Journal of Organometallic Chemistry, 371 (1989) 35–41
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09945

Syntheses and molecular structures of complexes formed in the reaction of dichlorobis[(π-cyclopentadienyl)-dicarbonyliron]tin(IV) with polydentate *o*-(nuclear substituted α-hydroxybenzylidenehydrazonomethyl)phenols

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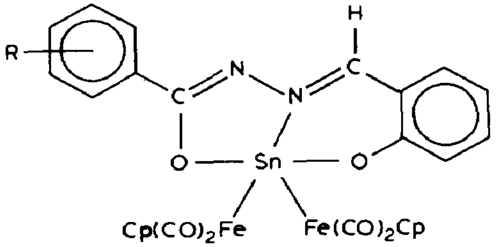
(Received January 9th, 1989)

Abstract

Eleven complexes having the general formula, $[\pi\text{-}C_5H_5Fe(CO)_2]_2[RC_6H_4C(O)N_2\text{-}CHC_6H_4O]Sn$ (R = H, *p*-NO_2, *p*-Cl, *p*-Br, *p*-I, *p*-CH_3, *p*-OCH_3, *m*-NO_2, *m*-OCH_3, and 3,5-dinitro) have been synthesized. These complexes have been characterized by ^1H NMR, IR and MS, and by elemental analysis. A single crystal X-ray diffraction study (R = *o*-NH_2) confirmed their molecular structures and revealed that the *o*-(nuclear substituted α-hydroxybenzylidenehydrazonomethyl)phenols are tridentate planar ligands. The crystals are monoclinic, space group $P2_1/n$ with a 13.495(4), b 13.058(2), c 18.311(3) Å, β 94.90(2)°, V 3214.9 Å^3, $Z = 4$, D_c 1.66 g/cm^3. Final discrepancy factors of $R = 0.033$ and $R_w = 0.039$ were obtained for 3075 observed independent reflections. The tin atom has a distorted trigonal bipyramidal coordination. Sn–Fe bond lengths are 2.5421 and 2.5242 Å (av. 2.5332 Å). In these complexes, the ligands exist in the enol-form.

Introduction

Some new organometallic compounds obtained by the substitution reactions of ligands in the polynuclear compounds help to elucidate the properties of metal–metal bonds in polynuclear compounds. Although there are some reports [1–4] on the substitution of chlorine atoms in dichlorobis(π-cyclopentadienyldicarbonyliron)tin (IV), the substituting ligands were limited to inorganic and a number of alkyl anions; the central tin atom in these complexes retains four coordination. We selected the *o*-(nuclear substituted α-hydroxybenzylidenehydrazonomethyl)phenols as the new ligands to substitute for the chlorine atoms and thereby obtained 11 new complexes containing Sn–Fe bonds. These complexes have been characterized by ^{1}H NMR, IR and MS, and by elemental analysis and have been formulated as follows:



where R = H, *p*-NO_2, *p*-Cl, *p*-Br, *p*-I, *p*-CH_3, *p*-OCH_3, *o*-NH_2, *m*-NO_2, *m*-OCH_3, and 3,5-dinitro. An X-ray diffraction study for R = *o*-NH_2 revealed that the tin atom in these new complexes has five coordination in a trigonal bipyramidal structure.

Results and discussion

The reactions of $[Cp(CO)_2Fe]_2SnCl_2$ with *o*-(nuclear substituted α-hydroxybenzylidenehydrazonomethyl)phenols give high yields (see Table 4) and can be carried out smoothly in the presence of triethyl amine as the acceptor of the hydrogen chloride which is the by-product from this reaction. Rigorous reaction conditions will result in lower yields because of the weak Sn–Fe bond present in the reactant, $[Cp(CO)_2Fe]_2SnCl_2$. Refluxing can remove the hydrogen chloride but the yield is much lower (about 30%). Addition of NaOH to the reaction system instead of refluxing can remove the hydrogen chloride, but the water formed by the neutralization would decompose the product and the reactant to result in a low yield.

