

PENTAMETHYLCYCLOPENTADIENYL RHODIUM COMPLEXES OF DIHYDRO-*s*-INDACENOPHANES: TRANSANNULAR INTERACTIONS

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Dedicated to Dr. R. Zahradnik on the occasion of his 60th birthday.

Transannular interactions in pentamethylcyclopentadienyl rhodium complexes ($\text{Me}_5\text{C}_5\text{Rh}$) of 18,22(18,20)-dihydro[2](4,4')biphenylo[2](2,6)-*s*-indacenophane (*IV*) and 12,16(12,18)-dihydro[2]paracyclo[2](4,8)-*s*-indacenophane (*IX*) were investigated. The capability of a $\text{Me}_5\text{C}_5\text{Rh}$ group to reduce electron density in both decks of these phanes was established. The deprotonation product *VII* of 18a,19,19a,22a,23,23a- η^6 -(18,22(18,20)-dihydro[2](4,4')biphenylo[2](2,6)-*s*-indacenophane)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) bis(hexafluoroantimonate) (*V*) was isolated as the first representative of a class of compounds whose existence had been previously postulated. Evidence for conformational flexibility of the biphenyl deck of *IV* and its derivatives was obtained. Comparative ^1H NMR studies led to a separation of transannular electronic interactions from magnetic anisotropy effects in 15a,16,17,18,18a- η^5 -(12-monohydro[2]paracyclo[2](4,8)-*s*-indacenophane)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) hexafluoroantimonate (*X*).

Transition metal complexes of phanes have been attracting increasing interest since a synthesis of one-dimensional metal phane polymers of potential practical value appears feasible¹. So far, a series of chromium, iron and ruthenium complexes of the $[2_n]$ cyclophanes¹ and iron complexes of a thiophenophane¹ and indenophanes² as well as [2]metacyclo- and [2]paracyclo[2](1,3)ferrocenophanes³ have been prepared and thoroughly studied. Useful insight into the extent of π -electron delocalization within these molecules and into the nature of the metal-phane bonding has thus been obtained.

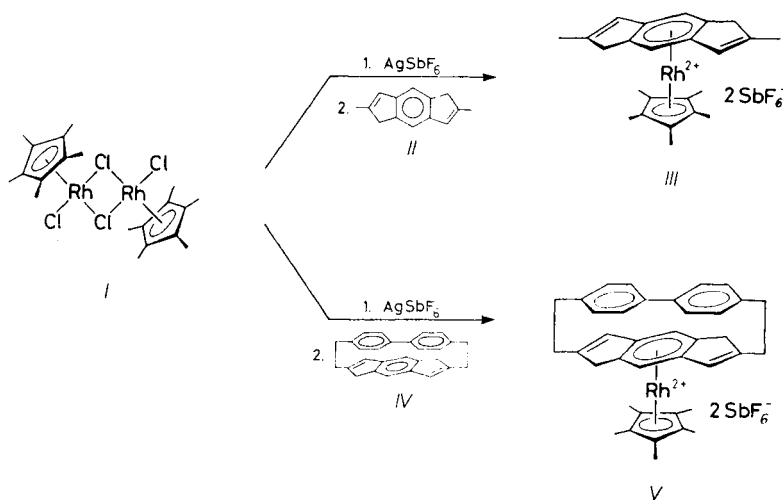
During our investigation of phanes derived from 1,5(1,7)-dihydro-*s*-indacene we observed⁴ that the Maitlis procedure for preparing η^5 -indenyl-pentamethylcyclopentadienyl rhodium salts⁵ is perfectly suited to provide the corresponding *s*-indacenophane transition metal complexes. The availability of certain stable η^6 -complexes, in which a $\text{Me}_5\text{C}_5\text{Rh}$ group is bound to the central arene ring of a dihydro-*s*-indacene, as well as of more conventional η^5 -complexes, bearing the $\text{Me}_5\text{C}_5\text{Rh}$

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group at one of the five-membered rings, promised to be of particular value for the elucidation of transannular interactions in those systems.

RESULTS AND DISCUSSIONS

We have demonstrated⁴, that the η^6 -dihydro-*s*-indacene complexes *III* and *V* can be obtained in reasonable yields when a suspension of bis(pentamethylcyclopentadienyl)-dichloro- μ -chlorodirhodium(III) (*I*) in acetone is subsequently treated with silver hexafluoroantimonate and 2,6-di-methyl-1,5(1,7)-dihydro-*s*-indacene (*II*) or 18,22-(18,20)-dihydro[2](4,4')biphenyl[2](2,6)-*s*-indacenophane (*IV*), respectively (Scheme 1).



