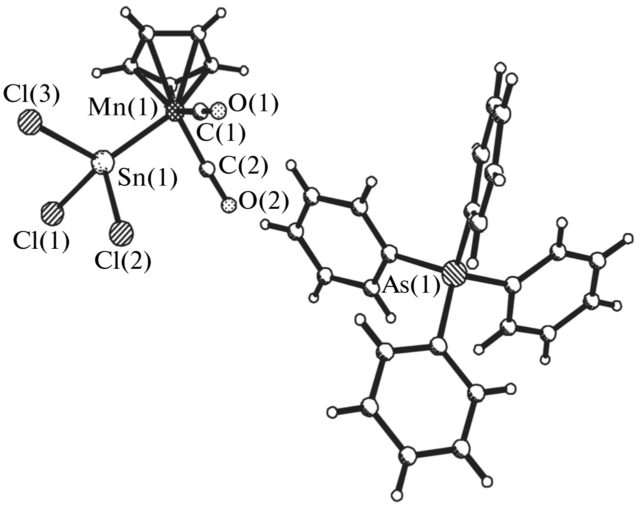


Fig. 1. Molecular structure of complex **I**. Bond lengths: Mn–Sn, 2.4457(4) Å; Sn–Cl(1), 2.3951(7) Å; Sn–Cl(2), 2.3986(7) Å; Sn(1)–Cl(3), 2.4116(6) Å.

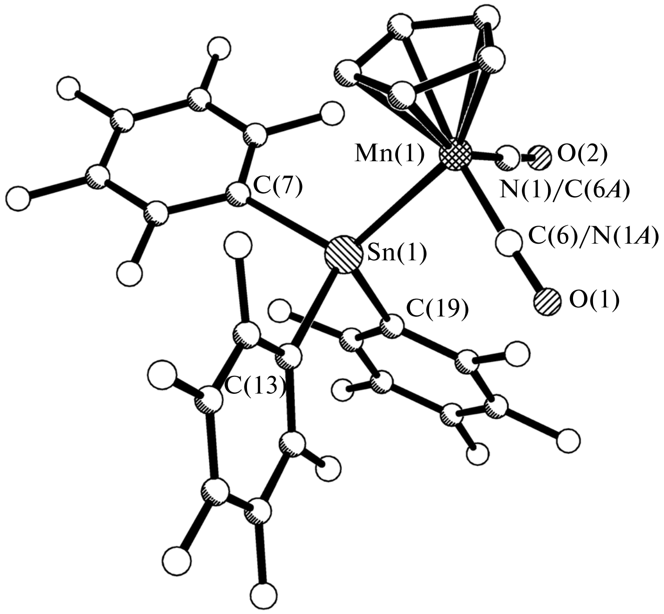


Fig. 2. Molecular structure of complex **II**. Selected bond lengths and bond angles: Mn(1)–Sn(1), 2.5494 Å; Mn(1)–N(1)/C(6*A*), 1.730 Å; Mn(1)–N(1*A*)/C(6), 1.734 Å; Sn(1)–C(7), 2.188 Å; Sn(1)–C(19), 2.198 Å; Sn(1)–C(13), 2.189 Å; C(7)Sn(1)C(13), 105.51°; C(7)SnC(19), 102.08°; C(13)SnC(19), 101.85°.

RESULTS AND DISCUSSION

Extensive investigations made in the 1960s into organometallic transition metal complexes and clusters containing the M–Sn bond have been reviewed in [1], with notice of shortening of these bonds. This general trend is due to dative interactions of the lone electron pair of a transition metal with the antibonding orbitals of the Sn–X bond or with the *d* orbitals of tin [1] and is complicated only in the presence of ligands that compete with tin for the coordination sites of a transition metal. For instance, in the 16-electron gold bisphosphine complex $[Au(PMe_2Ph)_2SnCl_3]$, the Au–Sn bond length (2.881 Å) [12] is greater than the sum of the covalent radii of these atoms ($r_{Au} + r_{Sn} = 1.36 + 1.39 = 2.75$ Å) [4], which suggests a considerable ionic character of this bond. Also in the 16-electron nickel complex $(2,2\text{-}iso\text{-}(Pr_2P)_2C_2H_4)Ni(\mu\text{-}C_2H_2)SnL_2]$ containing the four-membered ring $NiSnC_2H_2$ and bulky bis(trimethylsilyl)methyl groups L at the tin atom [13], the Ni–Sn bond length (2.625 Å) agrees with the sum of the covalent radii ($r_{Ni} + r_{Sn} = 1.24 + 1.39 = 2.63$ Å) [4], while this bond in $Ni(\eta^2\text{-}C_2H_4)_2(SnL_2)$ is formally a double one shortened to 2.387 Å [14].

