# Synthesis and Molecular Structures of Tris(thioand Selenophenyl)stannyl Complexes of Cyclopentadienylcarbonylnitrosylmanganese and Their Reaction Products with Tungsten Carbonyl

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**Abstract**—Reactions of CpMn(CO)(NO)SnCl<sub>3</sub> (I) with sodium benzenethiolate and sodium benzeneselenolate gave orange crystals of the complexes CpMn(CO)(NO)Sn(EPh)<sub>3</sub>, where E = S (II) or Se (III). Treatment of complex II with photochemically generated W(CO)<sub>5</sub>(THF) yielded the adduct CpMn(CO)(NO)Sn(SPh)<sub>3</sub>·W(CO)<sub>5</sub> (IV). A similar treatment of complex III resulted in the formation of the ditungsten complex W<sub>2</sub>(CO)<sub>4</sub>(SePh)<sub>6</sub> (V) with transfer of all chalcogenate groups from tin to tungsten. In reactions of complexes II and III with a Pt<sub>0</sub> complex with phosphine and acetylene, (PPh<sub>3</sub>)<sub>2</sub>Pt(Ph<sub>2</sub>C<sub>2</sub>), the chalcogenate groups are transferred from tin. Only the known Pt(II) complexes (PPh<sub>3</sub>)<sub>2</sub>Pt(EPh)<sub>2</sub>), where E = S (VI) or Se (VII). Molecular structures IV and V were characterized by X-ray diffraction. It has been found that the Mn–Sn bond in complex IV (2.5479(9) Å) is nearly the same length as that found earlier for complex II (2.5328(17) Å) and is substantially shorter than the sum of the covalent radii of Mn and Sn (2.78 Å). The Sn–S bond is noticeably lengthened (2.5217(11) Å) only for the S atom bound to tungsten (W–S, 2.5696(12) Å), while the other Sn–S bonds (2.4413(12) and 2.4291(12) Å) are virtually the same as in complex II (on average, 2.441 Å). Complex V contains the direct W–W bond (2.8153(16) Å) supplemented with four benzeneselenolate bridges in which the W–Se bonds (on average, 2.642(2) Å) are longer than the two terminal W–SePh bonds (2.571(2) Å). All the W–Se bonds are much shorter than the sum of the covalent radii of W and Se (2.82 Å).

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Among a variety of complexes containing transition metal-tin bonds [1], the carbonylcyclopentadienylnitrosylstannylmanganese complexes CpMn(CO) (NO)SnX<sub>3</sub> [2, 3] are of interest because of the chirality of the Mn atom surrounded by four different ligands (including the partially double Mn–Sn bond). This bond is shorter by 0.3 Å than the sum of the covalent radii of the corresponding metal atoms (2.78 Å [4]) and only slightly depends on the substituents X at the tin atom (X = Cl (I), SPh (II) [2], or C=CPh [3]). Earlier, we have obtained complex II from sodium benzenethiolate

and the ionic complex  $CpMn(CO)_2(NO)^+SnCl_3^-$  [2]. Here we describe the synthesis of complex II and its selenium analog  $CpMn(CO)(NO)Sn(SePh)_3$  (III) directly from covalent complex I, as well as reactions of complexes II and III with tungsten and platinum complexes.

#### EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of the complexes were carried out under

argon in dehydrated solvents. Complex I and  $(PPh_3)_2Pt(PhC=CPh)$  were prepared as described in [3] and [5], respectively. Silica gel for column chromatography was heated in vacuo at 100°C for 1 h for removal any air and moisture. IR spectra were recorded on a Specord 75 IR spectrophotometer (KBr pellets).

Synthesis of complex II. Sodium borohydride (0.025 g, 0.66 mmol) was added to a stirred solution of  $Ph_2S_2$  (0.07 g, 0.33 mmol) in ethanol (10 mL). After 1 h, solid-state CpMn(CO)(NO)SnCl<sub>3</sub> (0.09 g, 0.2 mmol) was added to the resulting transparent solution of sodium benzenethiolate. The solution turned dark vellow, immediately producing a white precipitate. The reaction mixture was stirred for 1 h and evaporated to dryness in a water aspirator vacuum. The yellow residue was subjected to extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the organic extract was filtered. TLC data: yellow spot,  $R_f$  0.44, CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (2:1). The mother liquor was diluted with light petroleum (10 mL) and the resulting solution was concentrated in vacuo until crystallization began and then kept at  $-5^{\circ}$ C for 24 h. The orange needle-like crystals

that formed were separated from the mother liquor and dried. The yield of complex II was 0.07 g (47.6%).

