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## Synthesis of slipped triple- and tetra-decker cationic ruthenium complexes with the $\mu, \eta^5 : \eta^6$ -indenyl ligand. X-Ray structure of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{-Ru}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$

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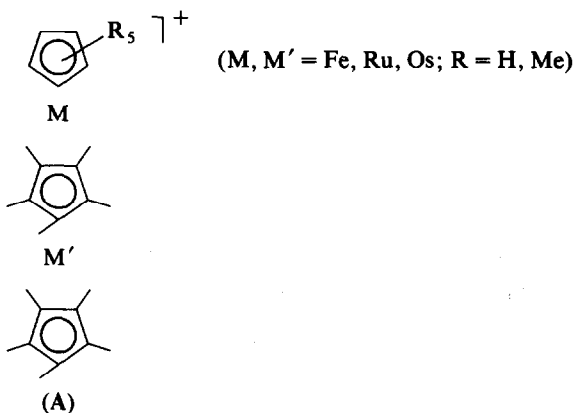
### Abstract

Slipped triple-decker complexes with a central indenyl ligand  $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{R}'_5)]\text{PF}_6$  ( $\text{R}, \text{R}' = \text{H}, \text{Me}$ ) were prepared by interaction of  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$  or  $\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_7)$  with  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  or  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]\text{PF}_6$ . The same reaction leads in the case of bis( $\eta^5$ -indenyl)ruthenium to the slipped triple-decker complexes  $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu, \eta^6 : \eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^5\text{-C}_9\text{H}_7)]\text{PF}_6$  ( $\text{R} = \text{H}, \text{Me}$ ) as well as to the tetra-decker complexes  $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu, \eta^6 : \eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{R}'_5)](\text{PF}_6)_2$  ( $\text{R}, \text{R}' = \text{H}, \text{Me}$ ). The structure of the complexes was confirmed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. An X-ray diffraction study of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$  provided supporting evidence.

### Introduction

We have already prepared some straight triple-decker complexes of the type A by addition of 12-electron coordinatively unsaturated species  $[\text{M}(\eta\text{-C}_5\text{R}_5)]^+$  ( $\text{M} = \text{Fe}, \text{R} = \text{H}; \text{M} = \text{Ru}, \text{R} = \text{H}, \text{Me}$ ) \* to decamethylmetallocenes based on metals of the iron group [1].

\* Complexes  $[\text{M}(\eta\text{-C}_5\text{R}_5)\text{L}]^+$  ( $\text{M} = \text{Fe}, \text{L} = \text{C}_6\text{H}_6; \text{M} = \text{Ru}, \text{L} = (\text{MeCN})_3$ ) were the sources of these species. When referring to addition of 12e species we do not imply that they are generated in an unsolvated form in the course of the reaction; we are describing the final results.



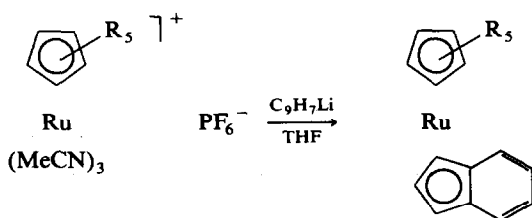
We have continued our study with a view to extending the number of carbocyclic systems which may be used as bridging ligands in multi-decker complexes. In the present work we used as starting materials ruthenium complexes with indenyl ligands such as  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$  and  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2^*$ . In these complexes the electrophilic particle may attack the  $\eta^5$ -coordinated five-membered ring (as happens in the case of methylated metallocenes) as well as the six-membered ring. In both cases the formation of triple-decker complexes would be expected: of the straight type similar to A in the first case, and of the slipped type in the second one.

### Results and discussion

We found earlier, when working on straight triple-decker complexes of the iron group metals with cyclopentadienyl ligands [1], that ruthenium compounds of this kind are much more stable than iron compounds. Therefore for the present study we chose ruthenium compounds. Complexes  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]^+$  [3,4] were taken as a source of 12e species, and mono- and bis-indenyl ruthenium complexes were used as substrates.

#### *Interaction of $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$ with mono-indenyl ruthenium complexes*

For the preparation of starting indenylcyclopentadienyl complexes **1** and **2** we used the reaction of the complexes  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]^+$  (R = H, Me) with indenyllithium:



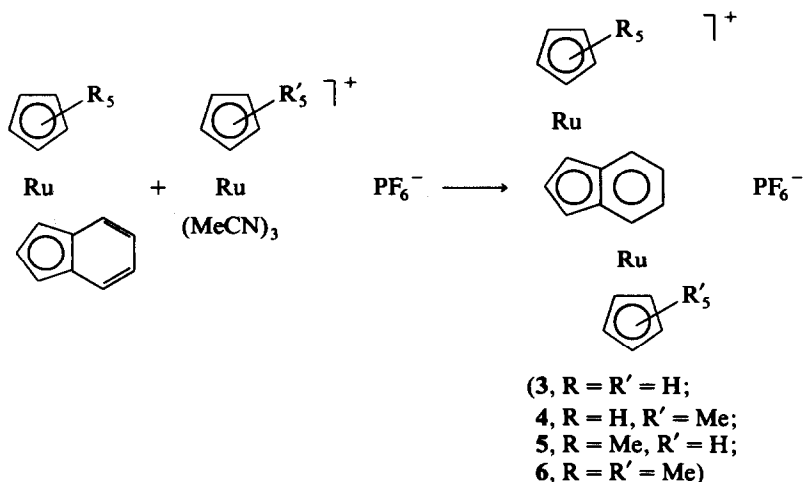
(1, R = H; 2, R = Me)

Compound **2** was also prepared by the reaction of complex  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  [5] with indenyllithium in the presence of Zn dust as a reducing agent although

\* For a preliminary communication see ref. 2.

addition of Zn dust is not necessary since in this case an excess of indenyllithium can act as a reducing agent\*.

Further reaction of compounds 1 and 2 with  $[\text{Ru}(\eta\text{-C}_5\text{R}'_5)(\text{MeCN})_3]^+$  ( $\text{R}' = \text{H}, \text{Me}$ ) proceeds in mild conditions (room temperature) in  $\text{CH}_2\text{Cl}_2$  or  $\text{MeNO}_2$  and leads to the 34-electron slipped triple-decker complexes 3–6:



The formation of the slipped triple-decker complexes thus reveals the six-membered ring of the indenyl ligand as the place of the attack by the cationic species  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$ .

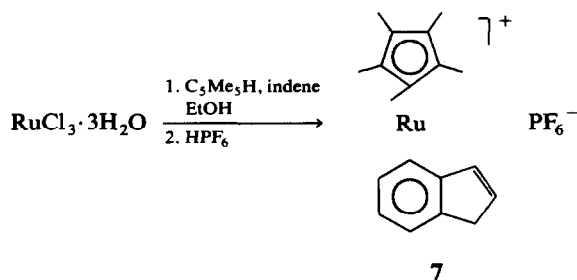
It is noteworthy that formation of straight triple-decker ruthenium complexes of type A (*vide supra*) in the analogous reaction of  $\text{Ru}(\eta\text{-C}_5\text{Me}_5)_2$  with  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]^+$  demands more drastic conditions (heating at  $100^\circ\text{C}$  in  $\text{MeNO}_2$ ). The mild conditions of the reaction of 1 and 2 with  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]^+$  seem to be connected with the essentially diene character of the six-membered ring in  $\eta^5$ -indenyl complexes (cf. for example ref. 7) that predisposes them to stepwise substitution of acetonitrile ligands. Meanwhile even in drastic conditions no product of any attack on the five-membered ring was observed for  $\eta^5$ -indenyl complexes. Thus the six-membered ring in 1 and 2 is much more nucleophilic than  $\eta^5$ -coordinated five-membered rings.

For addition of the permethylated  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$  fragment it is possible to use not only  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]^+$  but also the more readily available complex  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ . Treatment of  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  with Zn dust in THF gives  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}]_4$  which reacts further with 1 and 2 in the presence of  $\text{TIPF}_6$  giving compounds 4 and 6. Similar method using  $\text{KPF}_6$  was used earlier for the preparation of complexes of heterocycles [8].

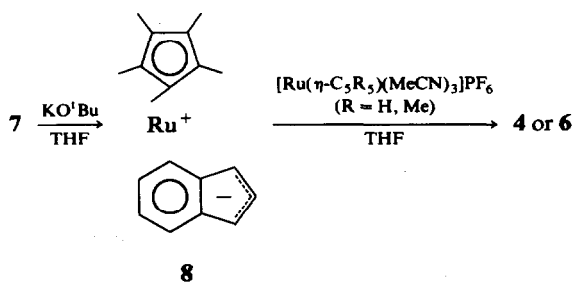
We have elaborated earlier a simple one-step method for synthesis of cationic complexes of the type  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-arene})]^+$  by interaction of ruthenium chloride with a mixture of pentamethylcyclopentadiene and arene in alcohol [9]. Using

\* Independently from our work [2], compound 2 has been prepared by other workers [6] using an excess of indenyllithium.

indene in this reaction we prepared  $\eta^6$ -indene complex **7** in high yield:



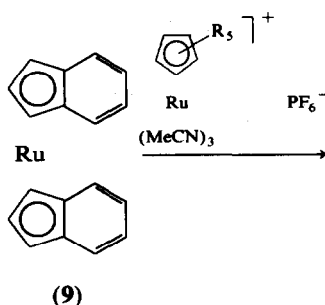
This complex was also prepared quantitatively by reaction of indene with  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  in alcohol. Further deprotonation of complex **7** with  $\text{KO}^t\text{Bu}$  in THF leads to  $\eta^6$ -indenyl complex **8** \* in nearly quantitative yield.



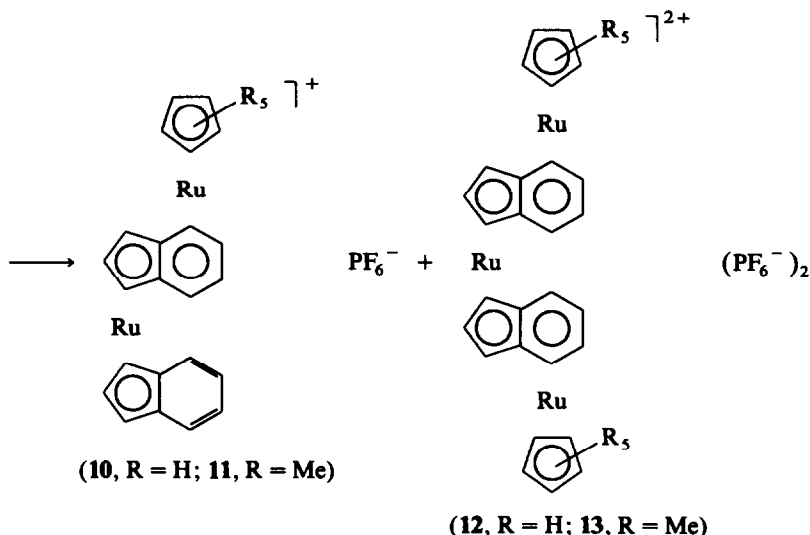
Similarly to isomeric complex **2**, compound **8** reacts with  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]\text{PF}_6$  giving slipped triple-decker complexes **4** and **6**.

