

191. Monoolefin and Diene Cycloaddition Induced by Transition-Metal Carbonyls. Cyclodimerization of 5,6-Dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene Catalyzed by Dodecacarbonyltriosmium

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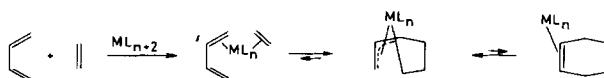
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Summary

The products generated by heating 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**) with $\text{Fe}_2(\text{CO})_9$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Cr}(\text{CO})_3(\text{MeCN})_3$, or $\text{W}(\text{CO})_5(\text{MeCN})$ or by treatment with Fe-atoms have been characterized by spectroscopic methods. Apart from the expected η^2 - and η^4 -complexes of the triene **1**, condensation products are formed which arise from the formal [4 + 2]-cycloaddition of **1** involving the endocyclic double bond of one molecule and the diene moiety of a second. The [4 + 2]-cycloaddition is catalyzed by $\text{Os}_3(\text{CO})_{12}$ in MeOH and gives 1,4-epoxy-7-methoxy-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene (**15**). Fe-Atoms induce a stereoselective [2 + 2]-cycloaddition of **1** which involves its endocyclic double bond and produces the dimer **8**.

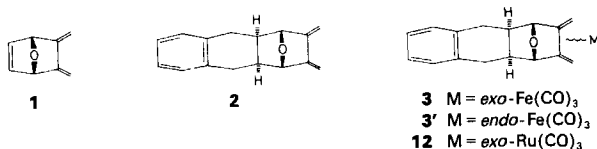
Introduction. – Consider the metal-assisted cycloaddition of a 1,3-diene to a transition-metal-coordinated monoolefin, as depicted in *Scheme 1*. One obstacle to the success of such a reaction is that the resulting cyclohexene complex is left coordinatively

Scheme 1



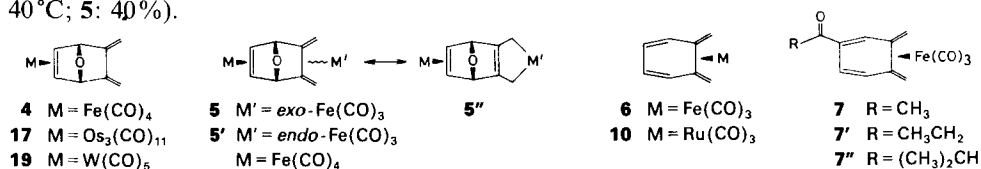
unsaturated. However, cyclization may occur if the required extra ligand is incorporated into the dienophile [1] or if the dienophile is a C,C-triple bond [2]. We have recently reported [3] on the first example of a formal [4 + 2]-cycloaddition in which the dienophile is complexed to an iron carbonyl, namely the reaction of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**) in the presence of $\text{Fe}_2(\text{CO})_9$, giving **2** and the corresponding *exo*- and *endo*- $\text{Fe}(\text{CO})_3$ diene complexes **3** and **3'**.

¹⁾ Part of Ph. D. dissertation of Ph. V., University of Lausanne, 1983.



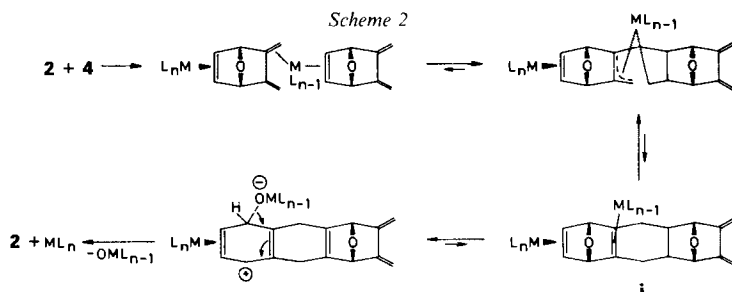
We have shown that cyclodimerization implies the intermediacy of the η^2 -Fe(CO)₄ complex **4** [3]. We have now completed the study of the reaction of **1** with iron carbonyls and Fe-atoms. As the cycloadduct **2** is a potential precursor for the synthesis of the antitumor agent 4-demethoxydaunomycinone [4], we have extended our investigation to other d⁸- and d⁶-metal carbonyls and report here on the catalytic cyclodimerization of **1** in the presence of osmium carbonyl cluster complexes.

