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## Synthesis and Structure of Octahedral Bis-Chelate Tin(IV) Derivative of the Ruthenocene Series

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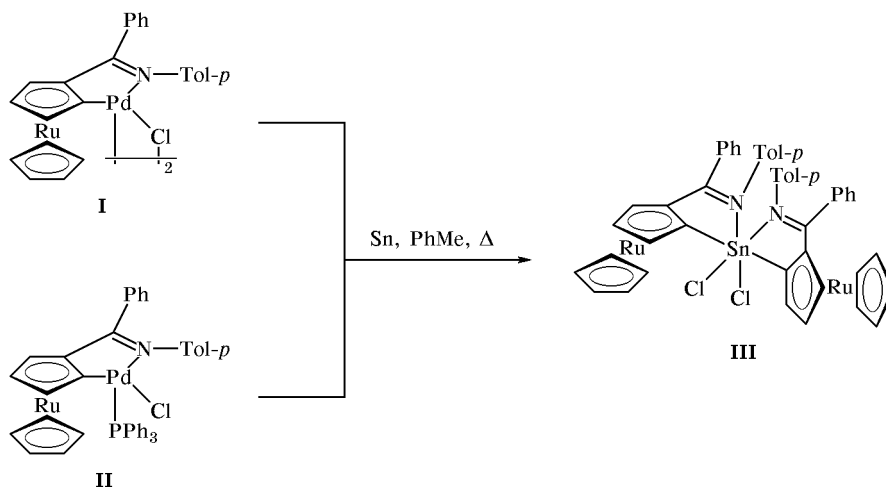
**Abstract**—Cyclopalladated  $\alpha$ -(*p*-tolylimino)benzylruthenocene reacts with metallic tin in a way similar to ferrocene analogs, yielding bis-chelate diruthenocenyln tin(IV) compound as a result of transmetalation.

Metallocenes having tin-containing substituents have been studied relatively poorly. These compounds can be synthesized by a conventional procedure through lithium derivatives. Provided that an electron-donor atom capable of forming a dative bond (e.g., nitrogen) is located in an appropriate position, chelate ring may be formed. Its strength depends to a large extent on the nature of other groups attached to the tin atom, but it is generally much weaker than analogous chelate rings formed by palladium or platinum [1]. We previously proposed a procedure for replacement of palladium in a chelate ring of ferrocene derivatives by tin (or silicon) via reaction with  $R_3SnLi$  [2]. These

reactions are not accompanied by change of valence state of the tin atom.

Yang Jie Wu *et al.* [3] recently reported on a new redox reaction of cyclopalladated Schiff bases derived from ferrocenyl ketones. These compounds were found to react with metallic tin powder to give bis-chelate tin(IV) derivatives. This reaction is also applicable to Schiff bases of the ruthenocene series, both dimeric cyclopalladation products like **I** and monomeric triphenylphosphine complexes like **II** (Scheme 1). Heating of the reactant mixture in boiling toluene is sufficient for the reaction to occur. On the other hand, cyclopalladated tertiary amines of the

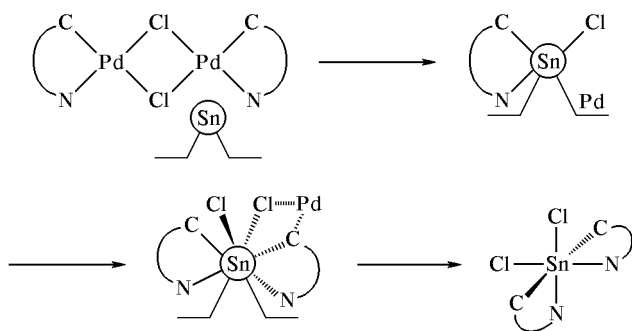
Scheme 1.



ferrocene or ruthenocene series gave no identifiable organotin compounds under analogous conditions. It should be emphasized that the final product is formed via a two-step process, successive oxidative addition  $\text{Sn}(0) \rightarrow \text{Sn}(\text{II}) \rightarrow \text{Sn}(\text{IV})$ .

