20. Polynuclear Iron and Rhodium Complexes of 7-Oxa[2.2.1]hericene (2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)

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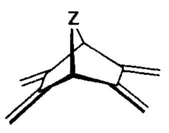
(2.XI.88)

μ-Carbonyl(Rh–Rh)di(η^5-indenyl)[(2*R*,3*S*)-*C*,2,3,*C*-η-(2,3,4,5-tetramethylidenebicyclo[2.2.1]heptan-7-one)]-dirhodium(I)(Rh–Rh) (**7**) and *cis*-μ-[(2*R*,3*S*,5*R*,6*S*)-*C*,2,3,*C*-η:*C*,5,6,*C*-η-(2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one)]bis[μ-carbonyldi(η^5-indenyl)dirhodium(I)(Rh–Rh)] (**8**) have been prepared. Complex **7** reacts with $Fe_2(CO)_9$ in hexane/MeOH and gives *cis*-μ-[(2*R*,3*S*,5*R*,6*S*)-] (**9**), *trans*-μ-[(2*R*,3*S*,5*S*,6*R*)-*C*,2,3,*C*-η: *C*,5,6,*C*-η-(2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one)]-μ-carbonyldi(η^5-indenyl)dirhodium(I)(Rh–Rh)-(tricarbonyliron) (**10**), and μ-carbonyl(Rh–Rh)[(2*R*,3*S*)-*C*,2,3,*C*-η-(2,3-dimethyl-5,6-dimethylidenebicyclo-[2.2.1]hept-2-en-7-one)]di(η^5-indenyl)dirhodium(I)(Rh–Rh) (**11**). Treatment of 7-oxa[2.2.1]hericene (**4**) with $Fe_2(CO)_9$ or $(cyclooctene)_2Fe(CO)_3$ gave a 1:2 mixture of *cis*-μ-[(2*R*,3*S*,5*R*,6*S*)-] (**12**) and *trans*-μ-[(2*R*,3*S*,5*S*,6*R*)-*C*,2,3,*C*-η:*C*,5,6,*C*-η-(2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one)]bis(tricarbonyliron)* (**13**).

Introduction. – Mononuclear transition metal-complexes of 1,3-dienes are well documented [1] [2]. In contrast, only a limited number of complexes of 1,3-dienes bonded to two [3] or more [4] adjacent metal centres have been reported. Although the synthetic methods for such species are not yet general and newer ones need to be developed, it is thinkable that the chemistry of these dinuclear complexes should become as interesting and useful as that of their monometallic analogues.

During the last ten years, we have developed efficient syntheses of new polyenes that possess two (*e.g.* **1** with $Z = CH_2$ [5], O [6], $Me_2C{=}C$ [7], CH_2CH_2, $CH{=}CH$ [8], $CH_2{=}C{-}CH_2$ [9]) or three (*e.g.* [2.2.2]hericene (**2**) [10]) exocyclic s-*cis*-butadiene units grafted onto bicyclic skeletons. Methods for the partial or/and complete complexation of these polyolefins by transition-metal carbonyls has already been presented [11] [12]. In some cases, the reactivity of these complexes has been explored [13]. With 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene, two different metalcarbonyls ($M^1 = Fe(CO)_3$,



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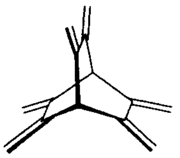

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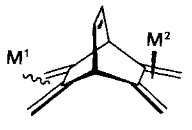

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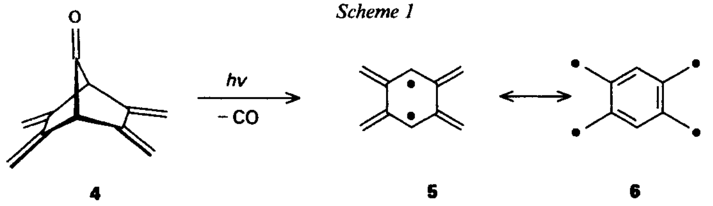
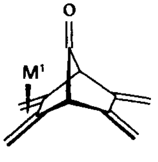
Scheme 1



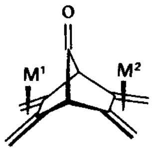
Ru(CO)$_3$; M^2 = M$_1$, Mo(CO)$_3$, W(CO)$_3$) could be attached selectively to the pentaene (see 3) [14]. Recently, we presented a synthesis of 7-oxa[2.2.1]hericene (**4**: 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one) [15], a precursor of the unstable 10-π-electron ligand **5**↔**6** *(Scheme 1)* [16] [17].