Results and Discussion. – 1. *Iron and Ruthenium Carbonyls.* The reaction of **1** with Fe₂(CO)₉ (pentane/Et₂O, 20°C) yields **4** and **5** in two consecutive steps [5]. These complexes are stable in non-polar solvents below *ca.* 50°C. Thermolysis of **5** (or **5'**) in toluene (95°C) gave CO₂ and **6** (60%) indicating the tendency of the Fe(CO)₄ group to abstract oxygen in a complex having an oxanorbornadiene ligand (limiting structure **5''**). Better yields of complexes **4**, **5**, and **5'** are now obtained by the reaction of **1** with Fe₂(CO)₉ (1:2) in 2-propanol (**4**: 45%; **5/5'**: 12%) and in THF (1/Fe₂(CO)₉ = 1:4; **4**: 40%; **5**: 40%).



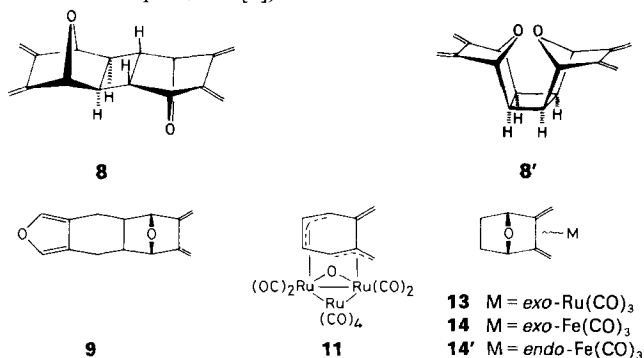
The best yields of adducts **2** (23%) and **3/3'** (18.5%) were obtained from the reaction of **1** with Fe₂(CO)₉ (1:1.5) in refluxing MeOH; adducts **2** and **3/3'** were accompanied by minor amounts of **5'**, **6**, and **7**. Complexes **3** and **3'** were easily oxidized by trimethylamine oxide (2 equiv., acetone) giving **2** (98%; total yield of **2** from **1**: 41%). Lower 1/Fe₂(CO)₉ ratios lowered the yield of **2** as **4** was further complexed to give **5/5'**. The tricarbonyl(*o*-xylylene)iron complexes **6** and **7** were shown to arise from the thermal decomposition of **5** and **5'** in MeOH. Heating **4** in MeOH at 50°C gave **2** (33%), **3** (11%), and **6** (14%), whereas the same reaction in the presence of **1** (1 equiv.) left the free ligand unreacted. This demonstrates that cyclodimerization of **1** implies the formation of **4**, since uncomplexed **1** cannot react with **4**.

The formation of **2** probably occurs through a 16-electron oxanorbornadiene intermediate (**i**, see *Scheme 2*) whose O-atom is abstracted by the Fe(CO)₃ group (or by

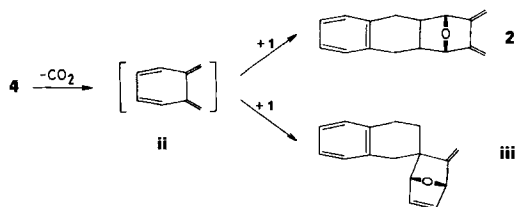


other metal carbonyls). The transient ML_n (e.g. $Fe(CO)_4$) is then trapped by **2** giving **3/3'**. Unfortunately, attempts to isolate an oxanorbornadiene complex such as **i** have been unsuccessful. The addition of extra ligands which are better π acceptors than oxygen to a solution of **1** and $Fe_2(CO)_9$ in MeOH gave $Fe(CO)_4L$ ($L = P(OCH_3)_3$, $P(Ph)_3$, CO) and **2** in low yields. Likewise no trace of **i** could be observed even not on subjecting a solution of **4** in MeOH to a pressure of 6500 bars, nor upon addition of bidentate ligands (ethylenediamine, ethyleneglycol) nor upon addition of protic acids (0.1–1 equiv.; AcOH, TsOH) or of a Lewis acid ($ZnCl_2$).