#### Interaction of $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$ with bis( $\eta^5$ -indenyl)ruthenium

In similar reactions we also used bis( $\eta^5$ -indenyl)ruthenium (**9**) [7,10]. It readily reacts with  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]\text{PF}_6$  giving a mixture of mono- and dicationic complexes as a result of addition of one or two  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  fragments:



\* Under strong UV irradiation in hexane or THF, complex **8** slowly undergoes  $\eta^6 \rightarrow \eta^5$  rearrangement giving the isomeric complex **2**.

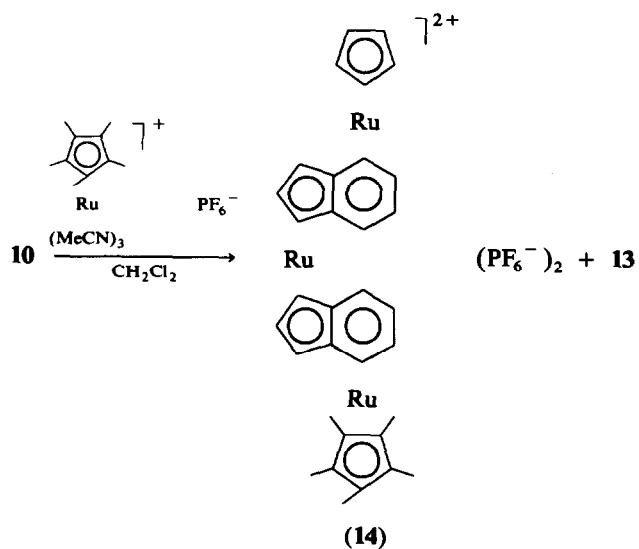


Reaction of **9** with  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  at a 1:1 ratio gives the monocationic triple-decker complex **10**, whereas if the ratio is 1:2, in mild conditions (20 °C) the dicationic tetra-decker complex **12** is also formed. At the same time reaction of **9** with  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]\text{PF}_6$  in mild conditions gives a mixture of mono- and dicationic multi-decker complexes **11** and **13** even when the ratio of reagents is 1:1, whereas at ratio 1:2, the tetra-decker dicationic complex **13** is formed almost exclusively. For selective preparation of triple-decker monocationic complex **11** the reaction was conducted at a 1:1 reagent ratio at 100 °C in  $\text{MeNO}_2$  since under such drastic conditions the tetra-decker complex **13** is probably destroyed with formation of triple-decker monocation **11**.

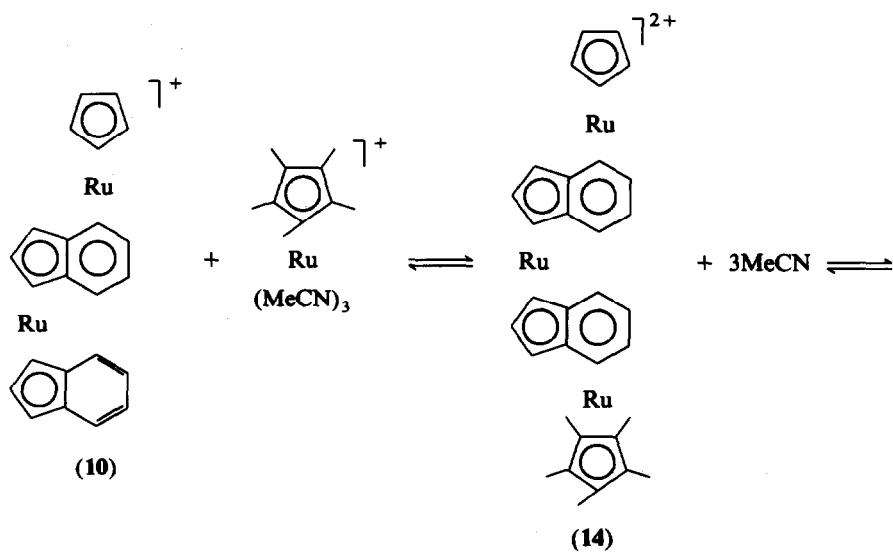
Tetra-decker dicationic complexes **12** and **13** may also be prepared stepwise by addition of cationic fragments  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  to previously prepared triple-decker monocationic complexes **10** and **11**:



The decamethylsubstituted complex **13** is much more stable than the parent compound **12** and is formed in higher yield. This stability is caused by stronger bonding of the six-membered ring with  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$  fragment than with the  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)]^+$  fragment. It was most clearly shown by an attempt to synthesise asymmetric tetra-decker complex **14** by reaction of the triple-decker complex **10** with the  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$  fragment, but instead of this a mixture of the expected complex **14** with the decamethylated analogue **13** (in ca. 2:1 ratio on the basis of  $^1\text{H}$  NMR data) was isolated from the reaction mixture after 24 h standing at room temperature:



This result suggests an equilibrium process:





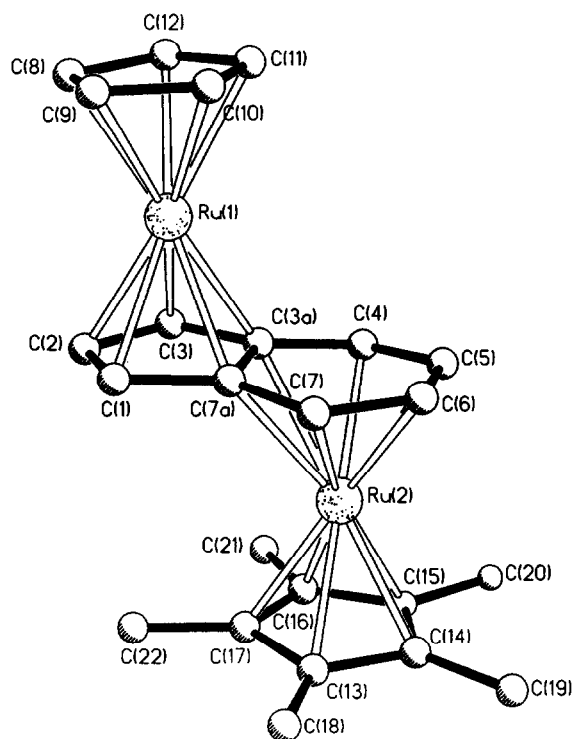


Fig. 1. The structure of the cation of 4-MeNO<sub>2</sub>.

Table 1

Analytical data for the slipped triple- and tetra-decker complexes

| Complex | Analysis (Found (calc.) (%)) |        |        | CH <sub>2</sub> Cl <sub>2</sub><br>molecules per molecule<br>of the complex |
|---------|------------------------------|--------|--------|---|
|         | C                            | H      | P      |   |
| 3       | 37.28                        | 2.87   | 5.29   | 0.25  |
|         | (37.67)                      | (2.87) | (5.05) |   |
| 4       | 39.25                        | 3.62   | 4.09   | 1.25  |
|         | (39.45)                      | (3.87) | (4.03) |   |
| 5       | 40.75                        | 3.56   | 4.35   | 0.75  |
|         | (40.93)                      | (3.91) | (4.26) |   |
| 6       | 46.47                        | 5.01   | 3.97   | 0.25  |
|         | (46.59)                      | (5.01) | (4.11) |   |
| 10      | 40.86                        | 2.78   | 4.34   | 0.5   |
|         | (41.20)                      | (2.94) | (4.52) |   |
| 11      | 46.08                        | 4.05   | 4.68   | 0.25  |
|         | (46.23)                      | (4.05) | (4.22) |   |
| 12      | 35.12                        | 2.60   | 6.41   | 0   |
|         | (35.26)                      | (2.54) | (6.50) |   |
| 13      | 41.93                        | 4.02   | 5.44   | 0   |
|         | (41.72)                      | (4.05) | (5.66) |   |
| 14      | 37.77                        | 3.47   | 5.81   | 0.5   |
|         | (37.74)                      | (3.31) | (5.81) |   |



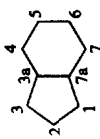
Table 2. <sup>1</sup>H NMR data for compounds 1–14 <sup>a,b</sup>.

| Compound | C <sub>5</sub> H <sub>5</sub> Ru <sup>+</sup>   |   |   | C <sub>5</sub> Me <sub>5</sub> Ru <sup>+</sup> |                  |                  |        |
|----------|---|---|---|--|------------------|------------------|--------|
|          | H(1), H(3)  | H(2)  | H(4), H(7)  | H(5), H(6)                                     | η <sup>5-c</sup> | η <sup>6-c</sup> |        |
| 1        | 5.27 d (2.5)  | 4.63 t (2.5)  | 7.42 <sup>d</sup>   | 6.81 <sup>d</sup>                              | 4.25 s           | —                |        |
| 2        | 4.78 d (2.5)  | 4.44 t (2.5)  | 7.12 <sup>d</sup>   | 6.85 <sup>d</sup>                              | —                | 1.66 s           |        |
| 3        | 5.56 d (2.8)  | 5.04 t (2.8)  | 7.33 <sup>d</sup>   | 5.74 <sup>d</sup>                              | 4.52 s           | —                |        |
| 4        | 5.50 d (2.7)  | 5.13 t (2.7)  | 6.78 <sup>d</sup>   | 5.55 <sup>d</sup>                              | 4.49 s           | 1.77 s           |        |
| 5        | 5.12 d (2.8)  | 4.93 t (2.8)  | 7.18 <sup>d</sup>   | 5.80 <sup>d</sup>                              | —                | 1.73 s           |        |
| 6        | 5.03 d (2.7)  | 4.97 t (2.7)  | 6.61 <sup>d</sup>   | 5.57 <sup>d</sup>                              | —                | 1.71 s           |        |
| 7        | H(1), H(1'): 3.14, 3.40 AB system<br>with additional triplet splitting<br>(J <sub>1,1'</sub> = 23.8, J <sub>1(1')/2</sub> = J <sub>1(1')/3</sub> = 2.1);<br>H(3): 6.75 br dt (J <sub>2/3</sub> = 5.7, J <sub>1(1')/3</sub> = 2.1) | 7.00 dt (J <sub>2/3</sub> = 5.7,<br>J <sub>1(1')/2</sub> = 2.1) | H(4): 6.40br d (5.1); H(7):<br>6.33 dd (J <sub>6/7</sub> = 4.7, J <sub>5/7</sub> = 1.8) | 5.91 m, 5.94 m                                 | —                | —                | 1.75 s |
| 8        | 6.09 d (3.6)  | 8.15 t (3.6)  | 5.78 <sup>d</sup>   | 4.52 <sup>d</sup>                              | —                | 1.38 s           |        |
| 9        | 4.90 d (2.4)  | 4.60 t (2.4)  | 6.69 <sup>d</sup>   | 6.55 <sup>d</sup>                              | —                | —                |        |
| 10       | η <sup>5</sup> -C <sub>9</sub> H <sub>7</sub> ; 5.25 d (2.4)  | 4.85 t (2.4)  | 7.11 <sup>d</sup>   | 6.96 <sup>d</sup>                              | —                | —                |        |
| 11       | μ, η <sup>5</sup> : η <sup>6</sup> -C <sub>9</sub> H <sub>7</sub> ; 5.19 d (2.7)<br>η <sup>5</sup> -C <sub>9</sub> H <sub>7</sub> ; 5.18 d (2.4)  | 5.06 t (2.7)<br>4.81 t (2.4)                                    | 6.90 <sup>d</sup><br>7.06 <sup>d</sup>  | 5.68 <sup>d</sup><br>6.91 <sup>d</sup>         | —<br>5.07 s      | —<br>—           | 1.70 s |
| 12       | μ, η <sup>5</sup> : η <sup>6</sup> -C <sub>9</sub> H <sub>7</sub> ; 5.11 d (2.7)  | 5.10 t (2.7)  | 6.33 <sup>d</sup>   | 5.44 <sup>d</sup>                              | —                | —                |        |
| 13       | 5.46 d (2.6)  | 5.35 t (2.6)  | 7.15 <sup>d</sup>   | 5.93 <sup>d</sup>                              | —                | —                |        |
| 14       | 5.33 d (2.7)  | 5.37 t (2.7)  | 6.58 <sup>d</sup>   | 5.66 <sup>d</sup>                              | 5.17 s           | —                |        |
|          | C <sub>9</sub> H <sub>7</sub> RuC <sub>5</sub> H <sub>5</sub> ; 5.40 d (2.7)  | 5.31 t (2.7)  | 7.11 <sup>d</sup>   | 5.88 <sup>d</sup>                              | —                | —                |        |
|          | C <sub>9</sub> H <sub>7</sub> RuC <sub>5</sub> Me <sub>5</sub> : H(1)–H(3):<br>5.38 ÷ 5.42 m <sup>c</sup>   |   | 6.64 <sup>d</sup>   | 5.72 <sup>d</sup>                              | —                | —                |        |

