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Cyclopenta[*b*]thienyl Ligand in Organometallic Chemistry. Synthesis of Cyclopenta[*b*]thiophene η^5-Complexes with Metal Coordination at the Thiophene Ring

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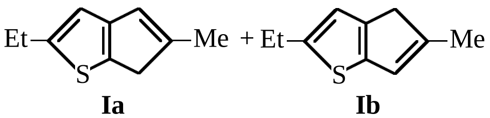
Abstract—Unlike isoelectronic η^6-indenyl ruthenium, manganese, and chromium complexes, heating of $Mn(CO)_5OTf$, $[Ru(Cp^*)Cl_4]$, and $Cr(C_{10}H_8)(CO)_3$ with isomeric 2-ethyl-5-methylcyclopenta[*b*]thiophenes leads to the corresponding η^5-complexes where the metal is coordinated at the C_5-carbocycle. The structure of the complex $Mn(Th)(CO)_3$ (Th = 2-ethyl-5-methylcyclopenta[*b*]thienyl) was proved by X-ray analysis.

Current studies in the field of organometallic chemistry are characterized by increased interest in the synthesis and reactivity of σ and π complexes formed by transition and nontransition metals with heterocycic ligands. This interest is explained prmarily by the fact that introduction of a heteroatom into π-electronic system of a ligand could give rise to appreciable anisotropy of electron density, which should in turn affect the reactivity of the heterocyclic ligand and also other ligands in the metal coordination sphere. Therefore, the use of heterocyclic ligands is promising from the viewpoint of discovering new reaction types that do not occur with the corresponding carbocyclic analogs. In partuclar, new generations of highly efficient metal-complex catalysts for various processes may be developed on the basis of fused heterocyclic systems.

We previously started a systematic study of σ- [1] and π-organometallic derivatives [2–4] of 2-ethyl-5-methylcyclopenta[*b*]thiophenes **Ia** and **Ib** which, for the sake of brevity, are referred to as thiapentalenes in the further treatment.

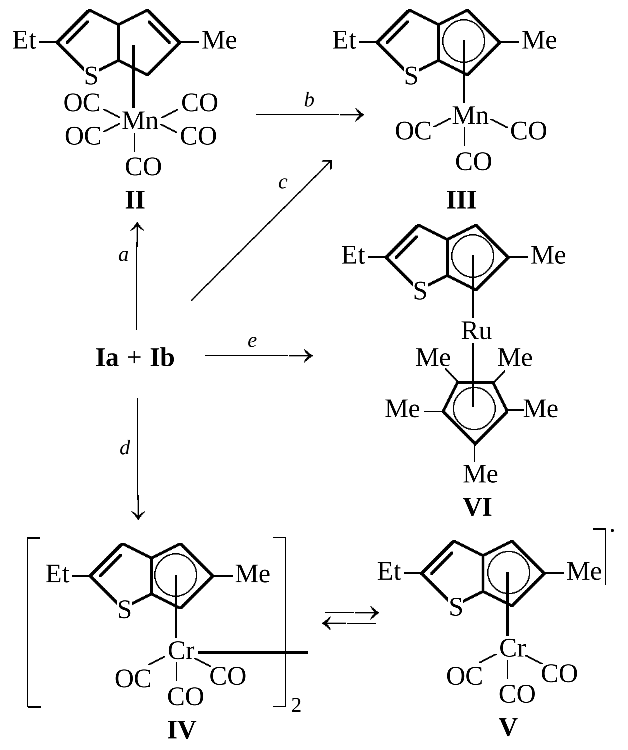


Ia **Ib**

The present work continues our studies in this line and extends them to include chromium, manganese, and ruthenium complexes. It seemed reasonable to compare the results with those obtained previously for indene complexes of transition metals, taking into account that thiapentalene and indene ligands are isooelectronic to each other [5–11], as well as for the simplest thiophene complexes with the same metals [11–16]. We have synthesized three new thiapentalene π-complexes with transition metals: chromium, manganese, and ruthenium. The structure of the initial organometallic compounds and the synthetic procedure allowed us to anticipate formation of complexes with two possible modes of metal coordination: at the cyclopentadiene and thiophene rings. However, regardless of the method of preparation, in all complexes the metal was coordinated to the cyclopentadiene ring of the ligand molecule.