SCHEME 1

Comparative ¹H NMR studies of hydrocarbons *II* and *IV* and complexes *III* and *V* readily reveal the substantial electron withdrawing capability of the double-charged Me₅C₅Rh group. As can be seen from Fig. 1, all resonances of complex *III* are shifted downfield in comparison to the corresponding values of *II*. The observed shift changes range from 0.60 ppm for the protons attached to the six-membered ring to 0.36 ppm for methyl groups at carbons 2 and 6 of the *s*-indacene framework. Since these methyl groups are sufficiently far removed from the metal, the latter value allows a direct estimate of the change in the electron density at those sites. Usually, complexation of an arene ring to a transition metal fragment results in an upfield shift of the aromatic protons due to a change in bond order for the aromatic carbons and a reduction of the ring current^{1,6}. In the present case, however, this effect is overcome by the positive charge located at the rhodium. Thus, the reduction

of electron density at the arene must be considered substantially higher than that indicated by the observed shift difference.

In the case of phane complex *V*, the electron deficiency of the *s*-indacene moiety is diminished by interaction with the opposite deck. As compared to *IV*, a mean downfield shift of 0.3 ppm for both inner and outer biphenyl protons is observed. The reduction of electron density in the biphenyl deck, however, must be accompanied by appropriate increases at the *s*-indacene as well as at rhodium. Since the shift differences of the respective *s*-indacene protons may partially be due to various ring current effects, the resonance frequency of the $\text{Me}_5\text{C}_5\text{Rh}$ -singlet is the most unambiguous measure of the electron densities there. Some upfield shift is thus required to occur and is, in fact, observed.

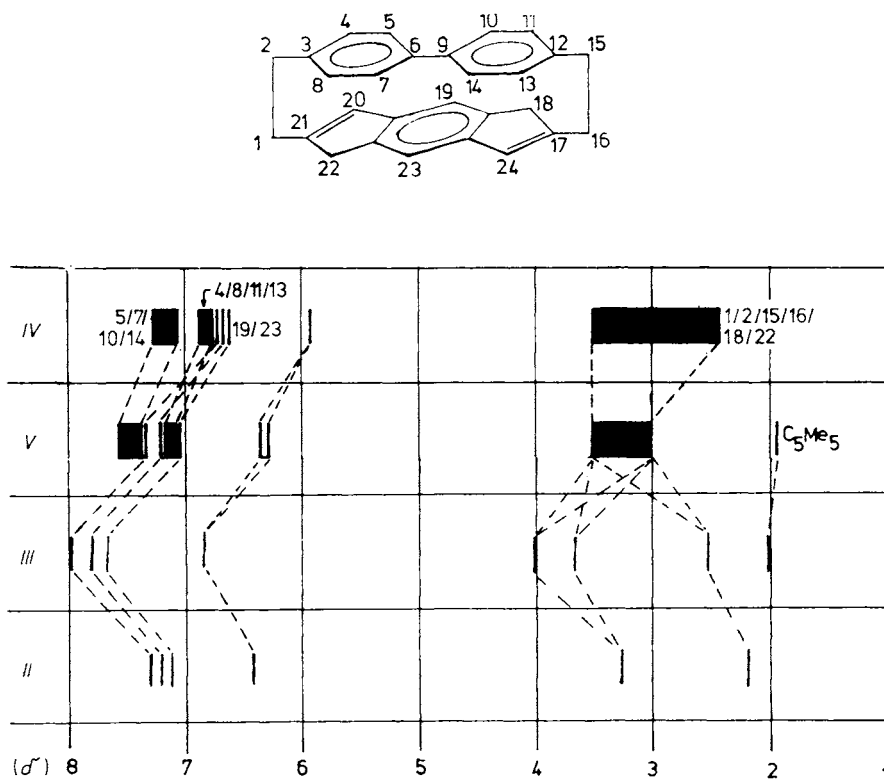
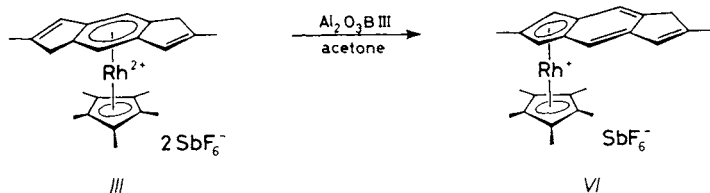


FIG. 1

Graphic representation of the chemical shift values obtained from the ^1H NMR spectra of hydrocarbons *II* and *IV* (CDCl_3) and η^6 -complexes *III* and *V* (hexadeuteroacetone). Extended multiplets are shown as bars

On treatment of η^6 -complex *III* with base, basic alumina being most convenient, deprotonation and subsequent migration of the $\text{Me}_5\text{C}_5\text{Rh}$ group from the six-membered to one of the five-membered rings occurs (Scheme 2).