While considering mechanisms of heterogeneous reactions involving a solid reagent, it should be kept in mind that some steps could occur on a surface where, at the sites of nanodefects (at the "edges"), the reactivity is enhanced. Octahedral tin(IV) derivatives formed in the reaction under study are characterized by *cis* arrangement of the chlorine atoms. We presume that the Sn–Cl bonds are formed when the Sn atom (which will become the octahedron center) is still bound to the metal surface; therefore, the two chlorine atoms are located in a single semisphere. Elimination of palladium is likely to be facilitated by its sorption on the tin surface. It would be premature to speak about details of the mechanism, but the general scheme of the two-step process is shown below (Scheme 2). According to [4], the reaction of 2-chloromercurioazobenzene with metallic tin also gives *cis* isomer of the corresponding octahedral complex  $\text{SnCl}_2[\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4]_2$ .

Scheme 2.



Structure **III** includes isolated molecules of the  $\text{Sn}(\text{L})_2\text{Cl}_2$  complex [ $\text{L} = p\text{-TolN}=\text{C}(\text{Ph})\text{CpRuCp}$ ] and solvent molecules ( $\text{Et}_2\text{O}$ ) (see figure). Molecule **III** consists of two geometrically equivalent ligand moieties in which the chelate and cyclopentadiene rings form planar bicyclic systems at a dihedral angle of  $109.9^\circ$  between each other. The planes of the phenyl and *p*-tolyl rings are turned, respectively, through angles of  $62.3$  and  $54.4^\circ$  (in one ligand) and  $87.1$  and  $52.7^\circ$  (in the other) with respect to the corresponding bicyclic system. The structure of the ruthenocene fragments is characterized by standard geometry: the cyclopentadiene rings are not coplanar, the average distance between the Ru atom and the Cp centroid is  $1.809 \text{ \AA}$ , and the Ru–C bond length ranges

from  $2.141(9)$  to  $2.207(8) \text{ \AA}$ . The tin coordination polyhedron is a distorted *cis*-octahedron  $\{\text{SnCl}_2\text{N}_2\text{C}_2\}$ ; the average Sn–Cl, Sn–N, and Sn–C bond lengths are, respectively,  $2.411(2)$ ,  $2.470(6)$ , and  $2.113(7) \text{ \AA}$ . Distortion of the octahedron is characterized by the following bond angles:  $\text{C}^1\text{SnC}^{1'}$   $155.3(3)^\circ$ ,  $\text{N}^1\text{SnCl}^2$   $162.0(1)^\circ$ ,  $\text{N}^{1'}\text{SnCl}^1$   $163.7(1)^\circ$ ; these values are considerably lower than the ideal value ( $180^\circ$ ). A similar structure is typical of the ferrocene analog of **III**,  $p\text{-TolN}=\text{C}(\text{Ph})\text{C}_5\text{H}_3\text{FeCp}_2\text{SnCl}_2$ . Crystals of the latter also contain a solvent molecule (hexane) [3] and are isostructural to the crystals of **III**.

The coordination polyhedron in the molecule of  $(\text{C}_6\text{H}_4\text{N}=\text{NPh})\text{SnCl}_2$  [5] (see above) is also a distorted *cis*-octahedron  $\{\text{SnCl}_2\text{C}_2\text{N}_2\}$ ; the phenyl ring and the chelate ring form a dihedral angle of  $38^\circ$ , which is smaller than the corresponding angle formed by the *p*-tolyl ring in molecule **III** and its ferrocene analog ( $55^\circ$ ). This may be due to increased steric hindrance in molecules of metallocene derivatives having one more phenyl substituent in the chelate ring. Comparison of the structures of cyclopalladated tertiary amines and Schiff bases suggests that the difference in their reactivities toward metallic tin originates from steric hindrances created by substituents at the tetrahedral nitrogen atom, as well as from the different electronic properties of these compounds.

