Exo-H- and *endo-H*-η^4-pentamethylcyclopentadiene complexes of platinum

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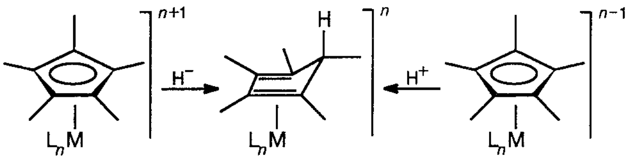
A mixture of *endo-H* and *exo-H* isomers (**1a** and **1b**) of the (η^4-C_5Me_5H)$PtCl_2$ complex was prepared by the reaction of K_2PtCl_4 with C_5Me_5H in MeOH. The mixture of isomers reacts with CpTl in the presence of $TlBF_4$ to give a novel complex, $[(\eta^4\text{-}C_5Me_5H)Pt(\eta^5\text{-}C_5H_5)]^+BF_4^-$, as a mixture of *endo-H-* and *exo-H*-isomers (**2a** and **2b**). The data of ^1H and ^{13}C NMR spectroscopy of the resulting complexes are discussed.

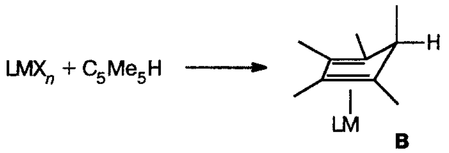
Key words: η^4-pentamethylcyclopentadiene, platinum complexes; synthesis; *endo-H-* and *exo-H*-isomers.

Transition metal complexes containing a η^4-coordinated pentamethylcyclopentadiene ligand have been studied to a substantially lesser degree than compounds with other dienes. Two main approaches to the preparation of compounds of this type are known. One of them consists of the modification of a coordinated η^5-cyclopentadienyl ligand by the action of complex hydrides[1] or acids;[2] in these cases, *exo-H*-isomers (**A**) of the corresponding η^4-cyclopentadiene compounds were shown or assumed to form.



A

The second route for the synthesis of η^4-pentamethylcyclopentadiene complexes is based on the reactions of pentamethylcyclopentadiene (or Dewar hexamethylbenzene in earlier works) with inorganic or organometallic halides.[3—5]

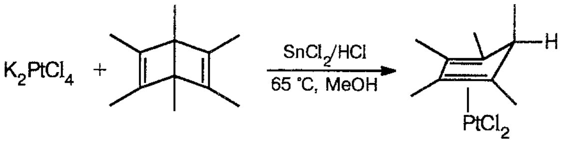


B

Compounds prepared according to this route are *endo-H*-isomers (**B**).

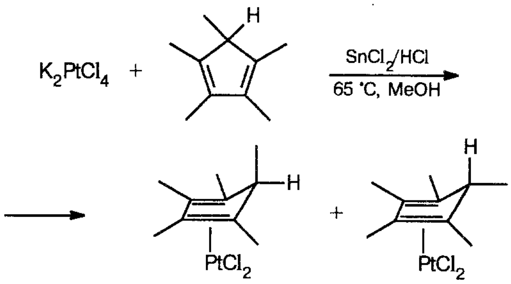
Only a few examples of complexes exist for which both the *exo-* and *endo*-isomers have been prepared.[1]

It has been found previously[3] that the reaction of Dewar hexamethylbenzene with K_2PtCl_4 in MeOH in the presence of catalytic amounts of an HCl solution of $SnCl_2$ yields only the *endo-H*-isomer of dichloro(η^4-pentamethylcyclopentadiene)platinum (**1a**).



1a

The investigation carried out by us showed that the use of pentamethylcyclopentadiene, rather than Dewar hexamethylbenzene, results in the formation of a mixture of *endo-H* and *exo-H* isomers (**1a** and **1b**) in a ~3 : 1 ratio (according to ^1H NMR). The presence of $SnCl_2$ as a catalyst is still necessary.



1a **1b**

The mixture of isomers **1a,b** reacts with cyclopentadienylthalium (CpTl) to give unstable cyclopentadienyl derivatives, which were characterized only by ^1H NMR spectroscopy.