For 
$$C_{24}H_{20}NO_2S_3MnSn \cdot CH_2Cl_2$$
 (*M<sub>r</sub>* 709.17).  
anal. calcd., %: C, 42.34; H, 3.13; N, 1.98; S, 13.56.  
Found, %: C, 42.89; H, 2.85; N, 2.29; S, 13.29.

IR (KBr, v, cm<sup>-1</sup>): 2000 s (v(CO)), 1760 s (v(NO)), 1005 m (C<sub>5</sub>H<sub>5</sub>), 835 m.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 7.61, 7.59, 7.25, 7.22, 7.20 s (17H), 4.43 s (5H).

Synthesis of complex III. Sodium borohydride (0.04 g, 1.2 mmol) was added to a stirred yellow solution of  $Ph_2Se_2$  (0.17 g, 0.6 mmol) in ethanol (10 mL). After 10 min, solid-state CpMn(CO)(NO)SnCl<sub>3</sub> (0.15 g, 0.2 mmol) was added to the resulting transparent solution of sodium benzeneselenolate. The solution turned dark yellow, immediately producing a white precipitate. The reaction mixture was stirred for 1 h and concentrated in vacuo. The yellow residue was subjected to extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). TLC data: yellow spot,  $R_f 0.52$ , CH<sub>2</sub>Cl<sub>2</sub>-hexane (2 : 1). The product was isolated by column chromatography (column height 5 cm, column diameter 2 cm) on silica gel with preliminary elution of the unreacted Ph<sub>2</sub>Se<sub>2</sub> with hexane and CH<sub>2</sub>Cl<sub>2</sub>-hexane (40 mL). The dark yellow reaction product was eluted with  $CH_2Cl_2$  (40 mL). The eluate was evaporated to dryness and the residue was dissolved in hot hexane (15 mL). The resulting solution was left at room temperature for 2 h. The dark yellow needle-like crystals that formed were separated from the mother liquor and dried in a water aspirator vacuum. The yield of complex III was 0.08 g (45%).

For  $C_{24}H_{20}NO_2Se_3MnSn (M_r 764.94)$ 

anal. calcd., %:	C, 37.68;	Н, 2.64;	N, 1.83.
Found, %:	C, 38.69;	Н, 1.87;	N, 1.62.

IR (CH<sub>2</sub>Cl<sub>2</sub>, v, cm<sup>-1</sup>): 1990 s (v(CO)), 1755 s (v(NO)).

Synthesis of complex IV. Pentacarbonyltetrahydrofurantungsten (0.28 g, 0.80 mmol) was added dropwise at 0°C to a stirred yellow solution of complex II (0.5 g, 0.80 mmol) in THF (40 mL). After the addition was completed, the resulting dark red solution was stirred for 1 h and concentrated in vacuo. The red residue was subjected to extraction with heptane (90 mL). TLC data: orange spot,  $R_f$  0.47, CH<sub>2</sub>Cl<sub>2</sub>-heptane (1 : 1). The extract was concentrated in vacuo until crystallization began and then kept at  $-5^{\circ}$ C for 24 h. The red prismatic crystals that formed were separated from the mother liquor and dried in vacuo. The yield of complex IV was 0.17 g (23.7%).

For C<sub>29</sub>H<sub>20</sub>NO<sub>7</sub>S<sub>3</sub>MnSnW (*M<sub>r</sub>* 948.14)

anal. calcd., %:	C, 36.74;	Н, 2.13;	N, 1.48;	S, 10.14.
Found, %:	C, 36.80;	H, 2.36;	N, 2.53;	S, 10.57.