Rastogi et al. [5] discussed the IR spectra of benzoyl hydrazones in detail and concluded that this kind of ligand is present in the keto-form. However, these ligands are capable of undergoing keto–enol tautomerism and thus can coordinate with a metal atom in either of these two forms depending on the experimental conditions. A comparison of the IR spectra of the free ligands with those of the relevant complexes, several obvious differences are apparent. a) The medium bands in the region 3060–3370 cm^{-1} which are usually assigned to the imine (due to ν(N–H)) in the spectra of the free ligands disappear from the spectra of the complexes. b) The spectra of the complexes show new bands at ca. 1587 cm^{-1} which can be assigned to the stretching vibration mode of the conjugate $>C{=}N{-}N{=}C<$ group [6]. c) The broad weak bands at ca. 2750 cm^{-1} due to the interaction between intramolecular hydrogen bond (–N · · · H–O–) are absent in the spectra of the complexes. d) The new bands at ca. 510 cm^{-1} and 457 cm^{-1} in the spectra of the complexes indicate that there are Sn–O and Sn–N bonds in these complexes. In light of these differences, it can be inferred that the ligands coordinate with the tin atom by the phenolic- and enolic-oxygen atoms through deprotonation. This inference is supported by the results of an X-ray diffraction study.

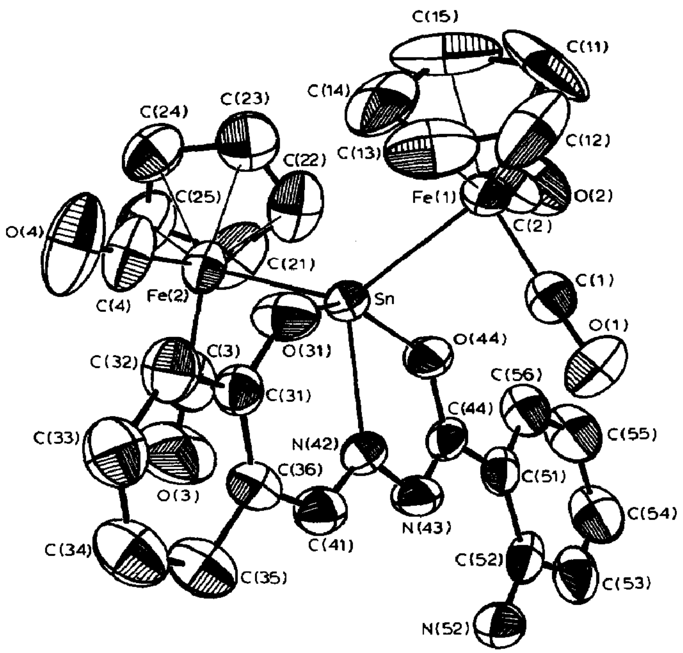


Fig. 1. Molecular structure of the complex (R = *o*-NH_2).