<sup>a</sup> Spectra were recorded for 1, 2 and 9 in CDCl<sub>3</sub>, for 8 in C<sub>6</sub>D<sub>6</sub> and for 3–7 and 10–14 in (CD<sub>3</sub>)<sub>2</sub>CO relative to residual protons of the solvent, δ (ppm) and multiplicity with J (Hz) in parentheses. <sup>b</sup> s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. <sup>c</sup> Bonding mode of [C<sub>5</sub>R<sub>2</sub>Ru]<sup>+</sup> fragment with indenyl framework. <sup>d</sup> Protons H(4), H(7) and H(5), H(6) are observed as multiplets characteristic of A and B parts of AA'BB' spin system. <sup>e</sup> Multiplet signals of protons H(1)–H(3) of fragment C<sub>9</sub>H<sub>7</sub>RuC<sub>5</sub>Me<sub>5</sub> in region δ = 5.38 ÷ 5.42 ppm are overlapped with doublet signal (δ = 5.40) of protons H(1), H(3) of fragment C<sub>9</sub>H<sub>7</sub>RuC<sub>5</sub>H<sub>5</sub>.

Table 3

 $^{13}\text{C}\{^1\text{H}\}$  NMR data for compounds 1–14 <sup>a</sup>

| Compound |  |        |                          |                         |              |                   |                   | $\text{C}_5\text{H}_3\text{Ru}^+$ |                   | $\text{C}_5\text{Me}_3\text{Ru}^+$ |                   | $\text{C}_5\text{Me}_5\text{Ru}^+$ |  |
|----------|---|--------|--------------------------|-------------------------|--------------|-------------------|-------------------|-----------------------------------|-------------------|------------------------------------|-------------------|------------------------------------|--|
|          | C(1), C(3)  | C(2)   | C(4), C(7) <sup>b</sup>  | C(5), C(6) <sup>b</sup> | C(3a), C(7a) | $\eta^5\text{-c}$ | $\eta^6\text{-c}$ | $\eta^5\text{-c}$                 | $\eta^6\text{-c}$ | $\eta^5\text{-c}$                  | $\eta^6\text{-c}$ |                                    |  |
| 1        | 65.74   | 72.57  | 126.81                   | 122.62                  | 92.46        | 69.86             | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
| 2        | in $(\text{CD}_3)_2\text{CO}$ : 68.35   | 76.84  | 125.18                   | 120.93                  | 92.36        | —                 | —                 | 82.20                             | —                 | 10.42                              | —                 |                                    |  |
|          | in $\text{C}_6\text{D}_6$ : 68.53   | 76.97  | 125.34                   | 121.18                  | 92.48        | —                 | —                 | 82.27                             | —                 | 11.04                              | —                 |                                    |  |
| 3        | 64.44   | 84.30  | 80.84                    | 84.01                   | 63.58        | 71.96             | 79.62             | —                                 | —                 | —                                  | —                 |                                    |  |
| 4        | 62.22   | 82.95  | 82.24                    | 86.92                   | 65.24        | 71.55             | —                 | —                                 | 94.01             | —                                  | 9.21              |                                    |  |
| 5        | 66.86   | 88.69  | 80.06                    | 82.77                   | 64.38        | —                 | 78.87             | 85.97                             | —                 | 10.50                              | —                 |                                    |  |
| 6        | 64.71   | 87.53  | 81.74                    | 86.01                   | 66.27        | —                 | —                 | 85.64                             | 93.38             | 10.55                              | 9.30              |                                    |  |
| 7        | C(1)(CH <sub>2</sub> ): 36.90   | —      | C(4)–C(7): 82.55, 84.52, | —                       | 104.43 and   | —                 | —                 | —                                 | 94.28             | —                                  | 8.67              |                                    |  |
|          | C(2) and C(3): 127.11 and 140.51  | —      | 85.37 and 85.87          | —                       | 107.56       | —                 | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
| 8        | 92.08   | 134.15 | 79.76                    | 77.94                   | 100.48       | —                 | —                 | —                                 | 85.62             | —                                  | 9.07              |                                    |  |
| 9        | 65.18   | 71.44  | 123.80                   | 121.05                  | 90.51        | —                 | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
| 10       | $\eta^5\text{-C}_9\text{H}_7$ : 67.13   | 73.79  | 125.25                   | 124.64                  | 92.46        | —                 | 79.24             | —                                 | —                 | —                                  | —                 |                                    |  |
|          | $\mu, \eta^5$ : $\eta^6\text{-C}_9\text{H}_7$ : 63.10                               | 82.45  | 79.17                    | 83.24                   | 63.50        | —                 | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
| 11       | $\eta^5\text{-C}_9\text{H}_7$ : 66.88   | 73.56  | 125.30                   | 124.46                  | 92.40        | —                 | —                 | —                                 | 94.10             | —                                  | 9.31              |                                    |  |
|          | $\mu, \eta^5$ : $\eta^6\text{-C}_9\text{H}_7$ : 61.18                               | 81.50  | 80.83                    | 86.39                   | 65.26        | —                 | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
| 12       | 65.10   | 85.47  | 80.07                    | 85.16                   | 64.38        | —                 | 80.38             | —                                 | —                 | —                                  | —                 |                                    |  |
| 13       | 62.81   | 83.91  | 81.31                    | 87.73                   | 65.70        | —                 | —                 | —                                 | 95.15             | —                                  | 9.27              |                                    |  |
| 14       | $\text{C}_9\text{H}_7\text{RuC}_5\text{H}_5$ : 64.76                                | 85.08  | 79.92                    | 84.97                   | 64.20        | —                 | —                 | —                                 | —                 | —                                  | —                 |                                    |  |
|          | $\text{C}_9\text{H}_7\text{RuC}_5\text{Me}_5$ : 63.23                               | 84.32  | 81.43                    | 87.91                   | 65.84        | —                 | 80.22             | —                                 | 95.35             | —                                  | 9.33              |                                    |  |

<sup>a</sup> Spectra were recorded relative to solvent signals: for 1, 3–7 and 10–14 in  $(\text{CD}_3)_2\text{CO}$ , for 8 and 9 in  $\text{C}_6\text{D}_6$  and for 2 in  $(\text{CD}_3)_2\text{CO}$  as well as in  $\text{C}_6\text{D}_6$ ,  $\delta$  (ppm).<sup>b</sup> Assignment of C(4), C(7) and C(5), C(6) signals was made by means of selective heteronuclear  $^{13}\text{C}$ - $^1\text{H}$  resonance on examples of compounds 2, 8, 9, 10 and 13.<sup>c</sup> Bonding mode of  $[\text{C}_5\text{R}_5\text{Ru}]^+$  fragment with indenyl framework.

of  $\mu$ -indenyl ligand are shifted upfield relative to the corresponding protons of the terminal indenyl ligand:  $\Delta\delta \approx -0.2 \div -0.7$  ppm for H(4), H(7) and  $\Delta\delta \approx -1.3 \div -1.5$  ppm for H(5), H(6) while shifts of the signals of five-membered ring protons of  $\mu$ -indenyl ligand relative to those of terminal indenyl ligand are  $\Delta\delta \approx -0.1$  ppm for H(1), H(3) and  $\Delta\delta = 0.2 \div 0.3$  ppm for H(2). Summarizing these data one can note that the transition of the indenyl ligand from terminal to bridging position is accompanied by the strongest shift of signals of six-membered ring protons H(5), H(6). The direction and value of this shift suggest that this six-membered ring is bonded with  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  fragment. The same picture was observed for proton signals of  $\mu$ -indenyl ligands in tetra-decker dicationic complexes 12–14.

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra (Table 3) proved to be still more informative. Comparison of the spectra of compounds 3–6 with those of initial mononuclear  $\eta^5$ -indenyl complexes 1, 2 shows that signals from the six-membered ring carbon atoms of the  $\mu$ -indenyl ligand are strongly shifted upfield relative to the corresponding signals of the terminal indenyl ligand. The shifts are  $\Delta\delta \approx -43 \div -46$  ppm for C(4), C(7),  $-35 \div -39$  ppm for C(5), C(6) and  $-26 \div -29$  ppm for indenyl ligand bridgehead carbon atoms C(3a), C(7a). At the same time signals of five-membered ring carbon atoms of indenyl ligand are shifted to a much lower extent and the maximum shift  $\Delta\delta \approx 10 \div 12$  ppm is observed for C(2). For comparison it should be noted that signals of benzene ring carbon atoms in complexes  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta\text{-C}_6\text{H}_6)]\text{BF}_4$  ( $\delta = 86.1$  ppm (R = H, in  $\text{CDCl}_3$ ) and  $\delta = 88.3$  ppm (R = Me, in  $\text{Me}_2\text{CO}-d_6$ ) [12]) are shifted upfield relative to that of free benzene ( $\delta = 128.7$  ppm [11]) on  $\Delta\delta \approx -40 \div -43$  ppm. These data unambiguously confirm coordination of the  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  fragment with the six-membered ring of indenyl ligand. Final proof of this fact was obtained by an X-ray diffraction study of compound 4.

One can notice that the position of signals of bridgehead carbon atoms C(3a), C(7a) of  $\mu$ -indenyl ligand in slipped triple-decker complexes is very different from the position of signals of atoms C(4)–C(7) in these compounds. This is however not surprising since bridgehead carbon atoms C(3a), C(7a) are simultaneously bonded with two  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  fragments i.e. they bridge between two ruthenium atoms, whereas atoms C(4)–C(7) are bonded with only one such fragment. Similar variance in the signal position of six-membered ring carbon atoms is also observed in the case of mononuclear  $\eta^5$ -indenyl complexes 1, 2 and 9, in which bridgehead carbon atoms C(3a), C(7a) of indenyl ligand are bonded with metal, while atoms C(4)–C(7) are not bonded.