The direct condensation of Fe-atoms into a solution of **1** in methycyclohexane at $-120^\circ C$ using a rotating reactor [6] gave **8** (10%) instead of **2**. Thus, Fe-atoms promote a formal $[2 + 2]$ -cycloaddition in this case. However, metal-vapor synthesis (MVS) seems unsuited to ligands bearing an O-atom such as **1** as extensive O-abstraction took place giving iron oxide. The relative *endo*-configuration of the H-atoms of the cyclobutane ring of **8** was indicated by the absence of vicinal coupling constants with the adjacent bridgehead protons in the 1H -NMR spectrum. The other 1H - and ^{13}C -NMR data were consistent with **8** or the isomeric dimer **8'**. The latter structure was not considered feasible due to the unfavourable steric interactions between the two O-atoms (for similar examples, see [7]).



Cyclodimerization of **1** is also assisted by other d^8 -metal carbonyls. The reaction of **1** with $Ru_3(CO)_{12}$ (1:2; toluene, $65^\circ C$) gave **2** (7%) and **9** (8%), besides minor quantities of **10** [8] and **11**. The observation of **9** which probably is the product of a *retro-Diels-Alder* reaction of intermediate **i** lends support to the proposed mechanism of cyclodimerization (Scheme 2). The reaction of **1** with $Ru_3(CO)_{12}$ in more coordinating solvents than toluene (e.g. refluxing MeCN) gave the products **2** and **12** (7%), as well as minor quantities of **13**. Since we found that thermolyses of **4** (or **5**) generates **6**, one might invoke a possible mechanism for the formation of **2** that involves the *o*-xylylene **ii** as an intermediate. However, as no products of *Diels-Alder* additions such as **iii** could be observed as side-products, this mechanism is difficult to maintain at this stage of our studies.



The *exo*-coordination of the Ru(CO)₃ group in **12** is based on a comparison of its NMR parameters with those of **3** and **3'**. It is known that an *exo*-M(CO)₃ group pushes the methyldiene protons *trans* with respect to C(2),C(3) towards the *exo*-face of a bicyclic diene [9]. This leads to a smaller dihedral angle between these protons and the bridgeheads protons H–C(1) and H–C(4). As a consequence, larger ⁴J_{H,H} or ⁵J_{H,H} coupling constants are observed between them (0.6 Hz in **12**; 0.8 Hz in **3** whose structure has been ascertained by X-ray analysis [10]) compared with those in the free ligands (≈ 0 Hz). In the *endo*-isomer **3'**, the corresponding coupling constant is < 0.2 Hz.

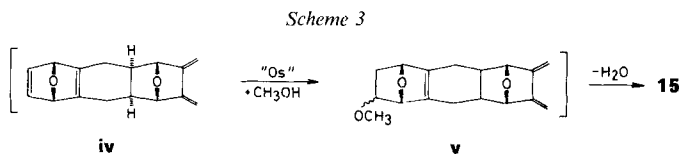
Complex **11** is a new type of Ru-cluster formed by O-abstraction from **1**. The isotopic distribution (MS) of the molecular 'envelope' corresponds to 3 Ru-atoms per cluster. The molecular mass is in agreement with that deduced from measurements of the unit cell volume (7782 Å³; Z = 16) and of the density (2.14 g·cm⁻³) of a crystalline sample. All CO's are terminal (IR) and magnetically nonequivalent (eight δ_C's). Its ¹H- and ¹³C-NMR data indicate that the organic ligand is a 6-membered planar ring with one uncoordinated double bond (CH₂=C(5): *t* at 106.9 ppm), a coordinated endocyclic allylic system (assigned by comparison with allylic iron systems [11]), and with a coordinated exocyclic allylic system (CH₂=C(6): *t* at 59.5 ppm). Although we have no direct evidence for the O-bridge, its presence is required by the analytical data and is in agreement with the 18-electron rule. Complex **11** is non-fluxional (–50 < *T* < 70°C) as opposed to bis(allyl)-*triangulo*-ruthenium analogs exempt of O-bridges (e.g. (pentalene)Ru₃(CO)₈ [12]).