Fig. 1 is a perspective drawing of [π-$C_5H_5Fe(CO)_2]_2[NH_2C_6H_4C(O)N_2CHC_6H_4$-O]Sn showing the labelling scheme. The final fractional coordinates of non-hydrogen atoms with equivalent isotropic thermal parameters are listed in Table 1. Tables 2 and 3 show the selected bond distances and angles, respectively. From Fig. 1 it can be seen that *o*-(α-hydroxy-*o*-aminobenzylidenehydrazonomethyl)phenol is a tridentate planar ligand. The tin atom lies in this plane and forms a five- and six-membered chelate ring with the polydentate ligand. The tin atom has a distorted trigonal bipyramidal coordination with two oxygen atoms occupying the axial positions and two iron atoms and one nitrogen atom occupying the equatorial positions. The tin atom is displaced by 0.12 Å from the equatorial plane in the direction of the phenolic-oxygen atom. This arrangement is in accord with that in which more electronegative ligands occupy the axial positions preferentially in the complexes containing five coordinated tin [7]. It has been reported [4] that the Sn–Fe bond length shortens as the effective electronegativity of the substituents on the tin atom increases for the complexes of general formula [π-$Cp(CO)_2Fe]_2SnR_2$ in the range of 2.60 Å (R = Me) [2] to 2.492 Å (R = Cl) [8]. In our complex (R = *o*-NH_2), the Sn–Fe bonds are 2.5242 Å and 2.5421 Å (av. 2.5332 Å), which lie in the middle of the above-mentioned range and are close to those for [π-$Cp(CO)_2Fe]_2Sn$(*p*-$CH_3C_6H_4$)Br [9]. As in [π-$Cp(CO)_2Fe]_2SnCl_2$, each iron in the product molecule keeps an approximately octahedral environment; the cyclopentadienyl group occupies three coordination sites and the tin and two carbonyls occupying the other three sites. Two [π-$Cp(CO)_2Fe$] groups maintain an approximate C_2 symmetry around an axis passing through the tin atom and the coordinating nitrogen atom. In the ORTEP drawing, the 50% probability ellipsoids (Fig. 1), corresponding to the carbon atoms of cyclopentadienyl rings have the long axes

Table 1

Fractional coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	$B_{eq.}$ ($Å^2$)
Sn	0.11246(3)	0.16172(4)	0.33737(3)	3.077(9)
Fe(1)	−0.05088(7)	0.06590(8)	0.34185(6)	3.44(2)
Fe(2)	0.22716(7)	0.17063(9)	0.23565(6)	4.20(2)
C(11)	−0.1421(6)	−0.0618(7)	0.325(1)	12.0(5)
C(12)	−0.894(8)	−0.0643(6)	0.3981(6)	9.2(2)
C(13)	0.0074(8)	−0.0681(6)	0.3893(6)	7.2(3)
C(14)	0.0231(8)	−0.0696(6)	0.3199(6)	7.5(3)
C(15)	−0.0631(9)	−0.0662(7)	0.2786(6)	8.7(3)
C(1)	−0.0687(5)	0.1489(6)	0.4140(4)	3.8(2)
C(2)	−0.1053(5)	0.1474(6)	0.2738(4)	4.7(2)
O(1)	−0.0821(4)	0.2024(4)	0.4625(3)	5.8(1)
O(2)	−0.1446(4)	0.1986(5)	0.2292(4)	7.3(2)
C(21)	0.1799(8)	0.2665(8)	0.1472(5)	7.2(3)
C(22)	0.0998(7)	0.2001(8)	0.1650(5)	6.8(3)
C(23)	0.1289(7)	0.0960(8)	0.1564(5)	6.3(2)
C(24)	0.2274(7)	0.0980(8)	0.1320(5)	6.5(2)
C(25)	0.2592(7)	0.2013(8)	0.1263(5)	6.6(2)
C(3)	0.2886(6)	0.2696(7)	0.2852(5)	6.2(2)
C(4)	0.3030(6)	0.0736(8)	0.2778(5)	6.6(2)
O(3)	0.3301(5)	0.3357(6)	0.3166(5)	10.0(2)
O(4)	0.3553(5)	0.0111(6)	0.3043(4)	10.0(2)
O(31)	0.1920(4)	0.0634(4)	0.4161(3)	4.9(1)
C(31)	0.2647(5)	0.0796(6)	0.4673(4)	3.6(2)
C(32)	0.3220(6)	−0.0052(6)	0.4937(5)	4.7(2)
C(33)	0.3985(6)	0.0077(7)	0.5497(5)	5.5(2)
C(34)	0.4189(7)	0.1032(7)	0.5808(5)	6.2(2)
C(35)	0.3612(6)	0.1876(7)	0.5567(5)	5.4(2)
C(36)	0.2831(5)	0.1760(6)	0.4991(4)	3.7(2)
C(41)	0.2263(5)	0.2670(6)	0.4795(4)	4.0(2)
N(42)	0.1572(4)	0.2756(4)	0.4261(3)	3.3(1)
N(43)	0.1146(4)	0.3725(4)	0.4209(3)	3.8(1)
C(44)	0.0527(5)	0.3813(5)	0.3612(4)	3.4(1)
O(44)	0.0379(3)	0.3091(3)	0.3136(3)	4.0(1)
C(51)	−0.0008(5)	0.4788(5)	0.3470(4)	3.8(2)
C(52)	0.0088(5)	0.5645(5)	0.3960(4)	4.2(2)
C(53)	−0.0493(6)	0.6528(6)	0.3758(5)	5.8(2)
C(54)	−0.1115(6)	0.6566(7)	0.3109(6)	6.6(2)
C(55)	−0.1202(7)	0.5723(7)	0.2628(6)	6.4(2)
C(56)	−0.0650(6)	0.4838(6)	0.2810(5)	4.9(2)
N(52)	0.0725(5)	0.5682(5)	0.4578(4)	4.6(1)
C(61)	0.7403(8)	0.3612(9)	0.3898(6)	8.2(3)
C(62)	0.6765(9)	0.2789(9)	0.3977(8)	9.3(4)
C(63)	0.5824(9)	0.2963(9)	0.4222(7)	9.4(4)
C(64)	0.5557(9)	0.397(1)	0.4381(7)	9.0(3)
C(65)	0.6196(9)	0.4778(9)	0.4277(7)	8.8(3)
C(66)	0.7125(8)	0.4587(9)	0.4042(6)	8.0(3)