IR (KBr, v, cm<sup>-1</sup>): 2055 m, 2015 m, 1980 m, 1925 s, 1875 s (v(CO)), 1780 s (v(NO)), 835 s, 1015 m (C<sub>5</sub>H<sub>5</sub>).

Synthesis of complex V. Pentacarbonyltetrahydrofurantungsten (0.23 g, 0.65 mmol) was added dropwise at -5°C for 20 min to a stirred yellow solution of complex III (0.5 g, 0.65 mmol) in THF (20 mL). The resulting brown solution was concentrated in vacuo for 1 h. The brown residue was dissolved in  $CH_2Cl_2$ (15 mL). TLC data: brown spot,  $R_f 0.43$ , CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:1). The product was isolated by column chromatography (column height 15 cm, column diameter 2.5 cm) on silica gel with preliminary elution of  $W(CO)_6$  and impurities with heptane and  $CH_2Cl_2$ heptane (40 mL). The brown reaction product was eluted with  $CH_2Cl_2$  (40 mL) and left for crystallization in a mixture of  $\tilde{C}H_2Cl_2$  (15 mL) and heptane (1 mL) at  $-5^{\circ}$ C for 24 h. The brown hexagonal prismatic crystals that formed were separated from the mother liquor and dried. The yield of complex V was 0.51 g (52%).

For $C_{40}H_{30}O_4Se_6W_2 \cdot C$	$CH_2Cl_2(M_r, 1501.07)$	
anal. calcd., %:	C, 32.81;	Н, 2.15.
Found, %:	C, 32.93;	H, 2.19.

IR (KBr, v, cm<sup>-1</sup>): 1985 s, 1935 s (v(CO)), 1010 m (Ph), 840 m.

Synthesis of complex VI. A colorless solution of  $(PPh_3)_2Pt(PhC=CPh)$  (0.14 g, 0.16 mmol) in THF (10 mL) was added to a stirred yellow solution of complex II (0.1 g, 0.16 mmol) in THF (15 mL). The reaction mixture was stirred for 1 h, producing a beige precipitate. The solvent was removed in vacuo and the yellow residue was dissolved in diethyl ether (15 mL). The resulting solution was filtered and diluted with heptane (5 mL). TLC data: yellow spot,  $R_f$  0.53, diethyl ether—heptane (1 : 1). The solution was kept at  $-5^{\circ}C$  for 24 h. The yellow tetragonal prismatic crystals that formed were separated from the mother liquor and dried. The yield of complex VI was 0.08 g (49%).

For	C₄ଃł	H <sub>40</sub> P	$^{\prime}{}_{2}S_{2}$	Pt (	$(M_r)$	937.	.99)
	~48-	-40-	$\gamma \sim \gamma$		p		~ ~ ,

anal. calcd., %:	C, 61.46;	H, 4.30;	S, 6.84.
Found, %:	C, 61.28;	H, 3.89;	S, 6.82.

IR (KBr, v, cm<sup>-1</sup>): 740 s, 690 m (Ph).

**Complex VII** was obtained from complex **III** (0.1 g, 0.13 mmol) and  $(PPh_3)_2Pt(PhC=CPh)$  (0.12 g, 0.13 mmol) as described above for the synthesis of complex **VI**. The yield of complex **VII** was 0.07 g (52%).

For  $C_{48}H_{40}P_2Se_2Pt$  ( $M_r$  1031.79).

anal. calcd., %:	C, 55.88;	H, 3.91.
Found, %:	C, 55.81;	Н, 3.79.

IR (KBr, v, cm<sup>-1</sup>): 740 s, 685 m (Ph).



**Fig. 1.** Molecular structure of complex **IV**. Selected bond lengths: Sn(1)-Mn(1), 2.548(2) Å; W(1)-S(3), 2.568(3) Å; Sn(1)-S(1), 2.443(3) Å; Sn(1)-S(2), 2.429(3) Å; Sn(1)-S(3), 2.521(3) Å.



Fig. 2. Complex IV: plots of (a) the heat flux and (b) the weight vs. the temperature in the  $50-450^{\circ}$ C range and (c) the DTG curve in the  $50-200^{\circ}$ C range.