Complex **13** was probably formed by hydrogenation of **1** by traces of hydridoruthenium carbonyls and was identified by comparison with an authentic sample obtained by the direct reaction of 2,3-dimethyldiene-7-oxabicyclo[2.2.1]heptane with Ru₃(CO)₁₂ (1:3; toluene, 60°C) and with the corresponding iron isomers **14** and **14'**. The *exo*-coordination in **13** is based on the same arguments as for **12** (⁴J_{H,H} or ⁵J_{H,H} between H–C(1) and H of =CH₂ *trans* with respect to C(2),C(3): 0.7, 0.8 and *ca.* 0 Hz for **13**, **14**, and **14'**, resp.).

2. *Cyclization Catalyzed by an Osmium Cluster Complex.* We found that heating **1** in presence of catalytic amounts of Os₃(CO)₁₂ (114:1; 65°C) in MeOH gave the methoxy adduct **15** (25%; 28.5 mol per mol of Os) and α,α'-dimethoxy-*o*-xylene (30%). This is the first example of a formal [4 + 2]-cycloaddition of a monoolefin to a diene catalyzed by a transition-metal carbonyl. The reaction of **1** with Os₃(CO)₁₂ in THF (1.5:1; 65°C) gave cluster complex **17** (14%) and adduct **16** (7%), the latter being

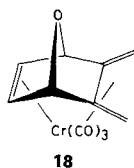


probably formed by hydrogenation of intermediate **iv** (*Scheme 3*) by traces of hydrido-osmium cluster complexes (analogous hydrogenations of olefins have been observed by *Ferrari et al.* [13]). Cluster complex **17** (obtained by the reaction of **1** with Os₃(CO)₁₁(MeCN) in CH₂Cl₂) did not dimerize when heated in THF or in MeOH (60°C). However, adduct **16** (*ca.* 10%) was formed when heating **17** in MeOH (60°C) in the presence of 2 equiv. of **1**. A possible explanation for the formation of **15** is presented in *Scheme 3*. The hypothetical oxanorbornadiene intermediate **iv** adds 1 equiv. of MeOH onto the less hindered double bond under catalysis by osmium carbo-



nyls [14]. The oxanorbornene intermediate **v** then eliminates 1 equiv. of H₂O (for analogies, see [15]) giving the aromatic derivatives **15**. Further investigations are required to substantiate these hypotheses.

3. *Chromium and Tungsten Carbonyls*. The thermal cyclodimerization of **1** by d⁶-metal carbonyls gave only low product yields. The reaction of **1** with W(CO)₃(MeCN) (1:2; hexane/Et₂O 2:1, 40°C) gave **2** (3%) and unidentified polymers. The reaction of **1** with Cr(CO)₃(MeCN)₃ (1:2; 30°C) gave **18** (51%), **2** (5.5%) and **16** (2.5%). Extensive polymerization took place during the corresponding reaction with W(CO)₃(MeCN)₃ or W(CO)₃(NH₃)₃.



Conclusion. – Transition-metal (d⁶ and d⁸) carbonyls are capable of inducing the dimerization of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**). The process involves initial coordination of the endocyclic C(2),C(3) double bond of the triene. This reaction is faster than coordination of the exocyclic diene moiety at C(5),C(6). A second carbonyl of the η²-complex intermediate is then probably displaced by a double bond of the diene moiety of a further molecule of triene. At this stage, a formal [4 + 2]-cycloaddition leads to formation of the observed products. Most interesting is the discovery that Os₃(CO)₁₂ induces the cyclization catalytically. Our results open a new field for synthetic applications of **1**, a compound readily available from furan and maleic anhydride.

We thank the *Swiss National Science Foundation* for financial support. We are grateful to Dr. *Philippe Narbel* for the preparation of complex **11** and to Dr. *D. Stahl* (Institut de chimie physique, EPFL) for the measurements of MS isotopic distributions.