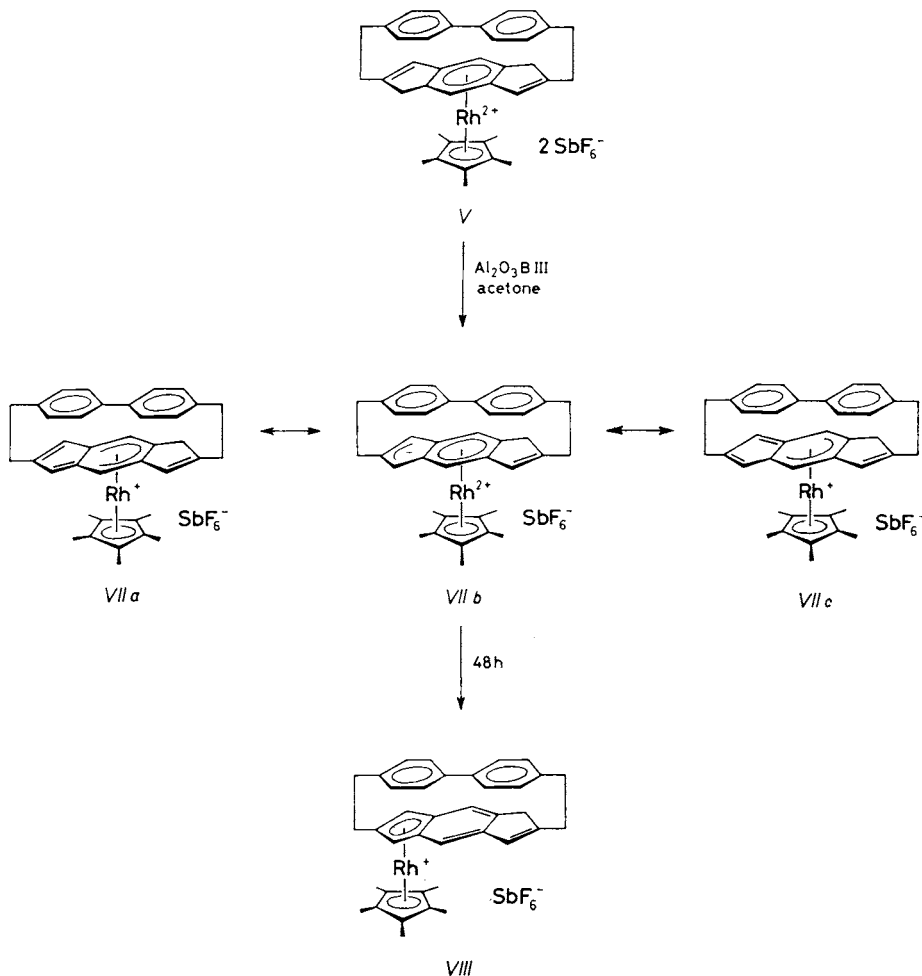


SCHEME 2

When complex *V* was treated similarly, the yellow color of the reaction mixture surprisingly turned grey. Addition of ether led to the precipitation of dark grey needles. Only when the solution was kept at room temperature for 48 h did a yellow color return and yellow crystals were then obtained upon addition of ether (Scheme 3).

The ^1H NMR spectra of both of these new compounds (Fig. 2) readily disclose their molecular constitutions. In fact, the yellow product is shown to be the expected η^5 -complex *VIII*, while the grey compound is identified as the deprotonation product *VII* of starting material. The existence of this type of species had originally been postulated by Maitlis et al.⁵ — based on kinetic evidence obtained from similar rearrangements of indene- into indenyl-complexes. Furthermore, a potential use of this class of compounds to study the course of haptotropic rearrangements has recently been proposed by Hoffmann, Albright and their collaborators⁷.