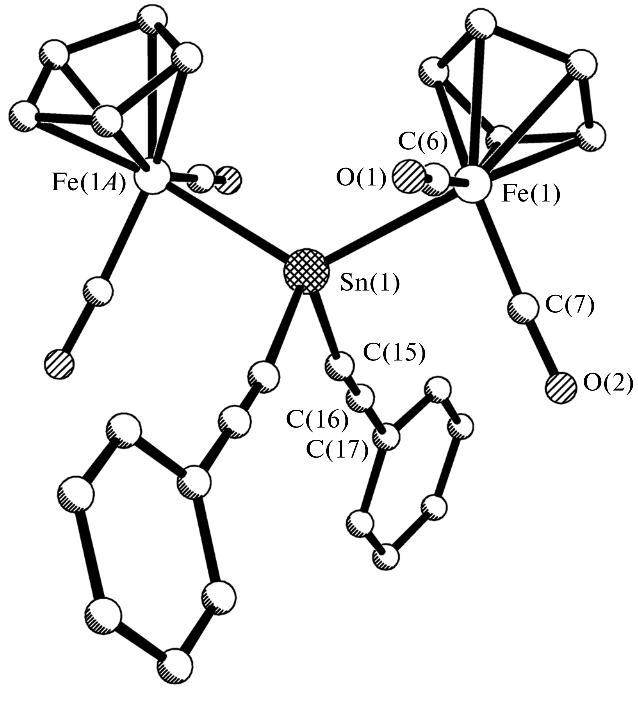


Fig. 3. Molecular structure of complex **III**. Selected bond lengths and bond angles: Fe(1)–Sn(1), 2.5457(3) Å; C(15)–Sn(1), 2.131(2) Å; C(16)–C(15), 1.202(3) Å; Fe(1)Sn(1)Fe(1*A*), 122.55(1)°; C(15)Sn(1)C(15*A*), 102.55(7)°; C(16)C(15)Sn(1), 166.1(2)°.

We found that $CpMn(CO)_2(THF)$ reacts with the salt $AsPh_4^+SnCl_3^-$ in THF to form ionic complex **I**, in which the THF molecule is displaced by the $SnCl_3^-$ anion. In the IR spectrum of complex **I** (in CH_2Cl_2), the frequencies of the CO stretching vibrations (1910 and 1840 cm^{-1}) are lower by 120 cm^{-1} than those for $CpMn(CO)_3$. According to X-ray diffraction data (Fig. 1), the complex contains the Mn–Sn bond (2.4457(4) Å) strongly shortened compared to the sum

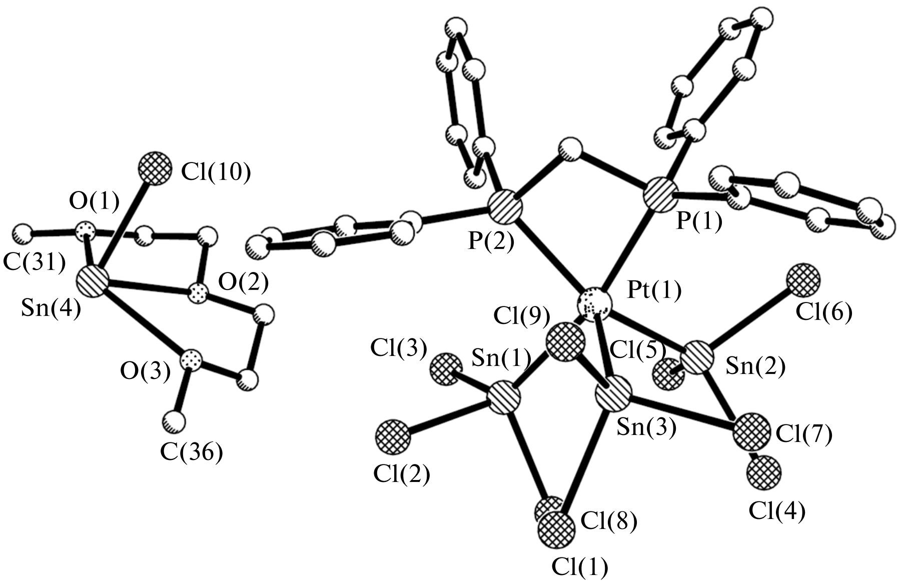
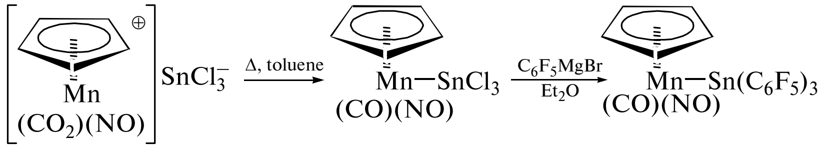