Experimental Part

1. General Remarks. – See [16]. The preparations of **1** and **4–6** have been reported previously [5]. The procedures reported below have not been optimized.

2. Reactions with Iron Carbonyls and Iron Atoms. – 2.1. Fe₂(CO)₉ (6.5 g, 17.8 mmol) was added portionwise to a solution of **1** (1.5 g, 12.5 mmol) in MeOH (100 ml) heated to reflux. After 3 h, the solvent was evaporated *i.v.*, the residue taken up in hexane/Et₂O 1:1 and chromatographed on *Florisil* (80 × 2 cm column) with hexane, then with hexane/Et₂O 95:5. Recrystallization of 6 yellow fractions from hexane at –25° gave **6** (250 mg, 6.5%), **5'** (113 mg, 2.2%), **2** (390 mg, 23%), **3** (414 mg, 18.1%), **3'** (7 mg, 0.3%), and **7** (100 mg, 2.7%). Complexes **3** and **3'** were then oxidized with Me₃NO (1 equiv.) in acetone (15 ml) at 20° giving **2** (98%; overall yield of **2** from **1**: 41%).

The same reaction under 1 atm CO (1.5 g of **1**, 9 g of $\text{Fe}_2(\text{CO})_9$, 100 ml of MeOH, 50°, 3 days) followed by the same workup gave **2/3/3'** in lower yield (27%), **6** (10%), and **7** (12.3%). The same reaction in EtOH (2 g of **1**, 8 g of $\text{Fe}_2(\text{CO})_9$, 100 ml, 50°, 9 h) gave **6** (1.2%), **4** (26%), **5/5'** (10%), **2** (26%), **3** (5%), **3'** (5%), and traces of **7'**.

The highest yields of **4**, **5**, and **5'** were obtained by the following procedure: a suspension of **1** (1.5 g, 12.5 mmol) and $\text{Fe}_2(\text{CO})_9$ (10 g, 27 mmol) in 2-propanol (150 ml) was stirred at 20° for 70 h. Then the solvent was evaporated *i.v.*, the residue taken up in hexane and column chromatographed (50 × 2 cm) on *Florisil* with hexane. Recrystallization from hexane at –25° gave **6** (1.5%), **4** (1.6 g, 45%) and **5/5'** (0.64 g, 12%).

2.2. *Cyclodimerization of 4*. A solution of **4** (0.6 g, 2.83 mmol) in MeOH (50 ml) was heated to 50° for 2 days, then evaporated *i.v.* Column chromatography on *Florisil* (20 × 1 cm) and recrystallization from hexane at –25° gave **2** (105 mg, 33%), **3** (57 mg, 11%), and **7** (120 mg, 14%). The same reaction in presence of **1** (0.35 g, 2.8 mmol) gave the same products and left **1** unreacted (0.32 g, 95%).

2.3. *Preparation of 7, 7', and 7''*. A solution of **5** (or **5'**) (0.8 g, 1.87 mmol) in MeOH (40 ml) was heated to 40° for 5 days, then evaporated *i.v.* Column chromatography on *Florisil* (15 × 1 cm) and recrystallization from hexane at –25° gave **6** (46 mg, 10%) and **7** (456 mg, 81%). The same reaction in EtOH gave **6** (161 mg, 35%) and **7'** (325 mg, 55%). The same reaction in 2-propanol gave **6** (35%) and **7''** (235 mg, 38%). The corresponding amides were not obtained upon heating **5** in dioxane in the presence of NH_3 or Et_2NH .

2.4. *Thermolysis of 5'*. A solution of **5'** (0.5 g, 1.17 mmol) in toluene (20 ml) was heated to 95° for 20 min. Evolution of CO_2 was observed (IR). Evaporation *i.v.*, filtration and recrystallization from hexane at –25° gave **6** (186 mg, 65%).