Which of the three resonance structures *VIIa*, *VIIb*, and *VIIc* most accurately represents the actual constitution of *VII* cannot yet be evaluated from the available data. The fact that the protons on the deprotonated five-membered rings of both complexes *VII* and *VIII* display two separate singlets in each NMR spectrum, however, requires further consideration. A comparison with the corresponding spectrum of the η^5 -2,6-dimethyl-*s*-indacene complex *VI* reveals that a direct influence of the position of the double bond in the non-deprotonated five-membered ring of the *s*-indacene deck cannot sufficiently explain this observation. Obviously then, the two protons in question in each of the two complexes *VII* and *VIII* are differentiated by interaction with the opposing biphenyl decks. Therefore, it must be concluded that the deprotonated five-membered ring of the *s*-indacene deck and the opposing benzene ring of the biphenyl deck are tilted with respect to each other. Consequently, the same must hold true regarding both benzene rings of the biphenyl deck. It appears highly probable then, that these deviations from planarity are also characteristic

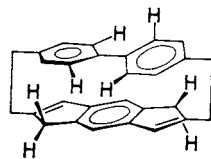


SCHEME 3

for 18,22-dihydro[2](4,4')biphenyl[2](2,6)-s-indacenophane (*IV*) (Scheme 4) itself.*

The conformational flexibility of phane *IV* and its derivatives severely limits the use of their NMR spectra to determine transannular electronic interactions. It must be noted, however, that the chemical shifts of the $\text{Me}_5\text{C}_5\text{Rh}$ groups and hence their

* The exact conformation of the biphenyl deck of phane *IV* varies depending on the actual positions of the double bonds in the *s*-indacene deck. Different chemical shifts for the vinyl protons of each of the two tautomers can thus be observed⁸.



IV

SCHEME 4

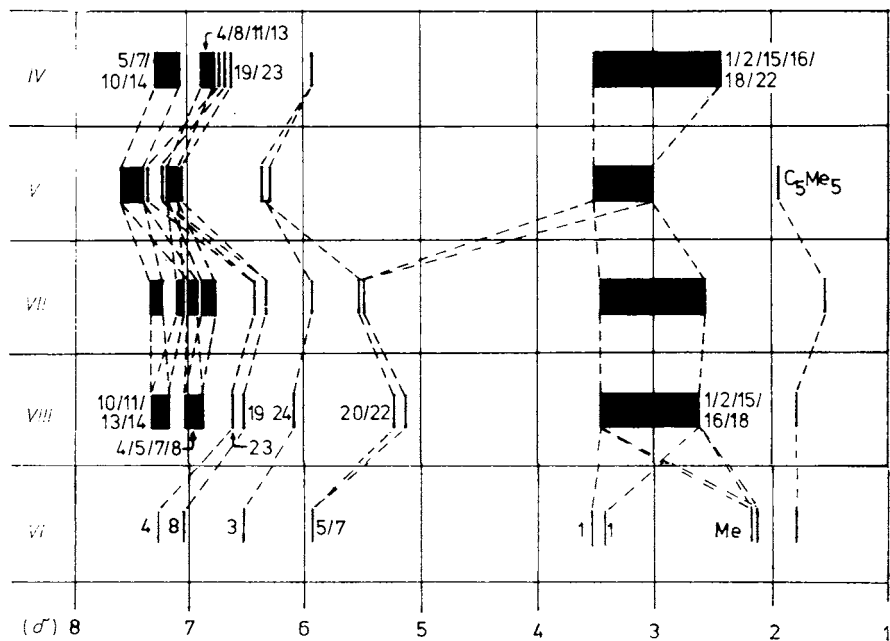
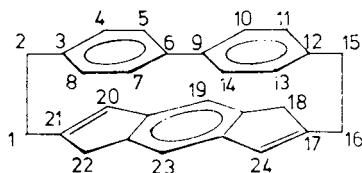
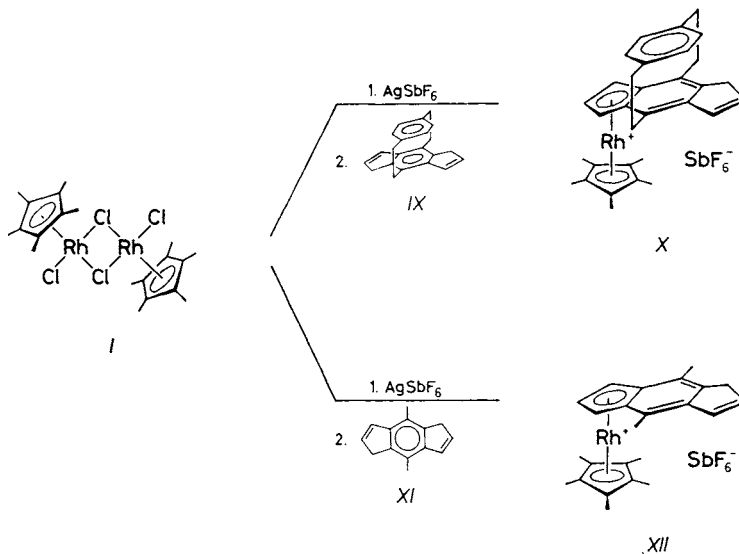