In triple-decker complexes 10 and 11, which contain two indenyl ligands, the signals of six-membered ring carbon atoms of terminal indenyl ligand C(4)–C(7) and C(3a), C(7a) practically coincide with those of the neutral mononuclear indenyl complexes 1, 2 and 9. This probably testifies that the influence of positive charge of the fragment  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  on the free six-membered ring of terminal indenyl ligand is weakly transmitted through the system of coordination bonds. Therefore it is not surprising that triple-decker monocations 10, 11 readily add a second cationic fragment  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  giving dicationic tetra-decker complexes.

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra as well as  $^1\text{H}$  NMR spectra of tetra-decker complexes 12–14 are quite similar to those of triple-decker complexes, and even their signal positions differ only slightly. In accordance with these spectra, in complexes 12–14 the fragments  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  are also bonded with six-membered rings.

Finally it is notable that the positions of  $^{13}\text{C}$  NMR signals of terminal cyclo-

pentadienyl ring carbon atoms in the slipped triple-decker and tetra-decker complexes practically coincide with that of other cationic sandwich compounds. Thus, for the fragments  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  coordinated with the six-membered ring of the indenyl ligand, positions of signals are almost the same as in the complexes  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta\text{-C}_6\text{H}_6)]^+$  [3,4,12] and for fragments  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)]^+$  coordinated with five-membered ring the signals coincide with those of terminal cyclopentadienyl rings in straight triple-decker complexes of ruthenium [1]. The signals of methyl groups of fragments  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$  also lie in the usual region \*.

#### *X-ray structural study of 4 · MeNO<sub>2</sub>*

In crystals of the nitromethane solvate 4 · MeNO<sub>2</sub> two symmetrically independent cations A and B have quite similar geometrical characteristics \*\*. Individual bond lengths in the structure are listed in Table 4, average values are quoted in the following discussion. The structure of the cation is presented in Fig. 1.

The cation 4 represents an example of a structurally characterized triple-decker complex with a central  $\eta^5 : \eta^6$ -indenyl ligand. The mean planes of all three decks are approximately parallel. The peculiar feature of this cation is the presence of the structural fragment M<sub>2</sub>C<sub>2</sub> formed by two bridgehead carbon atoms of indenyl ligand, which are simultaneously bonded from opposite sides with two metal atoms. Such a structural fragment is characteristic of slipped triple-decker complexes in contrast to straight (normal) triple-deckers, wherein all atoms of the central ring are bonded with both metal atoms. The structures of several slipped triple-decker complexes  $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\mu, \eta^6 : \eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\eta\text{-C}_6\text{H}_6)$  [13],  $(\eta\text{-C}_3\text{H}_5)\text{V}(\mu, \eta^6 : \eta^6\text{-C}_{10}\text{H}_8)\text{V}(\eta\text{-C}_3\text{H}_5)$  [14],  $(\eta\text{-C}_3\text{Me}_5)\text{Fe}(\mu, \eta^5 : \eta^5\text{-C}_8\text{H}_6)\text{Fe}(\eta\text{-C}_3\text{Me}_5)$  [15] and  $(\eta\text{-C}_3\text{H}_5)\text{Ni}(\mu, \eta^5 : \eta^5\text{-C}_8\text{H}_6)\text{Ni}(\eta\text{-C}_3\text{H}_5)$  [16] \*\*\* have been reported earlier. In this series of compounds, naphthalene or pentalenyl-dianion plays the role of bridging ligand and two bridgehead carbon atoms of these ligands simultaneously bonded with two metal atoms represent the specific "triple-decker fragment", quite similar to that in the indenyl derivative 4.

In complex 4 the Ru atoms are not quite symmetrically coordinated with five- and six-membered cycles of the indenyl ligand, the distances from the Ru atoms to the bridgehead C(3a) and C(7a) atoms being noticeably longer than other Ru-C distances. Thus the Ru(1)–C(3a) and Ru(1)–C(7a) bond lengths are equal to 2.220(7) and 2.221(6) Å respectively, whereas the Ru(1)–C(1), Ru(1)–C(2) and Ru(1)–C(3) distances amount to 2.177(7), 2.205(8) and 2.179(8) Å. The coordination of the Ru(2) atom with the six-membered ring is even more asymmetric: the Ru(2)–C(3a) and Ru(2)–C(7a) distances (2.298(7) and 2.310(6) Å) are longer than other Ru(2)–C distances involving the carbon atoms of this cycle by ca. 0.1 Å (Ru(2)–C(4–7) 2.218(7), 2.220(8), 2.202(7), 2.191(8) Å). Similar elongation of the M–C bond distances for the bridgehead carbon atoms of the fused aromatic ligand has been also reported in the slipped triple-deckers with bridging naphthalene

\* In ref. 1 a mistake was made in assignment of signals of the methyl groups in <sup>13</sup>C NMR spectra of straight triple-decker complexes with central C<sub>3</sub>Me<sub>5</sub> ligand. In reality the methyl group signals of the central ring (ca. 12 ÷ 14 ppm) are shifted downfield relative to the signals of methyl groups of the terminal rings (ca. 8 ÷ 10 ppm).

\*\* It is noteworthy that the coordinates of the corresponding atoms in cations A and B are related by the approximate non-crystallographic inversion operation  $x' = 1 - x$ ,  $y' = 0.25 - y$ ,  $z' = 0.5 - z$ .

\*\*\* Only the Ni–Ni bond distance has been reported for the nickel complex.

Table 4

Bond lengths (Å) with estimated standard deviations in parentheses for compound 4·MeNO<sub>2</sub>

|             | Cation A | Cation B |                                | Cation A | Cation B |
|-------------|----------|----------|--------------------------------|----------|----------|
| Ru(1)–C(1)  | 2.182(7) | 2.172(7) | C(6)–C(7)                      | 1.41(1)  | 1.40(1)  |
| Ru(1)–C(2)  | 2.196(8) | 2.213(8) | C(7)–C(7a)                     | 1.44(1)  | 1.42(1)  |
| Ru(1)–C(3)  | 2.169(8) | 2.188(7) | C(8)–C(9)                      | 1.40(1)  | 1.40(1)  |
| Ru(1)–C(3a) | 2.221(6) | 2.219(7) | C(8)–C(12)                     | 1.40(1)  | 1.40(1)  |
| Ru(1)–C(7a) | 2.212(6) | 2.230(6) | C(9)–C(10)                     | 1.39(1)  | 1.44(1)  |
| Ru(1)–C(8)  | 2.157(8) | 2.138(8) | C(10)–C(11)                    | 1.43(1)  | 1.44(1)  |
| Ru(1)–C(9)  | 2.188(7) | 2.169(8) | C(11)–C(12)                    | 1.39(2)  | 1.42(2)  |
| Ru(1)–C(10) | 2.184(8) | 2.163(8) | C(13)–C(14)                    | 1.43(1)  | 1.45(1)  |
| Ru(1)–C(11) | 2.172(9) | 2.196(8) | C(13)–C(17)                    | 1.43(1)  | 1.41(1)  |
| Ru(1)–C(12) | 2.163(8) | 2.175(8) | C(13)–C(18)                    | 1.55(1)  | 1.45(1)  |
| Ru(2)–C(3a) | 2.297(7) | 2.299(7) | C(14)–C(15)                    | 1.42(1)  | 1.44(1)  |
| Ru(2)–C(4)  | 2.229(7) | 2.207(7) | C(14)–C(19)                    | 1.45(1)  | 1.54(1)  |
| Ru(2)–C(5)  | 2.218(8) | 2.222(8) | C(15)–C(16)                    | 1.49(1)  | 1.37(1)  |
| Ru(2)–C(6)  | 2.213(7) | 2.191(7) | C(15)–C(20)                    | 1.49(1)  | 1.48(1)  |
| Ru(2)–C(7)  | 2.194(7) | 2.188(8) | C(16)–C(17)                    | 1.38(1)  | 1.48(1)  |
| Ru(2)–C(7a) | 2.327(6) | 2.292(6) | C(16)–C(21)                    | 1.49(1)  | 1.50(1)  |
| Ru(2)–C(13) | 2.149(7) | 2.189(7) | C(17)–C(22)                    | 1.50(1)  | 1.50(1)  |
| Ru(2)–C(14) | 2.147(7) | 2.158(7) |                                |          |          |
| Ru(2)–C(15) | 2.195(7) | 2.190(7) |                                | Anion A  | Anion B  |
| Ru(2)–C(16) | 2.177(7) | 2.181(7) | P–F(1)                         | 1.572(6) | 1.586(6) |
| Ru(2)–C(17) | 2.158(8) | 2.181(7) | P–F(2)                         | 1.580(6) | 1.575(6) |
| C(1)–C(2)   | 1.40(1)  | 1.43(1)  | P–F(3)                         | 1.578(6) | 1.587(6) |
| C(1)–C(7a)  | 1.42(1)  | 1.45(1)  | P–F(4)                         | 1.589(6) | 1.587(6) |
| C(2)–C(3)   | 1.40(1)  | 1.43(1)  | P–F(5)                         | 1.535(7) | 1.587(6) |
| C(3)–C(3a)  | 1.45(1)  | 1.43(1)  | P–F(6)                         | 1.566(6) | 1.603(6) |
| C(3a)–C(4)  | 1.45(1)  | 1.44(1)  |                                |          |          |
| C(3a)–C(7a) | 1.477(9) | 1.485(9) |                                |          |          |
| C(4)–C(5)   | 1.40(1)  | 1.40(1)  | Nitromethane solvate molecules |          |          |
| C(5)–C(6)   | 1.43(1)  | 1.42(1)  | O(1)–N                         | 1.21(1)  | 1.22(1)  |
|             |          |          | O(2)–N                         | 1.19(1)  | 1.22(1)  |
|             |          |          | N–C                            | 1.48(1)  | 1.49(1)  |

( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cr( $\mu$ , $\eta^6$ : $\eta^6$ -C<sub>10</sub>H<sub>8</sub>)Cr( $\eta$ -C<sub>6</sub>H<sub>6</sub>) [13] and pentalenyl-dianion ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Fe( $\mu$ , $\eta^5$ : $\eta^5$ -C<sub>8</sub>H<sub>6</sub>)Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>) [15]. The elongation of these bonds does not seem very surprising taking into account that, on the one hand, some asymmetry has always been observed in mononuclear complexes with fused aromatic ligands, e.g. in bis( $\eta^5$ -indenyl)ruthenium [17] or benzenenaphthalenechromium [18], and, on the other hand, M–C bonds somewhat longer than usual are typical of the triple-decker fragment in general. Such bond elongation has been observed in the straight triple-deckers with cyclopentadienyl ligands [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni( $\mu$ , $\eta$ -C<sub>5</sub>H<sub>5</sub>)Ni( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]BF<sub>4</sub> [19] and [( $\eta$ -C<sub>5</sub>R<sub>5</sub>)Ru( $\mu$ , $\eta$ -C<sub>5</sub>Me<sub>5</sub>)M( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]PF<sub>6</sub> (M = Ru, R = Me; M = Os, R = H) [20], wherein the M–C bonds for the bridging cyclopentadienyl ring are noticeably longer (by ca. 0.04–0.06 Å) than those for the terminal rings. Similar elongation of M–C bonds for carbon atoms of the central six-membered ring has been observed in ( $\eta$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)Cr( $\mu$ , $\eta$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)Cr( $\eta$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>) [21]. Such elongation is obviously due to some loosening of bonds in the triple-decker fragment.