2.5. *MVS Experiment*. The stainless steel rotatory reactor used has been described elsewhere [17]. Fe pellets (1.3 g, 23 mmol) were evaporated (45 A, 4 V, 2×10^{-3} Torr, 80 min) towards the upper rotating liquid film coating the surface of a 6-l pyrex flask containing a solution of **1** (2 g, 16 mmol) in methylcyclohexane (120 ml; exempt of toluene) at –120°. The mixture was transferred and rapidly filtered on *Kieselguhr* at –78° under Ar. Excess $\text{P}(\text{OMe})_3$ (80 mmol) was added, and the solution was stirred for 12 h, then reduced at –40°/0.1 Torr to a small volume and filtered through degassed alumina (2 g). The solvent was evaporated *i.v.*, and the residue was column chromatographed on degassed silica gel (50 × 2 cm) with $\text{AcOEt}/\text{hexane}$ 1:4. Recrystallization from hexane at –40° gave **8** (384 mg, 10%) and an unidentified polymeric material.

2.6. *Data of 1–8 and 11*. The m.p., IR, MS, ^1H - and ^{13}C -NMR data of **2**, **3**, **3'**, **5'**, **7**, **7'**, **7''**, and **11** have been reported in a preliminary communication [3]. For **1** and **4–6**, see [5]. Elemental analyses: Calc. for **2**, $\text{C}_{16}\text{H}_{16}\text{O}$ (224.304): C 85.68, H 7.19; found: C 85.80, H 7.13. Calc. for **3**, $\text{C}_{19}\text{H}_{16}\text{FeO}_4$ (364.184): C 62.66, H 4.43; found: C 62.37, H 4.40. Calc. for **3'**, $\text{C}_{19}\text{H}_{16}\text{FeO}_4$ (364.184): C 62.66, H 4.43; found: C 62.50, H 4.31. Calc. for **5'**, $\text{C}_{13}\text{H}_8\text{Fe}_2\text{O}_8$ (427.923): C 42.10, H 1.88; found: C 42.47, H 1.87. Calc. for **7**, $\text{C}_{13}\text{H}_{10}\text{FeO}_5$ (302.070): C 51.69, H 3.37; found: C 51.78, H 3.49. Calc. for **7'**, $\text{C}_{14}\text{H}_{12}\text{FeO}_5$ (316.097): C 53.20, H 3.83; found: C 53.17, H 3.71. Calc. for **7''**, $\text{C}_{15}\text{H}_{14}\text{FeO}_5$ (330.124): C 54.58, H 4.28; found: C 54.82, H 4.31.

(IR, *4S,4aS,4bS,5R,8S,8aR,8bR*)-1,4,5,8-Diepoxy-2,3,6,7-tetramethylideneperhydrobiphenylene (**8**). Colourless crystals, m.p. 250° (dec.). IR (KBr): 3080, 1800, 1650, 1460, 1440, 1425, 1300, 1280, 1260, 1245, 1200, 1190, 1135, 1025, 1015, 970, 950, 900, 830, 800, 720, 585, 560, 500, 400. ^1H -NMR (CDCl_3): 5.19, 4.91 (2s, 8H, 4 = CH_2); 4.67 (s, 4 bridge head H); 2.27 (s, 4H). ^{13}C -NMR (CDCl_3): 146.5 (s, C(2), C(3), C(6), C(7)); 101.5 (t, $J = 159$, = CH_2); 83.3 (d, $J = 161$, $^3J = 5$, C(1), C(4), C(5), C(8)); 44.0 (d, $J = 146$). MS (70 eV): 240 (32, M^+), 211 (9), 174 (57), 172 (57), 131 (27), 118 (25), 100 (64), 91 (64), 81 (100). Anal. calc. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ (240.304): C 79.97, H 6.71; found: C 79.15, H 6.85.