FIG. 2

Graphic representation of the chemical shift values obtained from the ^1H NMR spectra of phane *IV* (CDCl_3), η^6 -complex *V*, deprotonation product *VII*, and η^5 -complexes *VI* and *VIII* (hexa-deuteroacetone). Extended multiplets are shown as bars

respective electron densities are virtually the same in both, *s*-indacene *VI* and phane complex *VIII* (Fig. 2).

An evaluation of mutual electronic influences appears possible, however, when a more rigid phane molecule than *IV* is used. Therefore, we have submitted 12,16-(12,18)-dihydro[2]paracyclo[2](4,8)-*s*-indacenophane (*IX*)* to similar reaction conditions and directly isolated η^5 -complex *X*. Finally, complex *XII* was obtained from 4,8-dimethyl-1,5(1,7)-dihydro-*s*-indacene (*XI*)* for comparative purposes (Scheme 5).



SCHEME 5

The ^1H NMR spectra of compounds *IX*, *X*, *XI*, and *XII* are represented in Fig. 3. The aromatic protons of the benzene deck of phane *IX* resonate as one multiplet centered at 6.26 ppm, while the corresponding protons of phane complex *X* give rise to an AB-pattern at 6.39–6.48 ppm and a singlet at 6.13 ppm. Undoubtedly, the AB-pattern originates in the two protons next to the noncomplexed five-membered ring. Its mean upfield shift of almost 0.2 ppm relative to the center of the corresponding multiplet of *IX* thus indicates some reduction of electron density in the benzene deck of *X* as compared to *IX*. As expected, this effect is accompanied by an upfield shift of the $\text{Me}_5\text{C}_5\text{Rh}$ singlet of *X* relative to the corresponding signal

* Various substituted dihydro-*s*-indacenes, dihydro-*s*-indacenophanes, and their corresponding anions have been synthesized and investigated⁸.

of complex *XII* revealing an increase of electron density at this site. On the other hand, the singlet at 6.13 ppm arises from the benzene protons next to the complexed five-membered ring. Its chemical shift, however, is influenced by the anisotropy of the rhodiocene moiety, which overcompensates the effect due to reduction of electron density in the benzene deck and leads to the observed upfield shift of about 0.1 ppm relative to *IX*.

Phane complex *X* thus represents an interesting example in which a separation of transannular electronic interaction from magnetic anisotropy effects has been achieved. So far, similar investigations had been restricted to transition metal complexes of *anti*-[2.2]metacyclophane⁶.

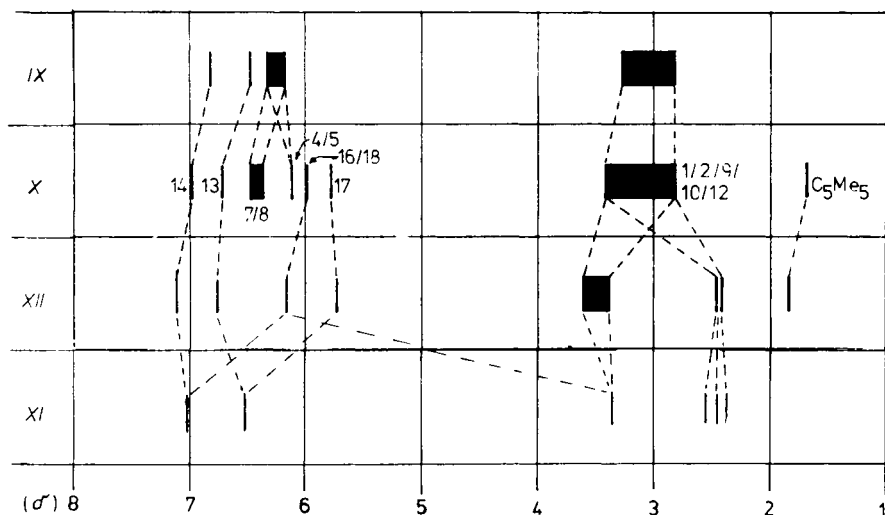
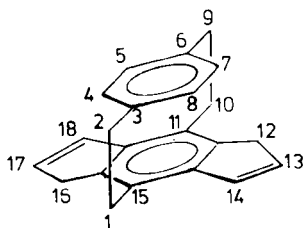