Fig. 4. Structures of the cation and the anion in complex **IV**. The hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles: Pt(1)–Sn(1), 2.5576(2) Å; Pt(1)–Sn(2), 2.5807(2) Å; Pt(1)–Sn(3), 2.6448(2) Å; Sn(4)–O(1), 2.4304(17) Å; Sn(4)–O(2), 2.3757(17) Å; Sn(4)–O(3), 2.525(2) Å; Pt(1)–P(1), 2.3147(5) Å; Pt(1)–P(2), 2.3150(5) Å; Sn(1)Pt(1)Sn(2), 87.77(1)°; Sn(2)Pt(1)Sn(3), 102.46(1)°; Sn(1)Pt(1)Sn(3), 93.86(1)°; Sn(1)Pt(1)P(1), 166.51(1)°; Sn(1)Pt(1)P(2), 96.50(1)°; Cl(10)Sn(4)O(1), 90.26(5)°; Cl(10)Sn(4)O(2), 82.86(5)°; Cl(10)Sn(4)O(3), 90.48(5)°.

of the covalent radii of these atoms (2.78 Å) [4]. When comparing structure **I** with the neutral complex $CpMn(CO)(NO)SnCl_3$ (Mn–Sn 2.5178 Å) described earlier, one can see that this bond is substantially shorter in structure **I**, probably because of a stronger dative Mn → Sn interaction in the anionic complex.

Treatment of the neutral stannylene complex $CpMn(CO)(NO)SnCl_3$ with a Grignard reagent prepared from bromopentafluorobenzene and activated metallic magnesium afforded complex **II** containing three C_6F_5 groups. This complex was characterized by X-ray diffraction (Fig. 2) and IR and NMR spectroscopy. In the IR spectrum of complex **II**, the frequencies of the CO (2000 cm^{-1}) and NO stretching vibrations (1780 cm^{-1}) are lower than those in the spectrum of the starting complex (2025 and 1790 cm^{-1}, respectively).



According to X-ray diffraction data, the Mn–Sn bond in complex **II** is only slightly (by 0.03 Å) longer than that in the starting trichloride complex; however, it is shorter than the sum of the covalent radii of Mn and Sn. The angles CSnC (on average, 103.04°) are much smaller than those in similar complexes containing no transition metal (on average, 113.4° for $ClSn(C_6F_5)_3$ and 109.06° for $Sn_2(C_6F_5)_6$). The CO and NO groups in the crystal of complex **II** are disordered with equal occupancies.

The ^{19}F NMR spectrum of complex **II** shows three signals, which suggests unrestricted rotation about the Mn–Sn bond. The chemical shifts (δ –121.2, *ortho*; –149.8, *para*; –159.4, *meta*) are in the range typical of $Sn(C_6F_5)_3$-containing complexes (δ –121.9, *ortho*; –145.0, *para*; –157.2, *meta* for $ClSn(C_6F_5)_3$ and δ –125.6, *ortho*; –150.0, *para*; –161.8, *meta* for $Sn_2(C_6F_5)_6$ [15]).