The significant elongation of the C–C bond between the bridgehead atoms of the indenyl ligand as compared to other C–C bonds is also noteworthy. In both

independent cations A and B the C(3a)–C(7a) bonds have in fact the same lengths (1.477(9) and 1.485(9) Å) and, just as in the  $\mu$ -naphthalene chromium [13] and  $\mu$ -pentalenyl iron [15] complexes, are longest in the bicyclic ligand. All indenyl C–C bond lengths with the exception of C(3a)–C(7a) have much closer values than in the mononuclear  $\eta^5$ -indenyl complexes (see e.g. ref. 22) and vary within the range  $1.40 \div 1.45$  Å which spans only 5 standard deviations (see Table 4). The elongation of the bond between the bridging atoms is probably also due to the loosening of bonds caused by the electron deficiency of the triple-decker moiety  $MC_2M$ . In other words coordination of two bridgehead atoms of the fused aromatic ligands by two metal atoms leads to considerable decrease of the  $\pi$ -character of the bond between these C atoms and results in a decrease of its bond order as compared with that in the same ligand coordinated by only one metal atom. Similarly in the straight triple-decker complexes elongation of C–C bonds of the central cyclopentadienyl or benzene ring by ca. 0.02–0.06 Å as compared with those of the terminal rings is usually observed [19–21].

The conformation of the indenyl ligand in the cation 4 is almost planar (in both independent cations the maximum displacement of the C(7) atom from the mean plane of all indenyl atoms is 0.07 Å). Nevertheless the observed deviations from planarity exceed the experimental standard deviations and have similar character in both independent cations. Thus the C(2) atom is displaced from the (planar within 0.03 Å) group C(1)C(3)C(3a)C(4)C(7)C(7a) by 0.111(7) Å in the direction opposite to the Ru(1) atom, whereas the C(5) and C(6) atoms are displaced from this plane by 0.129 (7) and 0.103(7) Å in the direction opposite to the Ru(2) atom. Thus, the five- and six-membered rings are folded along the lines C(1) ... C(3) and C(4) ... C(7), the dihedral angles being equal to 4.7 and 7.5° respectively. It should be mentioned that an analogous violation of planarity has been found for the naphthalene ligand of the centrosymmetric molecule  $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\mu, \eta^6: \eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\eta\text{-C}_6\text{H}_6)$  [13], wherein the naphthalene  $\beta$ -atoms are displaced from the other six atoms of the ligand by 0.123 and 0.120 Å. The corresponding dihedral angle is 5.8°. It is likely that such violation of planarity of fused aromatic ligand is associated with the above-mentioned elongation of M–C bonds involving bridgehead carbon atoms of the ligand.

Ceccon et al. have described the  $\mu$ -indenyl complex  $(\eta^4\text{-C}_8\text{H}_{12})\text{Rh}(\mu, \eta^3: \eta^6\text{-C}_9\text{H}_7)\text{Cr}(\text{CO})_3$ , in which they believe the indenyl ligand to be  $\eta^3$ -coordinated with the rhodium atom [23]. This conclusion has been made mainly on the basis of  $^{13}\text{C}$  NMR spectra, but the correlations between hapticity of indenyl ligand and  $^{13}\text{C}$  NMR shifts have been made earlier only for the complexes with terminal indenyl ligand [22] and application of such correlations to bridging indenyl ligand seems to be incorrect. According to the X-ray data for this compound distances from Rh to bridgehead carbon atoms C(3a) and C(7a) are longer by about 0.15 Å than distances to other carbon atoms of the five-membered ring (for the chromium atom similar elongation is about 0.10 Å). The fold dihedral angle of the five-membered ring is equal to 8.2°. Both the elongation of M–C distances and the fold dihedral angle for the five-membered ring in this compound are slightly greater than those in compound 4 or in  $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\mu, \eta^6: \eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\eta\text{-C}_6\text{H}_6)$  [13]. Nevertheless, this is not the reason to consider the five-membered ring of indenyl ligand to be  $\eta^3$ -coordinated with rhodium atom. In three real examples of complexes with  $\eta^3$ -indenyl ligand  $\text{W}(\eta^3\text{-C}_9\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2$  [24],  $\text{Ir}(\eta^3\text{-C}_9\text{H}_7)(\text{PMe}_2\text{Ph})_3$  [25] and  $[\text{Fe}(\eta^3\text{-C}_9\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2]^{2+}$  [26], the distances from the metal atom to the bridgehead carbon atoms are longer than those to the other carbon atoms of the five-membered ring, but the fold dihedral angle is smaller than in compound 4.

$C_9H_7(CO)_3]^-$  [26] the elongations of M–C distances amount to  $0.7 \div 0.8 \text{ \AA}$  and fold dihedral angles are equal to 26, 28 and  $22^\circ$  respectively. These examples show that Cecon's compound is best formulated as having bridging  $\eta^5 : \eta^6$ - or (distorted  $\eta^5$ ):  $\eta^6$ -indenyl ligand \* and so is closely related to the slipped triple-decker complexes of ruthenium. The same obviously applies to another similar complex which has been previously formulated as  $(\eta^4-C_8H_{12})Rh(\mu, \eta^3 : \eta^6-C_9H_7)Re(\eta^6-C_9H_8)$  [29]. Unfortunately, X-ray data for this compound are absent.

Although mean planes of all three decks in slipped triple-decker 4 are approximately parallel to each other, in both independent cations the indenyl ligand plane forms a somewhat larger dihedral angle with the plane of the unsubstituted ( $5.2^\circ$ ) than with the plane of the permethylated ( $1.3^\circ$ ) cyclopentadienyl ligand. The C(8) atom, whose projection eclipses the C(2) atom of the indenyl group, is in fact closer to the mean plane of the indenyl ligand than to any other atom of the unsubstituted cyclopentadienyl ligand.

Two 5-membered cycles coordinated by the Ru(1) atom in complex 4 as well as in the bis(indenyl)ruthenium molecule [17] are in the eclipsed conformation, the C(2)Cp(1)CpC(8) \*\* torsion angle being  $3.8^\circ$ . The distances of the Ru(1) atom from the planes of the cyclopentadienyl and indenyl ligands are 1.809(1) and 1.829(1)  $\text{\AA}$ . The pentamethylated cyclopentadienyl ligand is symmetrically arranged relative to the 6-membered cycle of the indenyl ligand, the C(4)Bz(1)Cp(M)C(15) \*\*\* torsion angle being  $4.4^\circ$ . As would be expected the distance from the Ru(2) to the plane of the six-membered ring (1.724(1)  $\text{\AA}$ ) is noticeably shorter than the distance of the same atom from the plane of the permethylated cyclopentadienyl ligand (1.802(1)  $\text{\AA}$ ). At the same time the latter does not differ significantly from the above-mentioned distances of the Ru(1) atom from the planes of  $C_5H_5$  ring and five-membered ring of indenyl ligand. The complex  $V_2(\mu, \eta^5 : \eta^6-C_9H_7)_2$ , prepared by Jonas [30], is a very interesting compound of another type with a bridging indenyl ligand. In this compound two vanadium atoms, bonded together, lie between two approximately parallel indenyl ligands. Unlike slipped triple-decker complexes which have metal atoms in *trans*-position, in the vanadium compound metal atoms are *cis*-orientated relative to both indenyl ligands. Similar to slipped triple-decker complexes in the vanadium compound each metal atom is bonded with the five- and six-membered rings of indenyl ligands so that two bridgehead carbon atoms of each indenyl ligand are bonded simultaneously with both vanadium atoms. Some elongation of V–C distances to bridgehead carbon atoms as compared with those for other carbon atoms, as well as a folding of the rings have also been observed for this compound [30].

Data presented here show that bridging between two metal atoms (*trans* or *cis*), as a mode of bonding of two ring fused aromatic ligands, is always characterized by some slip-fold distortion of metal bonding with aromatic ligand rings. This distortion must be somewhat greater than in related mononuclear complexes with the same ligand encirclement.

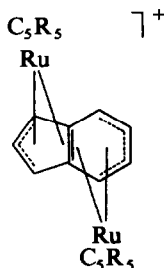
\* It is noteworthy that distorted  $\eta^5$ -indenyl complexes are quite typical of rhodium [27,28].

\*\* Cp(1) and Cp represent the centroids of 5-membered indenyl and unsubstituted cyclopentadienyl rings respectively.

\*\*\* Bz(1) and Cp(M) represent centroids of 6-membered indenyl and permethylated cyclopentadienyl rings respectively.

*Electron count in slipped multi-decker complexes with central fused aromatic ligands*

Slipped triple-decker complexes with fused aromatic systems as a central ligand can be regarded as compounds in which the role of bridge between two metal atoms belongs essentially to an ethylene fragment. Related complexes involving ethylene in this way include the zirconium compounds  $(\eta\text{-C}_5\text{H}_5)_2(\text{ClAlEt}_3)\text{Zr}(\mu, \eta\text{-C}_2\text{H}_4)\text{Zr}(\text{ClAlEt}_3)(\eta\text{-C}_5\text{H}_5)_2$  [31] and  $(\text{PEt}_3)_2\text{X}_3\text{Zr}(\mu, \eta\text{-C}_2\text{H}_4)\text{ZrX}_3(\text{PEt}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [32], and the platinum-ytterbium compound  $(\text{PPh}_3)_2\text{Pt}(\mu, \eta\text{-C}_2\text{H}_4)\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2$  [33]. In these compounds the ethylene molecule is a bridging ligand, bonded from opposite sides with two metal atoms. Such compounds are rather labile. The stability of the slipped triple-decker complexes of ruthenium can be attributed to the ruthenium atoms bonding not only with the ethylene fragment but also in the case of one ruthenium atom with the allyl fragment and with the diene fragment in the case of the other:



Such a description of bonding in these compounds, though simplified, is very useful since it allows us to understand what must be the number of valence electrons in these systems. For ruthenium, as well as for chromium and iron, the 18-electron rule is observed rather strictly. Therefore, each metal atom in the corresponding slipped triple-decker complexes must be surrounded by 18 electrons, a sum for both metal atoms of 36 electrons. But, since two electrons, which are donated by the ethylene fragment, are common to both metal atoms, the number of valence electrons in slipped triple-decker complexes must be  $36 - 2 = 34$ . In fact, triple-decker complexes  $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{R}'_5)]^+$ ,  $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\mu, \eta^6 : \eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\eta\text{-C}_6\text{H}_6)$  [13] and  $(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\mu, \eta^5 : \eta^5\text{-C}_8\text{H}_6)\text{Fe}(\eta\text{-C}_5\text{Me}_5)$  [15] are known to contain 34 valence electrons\*. Similarity of electron configurations leads to structural similarity of these compounds.