We report here our preliminary results on the complexation of **4** with Fe and Rh moieties. Unusual di-, tri-, and tetranuclear complexes have been obtained.

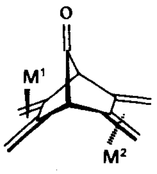
Results and Discussion. – Tetraenone **4** is an unstable compound that undergoes quick polymerization, even when diluted in degassed solvents. Therefore, complexation of **4** requires relatively smooth reaction conditions. We have found that treatment of **4** with tri(μ_2-carbonyl)tri(η^5-indenyl)triangulotrirhodium [18] [19] (toluene, 80°, 1 h) gave a mixture of the dinuclear Rh(I)complex **7** (45%, isolated) and the tetranuclear Rh(I)complex **8** (40%, isolated). The complexation occurred exclusively onto the *exo*-face of the s-*cis*-butadiene moieties, no trace of the isomeric *endo*-complexes could be detected in the reaction mixture.



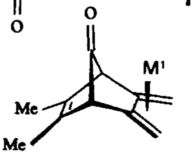
7 M^1 = (Ind)Rh–Rh(Ind) (μ-CO: O)



8 M^1 = M^2 = (Ind)Rh–Rh(Ind)
9 M^1 = (Ind)$_2$Rh$_2$(CO); M^2 = Fe(CO)$_3$
12 M^1 = M^2 = Fe(CO)$_3$



10 M^1 = (Ind)$_2$Rh$_2$(CO); M^2 = Fe(CO)$_3$
13 M^1 = M^2 = Fe(CO)$_3$



11 M^1 = (Ind)Rh–Rh(Ind)

Ind = η^5-indenyl

The ^{1}H- and ^{13}C-NMR spectra of **7** and **8** were temperature-independent between −60 and +60°, consistent with the structures proposed (see *Exper. Part*) [19]. The *exo*-configuration of the metallic moieties in **8** is retained, because the isomeric *endo*-C_{2v} species cannot exist due to the bulk of the two *endo*-μ-carbonyldi(η^5-indenyl)dirhodium groups. The *exo*-configuration of the dinuclear complex **7** is not established unambiguously.

Nevertheless, for steric reasons also, the isomeric *endo*-complex is expected to be less stable than **7**. The structure of **7** was confirmed by the fact that it was transformed into **8** exclusively. Further confirmation was obtained by the following experiment.

On heating **7** with $Fe_2(CO)_9$ in hexane/MeOH 5:1 (25 h, 30 h), a mixture was obtained from which the polynuclear complexes **9** (21%), **10** (10%), the product of 1,4-hydrogenation **11** (13%), and an unidentified (diene)bis(indenyl)dirhodium complex were isolated. The *exo*-configuration of the $Fe(CO)_3$ moiety in **9** was given by the observation of a typical ^4J coupling constant of 0.4 Hz (*M* type of coupling) between the *syn*-periplanar bridgehead protons H–C(1), H–C(4), and the adjacent methylidene protons $H_2C{=}C(5)$ and $H_2C{=}C(6)$ *trans* to C(5), C(6) [11b] [12b] [20]. This coupling constant was not observed in the ^{1}H-NMR spectrum of the iron endo-complex **10**.

The structure of **11** was elucidated from its spectral data (see *Exper. Part*) and elemental analysis. Product **11** was also obtained in 68% yield on treating **7** with $H_2Os_3(CO)_{10}$ [21] in cyclohexane at 20°.

Tetraenone **4** reacted with $Fe_2(CO)_9$ in MeOH (20°, 12 h) to give a 1:2 mixture of the dinuclear complexes **12** and **13** in 18% yield. When using $[Fe(CO)_3(\eta^2\text{-cyclooctene})_2]$ [22] in hexane at –40° (20 min), the same mixture **12**/**13** was obtained in a somewhat better yield (30%). Under both modes of Fe coordination, mononuclear complexes were not formed in significant amount, perhaps because of their lability. The *exo*-configuration of the $Fe(CO)_3$ moieties in **12** and **13** was established by the observation of a long-range coupling constant $^4J = 0.4$ Hz between the bridgehead protons and the adjacent *syn*-periplanar protons of the diene $Fe(CO)_3$ units.