Heating of $Mn(CO)_5OTf$ with 2 equiv of isomers **Ia** and **Ib** in methylene chloride gave only 12% of complex **III** (Scheme 1, reaction *c*). Complex **III** was also synthesized in 65% yield by reaction of thiapentalene lithium salt with an equimolar amount of $Mn(CO)_5OTf$ (Scheme 1, reactions *a* and *b*). According to the IR data, the reaction involves formation of η^1-thiapentalenyl intermediate **II** which is characterized by the following absorption bands arising from the carbonyl ligands, ν, cm^{-1}: 2107 m, 2046 s, 2017 s, 1991 s, 1964 w. These data indicate the presence of an $Mn(CO)_5$ moiety. The exact position of the manganese atom in complex **II** is unknown. Complex **III** was isolated as yellow crystals. Its IR spectrum contained three absorption bands from the $Mn(CO)_3$ fragment at 2021, 1944, and 1937 cm^{-1}. In the ^1H NMR spectrum we observed slightly broadened singlets from the 4-H and 6-H protons of the cyclopentadiene ring at δ 4.74 and 4.92 ppm, respectively. The ^{13}C chemical shifts of the C_5 ring in **III** are as follows, δ_C, ppm: 69.7 (C^4), 70.7 (C^6), 104.1 (C^5), 108.0 (C^8), 112.0 (C^7); the C^3 signal appears in the spectrum at δ_C 112.7 ppm. The structure of complex **III** was also confirmed by mass spectrometry. Its mass spectrum contained the molecular ion peak with

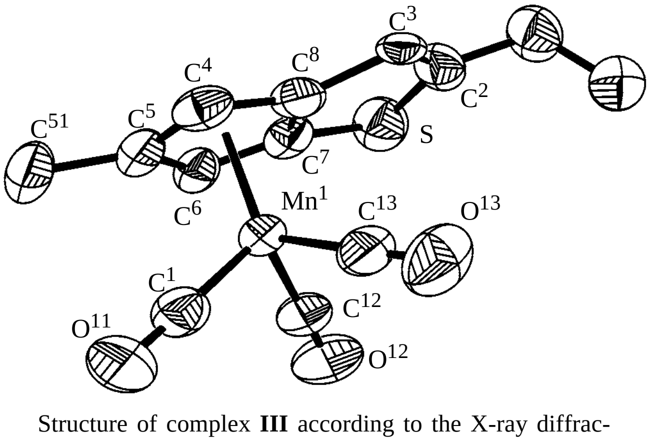
Scheme 1.



(*a*) (1) *n*-BuLi, (2) $Mn(CO)_5OTf$; *b*: Δ; (*c*) Mn(CO)5OTf; (*d*) $Cr(\eta^6\text{-}C_{10}H_8)(CO)_3$, MeOBu; *e*: (*1*) *n*-BuLi, (*2*) $[Cp^*RuCl_2]_2$ or $[Cp^*RuCl]_4$.

m/*z* 302 (M^+), three peaks corresponding to successive elimination of CO ligands [*m*/*z* 274 (M^+ – CO), 246 (M^+ – 2CO), and 218 (M^+ – 3CO)], and a peak with *m*/*z* 163 arising from the thiapentalenyl ligand.

Complex **III** is relatively stable to oxidation and hydrolysis. According to the X-ray diffraction data (see figure and Table 1), molecule **III** is characterized by slightly distorted η^5-coordination of the thiapentalenyl ligand: the distances Mn–C^4, Mn–C^5, Mn–C^6, Mn–C^7, and Mn–C^8 are 2.141(5), 2.130(5), 2.138(5), 2.185(5), and 2.197(5) Å, respectively. The principal bond lengths and bond angles in molecule **III** are collected in Table 2.



Structure of complex **III** according to the X-ray diffraction data (thermal ellipsoids with a 50% probability are shown).

The angle between the $SC^2C^3C^7C^8$ and $C^4C^5C^6$ planes in molecule **III** is about 5°. Complex **III** in crystal exists as two enantiomers in a ratio of 1 : 1. As a result, the structure is disordered with respect to C^3/S. This leads to “unusual” lengths of the C^2–S and C^2–C^3 bonds [1.648(8) and 1.564(8) Å, respectively] and anomalous C^7SC^2 [91.2(3)°] and $C^2C^3C^8$ angles [95.8(4)°]. The other bond lengths and bond angles fall into the corresponding standard ranges [17]. Analogous disordered structures were observed previously for benzo[*b*]thiophene complexes of chromium [11, 12], ruthenium [18], and iridium [13]. The projection of the manganese atom in complex **III** onto the C_5 ring plane almost coincides with its centroid (the deviation is ~0.05 Å toward C^5). These data are consistent with those reported for analogous (tricarbonyl)(indenyl)manganese complexes [17]. For example, the projection of the manganese atom onto the C_5-ring plane in $Mn(\eta^5\text{-indacenyl})(CO)_3$ deviates from the ring centroid by 0.07 Å toward C^2.