parallel to the ring planes, which indicates a large libration of these rings around the axis passing through the iron and the centre of the ring.

Fig. 2 is the unit cell drawing of the complex (R = *o*-NH_2). The crystal consists of discrete complex and solvent (C_6H_6) molecules in ratio of 1 : 1. Molecular

Table 2

The selected bond distances (Å)

Sn–Fe(1)	2.5421(8)	C(11)–C(15)	1.42(1)
Sn–Fe(2)	2.5242(7)	C(12)–C(13)	1.34(2)
Sn–O(31)	2.149(5)	C(13)–C(14)	1.305(9)
Sn–N(42)	2.247(4)	C(14)–C(15)	1.33(2)
Sn–O(44)	2.198(4)	C(1)–O(1)	1.156(7)
Fe(1)–C(11)	2.081(7)	C(2)–O(2)	1.151(7)
Fe(1)–C(12)	2.077(6)	C(21)–C(22)	1.44(2)
Fe(1)–C(13)	2.077(6)	C(21)–C(25)	1.44(1)
Fe(1)–C(14)	2.087(6)	C(22)–C(23)	1.43(1)
Fe(1)–C(15)	2.078(6)	C(23)–C(24)	1.439(9)
Fe(1)–C(1)	1.741(5)	C(24)–C(25)	1.422(8)
Fe(1)–C(2)	1.752(5)	C(3)–O(3)	1.156(9)
Fe(1)–Cp(1)	1.722(8)	C(4)–O(4)	1.158(8)
Fe(2)–C(21)	2.103(6)	O(31)–C(31)	1.315(8)
Fe(2)–C(22)	2.096(7)	C(36)–C(41)	1.443(6)
Fe(2)–C(23)	2.118(6)	C(41)–N(42)	1.297(5)
Fe(2)–C(24)	2.122(6)	N(42)–N(43)	1.391(6)
Fe(2)–C(25)	2.123(6)	N(43)–C(44)	1.323(6)
Fe(2)–C(3)	1.748(7)	C(44)–O(44)	1.288(6)
Fe(2)–C(4)	1.765(7)	C(44)–C(51)	1.476(5)
Fe(2)–Cp(2)	1.723(9)	C(52)–N(52)	1.36(1)
C(11)–C(12)	1.47(1)		

Table 3

The selected bond angles (°)