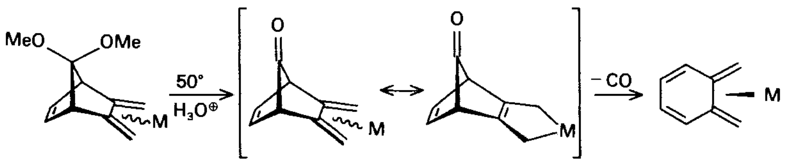
Tentative oxidations of the Fe moieties in **12** and **13** with Me_3N oxide in acetone or benzene [23] led only to decomposition, in contrast with bis(tricarbonyliron) complexes of 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-yl derivatives which were shown to undergo selective decomplexations under these conditions, yielding the corresponding monotricarbonyliron complex stereoselectively [13b] [24].

The structural [11b] and chemical properties [11e] [25] of [Fe(CO)$_3$(diene)]complexes can be described by invoking the limiting structures **14**↔**15** [26] (*Scheme 2*). The σ-bonded $Fe(CO)_3$ structure **15** interprets the property of the transition metal to retrodonate electrons into the LUMO of the π system [27]. Because of that, the complexes of tricarbonyl(5,6-dimethylidenebicyclo[2.2.1]hept-2-en-7-one)iron (**17**) derived from acidic hydrolysis of the corresponding acetals **16** could not be isolated, as they underwent fast cheletropic eliminations of CO to give tricarbonyl(orthoquinodimethane)iron (**19**) [28] (*Scheme 3*). The relative ease of the reaction **17**→**19** can be interpreted by the limiting structures **18** which confer a character of bicyclo[2.2.1]hept-2,5-dien-7-one to **17**, the latter system being known for its facile CO elimination to give the corresponding benzene derivative [29].

Scheme 2

14 **15**

Scheme 3



16 **17** **18** **19**

M = $Fe(CO)_3$

It was, thus, surprising to find that the dinuclear iron complexes **12** and **13** were quite stable species up to 110° (degassed toluene or decane). At higher temperature, only decomposition was observed. Similarly, irradiation (*Pyrex* or quartz vessel, Et_2O, acetone or toluene, –40°) led to demetallation and polymerization of the ligand. Since the metal-diene retrodonation in μ-carbonyl(diene)di(η^5-indenyl)dirhodium is less important than in $Fe(CO)_3$ derivatives [19], the dirhodium complex **11** did not expel the organic CO group easily. On heating (110°, toluene) or on irradiating (high-pressure Hg lamp, –30°, Et_2O/pentane) **11** led to demetallation and recovery of 2,3-dimethyl-5,6-dimethylidenebicyclo[2.2.1]hept-2-en-7-one.

The trinuclear irondirhodium complexes **9**, **10**, and the tetranuclear rhodium complex **8** did not expel the ketone CO more easily either on heating or irradiating, and, thus, failed to give us the expected polymetallic complexes of '1,2,4,5-tetramethylidenebenzene' (**6**). We are exploring further complexation of 7-oxa[2.2.1]hericene (**4**), hoping to generate such species.

We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous financial support.

Experimental Part

General. See [30].

Complexation of **4** *with [$Rh_3(CO)_3$(indenyl)$_3$]*. A degassed soln. of **4** [15] (50 mg, 0.32 mmol) and tri(μ_2-carbonyl)tri(η^5-indenyl)triangulotrirhodium (110 mg, 0.15 mmol) [18] in anh. toluene (70 ml) was sealed in a *Pyrex* tube under vacuum. The green soln. was heated to 80° for 1 h. After cooling to –20°, the tube was opened, and the brownish mixture was separated by column chromatography on silica gel (CH_2Cl_2/hexane 1:1) yielding 42 mg (45%) of **7** (R_f 0.5; TLC: SiO_2, CH_2Cl_2/hexane 2:1) and 65 mg (40%) of **8** (R_f 0.25; *idem*).