The reaction of $Cr(\eta^6\text{-}C_{10}H_8)(CO)_3$ with 2 equiv of thiapentalenes **Ia** and **Ib** in methyl *tert*-butyl ether in the presence of a catalytic amount of THF (to activate replacement of the naphthalene ligand) gave 47.5% of dimeric complex $[Cr(\eta^5\text{-Th})(CO)_3]_2$ (**IV**) as an equimolar mixture of isomers differing by orientation of the sulfur atoms in the thiapentalene ligands with respect to the metal–metal bond (*cis* or *trans*) (Scheme 1, reaction *d*). The structure of complex **IV** was confirmed by the IR and NMR spectra. Absorption bands of the carbonyl ligands appeared in the IR spectrum at 1987, 1944, and 1931 cm^{-}1. The Cr–Cr bond in complex **IV** is fairly weak; therefore, it readily dissociates in solution with formation of paramagnetic radical species $^{\cdot}Cr(\eta^5\text{-Th})(CO)_3$ (**V**). As a result, signals in the ^{1}H NMR spectrum are broadened. chastits. We succeeded in recording a satisfactory ^{1}H NMR spectrum at 0°C. The 4-H and 6-H protons in the two isomers give rise to a broadened singlet at δ 4.29 ppm. In the $^{13}C–\{^1H\}$ NMR spectrum, two pairs of signals corresponding to C^4 and C^6 are located at δ_C 78.7, 78.9, 79.6, and 79.9 ppm. The signals from C^5, C^7, and C^8 are obsrved in the δ_C range from 107 to 129 ppm, and the carbonyl ligands give rise to signals at δ_C 201.5 and 205.6 ppm.

Analogous ruthenium complex **VI** (Scheme 1, reaction *e*) was synthesized by heating of

Table 1. Crystallographic parameters of complex **III**

Parameter	Value
Formula	$C_{11}H_{13}MnO_3S$
M	302
T, K	294 (2)
λ, Å	0.71
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a, Å	8.716 (8)
b, Å	13.213 (7)
c, Å	11.480 (9)
β, deg	94.53 (6)
V, Å^3	1317.9 (6)
Z	4
d_{calc}, mg/mm^3	1.523
Absorption coefficient, mm^{-1}	1.16
F(000)	616
Crystal size, mm	$0.33 \times 0.20 \times 0.13$
θ range, deg	2.02 to 55
hkl range	$-1 \le h \le 11$, $-17 \le k \le 1$, $-14 \le l \le 14$
Number of reflections	2330
Number of independent reflections	2033 [R(int) = 0.0219]
Number of observed reflections [$I > 3\sigma(I)$]	1464
Correction for absorption	psi scan
Weight coefficients	0.0786 and 0.87989
Refinement method	Least-squares procedure with respect to F^2
Number of reflections/number of independent reflections ratio	2033/166
GODF	1.076
R [$I > 4\sigma(I)$]	R_1 = 0.0546, wR_2 = 0.1588
R (all reflections)	R_1 = 0.0802, wR_2 = 0.1763

Table 2. Principal bond lengths (*d*) and bond angles (ω) in the molecule of complex **III**

Bond	d, Å	Bond	d, Å
$S–C^2$	1.648 (8)	$Mn–C^6$	2.138 (5)
$C^2–C^3$	1.564 (8)	$Mn–C^7$	2.185(4)
$Mn–C^4$	2.141 (5)	$Mn–C^8$	2.197 (5)
$Mn–C^5$	2.130 (5)		
Angle	ω, deg	Angle	ω, deg
SC^2C^3	123.0 (4)	$C^2C^3C^8$	95.8 (4)