Fe(1)–Sn–Fe(2)	129.38(3)	Fe(2)–C(3)–O(3)	178.6(5)
Fe(1)–Sn–O(31)	94.0(1)	Fe(2)–C(4)–O(4)	177.8(5)
Fe(1)–Sn–N(42)	118.8(1)	Sn–O(31)–C(31)	133.0(4)
Fe(1)–Sn–O(44)	93.1(1)	O(31)–C(31)–C(32)	118.1(5)
Fe(2)–Sn–O(31)	102.7(1)	O(31)–C(31)–C(36)	122.5(5)
Fe(2)–Sn–N(42)	111.1(2)	C(32)–C(31)–C(36)	119.3(5)
Fe(2)–Sn–O(44)	96.5(1)	C(31)–C(36)–C(35)	119.6(4)
O(31)–Sn–N(42)	79.7(2)	C(31)–C(36)–C(41)	124.4(4)
O(31)–Sn–O(44)	148.2(2)	C(35)–C(36)–C(41)	115.9(4)
Sn–Fe(1)–Cp(1)	120.4(4)	C(36)–C(41)–N(42)	126.2(3)
Sn–Fe(1)–C(1)	84.0(1)	Sn–N(42)–C(41)	128.3(3)
Sn–Fe(1)–C(2)	89.4(2)	Sn–N(42)–N(43)	117.9(3)
Cp(1)–Fe(1)–C(1)	128.0(5)	C(41)–N(42)–N(43)	113.5(3)
Cp(1)–Fe(1)–C(2)	127.2(2)	N(42)–N(43)–C(44)	111.4(3)
C(1)–Fe(1)–C(2)	94.9(2)	N(43)–C(44)–O(44)	123.1(4)
Sn–Fe(2)–Cp(2)	120.2(3)	N(43)–C(44)–C(51)	119.1(3)
Sn–Fe(2)–C(3)	86.8(2)	O(44)–C(44)–C(51)	117.9(4)
Sn–Fe(2)–C(4)	90.8(2)	Sn–O(44)–C(44)	117.7(3)
Cp(2)–Fe(2)–C(3)	127.7(5)	C(44)–C(51)–C(52)	123.2(5)
Cp(2)–Fe(2)–C(4)	125.9(5)	C(44)–C(51)–C(56)	116.2(4)
Fe(1)–C(1)–O(1)	178.4(5)	N(52)–C(52)–C(51)	124.3(6)
Fe(1)–C(2)–O(2)	177.2(5)	N(52)–C(52)–C(53)	118.7(6)

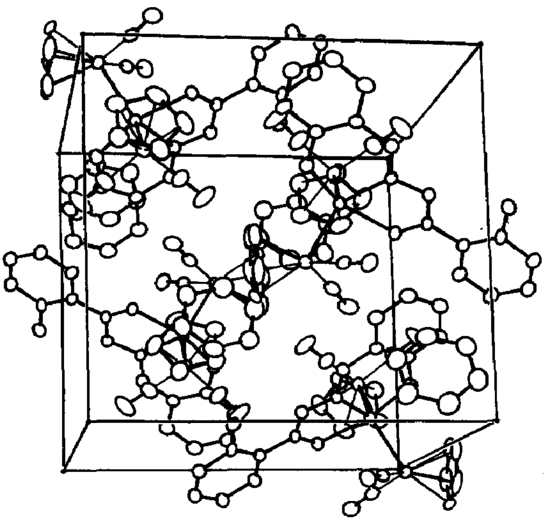


Fig. 2. Packing of molecules in a unit cell.

interactions are of the normal van der Waals type with no abnormally short inter- or intra-molecular contacts.

Experimental

Syntheses

The reagents and solvents were dried and purified by standard methods. The ligands and $[Cp(CO)_2Fe]_2SnCl_2$ were prepared by published procedures [5,10]. All reactions were carried out under dry argon.