*μ-Carbonyl(Rh–Rh)di(η^5-indenyl)[(2*R*,3*S*)-*C*,2,3,*C*-η-(2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one)]dirhodium(I)(Rh–Rh)* (**7**). Red-brownish crystals, m.p. 188–190° (dec.). IR (KBr): 3040, 2960, 1770, 1470, 1320, 1200, 800. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.55, 7.25 (2*m*); 6.16, 5.74, 5.48 (3*m*, 2 indenyl); 5.3, 4.9 (2*s*, CH_2=C(5), CH_2=C(6)); 2.48 (*s*, H–C(1), H–C(4)); 2.41 (*d*, J = 2.6, 1 H of H_2C=C(2), H_2C=C(3) *trans* to C(3) and C(2), resp.); 0.39 (*dd*, ^2J(H,H) = 2.6, ^2J(H,Rh) = 2.4, 1 H of CH_2=C(2), CH_2=C(3) *cis* to C(3) and C(2), resp.). ^{13}C-NMR (*t*, ^1J(C,Rh) = 50); 201.4 (*s*, C(7)=O); 144.7 (*s*, C(5),C(6)); 125.4, 125.0, 120.0, 119.9 (4*dd*, ^1J(C,H) = 162, ^3J(C,H) = 6, 8 arom. CH); 115.7, 112.8 (2*m*, arom. C); 103.9 (*t*, ^1J(C,H) = 160, 2 *C*H_2=C), 96.5, 79.4 (2*dt*), 80.2 (*dm*, ^1J(C,H) = 174, ^1J(C,Rh) = 5, allyl. C of indenyl); 77.2 (*dm*, ^1J(C,Rh) = 7, C(2),C(3)); 62.3 (*d*, ^1J(C,H) = 156, C(1),C(4)); 22.8 (*td*, ^1J(C,H) = 160, ^1J(C,Rh) = 12, *C*H_2=C(2), H*C*=C(3)). CI-MS (NH_3): 622 (2, M^+), 132 (7), 130 (7), 116 (100), 115 (54). Anal. calc. for $C_{30}H_{24}O_2Rh_2$ (622.33): C 57.90, H 3.88; found: C 57.75, H 4.04.

cis-μ-*[(2*R*,3*S*,5*R*,6*S*)-C,2,3,C-*η*:C,5,6,C-*η*-(2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)]bis[*μ*-carbonyldi(*η^5*-indenyl)dirhodium(I)(Rh–Rh)]* (**8**). Red-brownish crystals, m.p. > 200°. IR (KBr): 3040, 2960, 1790, 1660, 1480, 1320, 1200, 800, 760. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.58, 7.26 (2*m*, 16 arom. H); 6.16, 5.78, 5.50 (3*m*, 12 allyl. H); 2.36 (*d*, 1 H of CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6) *trans* to C(3), C(2), C(6), C(5), resp.); 1.72 (br. *s*, H–C(1), H–C(4)); 0.36 (*dd*, ^2J(H,Rh) = 2.4, ^2J(H,H) = 2.6, 1 H of CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6) *cis* to C(3), C(2), C(6), C(5), resp.). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 226.5 (*t*, ^1J(C,Rh) = 50); 201.4 (*s*, C(7)=O); 126.7, 125.7, 120.5, 120.4 (4*dd*, ^1J(C,H) = 162, ^3J(C,H) = 6, 16 arom. CH); 116.9, 114.3 (2*m*, 8 arom. C); 98.8, 81.4, 80.8 (3*d*, ^1J(C,H) = 174, 12 allyl. CH); 79.9 (br. *s*, C(2), C(3), C(5), C(6)); 63.8 (*d*, ^1J(C,H) = 160, C(1), C(4)); 22.9 (*td*, ^1J(C,H) = 160, ^1J(C,Rh) = 12, 4, H_2C=C). CI-MS (NH_3): 1086 (1, M^+), 840 (3), 622 (1), 231 (21), 132 (17), 16 (100). Anal. calc. for $C_{49}H_{38}O_3Rh_4$ (1086.47): C 54.17, H 3.53; found: C 54.93, H 4.05.

Complexation of **8** *with $Fe_2(CO)_9$.* $Fe_2(CO)_9$ (110 mg, 0.29 mmol) was added portionwise to a stirred soln. of **8** (60 mg, 0.095 mmol) in hexane/MeOH 5:1 (35 ml) under N_2 bubbling. After stirring for 15 h at 30° under N_2 bubbling (1 bubble/s), $Fe_2(CO)_9$ (100 mg, 0.28 mmol) was added and the mixture stirred another 10 h at 30°. The solvent was evaporated and the residue taken in CH_2Cl_2/hexane 1:1, filtered through paper, and separated by column chromatography (100 g, SiO_2, CH_2Cl_2/hexane 1:1) giving $Fe_3(CO)_{12}$ first, and a yellow fraction which was separated by HPLC (25 cm, *Lichrosorb Si60*, 10 atm., CH_2Cl_2/hexane 1:1) giving 16 mg (21%) of **9**, 8 mg (10%) of **10**, 8 mg (13%) of **11** and 8 mg (13%) of an unknown complex.