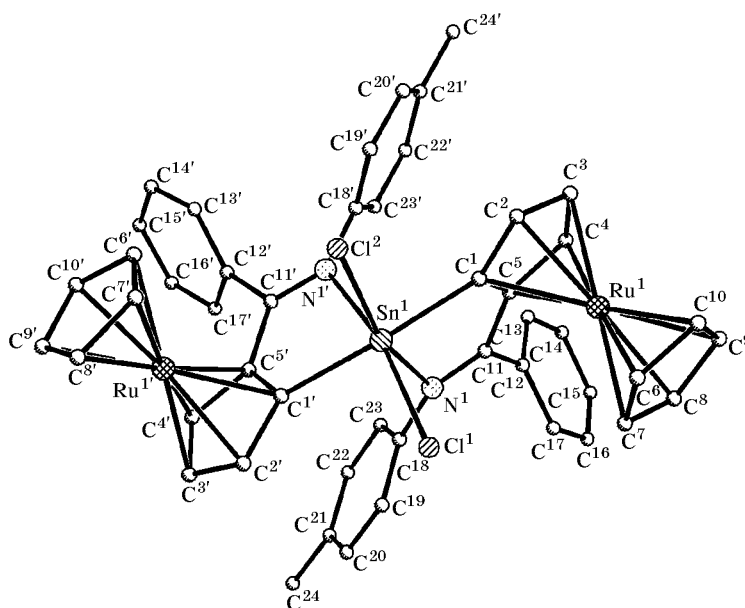
## EXPERIMENTAL

The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WP-200SY instrument from solutions in  $\text{CDCl}_3$ . In all the syntheses, dry solvents were used, which were purified by standard methods.

**Dichlorobis[2-( $\alpha$ -*p*-tolyliminobenzyl)ruthenocenylic-N]tin(IV) (III).** Freshly activated metallic tin,  $23.7 \text{ mg}$  ( $0.2 \text{ mol}$ ), was added to a suspension of  $22.9 \text{ mg}$  ( $0.04 \text{ mol}$ ) of cyclopalladated derivative **I** in toluene, and the mixture was heated under reflux for  $2.5 \text{ h}$ . The mixture was filtered and the filtrate was evaporated. The residue was recrystallized from diethyl ether to obtain  $8.5 \text{ mg}$  ( $41\%$ ) of compound **III**.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm:  $2.20 \text{ s}$  ( $3\text{H}$ ,  $\text{CH}_3$ ),  $4.31 \text{ d}$  ( $1\text{H}$ ),  $4.45 \text{ t}$  ( $1\text{H}$ ),  $4.75 \text{ s}$  ( $5\text{H}$ ,  $\text{C}_5\text{H}_5$ ),  $4.77 \text{ d}$  ( $1\text{H}$ ),  $6.48$  and  $6.81$  ( $4\text{H}$ ,  $\text{C}_6\text{H}_4$ , *AB* system,  $J = 8.0 \text{ Hz}$ ),  $7.25\text{--}7.27 \text{ m}$  ( $10\text{H}$ ,  $2\text{Ph}$ ). Found, %: C  $56.44$ ; H  $4.34$ .  $\text{C}_{48}\text{H}_{40}\text{Cl}_2\text{N}_2\text{Ru}_2\text{Sn}_1 \cdot \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ . Calculated, %: C  $56.23$ ; H  $4.54$ .

Following a similar procedure, compound **III** was synthesized from triphenylphosphine complex **II**. Yield  $93\%$ .

**X-Ray diffraction study.** Light yellow prisms.  $\text{SnCl}_2\text{C}_{48}\text{H}_{40}\text{RuN}_2 \cdot 0.5\text{Et}_2\text{O}$  ( $M$   $1073.61$ ). Monoclinic

Structure of octahedral tin(IV) complex **III**.

