

PENTAMETHYLCYCLOPENTADIENYL RHODIUM COMPLEXES OF  
 1,5- AND 1,7-DIHYDRO-S-INDACENES AND THEIR DERIVATIVES

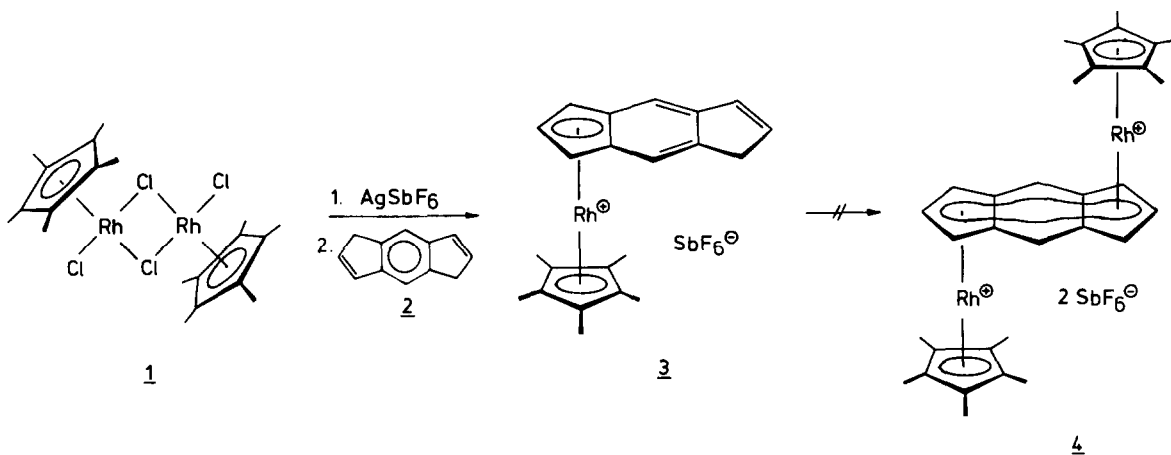
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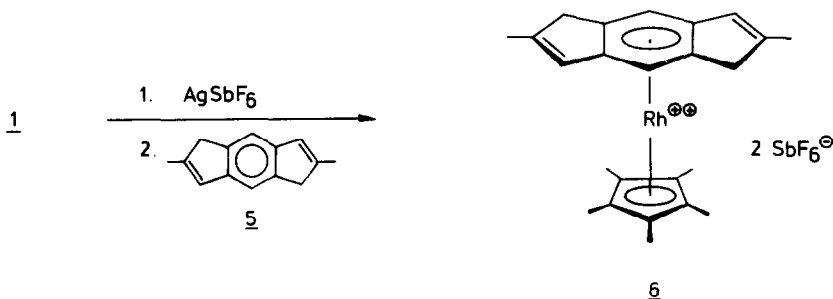
Summary: The reaction of  $(C_5Me_5RhCl_2)_2$  with  $AgSbF_6$  in the presence of 1,5- and 1,7-dihydro-s-indacenes or 2,6-dimethyl-1,5- and 1,7-dihydro-s-indacenes provides stable  $\eta^5$ - or  $\eta^6$ -monorhodium complexes, respectively. A novel phane rhodium complex is described.

Since 1,5-dihydro-s-indacene (2)<sup>1</sup> and its derivatives have become readily available<sup>2,3,4</sup>, they have been subject to several investigations including deprotonation<sup>2,5,6</sup>, carbene-addition<sup>6</sup>, and s-indacenophane-formation<sup>4</sup>. Here we want to report on their behavior in the formation of pentamethylcyclopentadienyl rhodium complexes.

Some years ago Maitlis and coworkers<sup>7</sup> observed that the reaction of  $(C_5Me_5RhCl_2)_2$  (1)<sup>8</sup> with  $AgPF_6$ <sup>9</sup> in the presence of indene or 4,6-dimethylindene provides  $C_5Me_5(\eta^5\text{-indenyl})RhPF_6$  or  $C_5Me_5(\eta^5\text{-4,6-dimethylindenyl})RhPF_6$  via the appropriate  $\eta^6$ -complexes in good yields. When we treated 1,5-dihydro-s-indacene (2) accordingly, the  $\eta^5$ -monohydro-s-indacene derivative 3 was isolated in 75 % yield. No sign for the formation of a possible di-rhodium complex 4 was found even when a two-fold excess of 1 was employed<sup>10</sup>.