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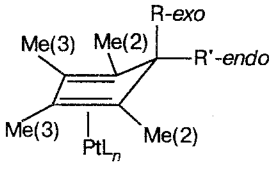
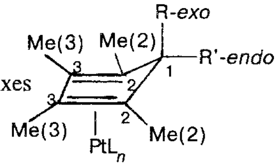
Table 1. ^{1}H NMR spectra of complexes 

, L_n = Cl_2 (**1a,b**) or η^5-C_5H_5 (**2a,b**) ($(CD_3)_2CO$, δ, *J*/Hz)

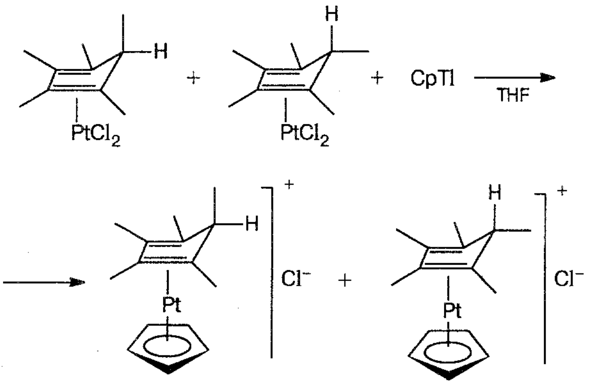
Comp-lex	R-*exo*	R'-*endo*	Me(2)	Me(3)	η^5-C_5H_5
1a	0.99(d, CH_3, J = 6.6)	3.41 (q, H, J = 6.6; J_{H-Pt} = 2.5)	1.40 (s, J_{H-Pt} = 9.4)	2.23 (s, J_{H-Pt} = 39.2)	—
1b	2.34 (q, H, J = 7.2)	1.58 (d, CH_3, J = 7.2; J_{H-Pt} = 4.6)	1.26 (s, J_{H-Pt} = 10.5)	2.26 (s, J_{H-Pt} = 37.6)	—
2a	0.70 (d, CH_3, J = 6.4)	3.90 (q, H, J = 6.4; J_{H-Pt} = 53.0)	1.96 (s, J_{H-Pt} = 36.2)	2.67 (s, J_{H-Pt} = 28.4)	6.18 (s, J_{H-Pt} = 25.2)
2b	5.70 (q, H, J = 6.6; J_{H-Pt} = 140.3)	1.41 (d, CH_3, J = 6.6; J_{H-Pt} = 6.0)	1.67 (s, J_{H-Pt} = 36.2)	2.70 (s, J_{H-Pt} = 28.0)	6.21 (s, J_{H-Pt} = 24.2)

Table 2. ^{13}C NMR spectra of complexes 

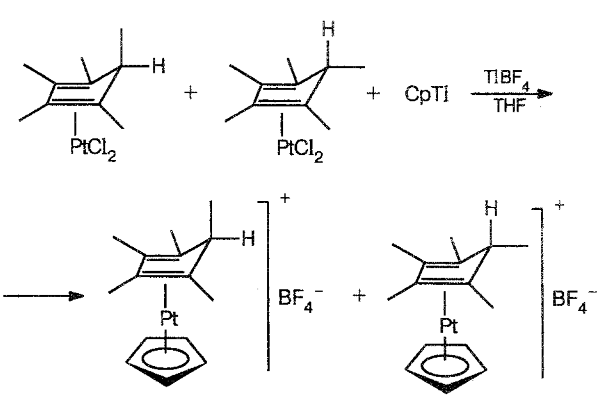
, L_n = Cl_2 (**1a,b**) or η^5-C_5H_5 (**2a,b**) ($CDCl_3$, δ, J_{C-Pt}/Hz)

Complex	R-*exo*	R'-*endo*	Me(2)	Me(3)	C(1)	C(2)	C(3)	η^5-C_5H_5
1a	21.9(57.8)	—	10.0(20)	13.0(3)	58.0(100)	103.4(118)	110.0(115)	—
1b*	—	29.8	9.8	12.6	55.4	101.3	110.0	—
2a	27.9(12.3)	—	10.6(22)	14.5(18)	59.9(123)	82.6(202)	104.7(105)	94.1(41)
2b	—	18.2(54)	10.4(22)	14.4(15)	54.3(122)	82.0(189)	105.1(105)	94.1(41)

* Spin-spin coupling constants (J_{C-Pt}) have not been determined due to low solubility of complexes **1a,b**.