**X-ray diffraction analysis.** Crystallographic parameters and the data collection and refinement statistics for structures **IV** and **V** are given in table. Structures **IV** and **V** were solved by the direct methods and refined anisotropically (isotropically for the H atoms) by the least-squares method on  $F^2$  with the SHELXTL program package [6]. The hydrogen atoms were located geometrically. Selected bond lengths in structures **IV** and **V** are given in the captions to Figs. 1 and 2, respec-

tively. The atomic coordinates and other parameters of structures **IV** and **V** have been deposited with the Cambridge Crystallographic Data Collection (nos. 814823 (**IV**) and 814824 (**V**); http://www.ccdc.cam.ac.uk/data\_request/cif).

The thermolysis of complex IV was examined by DSC and TGA on NETZSCH instruments. TG measurements were carried out under argon (flow rate 20 mL/min; Ar > 99.998%,  $O_2 < 0.0002\%$ ,  $N_2 <$ 

Crystallographic parameters and the data	a collection and refinement statistics for structures $\mathbf{IV}$ and $\mathbf{V}$

Demonstern	Value			
Parameter	IV	V		
M	948.12	1416.10		
Diffractometer	Bruker APEX II CCD			
Radiation ( $\lambda$ , Å)	$MoK_{lpha}$ (	0.71073)		
Т, К	296	5(2)		
Crystal system	Triclinic	Orthorhombic		
Space group	<i>P</i> 1	Pbca		
<i>a</i> , Å	10.863(3)	18.5701(9)		
b, Å	11.495(3)	10.9872(5)		
<i>c</i> , Å	15.438(3)	25.9794(13)		
α, deg	98.457(3)	90		
β, deg	103.538(3)	90		
γ, deg	115.882(3)	90		
V, Å <sup>3</sup>	1616.3(7)	5300.7(4)		
Ζ	2	4		
$\rho_{calcd}$ , g/cm <sup>3</sup>	1.948	1.774		
$\mu$ , mm <sup>-1</sup>	4.939	8.487		
<i>F</i> (000)	908	2616		
$\theta$ scan range $\omega$ , deg	2.05-29.00	2.19-29.00		
Ranges of $h$ , $k$ , and $l$ indices	-14 < h < 14,	0 < h < 25,		
	-15 < k < 15,	0 < k < 14,		
	-20 < <i>l</i> < 21	0 < 1 < 35		
Scan mode	C	0		
Number of independent reflections $(N_1)$	8557	7003		
Number of reflections with $I > 2(I) (N_2)$	5771	5377		
Number of parameters refined	388	235		
GOOF $(F^2)$	0.918	1.022		
$R_1$ for $N_2$	0.0374	0.0351		
$wR_2$ for $N_1$	0.0610	0.0788		
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$ , $e {\rm \AA}^{-3}$	1.032/-0.760	1.874-0.981		

0.001%, water vapor < 0.0003%, CH<sub>4</sub> < 0.0001%) in alundum crucibles on a TG 209 F1 instrument; the heating rates were 3, 5, and 10°C/min. The weights of samples were 0.5 to 3 mg. DSC experiments were carried out under argon on a DSC 204 F1 calorimeter in aluminum cells at a heating rate of 10°C/min. The weights of samples were 1 to 4 mg. The thermobalance and the calorimeter were temperature calibrated using the phase transition points of certified standards (C<sub>6</sub>H<sub>12</sub>, Hg, KNO<sub>3</sub>, In, Sn, Bi, and CsCl; 99.99% purity) in compliance with the norm ISO/CD 11357-1. Samples for TG and DSC experiments were weighed on a SARTORIUS RESEARCH R 160P analytical balance with an accuracy of 0.01 mg. TG and DSC data were processed according to the standards ISO 11357-1, ISO 11357-2, ISO 11358, and ASTM E 1269-95 with the NETZSCH Proteus Thermal Analvsis software.

X-ray powder diffraction analysis of the thermolysis products was carried out on a Guinier G670 camera (HUBER, Cu $K_{\alpha 1}$  radiation).