A 100-ml three-necked flask was charged with 0.0025 mol substituted benzoyl salicylahydrazone, 1.2 g $[Cp(CO)_2Fe]_2SnCl_2$ (0.0025 mol), and 60 ml benzene. Triethyl amine (0.007 mol) in benzene (10 ml) was added dropwise to the flask with stirring at room temperature. The solution was stirred for 3 h. The white precipitate of Et_3N–HCl that had formed was filtered and washed with 20 ml benzene, and the filtrate was concentrated to 5 ml. The orange crystals were collected after 7 ml petroleum ether (30–60 ° C) has been added to the filtrate. The orange solid was filtered and recrystallized from CH_2Cl_2/petroleum ether. Eleven new complexes were synthesized in this way. Their yields, physical constants, and the results of elemental analyses are listed in Table 4.

X-ray diffraction study

Crystals of the complex ($R = o\text{-}NH_2$) for the X-ray diffraction study were grown by slow evaporation of the solvent from CH_2Cl_2/petroleum ether at room temperature. A crystal of approximate dimensions 0.15 × 0.3 × 0.3 mm was mounted on an Enraf–Nonius DAC4 diffractometer equipped with a graphite monochromator. Preliminary examination and data collection were performed with Mo-K_α radiation (λ 0.71073 Å). A total of 4864 independent reflections were collected in the range of $2° \leqslant \theta \leqslant 25°$ by the w–2θ scan technique at room temperature, in which 3075 reflections with $I \geqslant 3\sigma(I)$ were considered observed and were used in the succeed-

Table 4

Physical constants and analytical data of the complexes

Entry	R	Mol wt.	Colour	m.p. (°C)	Yield (%)	Anal. (Found (Calcd.) (%))		
						C	H	N
1	H	711	orange-yellow	163–165	82	47.31 (47.33)	2.87 (2.81)	3.95 (3.94)
2	p-NO_2	756	orange	198–200	88	44.38 (44.51)	2.57 (2.51)	5.67 (5.56)
3	p-Cl	745	orange-yellow	174–176	81	45.28 (45.15)	2.58 (2.55)	3.81 (3.76)
4	p-Br	789	orange-yellow	195–197	91	42.59 (42.59)	2.39 (2.41)	3.62 (3.55)
5	p-I	836	orange-yellow	210–212	83	40.32 (40.19)	2.28 (2.27)	3.48 (3.34)
6	p-CH_3	725	orange-yellow	177–178	80	47.83 (47.93)	3.11 (3.03)	3.72 (3.86)
7	p-OCH_3	741	orange-yellow	166–168	81	47.11 (46.96)	2.94 (2.97)	3.87 (3.78)
8	o-NH_2	726	orange	95– 97	87	46.17 (46.28)	3.03 (2.89)	5.78 (5.79)
9	m-NO_2	756	orange-yellow	98–100	79	44.53 (44.51)	2.64 (2.51)	5.41 (5.56)
10	m-OCH_3	741	orange-yellow	163–165	95	46.79 (46.96)	3.08 (2.97)	3.75 (3.78)
11	3,5-dinitro	801	orange	260 dec.	81	41.90 (41.97)	2.32 (2.25)	7.09 (7.00)

ing refinements. The corrections for LP factors and for absorption based on a series of ψ scans were applied to the data. The crystals of this complex are monoclinic, the systematic absences of $\{0k0\}$ for k odd and $\{h01\}$ for $h+1$ odd suggest the space group $P2_1/n$. The cell parameters are a 13.495(4), b 13.058(2), c 18.311(3) Å, β 94.90(2)°, V 3124.9 Å^3; $Z=4$; D_c 1.66 g/cm^3.

The structure was solved by direct method (MULTAN 82). The Sn and two Fe atoms were located from an E-map. The coordinates of the remaining non-hydrogen atoms were found in subsequent difference Fourier syntheses. The hydrogen atoms were not included in the refinements. The final refinement by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged with unweighted and weighted agreement factors of 0.033 and 0.039, respectively. The highest peak on the final difference Fourier map had a height of 0.47 e/Å^3.

Acknowledgement

The authors are grateful to the National Science Foundation of China for support of this work.

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