A reaction of yellow-orange crystals of the complex $[CpFe(CO)_2]_2SnCl_2$ with a white suspension of

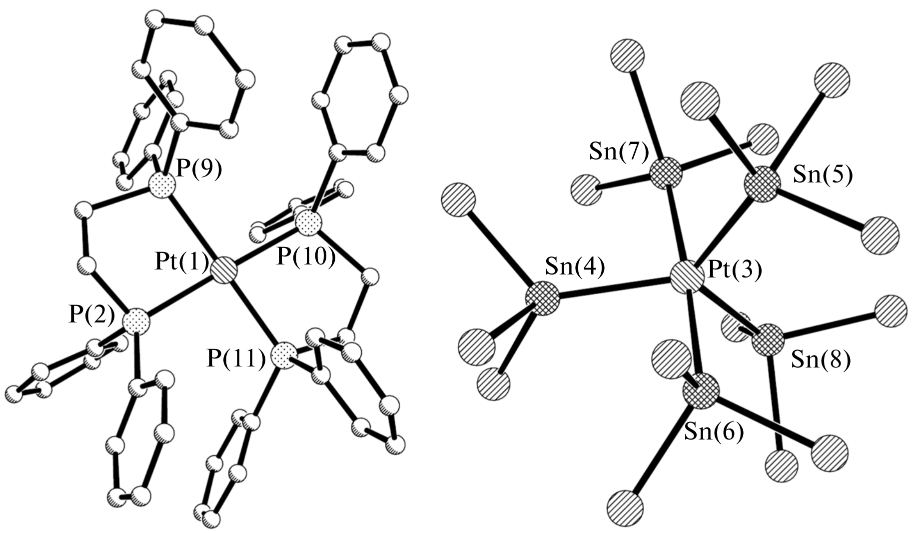
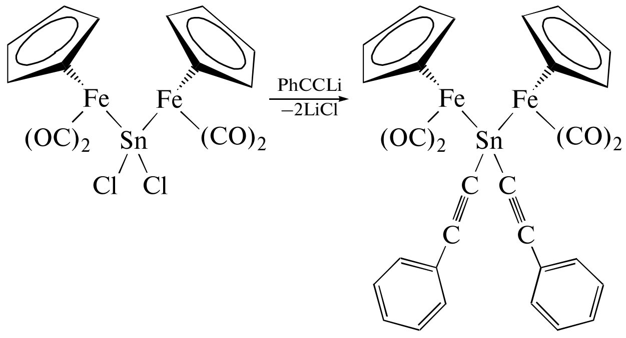


Fig. 5. Structures of the cation and the anion in complex **V**. The hydrogen atoms are omitted for clarity. Selected bond lengths: Pt(3)–Sn(4), 2.5503(15) Å; Pt(3)–Sn(5), 2.5655(15) Å; Pt(3)–Sn(6), 2.5552(17) Å; Pt(3)–Sn(7), 2.5421(17) Å; Pt(3)–Sn(8), 2.5655(17) Å; Pt(1)–P(11), 2.327(5) Å; Pt(1)–P(2), 2.330(5) Å; Pt(1)–P(9), 2.341(5) Å; Pt(1)–P(10), 2.344(5) Å.

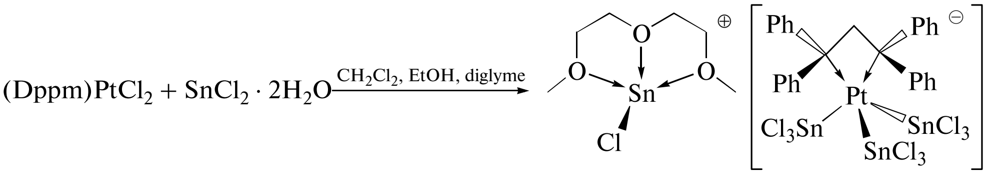
PhC≡CLi in cyclohexane gave complex **III**, which was confirmed by IR spectroscopy and X-ray diffraction.



This complex has been synthesized earlier [5] but not characterized by X-ray diffraction. Unfortunately, we failed to perform elemental analysis of complex **III** because of its strong tendency toward hydrolysis.

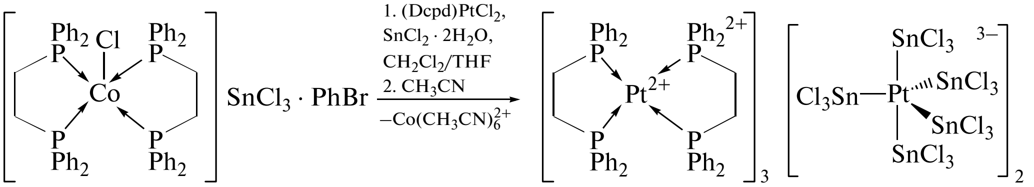
According to X-ray diffraction data (Fig. 3), the Fe–Sn bond (2.54 Å) is considerably shorter than the sum of the covalent radii of Fe and Sn (2.71 Å) [4]; its length remains virtually unchanged upon the replacement of two Cl atoms by two phenylacetylenide ligands. The C≡C bond (1.20 Å) has the same length as that in phenylacetylene. Structure **III** adopts a *syn*-conformation: the torsion angle C–Fe–Fe–C is 4.76(9)°; the angles CFeC between the CO groups are 93.05(8)°.