The vanadium complexes with  $\mu$ -naphthalene ligand  $(\eta\text{-C}_5\text{R}_5)\text{V}(\mu, \eta^6 : \eta^6\text{-C}_{10}\text{H}_8)\text{V}(\eta\text{-C}_5\text{R}_5)$  ( $\text{R} = \text{H}, \text{Me}$ ), prepared by Jonas [14], have only 30 valence electrons. Their electronic configuration is in good agreement with 16-electron encirclement around each metal atom, which is rather typical for vanadium and has been observed in related mononuclear complexes  $\text{V}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)$  [35] and  $\text{V}(\eta\text{-C}_5\text{R}_5)(\eta^6\text{-C}_{10}\text{H}_8)$  ( $\text{R} = \text{H}, \text{Me}$ ) [14,36]. That is why vanadium complexes are structurally related to the above-mentioned triple-decker complexes of ruthenium,

\* Bush and Lagowski [13] have noted, that the chromium compound conforms to the 30/34-electron rule for triple-decker complexes. Theoretical ground for this were provided by Hoffmann et al. [34], but these calculations were carried out for straight (usual) triple-decker systems with five-membered ring central ligands and therefore formal use of this rule in the case of slipped triple-decker complexes is not justified. Special calculations are necessary in this case and they have been carried out on the example of the iron slipped triple-decker complex with central pentalene ligand [15].



chromium and iron. In cobalt and nickel compounds with  $\mu$ -pentalene ligand  $(\eta\text{-C}_5\text{Me}_5)\text{M}(\mu, \eta^5: \eta^5\text{-C}_8\text{H}_6)\text{M}(\eta\text{-C}_5\text{Me}_5)$  (M = Co, Ni) [15] there are 36 and 38 valence electrons respectively. This fact can be explained if one supposes that each cobalt atom has 19-electron encirclement (as in cobaltocene) and each nickel atom has 20-electron encirclement (as in nickelocene) \*. Thus, the number of valence electrons in slipped triple-decker complexes with fused aromatic ligands should be  $2x - 2$ , where  $x$  is the number of valence electrons in the corresponding mononuclear compounds. In general, slipped  $n$ -decker complexes, which have  $n - 1$  metal atoms and  $n - 2$  bridging ligands, should contain  $x(n - 1) - 2(n - 2)$  valence electrons \*\*.

Jonas has also described the related 36-electron iron complex with central naphthalene ligand  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu, \eta^6: \eta^6\text{-C}_{10}\text{H}_8)\text{Fe}(\eta\text{-C}_5\text{H}_5)$  [14]. But, as noted above, stable slipped triple-decker complexes of iron should contain 34 valence electrons. Addition of two extra electrons to the system increases the asymmetry of bonding of both metal atoms with six-membered rings. The fold dihedral angle of these rings amounts to  $13.8^\circ$  [14]. Although greater than those in the 34-electron triple-decker complexes of ruthenium ( $4.7^\circ$  and  $7.5^\circ$ ) and chromium ( $5.8^\circ$ ) (*vide supra*) this value is much lower than that for the  $\eta^4$  ruthenium-coordinated six-membered ring of octamethylnaphthalene in  $\text{Ru}(\eta^4\text{-C}_{10}\text{Me}_8)(\eta\text{-C}_6\text{Me}_6)$  ( $41.5$  or  $43.3^\circ$ ) [40] \*\*\*. The increased distortion of the slipped triple-decker structure in the case of the 36-electron iron complex is undoubtedly connected with the forced repulsion of iron atoms which has the effect of decreasing interaction between their electronic systems since each of them already has 18 electrons. Otherwise, this iron compound can be considered to be the complex of "antiaromatic" naphthalene dianion  $\text{C}_{10}\text{H}_8^{2-}$  with two  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)]^+$  fragments. Indeed, in the dilithium derivative of this dianion (TMEDA)Li ( $\mu, \eta^6: \eta^6\text{-C}_{10}\text{H}_8$ )Li(TMEDA) the naphthalene moiety is also not planar (fold dihedral angle of each six-membered ring is equal to  $14.5^\circ$ ) and lithium atoms are markedly asymmetrically bonded with six-membered rings [41].

\* In these cases, as it has been noted [15], strong interaction between two metal atoms through pentalenyl ligand leads to coupling of electrons, which were unpaired in the parent mononuclear complexes.

\*\* In the case of straight (usual) triple-decker complexes the number of valence electrons is apparently also defined by the stable electronic configuration characteristic of this metal in the corresponding mononuclear compounds. Thus, in triple-decker complexes with central  $6\pi$ -electron ligands (e.g.  $\text{C}_5\text{H}_5^-$  or  $\text{C}_6\text{H}_6$ ) six  $\pi$ -electrons of this ligand are in common use by both metal atoms and therefore a number of valence electrons in straight triple-decker complexes should be  $2x - 6$ . In general,  $n$ -decker complexes with  $6\pi$ -electron ligands should have  $x(n - 1) - 6(n - 2)$  valence electrons. This may be illustrated by some examples. In ferrocene and nickelocene there are 18 and 20 valence electrons, respectively, and so the corresponding triple-decker compounds of these metals with central cyclopentadienyl ligand should have 30 and 34 valence electrons, and this is really observed for known complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu, \eta\text{-C}_5\text{Me}_5)\text{Fe}(\eta\text{-C}_5\text{Me}_5)]^+$  [1] and  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\mu, \eta\text{-C}_5\text{H}_5)\text{Ni}(\eta\text{-C}_5\text{H}_5)]^+$  [37]. In mononuclear arene complexes of vanadium  $\text{V}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)$  [35] and chromium  $\text{Cr}(\eta\text{-C}_6\text{H}_6)_2$  [38] there are 16 and 18 valence electrons and hence the corresponding triple-decker complexes of these metals should have 26 and 30 valence electrons respectively, and this is actually observed for compounds  $(\eta\text{-C}_5\text{H}_5)\text{V}(\mu, \eta\text{-C}_6\text{H}_6)\text{V}(\eta\text{-C}_5\text{H}_5)$  [39] and  $(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr}(\mu, \eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cr}(\eta\text{-C}_6\text{H}_3\text{Me}_3)$  [21]. The approach described here permits an understanding of how many valence electrons there should be in multi-decker complexes without carrying out rather complicated calculations.

\*\*\* For other examples of structurally characterised  $\eta^4$ -naphthalene complexes see ref. 14b.

Siebert et al. [42–44] have noted that there is strong electronic interaction between two metal atoms through the bridging ligand in the usual (straight) multi-decker complexes. They used this property for construction of specific low-dimensional materials with electron-conducting properties. It is obvious that such ligand mediated metal-metal interaction should also take place in slipped multi-decker complexes with bridging fused aromatic ligands, although in this case only a proportion of the bridging ligand electrons is common for two neighbouring metal atoms. In the case of the slipped triple-decker complexes with  $\mu$ -pentalenyl dianion  $(\eta\text{-C}_5\text{Me}_5)\text{M}(\mu, \eta^5: \eta^5\text{-C}_8\text{H}_6)\text{M}(\eta\text{-C}_5\text{Me}_5)$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) such interaction has been confirmed by the diamagnetism of the cobalt and nickel complexes, because it demands coupling of electrons at two metal atoms, as well as by the large values of  $E_{1/2}$  for their one- and two-electron oxidations [15]. Bush and Lagowski [45] have studied electrochemical properties of  $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\mu, \eta^6: \eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\eta\text{-C}_6\text{H}_6)$ , but their conclusion that electronic communication between chromium atoms is insignificant seems unconvincing to us. The electrochemical behaviour of the slipped triple- and tetra-decker complexes of ruthenium is now under investigation.

## Experimental

All reactions were carried out under argon. Isolation of products was performed in air unless otherwise stated. All solvents were predried and distilled under argon:  $\text{CH}_2\text{Cl}_2$  from  $\text{P}_2\text{O}_5$  or  $\text{CaH}_2$ , THF and  $\text{Et}_2\text{O}$  from  $\text{LiAlH}_4$  and hexane from Na. The starting materials  $\text{C}_5\text{Me}_5\text{H}$  [46],  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  [5],  $\text{Ru}(\eta\text{-C}_9\text{H}_7)_2$  [10], and  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]\text{PF}_6$  ( $\text{R} = \text{H}, \text{Me}$ ) [3,4] were prepared by published methods. In the latter case a mercury high-pressure immersion lamp was used in order to reduce irradiation time.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker WP 200 SY spectrometer relative to solvent signals.

### *Synthesis of mononuclear indenyl complexes*

#### *Preparation of $\text{Ru}(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_9\text{H}_7)$ (1)*

To a solution of indene (0.7 ml, 6 mmol) in THF (ca. 30 ml) was added at  $0^\circ\text{C}$  a solution of  $^n\text{BuLi}$  in hexane (3.8 ml of a 1.6 *N* solution, 6 mmol) and the mixture was stirred at this temperature for 1 h. To the prepared solution of indenyllithium  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  (2.17 g, 5 mmol) was added at  $0^\circ\text{C}$  and the mixture was stirred for 1 h at this temperature and then for 6 h at room temperature. Petroleum ether (ca. 100 ml) was added, and the resulting solution was filtered and evaporated *in vacuo*. The residue was extracted with petroleum ether and chromatographed on an alumina column (20–25 cm). Elution was performed with petroleum ether and then with petroleum ether/ $\text{Et}_2\text{O}$  (5/1) mixture. The main yellow band was evaporated *in vacuo* and the residue recrystallized from pentane at  $-78^\circ\text{C}$  to give air-stable yellow-orange crystals in ca. 70% yield. Anal. Found: C, 60.24; H, 4.31.  $\text{C}_{14}\text{H}_{12}\text{Ru}$  calc.: C, 59.77; H, 4.30%.

#### *Preparation of $\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_9\text{H}_7)$ (2)*

A mixture of  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  (1.535 g, 2.5 mmol) and Zn dust (ca. 0.5 g) in THF (ca. 20 ml) was stirred at room temperature for ca. 2 h. Colour of the mixture changed from red-brown to green and then returned to red-brown. A solution of

indenyllithium (6 mmol) in THF (ca. 20 ml) was added to  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}]_4$  generated and stirring was continued for 6 h. Petroleum ether (ca. 100 ml) was then added, the solution was filtered and the filtrate was evaporated *in vacuo*. The residue was chromatographed on an alumina column (ca. 20 cm) with petroleum ether as an eluent. Main yellow band was evaporated and the residue was recrystallized from pentane at  $-78^\circ\text{C}$  to give air-stable, yellow-orange crystals, yield 50–55%. Anal. Found: C, 64.80; H, 6.39.  $\text{C}_{19}\text{H}_{22}\text{Ru}$  calc.: C, 64.93; H, 6.31%.

Alternatively, this product was prepared in the same yield from  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  without Zn dust, but using two-fold excess of indenyllithium or in ca. 70% yield by interaction of indenyllithium with  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]\text{PF}_6$ .

#### Preparation of $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_8)]\text{PF}_6$ (7)

A solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (2.61 g, 10 mmol) in 100 ml of 90% alcohol was refluxed for ca. 30 min. Indene (3 ml, ca. 25 mmol) and pentamethylcyclopentadiene (3 ml, ca. 20 mmol) were then added and the reaction mixture was refluxed for 4 h. After cooling to room temperature excess of  $\text{HPF}_6$  solution (ca. 66%, 5 ml) was added followed by ether (250–300 ml). The mixture was left overnight at  $-20^\circ\text{C}$ . The precipitate was filtered off, washed with ether and dissolved in acetone. The solution was filtered through an alumina column (ca. 12 cm) and eluted with acetone. The filtrate was evaporated to a small volume *in vacuo* and ether was added. The colourless solid was filtered off and reprecipitated from  $\text{CH}_2\text{Cl}_2$  by ether or hexane. Yield ca. 80%. Anal. Found: C, 45.30; H, 4.49; P, 6.35.  $\text{C}_{19}\text{H}_{23}\text{F}_6\text{PRu}$  calc.: C, 45.88; H, 4.66; P, 6.23%. The same product was prepared in a similar manner in ca. 90% yield by refluxing  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  with indene in alcohol until disappearance of dark colour.