crystals, crystal habit  $0.40 \times 0.35 \times 0.25$  mm; at 163 K:  $a = 32.167(6)$ ,  $b = 14.644(2)$ ,  $c = 19.900(6)$  Å,  $\beta = 110.27(2)^\circ$ ;  $V = 8794(3)$  Å<sup>3</sup>;  $d_{\text{calc}} = 1.622$  g/cm<sup>3</sup>; space group  $C2/c$ ;  $Z = 8$ . The experimental set of 6621 reflections was obtained on a Syntex P21 four-circle automatic diffractometer at 163 K (MoK radiation, graphite monochromator,  $\theta_{\text{max}} = 46^\circ$ ). After averaging of equivalent reflections, 6128 independent reflections were obtained ( $R_{\text{int}} = 0.0212$ ). Absorption by the sample ( $\mu = 14.01$  cm<sup>-1</sup>) was not taken into

account. The structure was solved by the direct method and successive Fourier syntheses. The positions of non-hydrogen atoms were refined by the full-matrix least-squares procedure with respect to  $F_{hkl}^2$  in anisotropic approximation. The solvent (diethyl ether) molecule is disordered relative to the symmetry center. The coordinates of all hydrogen atoms were calculated from geometry considerations and were refined using the "rider" model [ $U_{\text{iso}}(\text{H}) = nU_{\text{eq}}(\text{C})$ , where  $n = 1.5$  and 1.2 for CH<sub>3</sub> and CH<sub>2</sub> groups, respectively;  $U_{\text{eq}}(\text{C})$

Principal bond lengths  $d$  and bond angles  $\omega$  in the molecule SnCl<sub>2</sub>L<sub>2</sub> (**III**)

| Bond                             | $d$ , Å  | Bond                               | $d$ , Å  | Bond                             | $d$ , Å  | Bond                              | $d$ , Å  |
|----------------------------------|----------|------------------------------------|----------|----------------------------------|----------|-----------------------------------|----------|
| Sn <sup>1</sup> –C <sup>1</sup>  | 2.099(7) | Sn <sup>1</sup> –C <sup>1'</sup>   | 2.126(7) | Sn <sup>1</sup> –Cl <sup>1</sup> | 2.440(2) | Sn <sup>1</sup> –Cl <sup>2</sup>  | 2.441(2) |
| Sn <sup>1</sup> –N <sup>1</sup>  | 2.465(6) | Sn <sup>1</sup> –N <sup>1'</sup>   | 2.474(5) | Ru <sup>1</sup> –C <sup>1</sup>  | 2.182(7) | Ru <sup>1'</sup> –C <sup>1'</sup> | 2.173(7) |