$[Ru(\eta^5\text{-}Cp^*)Cl]_4$ (which was prepared *in situ* by reduction of $[Ru(\eta^5\text{-}Cp^*)Cl_2]_2$ with zinc dust) with 3 equiv of thiapentalene **Ia**/**Ib** (reaction time 6 h, yield 64%). Complex **VI** was also obtained in 74% yield by reaction of $[Ru(\eta^5\text{-}Cp^*)Cl_2]_2$ with 4 equiv of thiapentalenyllithium. Komplex **VI** is moderately stable in air and readily soluble in organic solvents. Its structure was established by ^1H NMR spectroscopy. The ^1H NMR spectrum of **VI** contained singlets from the pentamethylcyclopentadienyl group and thiapentalene 4-H, 6-H, and 3-H protons at δ 1.65, 4.30, 4.37, and 6.10 ppm, respectively. The η^5-coordination mode is confirmed by the ^{13}C chemical shifts of the C_5-ring, δ_C, ppm: 78.4 (C^4), 79.9 (C^6), 89.2 (C^5), 108.4 (C^8), 110.1 (C^7).

Thus, the formation of η^5-complexes with metal coordination at the thiophene ring of thiapentalene ligand is thermodynamically less favorable than the formation of analogous η^6-indene complexes, which is consistent with published data on the reactivity of benzothiophene ligands [13, 18].

EXPERIMENTAL

The NMR spectra were recorded on a Varian-400 spectrometer. The IR spectra were measured on an IKS-29 instrument. Elemental compositions were determined at the Microanalysis Laboratory, Faculty of Chemistry, Moscow State University. The mass spectra (electron impact, 70 eV) were run on an MKh-1320 instrument.

All reactions were carried out in dry solvents under argon. Diethyl ether and tetrahydrofuran were dried by refluxing over metallic sodium in the presence of benzophenone; benzene and hexane were refluxed over metallic sodium; toluene was refluxed over potassium–sodium alloy, and methylene chloride was boiled over phosphoric anhydride. Lithium salts and organometallic derivatives of ruthenium, chromium, and manganese were synthesized using specially designed Schlenk glassware.

Isomeric thiapentalenes **Ia** and **Ib** [19], $Mn(CO)_5OTf$ [20], $Cr(\eta^6\text{-}C_{10}H_8)(CO)_3$ [21], and $[Ru(\eta^5\text{-}Cp^*)Cl_2]_2$ [22] were prepared by known methods. The structure of complex **III** was solved using SHELX 97 software package [23].

Tricarbonyl(η^5-thiapentalenyl)manganese(I) (III). To a solution of 0.4 g of isomer mixture **Ia**/**Ib** in 30 ml of ether we added at room temperature

0.98 ml of a 2.5 M solution of butyllithium in hexane. Pale yellow lithium salt immediately precipitated. The mixture was stirred for 12 h and cooled to –40°C, and 0.87 g of pentacarbonylmanganese(I) trifluoromethanesulfonate was added. The resulting red solution was stirred for 1 h at –40°C and then for 1 h at room temperature. The solvent was evaporated under reduced pressure, and 40 ml of hexane was added to the residue. The mixture was heated for 3 h under reflux, concentrated to a volume of 5 ml, and subjected to chromatography on silica gel 60 using hexane as eluent. The first fraction contained decacarbonyldimanganese. The second yellow fraction was collected and evaporated under reduced pressure. The residue was dissolved in 15 ml of methylene chloride, and 1 ml of trifluoroacetic acid was added. The solution immediately turned dark red. It was stirred for 15 min and filtered, and the filtrate was evaporated to dryness under reduced pressure. Yield 0.48 g (65%), yellow crystalline substance. IR spectrum (hexane), ν(CO), cm^{-1}: 2021, 1944, 1937. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.23 t (3H, CH_3CH_2, $^3J_{HH}$ = 7.5), 1.94 s (3H, Me), 2.67 q (2H, CH_3CH_2, $^3J_{HH}$ = 7.5), 4.74 s (1H, 4-H), 4.92 s (1H, 6-H), 6.43 s (1H, 3-H). ^{13}C–{^1H} NMR spectrum ($CDCl_3$), δ_C, ppm: 13.5 (CH_3CH_2), 14.8 (Me), 24.9 (CH_3CH_2), 69.7 (C^4), 70.7 (C^6), 104.1 (C^5), 108.2 (C^8), 112.0 (C^7), 112.7 (C^3), 154.7 (C^2), 225.6 (CO). Mass spectrum, *m*/*z* (I_{rel}, %): 302 (33) [M^+], 274 (26) $[M – CO]^+$, 246 (21) $[M – 2CO]^+$, 218 (100) $[M – 3CO]^+$, 163 (94) $[C_{10}H_{11}]^+$, 148 (100) $[C_{10}H_{11} – Me]^+$. Found, %: C 52.03; H 3.82; Mn 18.19. $C_{13}H_{11}MnO_3S$. Calculated, %: C 51.66; H 3.67; Mn 18.18.