The instability of the compounds obtained is obviously due to the interaction of the organometallic cation with the Cl$^-$ anion. In fact, when the same reaction was carried out in the presence of $TlBF_4$, we obtained a previously unknown platinum complex, (η^4-pentamethylcyclopentadiene)(η^5-cyclopentadienyl)platinum tetrafluoroborate, as a mixture of *endo-H* and *exo-H* isomers (**2a** and **2b**).



2a **2b**

Complexes **1a,b** and **2a,b** were characterized by the data of elemental analysis and ^{1}H and ^{13}C NMR spectroscopy, which are given in Tables 1 and 2. The appearance of the spectra is normal for this type of compound and is not in contradiction with the assumed structure. Nevertheless, a number of peculiarities can be observed. For example, the chemical shifts of the signals for the *endo-H* atoms in the ^{1}H NMR spectra of complexes **1a** and **2a** are relatively close (3.41 and 3.90 ppm), whereas the difference between the chemical shifts of the signals for the *exo-H* atoms in complexes **1b** and **2b** is quite pronounced (2.34 and 5.70 ppm). This considerable distinction is still difficult to explain, since there are practically no spectroscopic data for η^4-pentamethylcyclopentadiene complexes of platinum. In this connection it is interesting to compare the chemical shifts obtained by us with the known values for η^4-cyclopentadiene complexes of other metals (Table 3).

Based on a comparison of the values of δ of the signals for the *exo-H* atoms and Δδ ($\Delta\delta = \delta_{\text{exo-}H} - \delta_{\text{endo-}H}$), η^4-cyclopentadiene complexes may be divided into three groups. In the first group are compounds in which chemical shifts of the *exo-H* atoms lie within the interval 1.5—3.0 ppm and $\Delta\delta < 0$. To the second group we assign complexes with $2.5 < \delta_{\text{exo-}H} < 4.0$ and $0 < \Delta\delta < 1.5$. Compounds having $\delta_{\text{exo-}H} > 5.5$ ppm and $\Delta\delta > 1.5$ ppm comprise the third group. This division into groups practically coincides with the position of the central atom of a complex in the Periodic Table, *i.e.*, the first, second, and third groups consist of metals, from the first, second, and third transition metal series, respectively.*

If one considers η^4-pentamethylcyclopentadiene complexes on the basis of the same criteria, complexes **2a,b** turn out to belong to the third group, while complexes **1a,b** fall into the first group. The most pronounced distinction between the ^{13}C NMR spectra (see Table 2) of complexes **1a,b** and **2a,b** is observed for the C(2) atoms, whereas the chemical shifts of the signals for the Me groups attached to the coordinated carbon atoms (C(2) and C(3)) differ by no more than 5 ppm in all four of the compounds.

As was shown previously,[6] the signals from the C(2) atoms in the series of complexes $(\eta^4\text{-C}_5\text{H}_6)\text{M}(\text{C}_5\text{H}_5)$ (M = Co, Rh, Ir) undergo an upfield shift, which increases on going from Co to Rh and especially to Ir. The upfield displacement of the signals for C(2) and the downfield displacement of the signals for the *exo-H* atoms are likely to have the same cause and to be typical of both cyclopentadiene and pentamethylcyclopentadiene complexes. One of the possible reasons[6] for the upfield shift of the signals for C(2) is that on going from Co to Ir the dative bonding increases.

Table 3. Chemical shifts (δ) of the signals from the *exo-H* and *endo-H* atoms in complexes $(\eta^4\text{-C}_5\text{R}_5\text{H})\text{ML}_n$ (R = H, Me)