FIG. 3

Graphic representation of the chemical shift values obtained from the ^1H NMR spectra of hydrocarbons *IX* and *XI* (CDCl_3) and η^5 -complexes *X* and *XII*. Extended multiplets are shown as bars

EXPERIMENTAL

General comments. ^1H NMR spectra were determined with a Varian XL-100 and Bruker WM 300 spectrometer using tetramethylsilane as internal standard (δ -scale). UV spectra were obtained with a Beckman 5 240 spectrometer (nm, log ϵ). IR spectra were measured using a Beckman IR 5A instrument (cm^{-1}). Mass spectra were obtained with a Varian MAT 311A spectrometer (electron impact: MS-EI, 70 eV; field desorption: MS-FD). Elemental analyses were carried out in the microanalytical laboratory of the Institut für Organische Chemie, Technische Hochschule Darmstadt. Melting points are not given because all of these complexes decomposed without melting when heated above 250°C in an evacuated, sealed tube. All solvents were reagent grade and used without further purification. Dihydro-*s*-indacene derivatives *II*, *IV*, *IX*, and *XI* as well as rhodium complexes *III* and *V* were prepared as reported elsewhere^{4,8,9}.

4a,5,6,7,7a- η^5 -(2,6-Dimethyl-1-monohydro-*s*-indacene)- η^5 -(pentamethylcyclopentadienyl)-rhodium(III) Hexafluoroantimonate (*VI*)

A solution of 178 mg (0.02 mmol) of 3a,4,4a,7a,8- η^6 -(2,6-dimethyl-1,5(1,7)-dihydro-*s*-indacene)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) bis(hexafluoroantimonate) (*III*) in 4 ml of acetone was filtered over a short column of alumina B III. The formation of a dark violet band was observed which gradually turned yellow during elution with acetone. After the color of the eluate had turned completely yellow, the solution was concentrated to a few ml. Ether was added and the mixture was kept at -5°C for 24 h. Yellowish green crystals were collected upon filtration, yielding 111 mg (85%). For $\text{C}_{24}\text{H}_{28}\text{F}_6\text{RhSb}$ (655.14) calculated: 44.00% C, 4.31% H; found: 44.24% C, 4.23% H. IR (KBr, cm^{-1}): 1 460, 1 389, 653. UV (CH_3CN ; λ_{max} , nm (log ϵ): 219 (4.23), 234 (4.31), 267 (4.31), 312 (4.34), 368 sh (3.57), 417 sh (3.23). ^1H NMR (hexadeuteroacetone): 1.77 s, 15 H ($\text{C}_5(\text{CH}_3)_5$); 2.10 s, 3 H (CH_3 -6); 2.16 s, 3 H (CH_3 -2); 3.42 d, 1 H (H-1 *exo* or *endo*, $J = 23$ Hz); 3.51 d, 1 H (H-1, *exo* or *endo*, $J = 23$ Hz); 5.93 s, 2 H (H-5, H-7); 6.57 s, 1 H (H-3); 7.03 s, 1 H (H-8); 7.30 s, 1 H (H-4). ^{13}C NMR (hexadeuteroacetone): 9.04 s ($\text{C}_5(\text{CH}_3)_5$); 12.28 s (CH_3 -6); 17.16 s (CH_3 -2); 42.35 s (C-1); 81.92 d (C-5 or C-7, $J = 4.1$ Hz); 82.01 d (C-5 or C-7, $J = 4.4$ Hz); 100.05 d (C-6, $J = 8.2$ Hz); 101.88 d (C-4a or C-7a, $J = 4.7$ Hz); 104.92 d (C-4a or C-7a, $J = 6.2$ Hz); 105.32 d ($\text{C}_5(\text{CH}_3)_5$, $J = 6.4$ Hz); 108.46 s (C-4); 115.71 s (C-6); 127.79 s (C-3); 147.50 s (C-2); 152.91 s (C-3a). MS-FD: m/z 419 (100%, $\text{C}_{24}\text{H}_{28}\text{Rh}^+$).