#### Preparation of $\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_7)$ (8)

A mixture of  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_8)]\text{PF}_6$  (0.995 g, 2 mmol) and  $\text{KO}^t\text{Bu}$  (0.5 g, ca. 4 mmol) in THF (ca. 20 ml) was stirred for 2 h. Hexane (ca. 40 ml) was added and the solution was filtered. The filtrate was evaporated and the residue was recrystallized under argon by cooling the hot hexane solution to  $-20^\circ\text{C}$ . Orange crystals were obtained in ca. 90% yield. Anal. Found: C, 64.65; H, 6.50.  $\text{C}_{19}\text{H}_{22}\text{Ru}$  calc.: C, 64.93; H, 6.31%. The compound is stable in inert atmosphere but decomposes slowly in air.

#### Synthesis of the slipped triple- and tetra-decker complexes

Preparation of  $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{R}'_5)]\text{PF}_6$  ( $R = R' = \text{H}$  (3);  $R = \text{H}$ ,  $R' = \text{Me}$  (4);  $R = \text{Me}$ ,  $R' = \text{H}$  (5),  $R = R' = \text{Me}$  (6)).

From  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$ . (a) A mixture of  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$  ( $R = \text{H}$ ,  $\text{Me}$ ) (0.5 mmol) and  $[\text{Ru}(\eta\text{-C}_5\text{R}'_5)(\text{MeCN})_3]\text{PF}_6$  ( $R' = \text{H}$ ,  $\text{Me}$ ) (0.5 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 ml) and the solution was set aside for ca. 2 h. Hexane (ca. 50 ml) was added, the precipitate was filtered off and reprecipitated twice from  $\text{CH}_2\text{Cl}_2$ /hexane (3/2 or 2/1) mixture by hexane. The products, which are orange solids, were obtained in ca. 80% yield, and are air-stable except for compound 4, which slowly decomposes on prolonged storage in air. Elemental analysis data (see Table 1) suggest the presence of  $\text{CH}_2\text{Cl}_2$  solvate molecules in all triple- and tetra-decker complexes prepared except compounds 12 and 13.

(b) A mixture of  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$  (0.154 g, 0.25 mmol) and Zn dust (ca. 0.1 g) in THF (10 ml) was stirred at room temperature for ca. 1–2 h. The colour changes from red-brown to green and then returns to red-brown. Then  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$  (R = H, Me) (0.5 mmol) and  $\text{TlPF}_6$  (0.384 g, 1.1 mmol) were added to generated  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{Cl}]_4$  and the mixture was stirred for ca. 6 h. Hexane (ca. 30 ml) was added, the solid material was filtered off and extracted by  $\text{CH}_2\text{Cl}_2$ /hexane (3/2) mixture. Addition of hexane to each extract precipitates an orange solid, which was reprecipitated from the same solvent mixture by hexane to give complexes **4** and **6** in ca. 80% yield.

From  $\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_7)$ . A mixture of  $\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_9\text{H}_7)$  (0.176 g, 0.5 mmol) and  $[\text{Ru}(\eta\text{-C}_5\text{R}_5)(\text{MeCN})_3]\text{PF}_6$  (R = H, Me) (0.5 mmol) in THF (10 ml) was stirred for ca. 2 h. Hexane (ca. 30 ml) was added and the precipitate was filtered off and reprecipitated twice from  $\text{CH}_2\text{Cl}_2$ /hexane (3/2) mixture by hexane to give complexes **4** and **6** in 80–90% yield.

*Preparation of  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  (**10**)*

This orange-red compound was prepared in ca. 80% yield by reaction of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  with  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  as described above for the similar reaction of  $\text{Ru}(\eta\text{-C}_5\text{R}_5)(\eta^5\text{-C}_9\text{H}_7)$ . The triple decker complex **10** slowly decomposes on prolonged storage in air.

*Preparation of  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$  (**11**)*

A mixture of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  (0.364 g, 1.1 mmol) and  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]\text{PF}_6$  (0.504 g, 1.0 mmol) in  $\text{MeNO}_2$  (5 ml) was refluxed for 2 h. After cooling of the mixture the solvent was evaporated *in vacuo* and the residue was extracted with  $\text{CH}_2\text{Cl}_2$ /hexane (3/2) mixture. Addition of hexane to extracts gives orange precipitate, which was reprecipitated twice by hexane from the same solvent mixture with a yield of ca. 80%. The compound slowly decomposes on prolonged storage in air.

When this reaction was carried out in  $\text{CH}_2\text{Cl}_2$  at room temperature the triple-decker complex **11** was formed, mixed with the tetra-decker complex **13**.

*Preparation of  $[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\mu, \eta^6 : \eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{Me}_5)](\text{PF}_6)_2$  (**13**)*

A mixture of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  (0.166 g, 0.5 mmol) and  $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{MeCN})_3]\text{PF}_6$  (0.555 g, 1.1 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 ml) and the solution was set aside at room temperature for 2 h. Hexane (ca. 50 ml) was added and the precipitate was reprecipitated twice from  $\text{CH}_2\text{Cl}_2$ /hexane (3/2) mixture by hexane. An orange-red solid, quite stable in air, was obtained in ca. 80% yield.

Triple-decker complex **11** can be used instead of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  in this preparation.

*Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu, \eta^6 : \eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{H}_5)](\text{PF}_6)_2$  (**12**)*

Following the above procedure non-methylated compound was prepared, but only in low yield. Removal of acetonitrile as the reaction proceeds increases the yield. A solution of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  (0.166 g, 0.5 mmol) and  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  (0.477 g, 1.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was stirred for 1 h. Then the solvent was thoroughly removed *in vacuo*, a new portion of  $\text{CH}_2\text{Cl}_2$  was added and

Table 5  
 Non-hydrogen atomic coordinates ( $\times 10^5$  for Ru,  $\times 10^4$  for other atoms) and equivalent isotropic thermal parameters for compound 4-MeNO<sub>2</sub>

| Atom            | x        | y        | z        | $B_{eq}$ ( $\text{\AA}^2$ ) | x        | y        | z        | $B_{eq}$ ( $\text{\AA}^2$ ) |
|-----------------|----------|----------|----------|-----------------------------|----------|----------|----------|-----------------------------|
| <i>Cation A</i> |          |          |          |                             |          |          |          |                             |
| Ru(1)           | 21311(5) | 14296(3) | 79387(2) | 1.85(2)                     | 79264(5) | 10753(3) | 71479(2) | 1.79(1)                     |
| Ru(2)           | 28753(4) | 11858(3) | 61764(2) | 1.36(1)                     | 71831(4) | 13221(3) | 89051(2) | 1.38(1)                     |
| C(1)            | 1703(6)  | 2161(4)  | 7133(3)  | 2.4(2)                      | 8328(6)  | 333(4)   | 7942(3)  | 2.3(2)                      |
| C(2)            | 922(6)   | 1658(4)  | 7133(3)  | 2.3(2)                      | 9142(6)  | 828(5)   | 7957(3)  | 3.0(2)                      |
| C(3)            | 1248(6)  | 916(5)   | 7110(3)  | 2.9(2)                      | 8823(6)  | 1589(4)  | 7984(3)  | 2.5(2)                      |
| C(3a)           | 2265(6)  | 937(4)   | 7040(3)  | 1.8(2)                      | 7822(6)  | 1569(4)  | 8052(3)  | 1.7(2)                      |
| C(4)            | 2975(7)  | 370(4)   | 6951(3)  | 2.4(2)                      | 7130(7)  | 2138(4)  | 8148(3)  | 2.7(2)                      |
| C(5)            | 3933(6)  | 601(5)   | 6928(3)  | 2.9(2)                      | 6155(7)  | 1935(5)  | 8153(3)  | 2.9(2)                      |
| C(6)            | 4201(6)  | 1375(4)  | 6929(3)  | 2.4(2)                      | 5869(5)  | 1171(6)  | 8154(3)  | 2.8(2)                      |
| C(7)            | 3495(6)  | 1938(4)  | 6950(3)  | 1.9(2)                      | 6533(6)  | 588(4)   | 8129(3)  | 2.4(2)                      |
| C(7a)           | 2539(5)  | 1738(4)  | 7060(3)  | 1.7(2)                      | 7481(5)  | 777(4)   | 8026(3)  | 1.3(2)                      |
| C(8)            | 1645(7)  | 1638(5)  | 8785(3)  | 3.1(2)                      | 8409(6)  | 929(4)   | 6302(3)  | 2.5(2)                      |
| C(9)            | 2502(7)  | 2063(5)  | 8806(3)  | 2.8(2)                      | 7583(7)  | 466(5)   | 6278(3)  | 2.9(2)                      |
| C(10)           | 3287(7)  | 1590(5)  | 8778(3)  | 3.2(2)                      | 6767(7)  | 947(5)   | 6320(3)  | 3.5(2)                      |
| C(11)           | 2925(9)  | 839(6)   | 8757(4)  | 4.7(3)                      | 7117(8)  | 1707(5)  | 6342(3)  | 3.4(2)                      |
| C(12)           | 1927(7)  | 883(5)   | 8774(3)  | 3.3(2)                      | 8140(8)  | 1683(4)  | 6336(3)  | 3.6(2)                      |
| C(13)           | 3136(6)  | 1628(5)  | 5323(3)  | 2.8(2)                      | 6857(5)  | 858(4)   | 9754(3)  | 1.6(2)                      |
| C(14)           | 3161(5)  | 826(4)   | 5294(3)  | 2.0(2)                      | 6960(6)  | 1669(4)  | 9798(3)  | 2.4(2)                      |
| <i>Cation B</i> |          |          |          |                             |          |          |          |                             |