cis-μ-*[(2*R*,3*S*,5*R*,6*S*)-C,2,3,C-*η*:C,5,6,C-*η*-(2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)]*μ*-carbonyldi(*η^5*-indenyl)dirhodium(I)(Rh–Rh)(tricarbonyliron)* (**9**). Red-brownish crystals, m.p. 210–212° (dec.). IR (KBr): 2040, 1980, 1960, 1790, 1640, 1470, 1340, 1160. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.58, 7.24 (2*m*, 4 arom. CH); 6.22, 5.83, 5.64 (3*m*, 3 CH allylic); 2.61 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of CH_2=C(2), CH_2=C(3) *trans* to C(3), C(4), resp.); 2.53 (*s*, H–C(1), H–C(4)); 2.02 (*dd*, ^2J(H,H) = 3.2, ^4J(H,H) = 0.4, 1 H of CH_2=C(5), CH_2=C(6) *trans* to C(6), C(5), resp.); 0.25 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of H_2C=C(2), H_2C=C(3) *cis* to C(3), C(2), resp.). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 225.6 (*t*, ^1J(C,H) = 50, μ-CO); 208.6 (*s*, $Fe(CO)_3$); 193.5 (*s*, C(7)=O); 126.8, 125.9, 120.7, 120.1 (*dd*, ^1J(C,H) = 162, ^3J(C,H) = 6, 8 arom. CH); 107.4, 103.7 (2*m*, 4 arom. C); 108.1 (*s*, C(5),C(6)); 96.3, 81.2, 79.9 (3*d*, ^1J(C,H) = 174, 2 allyl. CH); 76.4 (br. *s*, C(2),C(3)); 58.9 (*d*, ^1J(C,H) = 160, C(1),C(4)); 35.6 (*t*, ^1J(C,H) = 160, H_2C=C(5), H_2C=C(6)); 23.4 (*td*, ^1J(C,H) = 160, ^1J(C,Rh) = 12, CH_2=C(2), CH_2=C(3)). CI-MS (NH_3): 762 (24, M^+), 761 (21), 621 (4), 506 (5), 435 (11), 134 (20), 116 (100). Anal. calc. for $C_{33}H_{24}FeO_5Rh_2$ (762.21): C52.00, H 3.17; found: C 51.09, H 3.15.

trans-μ-*[(2*R*,3*S*,5*S*,6*R*)-C,2,3,C-*η*:C,5,6,C-*η*-(2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)]-*μ*-carbonyldi(*η^5*-indenyl)dirhodium(I)(Rh–Rh)(tricarbonyliron)* (**10**). Red-brownish crystals, m.p. 216–218° (dec.). IR (KBr): 2040, 1980, 1970, 1780, 1320, 1180, 800. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.58 (*m*, 8 arom. H); 6.24, 5,83, 5.25 (3*m*, 6 allyl. H); 2.83 (*s*, H–C(1), H–C(4)); 2.58 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of CH_2=C(2), CH_2=C(3) *trans* to C(3), C(2), resp.); 2.05 (*d*, *J* = 3.2, 1 H of CH_2=C(5), CH_2=C(6) *trans* to C(6), C(5), resp.); 0.47 (*d*, *J* = 3.2, 1 H of CH_2=C(5), CH_2=C(6) *cis* to C(6),C(5), resp.); 0.37 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of CH_2=C(2), CH_2=C(3) *cis* to C(3),C(2), resp.). CI-MS (NH_3): 762 (13, M^+), 761 (9), 435 (5), 134 (18), 116 (100). Anal. calc. for $C_{33}H_{24}FeO_5Rh_2$ (762.21): C 52.00, H 3.17; found: C 51.61, H 3.21.