Complex	$\delta_{exo\text{-}H}$	$\delta_{endo\text{-}H}$	Δδ	Reference
$(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{PtCl}_2$ (**1a,b**)	2.34	3.41	−1.07	—
$(\eta^4\text{-C}_5\text{H}_6)\text{Co}(\text{C}_5\text{H}_5)$	1.83	2.61	−0.78	6
$(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_2(\text{PPh}_3)$	2.24	2.78	−0.54	7
$[(\eta^4\text{-C}_5\text{H}_6)\text{Ni}(\text{C}_5\text{H}_5)]^+$	3.06	3.53	−0.47	2
$(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3$	1.92	2.37	−0.45	8
$(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})(\text{dppe})$	2.75	3.03	−0.28	7
$(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Rh}(\text{C}_5\text{H}_5)$	2.82	2.71	0.11	1
$(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{CO})(\text{PPh}_3)_2$	2.94	2.51	0.43	9
$(\eta^4\text{-C}_5\text{H}_6)\text{Rh}(\text{C}_5\text{H}_5)$	3.21	2.77	0.44	6
$(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{tripod})$	4.01	3.54	0.47	7
$(\eta^4\text{-C}_5\text{H}_6)\text{Ru}(\text{triphos})$	3.57	2.58	0.99	7
$[(\eta^4\text{-C}_5\text{H}_6)\text{Mo}(\text{C}_5\text{H}_5)(\text{dppe})]^+$	3.58	2.51	1.07	10
$[(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Pt}(\text{C}_5\text{H}_5)]^+$ (**2a,b**)	5.70	3.90	1.80	—
$(\eta^4\text{-C}_5\text{H}_6)\text{Ir}(\text{C}_5\text{H}_5)$	5.63	3.68	1.95	6
$(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$	5.76	3.53	2.23	11
$(\eta^4\text{-C}_5\text{H}_6)\text{Ir}(\text{C}_5\text{Me}_5)$	5.63	3.28	2.35	1

Thus, the data of ^{1}H and ^{13}C NMR spectroscopy obtained for complexes **2a,b** reflect the peculiarities of η^4-cyclopentadiene complexes of the metals of the third transition series, while the results obtained for complexes **1a,b** are to a large measure characteristic of the first transition series compounds. One may assume that this distinction is due to the presence of two Cl atoms in the *trans*-position with respect to the pentamethylcyclopentadiene ligand in the 16-electron complexes **1a,b**, which results in a decrease in the dative bonding[12] and cancels the effect of the nature of the metal atom.

Experimental

All of the operations in the synthesis of the platinum complexes were carried out in an argon atmosphere using absolute solvents. ^{1}H and ^{13}C NMR spectra were recorded on Bruker WP-200SY and Varian VRX-300 spectrometers in CDCl_3 and $(\text{CD}_3)_2\text{CO}$. The chemical shifts are given in the δ scale with respect to TMS.

Dichloro(η^4-1,2,3,4,5-pentamethylcyclopentadiene)platinum (1a,b). $\text{C}_5\text{Me}_5\text{H}$ (5 mL, 42 mmol) and a solution of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (0.30 g, 2 mmol) in 60 mL of conc. HCl were added to a suspension of K_2PtCl_4 (4.20 g, 10 mmol) in 250 mL of MeOH, the mixture was boiled for 4 h, cooled to room temperature, and concentrated *in vacuo* to ~50 mL. The yellow precipitate was filtered off, washed with MeOH (3×5 mL) and Et_2O (3×20 mL), dried *in vacuo*, and reprecipitated from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture. Yield 3.35 g (83 %). Found (%): C, 29.84; H, 4.06; Cl, 17.60. $\text{C}_{10}\text{H}_{16}\text{Cl}_2\text{Pt}$. Calculated (%): C, 29,82; H, 4.00; Cl, 17.60.

(η^4-1,2,3,4,5-Pentamethylcyclopentadiene)(η^5-cyclopentadienyl)platinum fluoroborate (2a,b). $\text{C}_5\text{H}_5\text{Tl}$ (0.4 g, 1.5 mmol) and TlBF_4 (0.40 g, 1.5 mmol) were added to a suspension of complexes **1a,b** (0.61 g, 1.5 mmol) in 50 mL of acetone, the mixture was stirred for 2 h at room temperature and filtered, and the solution was concentrated and treated with 70 mL of ether. The precipitate was filtered off, washed with ether, and dried *in vacuo*. Yield 0.67 g (93 %). Found (%): C, 37,12; H, 4.02; F, 15.71. $\text{C}_{15}\text{H}_{21}\text{BF}_4\text{Pt}$. Calculated (%): C, 37,61; H, 4,32; F, 15.73.

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* Recently[6] it was suggested that the abnormal downfield shift of *exo-H* is unique to the metals of the third transition series.

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