19a,20,21,22,22a- η^5 -(18-Monohydro[2](4,4')biphenyl[2](2,6)-*s*-indacenophane)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) Hexafluoroantimonate (*VIII*) and 18a,19,19a,22a,23,23a- η^6 -(18-Monohydro[2](4,4')biphenyl[2](2,6)-*s*-indacenophane)- η^5 -pentamethylcyclopentadienylrhodium(III) Hexafluoroantimonate (*VII*)

A solution of 107 mg (0.01 mmol) of 18a,19,19a,22a,23,23a- η^6 -(18,22(18,20)-dihydro[2](4,4')biphenyl[2](2,6)-*s*-indacenophane)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) bis(hexafluoroantimonate) (*V*) in 3 ml of acetone was filtered over a short column of alumina B III. The resulting dark gray band was eluted with acetone. The eluate was concentrated to 2 ml and ether was added. After 24 h at -5°C , 69 mg (81%) of *VII* were obtained as grey needles. ^1H NMR (hexadeuteroacetone): 1.52 s, 15 H ($\text{C}_5(\text{CH}_3)_5$); 2.53–3.44 m, 10 H (CH_2); 5.52 s, 1 H (H-20 or H-22); 5.55 s, 1 H (H-20 or H-22); 5.93 s, 1 H (H-24); 6.33 s, 1 H (H-19); 6.43 s, 1 H (H-23); 6.81–6.90 m, 2 H (H-4, H-8); 6.95–7.05 m, 2 H (H-5, H-7); 7.06–7.11 m, 2 H (H-11, H-13); 7.24–7.33 m, 2 H (H-10, H-14). MS-FD: m/z 598 (100%, $\text{C}_{38}\text{H}_{38}\text{Rh}^+$). When the solution of complex *VII* in acetone was allowed to stand at room temperature for 48 h before ether was added, however, the color changed from grey into yellow and 67 mg (80%) of *VIII* were then

obtained upon addition of ether. For $C_{38}H_{38}F_6RhSb$ (833.37) calculated: 54.77% C, 4.60% H; found: 55.05% C, 4.44% H. IR (KBr, cm^{-1}): 1 460, 1 390, 654. UV (CH_3CN ; λ_{max} , nm (log ϵ): 212 (4.58), 275 (4.57), 286 sh (4.55), 316 sh (4.38), 388 (3.61), 435 sh (3.28). 1H NMR (hexadeuteroacetone): 1.76 s, 15 H ($C_5(CH_3)_5$); 2.61–3.44 m, 10 H (CH_2); 5.16 s, 1 H (H-20 or H-22); 5.26 s, 1 H (H-20 or H-22); 6.10 s, 1 H (H-24); 6.53 s, 1 H (H-19); 6.67 s, 1 H (H-23); 6.91–7.04 m, 4 H (H-4, H-5, H-7, H-8); 7.21–7.36 m, 4 H (H-10, H-11, H-13, H-14). MS-FD: m/z 598 (100%, $C_{38}H_{38}Rh^+$).

15a,16,17,18a- η^5 -(12-Monohydro[2]paracyclo[2](4,8)-*s*-indacenophane)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) Hexafluoroantimonate (*X*)

To a suspension of 154 mg (0.26 mmol) of rhodium complex *I* in 5 ml of acetone was added a solution of 344 mg (1.00 mmol) of silver hexafluoroantimonate in 5 ml of acetone. After 20 min of stirring at room temperature the precipitated silver chloride was filtered off and 171 mg (0.60 mmol) of 12,16(12,18)-dihydro[2]paracyclo[2](4,8)-*s*-indacenophane (*IX*) was added. After another 20 min the mixture was concentrated and passed over a short column of alumina to remove impurities. Ether was then added to the yellow filtrate until crystallization began. The mixture was stored at $-5^\circ C$ for 24 h after which the product was collected by filtration. Recrystallization from acetone/ether yielded 159 mg (44%) of dark yellow needles. For $C_{32}H_{34}F_6RhSb$ (765.28) calculated: 50.76% C, 4.53% H; found: 50.48% C, 4.60% H. IR (KBr, cm^{-1}): 1 455, 1 380, 654. UV (CH_3CN ; λ_{max} , nm (log ϵ): 225 (4.32), 235 (4.31), 263 (4.26), 286 (4.18), 331 (4.28), 400 sh (3.23). 1H NMR (hexadeuteroacetone): 1.67 s, 15 H ($C_5(CH_3)_5$); 2.78–3.42 m, 10 H (CH_2); 5.80 dt, 1 H (H-17, $J_1 = 2.6$ Hz, $J_2 = 1.2$ Hz); 6.01 mc, 2 H (H-16, H-18); 6.13 s, 2 H (H-4, H-5); 6.39–6.48 AB, 2 H (H-7, H-8, $J = 7.5$ Hz); 6.73 dt, 1 H (H-13, $J_1 = 5.8$ Hz, $J_2 = 2.0$ Hz); 7.02 dt, 1 H (H-14, $J_1 = 5.8$ Hz, $J_2 = 2.3$ Hz). MS-FD: m/z 521 (100%, $C_{32}H_{34}Rh^+$).