## **RESULTS AND DISCUSSION**

Complex I instantaneously reacts with sodium benzenethiolate; the reaction is accompanied by a color change and the formation of a white precipitate (Scheme 1). Complex II was isolated as orange needle-like crystals that are soluble in nonpolar solvents and are gradually hydrolyzed in air. The IR spectra and elemental analysis data for complex II are identical with those cited in [2]; however, its yield (47%) was twice as high. The frequencies of the v(CO) and v(NO) vibrations in complex II (1995 and 1765 cm<sup>-1</sup>, respectively) are virtually identical with those found for the complex CpMn(CO)(NO)Sn(C=CPh)<sub>3</sub> (2000 and 1765 cm<sup>-1</sup>, respectively) [3].



Thus, the fragment  $Sn(SPh)_3$  is comparable with  $Sn(C=CPh)_3$  in donor-acceptor properties. Therefore, it is no wonder that the Mn-Sn bond in complex II is shorter (2.5328(17) Å) than the sum of the covalent radii of these metals (2.78 Å). The single Sn-S bonds (on average, 2.441 Å) do not exceed the sum of the covalent radii (2.44 Å). Following [7], one can assume that the shortening of the formally single Mn-Sn bonds results from an additional dative inter-

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action of the *d* electrons of manganese with the vacant *d* orbitals of tin rather than with the antibonding  $\sigma^*$  orbitals of the Sn–X bonds.

A similar reaction of complex I with three equivalents of NaSePh in ethanol gave complex III (Scheme 2) as orange needle-like crystals that are also soluble in nonpolar solvents and are gradually hydrolyzed in air:



Complex **III** was characterized by elemental analysis and **IR** spectroscopy. We failed to grow its crystals suitable for X-ray diffraction. The absorption bands of the CO and NO stretching vibrations in complex **III** (1995 and 1765 cm<sup>-1</sup>, respectively) are similar to those in the spectrum of complex **II**.

In a reaction of complex I with NaTePh, the reaction product was detected in the reaction mixture by IR spectroscopy; however, attempted isolation resulted in its decomposition.

The presence of the lone electron pair at the S atoms in complex II allows its reaction with pentacarbonyltetrahydrofurantungsten, yielding adduct IV (Scheme 3):



Like the starting complex II, red complex IV is well soluble in nonpolar solvents (e.g., hexane) and thus can easily be isolated. Structure IV was characterized by elemental analysis, IR spectroscopy, and X-ray diffraction (Fig. 1, table). The IR spectrum of complex IV shows the increasing frequencies of the CO and NO stretching vibrations at the Mn atom to 2015 and 1780 cm<sup>-1</sup>, respectively, which is due to the coordination of the S atom to the electron-withdrawing pentacarbonyltungsten. In structure IV, this leads

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only to the lengthening of the corresponding Sn–S bond (2.5217(11) Å) compared to the other two Sn–S bonds (2.4413(12) and 2.4291(12) Å), the Mn–Sn bond remaining virtually intact (2.5479(9) Å). Note that the formally single W–S bond (2.5696(12) Å) is also noticeably shorter than the sum of the covalent radii of these elements (2.67 Å), probably because of an additional W  $\rightarrow$  S opposite bond. At the same time, the S–C bond (1.784(4) Å) is not influenced by the coordinated pentacarbonyltungsten: like the other two bonds (1.782(4) and 1.777(4) Å), it remains single and corresponds to the sum of the covalent radii (1.79 Å).

According to the DSC and TGA data, complex IV decomposes above  $107.2 \pm 2.0^{\circ}$ C (Figs. 2a, 2b). The DTG curve (Fig. 2c) shows an endothermic peak in a range from 107 to  $125^{\circ}$ C ( $Q = 130.3 \pm 2.5 \text{ kJ/mol}$ ). The weight loss  $\Delta m = 8.8 \pm 1.5\%$  suggests elimination of three out of six CO groups coordinated to tungsten