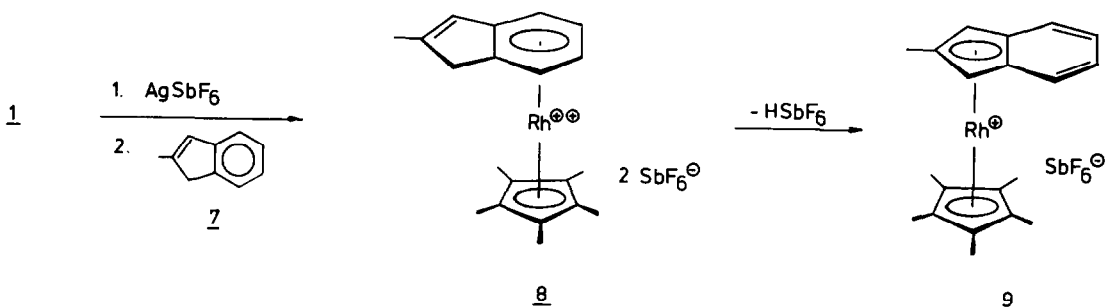


Surprisingly however, the reaction of 1 with 2,6-dimethyl-1,5-dihydro-s-indacene (5) stopped at the stage of the  $\eta^6$ -complex 6.



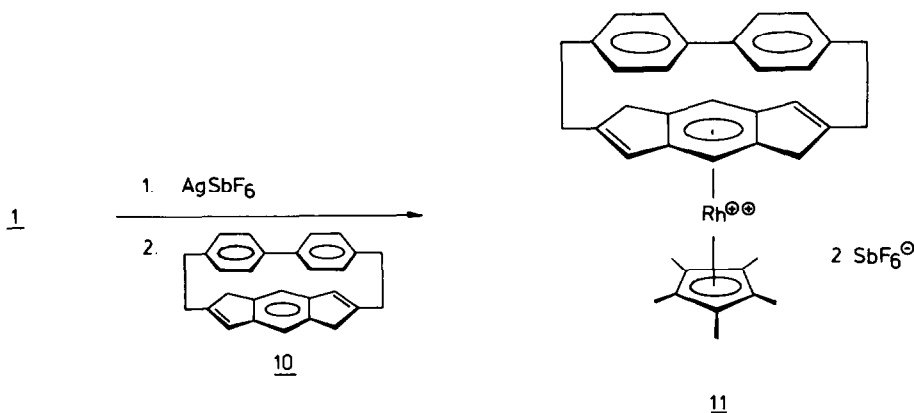
6 can be isolated in 58 % yield as stable yellow crystals (from acetone/ether). Its structure has been proven by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , IR, field desorption mass spectrometry, and combustion analysis. It shows only very little tendency to rearrange into the corresponding  $\eta^5$ -complex when kept in acetone solution for four weeks at room temperature, while it is more readily decomposed in the presence of acetonitrile or stronger coordinating reagents.

Hindrance of migration of the  $\text{C}_5\text{Me}_5\text{Rh}$ -moiety also was observed when the analogous reaction of 2-methylindene (7) was investigated. While  $\text{C}_5\text{Me}_5(\eta^6\text{-2-methylindene})\text{Rh}(\text{SbF}_6)_2$  (8) was isolated in 73 % yield by quenching the mixture with ether after 15 minutes, 81 % of the corresponding  $\eta^5$ -complex 9 was obtained after 36 hours.



Thus, the rate of rearrangement drops significantly in the following sequence of ligands: indene  $\approx 2 > 7 \gg 5$ .

In an application of these results, 1 was treated with 18,22-dihydro-[2](4,4')-biphenyl- [2](2,6)-s-indacenophane (10)<sup>4</sup> to give the expected  $\eta^6$ -complex 11 - a novel type of transition metal phane complex - as stable brownish-yellow needles in 78 % yield.



### Experimental:

Bis(pentamethylcyclopentadienyl)dichlorodi- $\mu$ -chlorodirhodium(III)<sup>8</sup> (1) (0.25 mmol), silver hexafluoroantimonate (1.00 mmol), and acetone (10 ml) were stirred at room temperature for 20 min. The precipitated AgCl was removed by filtration and 2-methylindene (7) or one of the dihydro-*s*-indacene derivatives 2, 5, or 10 (0.60 mmol) was added with stirring. After 30 min (8: 15 min; 9: 36 h) crystallization was induced by addition of ether (20 - 100 ml) and storing of the mixture at -5°C for 24 h. The product was collected by filtration. It was essentially pure.

2,6-Dimethyl-1,5(1,7)-dihydro-*s*-indacene (5) was obtained from 2,6-bis(chloromethyl)-1,5(1,7)-dihydro-*s*-indacene<sup>4</sup> after treatment with lithium triethylborohydride: colourless leaflets, mp. 117-119°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 7.36 (s, o.2H, syn: H-4); 7.26 (s, o.6H, anti: H-4, H-8); 7.14 (s, o.2H, syn: H-8); 6.47 (s-br, 2H, syn: H-3, H-5, anti: H-3, H-7); 3.25 (s, 4H, CH<sub>2</sub>); 2.14 (s, 6H, CH<sub>3</sub>).