In connection with our investigations of platinum–tin clusters as precursors of PtSn-containing catalysts for electrochemical oxidation of alcohols [16] as well as with the evidence that the catalytic systems Pt_3Ru_2Sn/C are more active in methanol oxidation than are the catalysts Pt/C or PtRu/C [17], here we obtained ionic complexes with different Pt : Sn ratios. For instance, a reaction of the diphosphine complex $(Dppm)PtCl_2$ with $SnCl_2 \cdot 2H_2O$ in CH_2Cl_2–ethanol in the presence of diglyme produced a yellow product, which was recrystallized from CH_2Cl_2 to give yellow complex **IV**. According to X-ray diffraction data (Fig. 4), the electron-rich anion $(Dppm)Pt(SnCl_3)_3^-$ has a distorted trigonal-bipyramidal geometry with formally single Pt–P and Pt–Sn bonds. However, they are substantially shorter (Pt–P, 2.3147(5)–2.3150(5) Å; Pt–Sn, 2.5576(2)–2.6448(2) Å) than the sum of the covalent radii of the corresponding atoms ($r_{Pt} + r_P = 1.36 + 1.07 = 2.43$ Å; $r_{Pt} + r_{Sn} = 1.36 + 1.39 = 2.75$ Å) [4].



The tin atom in the cation [η^3-$CH_3O(CH_2)_2O(CH_2)_2OCH_3)SnCl]^+$ is coplanar with the coordinated O atoms of the diglyme (Sn–O, 2.3757(17), 2.4304(17), and 2.525(2) Å). This plane is nearly perpendicular to the Sn–Cl bond (the corresponding ClSnO angles are 82.86°, 90.26°, and 90.48°). In the crystal of complex **IV**, the cations form dimeric Sn_2Cl_2 motifs containing single Sn–Cl bonds (2.4586(7) Å; $r_{Sn} + r_{Cl} = 1.39 + 1.02 = 2.41$ Å) and a long intermolecular Sn–Cl contact (3.236 Å) making an angle of 135.82° with the central Sn–O bond. This structure also shows a long symmetrical Sn–Cl contact (3.356 Å) with one of the $SnCl_3$ groups in the anion (angle ClSnO, 135.82°). Note that the presence of the tin atom in the cation leads to a total Pt : Sn ratio of 1 : 4 in complex **IV**.

On the other hand, the total Pt : Sn ratio proved to be 1 : 2 in cluster **V**, which is the product of unexpected transmetalation of $(Dcpd)PtCl_2$ with the salt $[(Dppe)_2CoCl][SnCl_3] \cdot PhBr$ in acetonitrile in the presence of $SnCl_2$. The resulting complex **V** crystallizes slowly to give red-orange crystals that are insoluble in common organic solvents.



According to X-ray diffraction data (Fig. 5), complex salt **V** consists of three electron-deficient 16e$^-$ platinum(II) dications $Pt(Dppe)_2^{2+}$ (Pt–P 2.327(5)–2.344(5) Å) and two trigonal-bipyramidal electron-rich anions $Pt(SnCl_3)_5^{3-}$. The Pt–P (2.327(5)–2.344(5) Å) and Pt–Sn bonds (2.5421(17)–2.5655 Å) are substantially shorter than the sum of the covalent radii of the corresponding atoms. Both the ions have been already documented separately; however, such a combination of them was found for the first time.

To sum up, X-ray diffraction study of complexes **I**–**V** revealed that the formally single bonds between the atoms of transition metals M (Mn, Fe, and Pt) and Main Group heavy elements (Sn and P) having vacant *d* orbitals are appreciably shortened. The M–Sn bond length in complexes **II** and **III** are virtually independent of the substituents at the tin atom and the Pt–Sn bond length in complexes **IV** and **V** is virtually independent of the Pt : Sn ratio.

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