| Ru <sup>1</sup> –C <sup>2</sup>  | 2.190(8) | Ru <sup>1'</sup> –C <sup>2'</sup>  | 2.207(8) | Ru <sup>1</sup> –C <sup>3</sup>  | 2.181(8) | Ru <sup>1'</sup> –C <sup>3'</sup> | 2.195(7) |
| Ru <sup>1</sup> –C <sup>4</sup>  | 2.170(8) | Ru <sup>1'</sup> –C <sup>4'</sup>  | 2.159(7) | Ru <sup>1</sup> –C <sup>5</sup>  | 2.166(7) | Ru <sup>1'</sup> –C <sup>5'</sup> | 2.149(7) |
| Ru <sup>1</sup> –C <sup>6</sup>  | 2.154(8) | Ru <sup>1'</sup> –C <sup>6'</sup>  | 2.141(9) | Ru <sup>1</sup> –C <sup>7</sup>  | 2.158(8) | Ru <sup>1'</sup> –C <sup>7'</sup> | 2.165(8) |
| Ru <sup>1</sup> –C <sup>8</sup>  | 2.178(8) | Ru <sup>1'</sup> –C <sup>8'</sup>  | 2.173(8) | Ru <sup>1</sup> –C <sup>9</sup>  | 2.196(8) | Ru <sup>1'</sup> –C <sup>9'</sup> | 2.172(8) |
| Ru <sup>1</sup> –C <sup>10</sup> | 2.189(8) | Ru <sup>1'</sup> –C <sup>10'</sup> | 2.165(9) | N <sup>1</sup> –C <sup>11</sup>  | 1.292(8) | N <sup>1'</sup> –C <sup>11'</sup> | 1.296(8) |
| N <sup>1</sup> –C <sup>18</sup>  | 1.423(8) | N <sup>1'</sup> –C <sup>18'</sup>  | 1.423(8) | C <sup>1</sup> –C <sup>2</sup>   | 1.416(9) | C <sup>1'</sup> –C <sup>2'</sup>  | 1.422(9) |
| C <sup>1</sup> –C <sup>5</sup>   | 1.426(9) | C <sup>1'</sup> –C <sup>5'</sup>   | 1.423(9) | C <sup>2</sup> –C <sup>3</sup>   | 1.43(1)  | C <sup>2'</sup> –C <sup>3'</sup>  | 1.42(1)  |
| C <sup>3</sup> –C <sup>4</sup>   | 1.40(1)  | C <sup>3'</sup> –C <sup>4'</sup>   | 1.41(1)  | C <sup>4</sup> –C <sup>5</sup>   | 1.44(1)  | C <sup>4'</sup> –C <sup>5'</sup>  | 1.435(9) |
| C <sup>5</sup> –C <sup>11</sup>  | 1.455(9) | C <sup>5'</sup> –C <sup>11'</sup>  | 1.467(9) | C <sup>6</sup> –C <sup>7</sup>   | 1.40(1)  | C <sup>6'</sup> –C <sup>7'</sup>  | 1.39(1)  |
| C <sup>6</sup> –C <sup>10</sup>  | 1.41(1)  | C <sup>6'</sup> –C <sup>10'</sup>  | 1.41(1)  | C <sup>7</sup> –C <sup>8</sup>   | 1.41(1)  | C <sup>7'</sup> –C <sup>8'</sup>  | 1.40(1)  |
| C <sup>8</sup> –C <sup>9</sup>   | 1.41(1)  | C <sup>8'</sup> –C <sup>9'</sup>   | 1.40(1)  | C <sup>9</sup> –C <sup>10</sup>  | 1.42(1)  | C <sup>9'</sup> –C <sup>10'</sup> | 1.40(1)  |
| C <sup>11</sup> –C <sup>12</sup> | 1.48(1)  | C <sup>11'</sup> –C <sup>12'</sup> | 1.49(1)  |                                  |          |                                   |          |