*μ-Carbonyl(Rh–Rh)(2*R*,3*S*)-C,2,3,C-*η*-(2,3-dimethyl-5,6-dimethylidenebicyclo[2.2.1]hept-2-en-7-one)]di-(*η^5*-indenyl)dirhodium(I)(Rh–Rh)* (**11**). Red crystals, m.p. 192–194° (dec.). IR (KBr): 2900, 1770, 1480, 1440, 1320, 1040. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.55, 7.24 (*m*, 2 × 4 H); 6.12, 5.89, 5.47 (3*m*, 6 allyl. H); 2.48 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of H_2C=C(2), H_2C=C(3) *trans* to C(3),C(2), resp.); 2.43 (*s*, H–C(1),H–C(4)); 1.76 (*s*, 2 Me); 0.33 (*t*, ^2J(H,H) = 3.2, ^2J(H,Rh) = 2.6, 1 H of CH_2=C(2), CH_2=C(3) *cis* to C(3),C(2), resp.). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 226.5 (*t*, ^1J(C,Rh) = 50, μ-CO); 201.4 (*s*, C(7)=O); 128.1 (*s*, C(5),C(6)); 125.7, 124.9, 120.0, 118.9 (4*dd*, ^1J(C,H) = 162, ^3J(C,H) = 6, arom. CH); 115.7, 112.2 (2*m*, arom. C); 96.4 (*dt*), 80.2, 79.2 (2*dm*, ^1J(C,H) = 174, ^1J(C,Rh) = 5, allyl. CH); 78.1 (*d*, ^1J(C,Rh) = 7, C(2),C(3)); 63.3 (*d*, ^1J(C,H) = 156, C(1),C(4)); 22.8 (*dt*, ^1J(C,H) = 160, ^1J(C,Rh) = 12, CH_2=C(2), CH_2=C(3)); 16.9 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 624 (14, M^+), 435 (15), 134 (32), 116 (100). Anal. calc. for $C_{30}H_{26}O_2Rh_2$ (624.35): C 57.71, H 4.20; found: C 57.14, H 4.23.

Complex **11** was obtained in 68% yield on treating **8** with $Os_3(CO)_{10}H_2$ in cyclohexane at 20°.

Complexation of **4** *with $Fe_2(CO)_9$.* $Fe_2(CO)_9$ (2 g, 5.5 mmol) was added portionwise to a stirred soln. of **4** (250 mg, 1.58 mmol) in MeOH (25 ml) and bubbled with N_2. After stirring at 20° for 12 h, the solvent was evaporated, and the residue purified and separated by column chromatography on silica gel (7.5 g, CH_2Cl_2/hexane 1:1) giving a first fraction (R_f 0.87) yielding 82 mg (12%) of **11** and a second fraction (R_f 0.83) yielding 34 mg (6%) of **12**. The same dinuclear complexes **11** and **12** were obtained in 30 and 15% yield, resp., on treating **4** with [$Fe(CO)_3$(cyclooctene)$_2$] [22] in anh. hexane at −30° for 1 h.

cis-μ-*[(2*R*,3*S*,5*R*,6*S*)-C,2,3,C-*η*:C,5,6,C-*η*-(2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)]bis(tricarbonyliron)* (**12**). Yellow crystals, m.p. 109–110° (hexane). UV (95% EtOH): 221 (38000, sh), 300 (13000), 327 (7500). IR (hexane): 2960, 1980, 1950, 1760, 1400, 1200, 1130. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.87 (*s*, H−C(1), H−C(4)); 2.47 (*d*, *J* = 3, 1 H of CH_2=C(2), CH_2=C(3), CH_2=C(5), CH_2=C(6) *trans* to C(3), C(2), C(6), C(5), resp.); 0.55 (*d*, *J* = 3, 4 H). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 212.3 (*s*, Fe(CO)); 207.8 (*s*, C(7)=O); 119.3 (*s*, C(2), C(3), C(5), C(6)); 52.3 (*d*, ^1J(C,H) = 155, C(1), C(4)); 32.1 (*t*, ^1J(C,H) = 160, 4 CH_2=C). MS (70 eV): 438 (1, M^+), 410 (12), 382 (13), 354 (19), 298 (47), 270 (75), 242 (59), 186 (17), 128 (25), 85 (50), 56 (100). Anal. calc. for $C_{17}H_{10}Fe_2O_7$ (437.96): C 46.62, H 2.30; found: C 46.50, H 2.34.

trans-μ-*[(2*R*,3*S*,5*S*,6*R*)-C,2,3,C-*η*:C,5,6,C-*η*-(2,3,5,6-Tetramethylidenebicyclo[2.2.1]heptan-7-one)]bis(tricarbonyliron)* (**13**). Yellow crystals, m.p. 112–113°(hexane). IR (KBr): 2040, 1980, 1950, 1780, 1480, 1240, 1130. ^{1}H-NMR (80 MHz, $CDCl_3$): 4.05 (*s*, H−C(1), H−C(4)); 2.42, 2.20 (2*d*, *J* = 3); 0.92, 0.52 (2*d*, *J* = 3). MS (70 eV): 438 (5, M^+), 410 (12), 382 (16), 326 (14), 298 (29), 270 (93), 242 (29), 184 (24), 158 (33), 101 (38), 59 (100). Anal. calc. for $C_{17}H_{10}Fe_2O_7$ (437.96): C 46.62, H 2.30; found: C 46.53, H 2.32.

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