Tricarbonyl(η^5-thiapentalenyl)chromium(0) dimer (IV). A Schlenk vessel was charged with 0.26 g of tricarbonyl(naphthalene)chromium(0), 0.49 g of thiapentalene **Ia**/**Ib**, and 10 ml of methyl *tert*-butyl ether. The mixture was stirred for 5 h at 50°C and diluted with petroleum ether. The solution was separated from the precipitate, and the latter was washed with several 10-ml portions of petroleum ether (by decanting) and dried for 5 h under reduced pressure. Yield 0.28 g (47%), dark green crystalline substance. IR spectrum (hexane), ν(CO), cm^{-1}: 1987, 1944, 1931. ^1H NMR spectrum (C_6D_6, 0°C), δ, ppm (*J*, Hz): 1.35 t (3H, 11-H, ^3J = 7.6), 1.99 s (6H, 9-H), 2.67 q (2H, 10-H, ^3J = 7.4), 4.29 m (4H, 4-H, 6-H), 6.25 s (2H, 3-H). ^{13}C–{^1H} NMR spectrum (C_6D_6, 0°C), δ_C, ppm: 14.2 and 15.4 (C^{11}); 13.8 and 14.5 (C^9); 30.7 and 31.5 (C^{10}); 78.8, 78.9, 79.6, and 79.9 (C^4, C^6); 113.7 and 130.9 (C^3); 107.4, 113.1, 113.8, 114.1, 116.7, and 130.0 (C^5, C^9, C^8); 159.9 and 156.0 (C^2); 201.5 and 205.6 (CO). Found, %: C 51.93; H 3.71; Cr 17.36. $C_{26}H_{22}CrO_6S_2$. Calculated, %: C 52.17; H 3.70; Cr 17.37.

(η^5-Pentamethylcyclopentadienyl)(η^5-thiapentalenyl)ruthenium (VI). *a*. A Schlenk vessel was charged with a solution of 0.42 g of thiapentalene **Ia**/**Ib** in 15 ml of diethyl ether, and 1.45 ml of a 2.02 M solution of butyllithium in hexane was quickly added. The mixture was stirred for 3 h at room temperature, and 0.26 g of $[Cp^*RuCl_2]_2$ was added. The mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure, and the residue was extracted with petroleum ether (3 × 15 ml). The solvent was removed under reduced pressure, and the residue was dried for 5 h in a vacuum. Yield 0.75 g (74%), light yellow crystals.

b. A Schlenk vessel was charged with 0.13 g of $[Cp^*RuCl_2]_2$, 0.16 g of zinc dust, and 20 ml of THF. The mixture was stirred for 1 h at room temperature, and it changed from red–brown to green and then to red–brown again. A solution of 0.42 mmol of thiapentalene lithium salt was added, the mixture was stirred for 1 h and evaporated under reduced pressure, and the residue was extracted with petroleum ether (3 × 5 ml). The solvent was removed from the extract under reduced pressure, and the residue was dried for 5 h in a vacuum. Yield 0.64 g (64%), light yellow crystals. ^1H NMR spectrum (C_6D_6), δ, ppm: (*J*, Hz): 1.24 t (3H, 11-H, ^3J = 7.4), 1.73 s (15H, Cp^*), 1.78 s (3H, 9-H), 2.10 q (2H, 10-H, ^3J = 7.4 Hz), 4.31 s (1H, 4-H), 4.46 s (1H, 6-H), 6.25 s (1H, 3-H). ^{13}C–{^1H} NMR spectrum ($CDCl_3$), δ_C, ppm: 13.7 (CH_3CH_2), 15.0 (Me), 16.0 (5-Me), 25.2 (CH_3CH_2), 78.4 (C^4), 78.9 (C^6), 89.2 (C^5), 108.4 (C^8), 110.1 (C^7), 112.7 (C^3), 114.4 (C_5Me_5), 152.5 (C^2). Found, %: C 59.98; H 6.56; Ru 25.36. $C_{20}H_{26}RuS$. Calculated, %: C 60.12; H 6.56; Ru 25.30.

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