Table. (Contd.)

| Angle   | $\omega$ , deg | Angle   | $\omega$ , deg | Angle   | $\omega$ , deg | Angle   | $\omega$ , deg |
|---|----------------|---|----------------|---|----------------|---|----------------|
| C <sup>1</sup> Sn <sup>1</sup> C <sup>1'</sup>  | 155.3 (3)      | Cl <sup>1</sup> Sn <sup>1</sup> Cl <sup>2</sup> | 99.28 (7)      | C <sup>1</sup> Sn <sup>1</sup> Cl <sup>1</sup>  | 102.4 (2)      | C <sup>1'</sup> Sn <sup>1</sup> Cl <sup>1</sup> | 94.2 (2)       |
| C <sup>1</sup> Sn <sup>1</sup> Cl <sup>2</sup>  | 92.8 (2)       | C <sup>1'</sup> Sn <sup>1</sup> Cl <sup>2</sup> | 102.6 (2)      | C <sup>1</sup> Sn <sup>1</sup> N <sup>1</sup>   | 73.4 (2)       | C <sup>1'</sup> Sn <sup>1</sup> N <sup>1</sup>  | 87.1 (2)       |
| C <sup>1</sup> Sn <sup>1</sup> N <sup>1'</sup>  | 86.6 (2)       | C <sup>1'</sup> Sn <sup>1</sup> N <sup>1'</sup> | 73.4 (2)       | Cl <sup>1</sup> Sn <sup>1</sup> N <sup>1</sup>  | 95.0 (1)       | Cl <sup>1</sup> Sn <sup>1</sup> N <sup>1'</sup> | 163.7 (1)      |
| Cl <sup>2</sup> Sn <sup>1</sup> N <sup>1</sup>  | 162.0 (1)      | Cl <sup>2</sup> Sn <sup>1</sup> N <sup>1'</sup> | 93.8 (1)       | N <sup>1</sup> Sn <sup>1</sup> N <sup>1'</sup>  | 74.4 (2)       | C <sup>11</sup> N <sup>1</sup> C <sup>18</sup>  | 122.2 (6)      |
| C <sup>11</sup> N <sup>1</sup> C <sup>18'</sup> | 123.3 (6)      | C <sup>11</sup> N <sup>1</sup> Sn <sup>1</sup>  | 112.2 (4)      | C <sup>11</sup> N <sup>1</sup> Sn <sup>1</sup>  | 112.3 (4)      | C <sup>18</sup> N <sup>1</sup> Sn <sup>1</sup>  | 124.8 (4)      |
| C <sup>18'</sup> N <sup>1</sup> Sn <sup>1</sup> | 124.2 (4)      | C <sup>2</sup> C <sup>1</sup> C <sup>5</sup>    | 107.8 (6)      | C <sup>2</sup> C <sup>1</sup> C <sup>5'</sup>   | 107.7 (6)      | C <sup>2</sup> C <sup>1</sup> Sn <sup>1</sup>   | 134.4 (5)      |
| C <sup>2</sup> C <sup>1</sup> Sn <sup>1</sup>   | 135.0 (5)      | C <sup>5</sup> C <sup>1</sup> Sn <sup>1</sup>   | 117.0 (5)      | C <sup>5</sup> C <sup>1</sup> Sn <sup>1</sup>   | 116.5 (5)      | Sn <sup>1</sup> C <sup>1</sup> Ru <sup>1</sup>  | 131.0 (3)      |
| Sn <sup>1</sup> C <sup>1</sup> Ru <sup>1'</sup> | 130.3 (3)      | N <sup>1</sup> C <sup>11</sup> C <sup>5</sup>   | 116.1 (6)      | N <sup>1</sup> C <sup>11</sup> C <sup>5'</sup>  | 116.1 (6)      | N <sup>1</sup> C <sup>11</sup> C <sup>12</sup>  | 125.5 (6)      |
| N <sup>1</sup> C <sup>11</sup> C <sup>12'</sup> | 125.1 (6)      | C <sup>5</sup> C <sup>11</sup> C <sup>12</sup>  | 118.4 (6)      | C <sup>5</sup> C <sup>11</sup> C <sup>12'</sup> | 118.4 (6)      | C <sup>23</sup> C <sup>18</sup> N <sup>1</sup>  | 122.7 (6)      |
| C <sup>23</sup> C <sup>18</sup> N <sup>1'</sup> | 122.2 (6)      | C <sup>19</sup> C <sup>18</sup> N <sup>1</sup>  | 118.2 (6)      | C <sup>19</sup> C <sup>18</sup> N <sup>1'</sup> | 118.1 (6)      |   |                |

is an equivalent isotropic factor of the carbon atom to which the given hydrogen atom is attached]. The final divergence factors were  $R_1 = 0.0476$  [calculated by  $F_{hkl}$  for 4174 reflections with  $I > 2\sigma(I)$ ],  $wR_2 = 0.0985$  (calculated by  $F_{hkl}$  for all reflections),  $F(000) = 4280$ , GOOF = 0.989; 532 refined parameters; maximal and minimal residual electron density peaks 0.442 and  $-0.436 \text{ e}/\text{\AA}^3$ , respectively. The coordinates of atoms are available from the authors; the bond lengths and bond angles are given in table. All calculations were performed with the aid of SHELXTL software package (version 5.1) [6].

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## REFERENCES

1. Marquarding, D., Klusacek, H., Gokel, G., Hoffmann, P., and Ugi, I., *J. Am. Chem. Soc.*, 1970, vol. 92, p. 5389.
2. Troitskaya, L.L., Bulygina, L.A., and Sokolov, V.I., *Metalloorg. Khim.*, 1990, vol. 3, p. 615.
3. Yang Jie Wu, Li Ding, Zhi Xian Zhou, Chen Xia Du, and Wen Ling Wang, *J. Organomet. Chem.*, 1998, vol. 564, p. 233.
4. Brianso, J.L., Solans, X., and Vicente, J., *J. Chem. Soc., Dalton Trans.*, 1983, p. 169.
5. *Cambridge Structural Database System*, Release April 2002.
6. Sheldrick, G.M., *SHELXTL Version 5.0. Software Reference Manual*, Madison: Siemens Industrial Automation, 1995.