Table 5 (continued)

| Atom                                  | x        | y        | z       | $B_{eq}$ ( $\text{\AA}^2$ ) | x        | y        | z       | $B_{eq}$ ( $\text{\AA}^2$ ) |
|---------------------------------------|----------|----------|---------|-----------------------------|----------|----------|---------|-----------------------------|
| <i>Cation A (continued)</i>           |          |          |         |                             |          |          |         |                             |
| C(15)                                 | 2209(6)  | 561(4)   | 5333(3) | 2.4(2)                      | 7950(6)  | 1880(4)  | 9759(3) | 2.4(2)                      |
| C(16)                                 | 1603(5)  | 1238(6)  | 5397(3) | 2.8(2)                      | 8453(5)  | 1237(6)  | 9687(3) | 3.3(2)                      |
| C(17)                                 | 2180(7)  | 1869(5)  | 5396(3) | 2.8(2)                      | 7785(6)  | 587(5)   | 9686(3) | 2.5(2)                      |
| C(18)                                 | 4032(8)  | 2128(7)  | 5281(4) | 4.7(3)                      | 5997(7)  | 421(6)   | 9805(4) | 3.9(3)                      |
| C(19)                                 | 3957(7)  | 351(6)   | 5186(4) | 4.0(3)                      | 6123(8)  | 2197(6)  | 9893(4) | 4.1(3)                      |
| C(20)                                 | 1929(10) | -249(6)  | 5321(4) | 6.0(4)                      | 8353(10) | 2654(6)  | 9784(4) | 5.4(4)                      |
| C(21)                                 | 550(7)   | 1237(10) | 5433(4) | 6.6(4)                      | 9506(6)  | 1219(10) | 9621(4) | 6.9(4)                      |
| C(22)                                 | 1805(10) | 2651(6)  | 5429(5) | 6.1(4)                      | 7989(10) | -232(6)  | 9618(4) | 5.6(4)                      |
| <i>Anion B</i>                        |          |          |         |                             |          |          |         |                             |
| P                                     | 5449(1)  | 1238(1)  | 1773(1) | 2.61(5)                     | 174(2)   | 1250(1)  | 3377(1) | 3.19(6)                     |
| F(1)                                  | 5441(5)  | 2119(3)  | 1793(4) | 7.1(2)                      | 1350(4)  | 1254(4)  | 3556(3) | 6.3(2)                      |
| F(2)                                  | 5436(5)  | 352(3)   | 1744(4) | 6.7(2)                      | -993(4)  | 1250(5)  | 3200(3) | 6.5(2)                      |
| F(3)                                  | 6598(4)  | 1222(5)  | 2067(3) | 7.1(2)                      | 177(5)   | 609(3)   | 3875(3) | 5.4(2)                      |
| F(4)                                  | 4280(4)  | 1246(4)  | 1524(3) | 6.4(2)                      | 184(6)   | 1885(3)  | 2876(3) | 5.7(2)                      |
| F(5)                                  | 5637(8)  | 1254(5)  | 1116(3) | 10.7(4)                     | 161(5)   | 1871(3)  | 3889(3) | 5.3(2)                      |
| F(6)                                  | 5284(6)  | 1189(7)  | 2449(3) | 8.9(3)                      | 190(5)   | 628(3)   | 2857(3) | 5.1(2)                      |
| <i>Nitromethane solvate molecules</i> |          |          |         |                             |          |          |         |                             |
| O(1)                                  | 4574(7)  | 1824(5)  | 3662(4) | 7.7(3)                      | 9733(6)  | 1828(4)  | 1257(3) | 5.2(2)                      |
| O(2)                                  | 4511(6)  | 626(5)   | 3625(4) | 7.0(3)                      | 9686(6)  | 626(4)   | 1209(3) | 4.9(2)                      |
| N                                     | 4214(5)  | 1234(5)  | 3449(3) | 3.8(2)                      | 9375(5)  | 1225(5)  | 1350(3) | 3.4(2)                      |
| C                                     | 3333(7)  | 1234(7)  | 2931(4) | 4.4(4)                      | 8469(7)  | 1226(6)  | 1607(4) | 4.5(3)                      |

Table 6

Hydrogen atomic coordinates ( $\times 10^3$ ) and isotropic thermal parameters for compound 4-MeNO<sub>2</sub>

| Atom                                  | x       | y       | z       | $B_{eq}$ ( $\text{\AA}^2$ ) | x       | y       | z       | $B_{eq}$ ( $\text{\AA}^2$ ) |
|---------------------------------------|---------|---------|---------|-----------------------------|---------|---------|---------|-----------------------------|
| <b>Cation A</b>                       |         |         |         |                             |         |         |         |                             |
| H(1)                                  | 168(6)  | 255(5)  | 716(4)  | 4(2)                        | 838(6)  | -22(4)  | 785(3)  | 2(2)                        |
| H(2)                                  | 34(5)   | 180(4)  | 714(3)  | 2(1)                        | 975(5)  | 75(4)   | 791(3)  | 2(1)                        |
| H(3)                                  | 81(5)   | 48(3)   | 710(3)  | 1(1)                        | 920(10) | 204(7)  | 801(5)  | 7(3)                        |
| H(4)                                  | 274(6)  | -11(4)  | 691(3)  | 2(2)                        | 733(5)  | 264(4)  | 819(3)  | 2(1)                        |
| H(5)                                  | 434(6)  | 17(4)   | 678(4)  | 3(2)                        | 581(6)  | 233(4)  | 820(3)  | 3(2)                        |
| H(6)                                  | 499(7)  | 151(5)  | 693(4)  | 5(2)                        | 519(5)  | 99(3)   | 818(3)  | 1(1)                        |
| H(7)                                  | 369(5)  | 244(4)  | 690(3)  | 2(1)                        | 628(5)  | 8(3)    | 819(3)  | 1(1)                        |
| H(8)                                  | 102(6)  | 180(4)  | 880(3)  | 3(2)                        | 900(4)  | 80(3)   | 625(2)  | 1(1)                        |
| H(9)                                  | 255(6)  | 257(4)  | 883(3)  | 3(2)                        | 757(6)  | -1(4)   | 628(3)  | 3(2)                        |
| H(10)                                 | 384(8)  | 170(5)  | 878(4)  | 5(2)                        | 619(8)  | 84(5)   | 634(4)  | 5(2)                        |
| H(11)                                 | 318(8)  | 40(5)   | 867(4)  | 6(3)                        | 681(6)  | 212(4)  | 643(3)  | 3(2)                        |
| H(12)                                 | 145(8)  | 43(5)   | 872(4)  | 5(2)                        | 853(6)  | 214(4)  | 630(3)  | 3(2)                        |
| H(181)                                | 447(5)  | 204(3)  | 541(3)  | 1(1)                        | 582(6)  | 0(4)    | 946(3)  | 2(2)                        |
| H(182)                                | 376(6)  | 271(4)  | 545(3)  | 3(2)                        | 525(5)  | 73(4)   | 966(3)  | 2(2)                        |
| H(183)                                | 399(5)  | 211(3)  | 482(3)  | 1(1)                        | 603(8)  | 12(6)   | 1006(5) | 6(3)                        |
| H(191)                                | 415(6)  | -3(4)   | 542(3)  | 3(2)                        | 558(5)  | 206(3)  | 964(3)  | 1(1)                        |
| H(192)                                | 473(6)  | 64(4)   | 531(3)  | 3(2)                        | 636(5)  | 279(4)  | 969(3)  | 2(1)                        |
| H(193)                                | 385(10) | 18(7)   | 490(6)  | 9(4)                        | 606(6)  | 220(5)  | 1032(4) | 4(2)                        |
| H(201)                                | 172(9)  | -34(6)  | 498(5)  | 8(3)                        | 794(4)  | 298(3)  | 981(2)  | 1(1)                        |
| H(202)                                | 142(9)  | -33(6)  | 548(5)  | 7(3)                        | 857(6)  | 274(4)  | 955(3)  | 4(2)                        |
| H(203)                                | 220(24) | -58(15) | 578(13) | 17(9)                       | 870(6)  | 275(4)  | 1017(4) | 4(2)                        |
| H(211)                                | 25(5)   | 143(4)  | 511(3)  | 2(2)                        | 879(5)  | 140(4)  | 996(3)  | 2(1)                        |
| H(212)                                | 39(8)   | 157(5)  | 572(4)  | 5(3)                        | 967(9)  | 147(6)  | 946(5)  | 5(3)                        |
| H(213)                                | 54(10)  | 84(6)   | 561(5)  | 8(4)                        | 951(7)  | 60(5)   | 929(4)  | 5(2)                        |
| H(221)                                | 141(5)  | 265(4)  | 570(3)  | 2(1)                        | 851(8)  | -23(5)  | 948(4)  | 6(2)                        |
| H(222)                                | 147(6)  | 281(4)  | 505(3)  | 3(2)                        | 829(6)  | -42(4)  | 995(3)  | 3(2)                        |
| H(223)                                | 207(7)  | 282(5)  | 536(4)  | 2(2)                        | 746(13) | -48(9)  | 924(7)  | 13(5)                       |
| <b>Nitromethane solvate molecules</b> |         |         |         |                             |         |         |         |                             |
| HC(1)                                 | 341(13) | 105(10) | 252(7)  | 10(5)                       | 798(5)  | 130(5)  | 120(3)  | 4(2)                        |
| HC(2)                                 | 257(17) | 83(13)  | 286(10) | 19(8)                       | 856(16) | 164(10) | 196(9)  | 18(6)                       |
| HC(3)                                 | 300(12) | 173(7)  | 296(6)  | 10(4)                       | 836(11) | 71(7)   | 162(6)  | 12(4)                       |

stirring was continued for 1 h. The solvent removal-compensation cycle followed by stirring for 1 h was repeated twice more. The precipitate was filtered off, washed in  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  ml) and reprecipitated twice from  $\text{CH}_2\text{Cl}_2/\text{MeNO}_2$  (10/1) mixture by hexane. A red-brown solid, quite stable in air, was obtained in ca. 80% yield. The triple-decker complex **10** can be used instead of  $\text{Ru}(\eta^5\text{-C}_9\text{H}_7)_2$  in this preparation.

*Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\mu, \eta^6 : \eta^5\text{-C}_9\text{H}_7)\text{Ru}(\mu, \eta^5 : \eta^6\text{-C}_9\text{H}_7)\text{Ru}(\eta\text{-C}_5\text{Me}_5)](\text{PF}_6)_2$  (**14**)*

The orange-red compound **14**, quite stable in air, was prepared in ca. 80% yield by reaction of the triple-decker complex **11** (0.356 g, ca. 0.5 mmol) with  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$  (0.239 g, 0.55 mmol) in  $\text{CH}_2\text{Cl}_2$  following the procedure for preparation of complex **12**.

*X-Ray structure analysis of  $4 \cdot \text{MeNO}_2$*

The single crystals of  $4 \cdot \text{MeNO}_2$  suitable for X-ray structural study were obtained by means of slow diffusion in the two-phase system, ether– $\text{MeNO}_2$  solution of **4**.

Crystals of  $4 \cdot \text{MeNO}_2$  are monoclinic. At 153 K:  $a = 13.835(3)$ ,  $b = 17.830(5)$ ,  $c = 22.135(5)$  Å,  $\beta = 102.81(2)^\circ$ ,  $V = 5324(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 1.815$  g cm<sup>-3</sup>, space group  $P2_1/c$ . The unit cell dimensions as well as the intensities of 4805 reflections with  $F^2 \geq 4\sigma$  were measured with an automatic 4-circle diffractometer Syntex P2<sub>1</sub> (153 K,  $\lambda(\text{Mo-K}_\alpha)$ , graphite monochromator,  $\theta/2\theta$ -scan,  $\theta \leq 25^\circ$ ).

The structure was solved by means of the standard heavy atom technique. The Patterson function revealed the coordinates of four independent Ru atoms, and all other non-hydrogen atoms of cations and anions were located in the subsequent approximations of the electron density syntheses. The structure was refined by the full-matrix least-squares technique at first in the isotropic and then in the anisotropic approximation. The eight highest peaks found in the difference Fourier synthesis were identified as the atoms of two solvate nitromethane molecules. These atoms were included in subsequent refinement after which a further difference Fourier synthesis revealed all hydrogen atoms of both independent cations and both solvate molecules. The final refinement in the anisotropic approximation for non-hydrogen and in the isotropic approximation for the H atoms converged to  $R = 0.035$ ,  $R_w = 0.041$ . All calculations were carried out with an Eclipse S/200 computer using the INEXTL program package [47]. The coordinates of non-hydrogen atoms are listed in Table 5, and hydrogen atomic coordinates are given in Table 6.

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