and manganese. The further weight loss  $\Delta m = 12.5 \pm$ 1.5% in a range from 125 to 145°C (before the exothermic effect) is due to elimination of the remaining three CO groups and one NO group coordinated to manganese. Another endothermic peak at 152–270°C  $(\Delta m = 18.0 \pm 1.5\%)$  can be attributed to elimination of  $Ph_2S_2$  and structural rearrangement. Finally, a diffuse endothermic peak appears at 270–400°C ( $\Delta m = 20.6 \pm$ 1.5%). This weight loss corresponds to elimination of the phenyl and cyclopentadienyl fragments, which leaves an X-ray amorphous solid of the formula MnSnSW (its mass is 41.5% of the starting complex IV; calcd.: 41.1%). A suggested general pattern of the thermolysis is shown in Scheme 4. Note that the final product combines tin and tungsten atoms, which are not easily compatible using conventional methods of solid-state chemistry because these metals have very different melting temperatures.

 $CpMn(CO)(NO)Sn(SPh)_{3}W(CO)_{5} \xrightarrow[-3CO]{105-111^{\circ}C} CpMn(NO)Sn(SPh)_{3}W(CO)_{3}$   $\xrightarrow{125-145^{\circ}C} CpMnSn(SPh)_{3}W \xrightarrow[-Ph_{2}S_{2}]{152-270^{\circ}C} CpMnSn(SPh)W \xrightarrow[-Cp,-Ph]{270-400^{\circ}C} MnSnSW.$ Scheme 4.

For the moment, we failed to isolate complex IV deprived of two CO groups. As implied by structure II [3], the relative positions of the lone electron pairs of the S atoms hinders coordination of the fragment  $W(CO)_3$  to all three chalcogen

atoms. The only example of the coordination of this fragment to three S atoms linked by methylene bridges with the Sn atom is cited in [8]; in this case, the bridges make the ligand flexible and fit for chelation (Scheme 5):

$$CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{3} \qquad CH_{2} \qquad CH_{2} \qquad CH_{3} \qquad CH_{2} \qquad CH_{3} \qquad CH_{2} \qquad CH_{3} \qquad C$$

Scheme 5.

A reaction of benzeneselenolate complex III with  $W(CO)_5$ THF unexpectedly gives dimeric ditungsten complex V (Scheme 6), which was isolated as brown prismatic crystals. Structure V was characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. The IR spectrum shows bands at 1985 and 1935 cm<sup>-1</sup> (CO stretching vibrations). According to X-

ray diffraction data (Fig. 3), structure V is symmetrical and contains two perpendicular planes ( $Se_2-W_1-Se_2-W_1$  and  $Se_3-W_1-Se_3-W_1$ ).

Although the bonds between the W atoms and the SePh bridges (on average, 2.642(2) Å) are longer than the terminal W–SePh bond (2.571(2) Å), all



**Fig. 3.** Molecular structure of complex **V**. Selected bond lengths: W–W, 2.8153(16) Å; W(1)–Se(1), 2.571(2) Å; W(1)–Se(3), 2.615(2) Å; W(1)–Se(2), 2.636(2) Å; W(1)–Se(2), 2.647(2) Å; W(1)–Se(3), 2.673(2) Å.

the bonds are substantially shorter than the sum of the covalent radii (2.82 Å). It is no wonder that the W–W bond (2.8153(16) Å) is also shorter than the double covalent radius of tungsten (3.24 Å). As for the cause of the cleavage of the Sn–Se bonds, the weakening of the tin– chalcogen bond was distinct in the formation of a short-

ened bond between sulfur and  $W(CO)_5$  in structure IV. Likewise, strengthening of the Se–W bonds in intermediate A (Scheme 6) will weaken the Sn–Se bonds and may result in their cleavage followed by the formation of dimer V (via elimination of one CO group from either Watom):



In reactions of complexes II and III with a  $Pt_0$  complex, Pt(0) is oxidized into Pt(II) to give the known complexes VI and VII, probably through inter-

mediate **B** (Scheme 7) (as in the preceding case, the destiny of the manganese—tin residue was not studied):

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Complexes VI and VII, which are resistant to moisture and atmospheric oxygen, were characterized by elemental analysis and IR spectroscopy. Their IR spectra show bands due to phenyl groups. Complex VII was additionally examined by X-ray diffraction; the parameters obtained are identical with those cited in [9].

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