4a,5,6,7,7a- η^5 -(1-Monohydro-4,8-dimethyl-*s*-indacene)- η^5 -(pentamethylcyclopentadienyl)rhodium(III) Hexafluoroantimonate (*XII*)

Following exactly the same procedure as described for the preparation of phane complex *X* using 154 mg (0.25 mmol) of *I*, 344 mg (1.00 mmol) of $AgSbF_6$ and 109 mg (0.60 mmol) of 4,8-dimethyl-1,5(1,7)-dihydro-*s*-indacene (*XI*), 92 mg (28%) of dark yellow needles were obtained. For $C_{24}H_{28}F_6RhSb$ (655.14) calculated 44.00% C, 4.31% H; found: 44.10% C, 4.28% H. IR (KBr, cm^{-1}): 1 452, 1 389, 654. UV (CH_3CN ; λ_{max} , nm (log ϵ): 228 (4.28), 254 (4.26), 266 (4.26), 286 sh (4.23), 315 (4.28), 413 sh (3.14). 1H NMR (hexadeuteroacetone): 1.81 s, 15 H ($C_5(CH_3)_5$); 2.39 s, 3 H (CH_3 -8); 2.44 s, 3 H (CH_3 -4); 3.41–3.60 AB, 2 H (CH_2 , $J = 24$ Hz); 5.77 dt, 1 H (H-6, $J_1 = 2.7$ Hz, $J_2 = 1.4$ Hz); 6.21 dd, 2 H (H-5, H-7, $J_1 = 2.7$ Hz, $J_2 = 0.9$ Hz); 6.78 dt, 1 H (H-2, $J_1 = 5.7$ Hz, $J_2 = 2.1$ Hz); 7.13 dt, 1 H (H-3, $J_1 = 5.7$ Hz, $J_2 = 2.3$ Hz). MS-FD: m/z (100%, $C_{24}H_{28}Rh^+$).

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REFERENCES

1. Bockelheide V.: Top. Curr. Chem. *113*, 87 (1983); Pure Appl. Chem. *58*, 1 (1986); and references therein.
2. El-Tamany S., Raulfs F.-W., Hopf H.: Angew. Chem. *95*, 631 (1983); Angew. Chem., Int. Ed. Engl. *22*, 633 (1983).

- Hopf H., Raulfs F.-W., Schomburg D.: *Tetrahedron* **40**, 1655 (1986).
Frim R., Raulfs F.-W., Hopf H., Rabinovitz M.: *Angew. Chem.* **98**, 160 (1986); *Angew. Chem., Int. Ed. Engl.* **25**, 174 (1986).
3. Hisatome M., Yoshihashi M., Yamakawa K., Iitaka Y.: *Tetrahedron Lett.* **24**, 5757 (1983).
 4. Bickert P., Hafner K.: *Tetrahedron Lett.* **23**, 2309 (1982).
 5. White C., Thompson S. J., Maitlis P. M.: *J. Chem. Soc., Dalton Trans.* **1977**, 1654; and references therein.
 6. Langer E., Lehner H.: *J. Organomet. Chem.* **173**, 47 (1979).
Laganis E. D., Voegeli R. H., Swann R. T., Finke R. G., Hopf H., Boekelheide V.: *Organometallics* **1**, 1415 (1982).
Swann R. T., Boekelheide V.: *J. Organomet. Chem.* **231**, 143 (1982).
 7. Albright T. A., Hofmann P., Hoffmann R., Lillya C. P., Dobosh P. A.: *J. Am. Chem. Soc.* **105**, 3396 (1983).
 8. Bickert P., Boekelheide V., Hafner K.: Unpublished results. Bickert P.: *Thesis*. Darmstadt 1983.
 9. Bickert P., Boekelheide V., Hafner K.: *Angew. Chem.* **94**, 308 (1982); *Angew. Chem., Int. Ed. Engl.* **21**, 304 (1982).