Physical data of the complexes 3, 6, 8, and 11<sup>11</sup>:

3: <sup>1</sup>H-NMR:  $\delta$  = 7.57 (s-br, 1H, H-4); 7.41 (s-br, 1H, H-8); 7.09-6.94 (m, 1H, H-3); 6.90-6.78 (m, 1H, H-2); 6.19 (d, 2.7 Hz, 2H, H-5, H-7); 5.78 (dt, 2.7 Hz, 1.5 Hz, 1H, H-6); 3.64-3.51 (m, 2H, CH<sub>2</sub>); 1.83 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)

IR(KBr): 1389, 1450 cm<sup>-1</sup>

C<sub>22</sub>H<sub>24</sub>F<sub>6</sub>RhSb (627.08) Calcd.: C 42.14 H 3.86 Found: C 42.01 H 3.93

6: <sup>1</sup>H-NMR:  $\delta$  = 7.98 (s, o.5H, syn: H-4); 7.86 (s, 1H, anti: H-4, H-8); 7.71 (s, o.5H, syn: H-8); 6.84 (s, 2H, syn: H-3, H-5, anti: H-3, H-7); 4.02 (d, 24.5 Hz, 2H), 3.63 (d, 24.5 Hz, 2H) (CH<sub>2</sub>); 2.50 (s, 6H, CH<sub>3</sub>-2/6); 1.99 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)

IR(KBr): 1379, 1450, 1592 cm<sup>-1</sup>

C<sub>24</sub>H<sub>29</sub>F<sub>12</sub>RhSb<sub>2</sub> (891.88) Calcd.: C 32.32 H 3.28 Found: C 32.34 H 3.20

- 8:  $^1\text{H-NMR}$ :  $\delta$  = 7.87 (d, 6.3 Hz, 1H), 7.72 (d, 6.5 Hz, 1H) (H-4, H-7); 7.54-7.41 (m, 2H, H-5, H-6); 6.90 (s-br, 1H, H-3); 4.04 (d, 24.5 Hz, 1H), 3.78 (d, 24.5 Hz, 1H) ( $\text{CH}_2$ ); 2.53 (s, 3H,  $\text{CH}_3$ -2); 2.22 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ )  
 IR(KBr): 1382, 1440, 1594  $\text{cm}^{-1}$   
 $\text{C}_{20}\text{H}_{25}\text{F}_{12}\text{RhSb}_2$  (839.81)      Calcd.: C 28.60    H 3.00      Found: C 28.61    H 2.87
- 9:  $^1\text{H-NMR}$ :  $\delta$  = 7.54-7.40 (m, 4H, H-4, H-5, H-6, H-7); 6.08 (s, 2H, H-1, H-3); 2.17 (s, 3H,  $\text{CH}_3$ -2); 1.82 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ )  
 IR(KBr): 1379, 1447  $\text{cm}^{-1}$   
 $\text{C}_{20}\text{H}_{24}\text{F}_6\text{RhSb}$  (603.06)      Calcd.: C 39.83    H 4.01      Found: C 39.90    H 3.86
- 11:  $^1\text{H-NMR}$ :  $\delta$  = 7.59-7.41 (m, 4H), 7.25-7.11 (m, 4H) (biphenyl-H); 7.40 (s, syn: H-23); 7.27 (s, anti: H-19, H-23), 7.10 (s, syn: H-19) (2H); 6.38 (s, o.8H), 6.32 (s, 1.2H) (syn: H-22, H-24, anti: H-20, H-24); 3.48-3.02 (m, 12H,  $\text{CH}_2$ ); 1.91 (s), 1.90 (s) (15H,  $\text{C}_5(\text{CH}_3)_5$ )  
 IR(KBr): 1380, 1450, 1581  $\text{cm}^{-1}$   
 $\text{C}_{38}\text{H}_{39}\text{F}_{12}\text{RhSb}_2$  (1070.12)      Calcd.: C 42.65    H 3.67      Found: C 42.87    H 3.61

#### Acknowledgment:

Support of this work by the Fonds der Chemischen Industrie, the Dr. Otto Röhm-Gedächtnisstiftung, and the Degussa, Frankfurt/Main, is gratefully acknowledged.

#### References and Notes:

- 1,5-dihydro-s-indacene and all of its derivatives occurred as a mixture of tautomers: e.g. 1,5-dihydro-s-indacene (anti), 1,7-dihydro-s-indacene (syn).
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- $\text{SbF}_6^-$  was used as counterion during these investigations.
- A comparable iron complex of a benzodicyclobutadiene derivative has been prepared by T. Butters, F. Toda, and W. Winter, *Angew. Chem.* **92**, 952 (1980); *Angew. Chem. Int. Ed. Engl.* **19**, 926 (1980).
- NMR spectra were recorded on Varian XL-100 or Bruker WM 300 spectrometers in hexadeuterioacetone with tetramethylsilane as internal standard. Correct field desorption mass spectra were obtained for all new rhodium complexes. Melting points are not given because all of these complexes decomposed without melting when heated above 250°C in an evacuated, sealed melting point tube.

(Received in Germany 18 March 1982)