3. *Reactions with Ruthenium Carbonyls*. 3.1. A suspension of **1** (1.5 g, 12.5 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (1.5 g, 23 mmol) in toluene (50 ml) was heated to 65° for 15 days, then evaporated *i.v.* The residue was taken up in hexane/ CH_2Cl_2 1:1, filtered, and column chromatographed on *Florisil* (80 × 2 cm) with hexane/ Et_2O 9:1. Recrystallization from hexane at –25° gave **10** [8] (50 mg, 1.3%), **2** (100 mg, 7%), **11** (0.6%), **15** (25 mg, 1%), **9** (107 mg, 8%), and traces of **16**. The same reaction in THF (150 ml; reflux, 60 h) and same workup gave **1** and **10** in lower yields as well as adduct **12** (1%) and **13** (1.2%).

3.2. *Preparation of 13, 14, and 14'*. A suspension of 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane (1 g, 8 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (1.7 g, 2.6 mmol) in toluene (50 ml) was heated to 65° for 48 h. Evaporation *i.v.* and column chromatography on *Florisil* (50 × 1 cm) with hexane gave **13** (1.05 g, 40%). The corresponding reaction with $\text{Fe}_2(\text{CO})_9$ (40 g, 110 mmol) in MeOH (600 ml; 8 g of ligand, 50°, 4 days) followed by chromatography on *Florisil* (80 × 2 cm) with hexane (elution of $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$), then with hexane/5 vol-% Et_2O and recrystallization from hexane at –20° gave **14** (10.5 g, 61%). In refluxing MeOH (2 days), **14'** was also obtained (10%).

3.3. *Data of 9-14. For 10, see [8]. Tricarbonyl[(1R,2S,3R,4S,4aS,9aR)-C,2,3,C- η -(1,4-epoxy-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene)]ruthenium (12).* Colourless crystals, m.p. 150.5-151.5°. IR: 2078, 1992, 1988 (CO). ¹H-NMR (CDCl₃): 7.18 (br. s, 4H, H-C(5), H-C(6), H-C(7), H-C(8)); 4.50 (m, 2H, H-C(1), H-C(4)); 3.05, 2.70 (2m, 4H, 2H-C(9), 2H-C(10)); 2.45 (m, 2H, H-C(4a), H-C(9a)); 2.07 (dd, 2H, H trans to C(2), C(3)); 0.56 (d, 2H, H cis to C(2), C(3)); ²J(endo,exo) = 13.5, J(endo,9a) = 5.0, J(9exo,9a) = 9.0, ⁴J(1,Htrans) or ⁵J(4,Htrans) = 0.6, ²J(Hcis, Htrans) = 2.8. ¹³C-NMR (CDCl₃): 195.6 (s, CO); 138.8 (s, C(8a), C(10a)); 127.1 (d, J = 154, C(5), C(6), C(7), C(8)); 110.1 (s, C(2), C(3)); 82.9 (d, J = 163, C(1), C(4)); 42.4 (d, J = 136, C(4a), C(9a)); 33.2 (t, J = 127, C(9), C(10)); 25.2 (t, J = 159, =CH₂). MS (70 eV): 410 (7, M⁺), 382 (43), 354 (100), 326 (60, M⁺ - 3 CO), 296 (89), 230 (32). Anal. calc. for C₁₉H₁₆O₄Ru (409.41): C 55.74, H 3.94; found: C 55.59, H 3.85.

(1R,2R,10S,11S)-12,13-Dimethylidene-6,14-dioxotetracyclo[9.2.1.0^{2,10}.0^{4,8}]tetradeca-4,7-diene (9). Colourless crystals, m.p. 115-116°. ¹H-NMR (CDCl₃): 7.16 (s, 2H, H-C(5), H-C(7)); 5.24, 5.00 (2s, 4H, 2 =CH₂); 4.58 (s, 2H, H-C(1), H-C(11)); 2.91, 2.31 (2m, 4H, CH₂(3), CH₂(9)); 2.16 (m, 2H, H-C(2), H-C(10)); ²J(3endo,3exo) = 13.5, ³J(3endo,2) = 6.0, J(3exo,2) = 9.5. ¹³C-NMR (CDCl₃): 147.7, 122.4 (2s); 135.9 (d, J = 154, C(5), C(7)); 101.1 (t, J = 159, =CH₂); 86.6 (dd, J = 158, ³J = 6, C(1), C(11)); 44.5 (d, J = 138, C(2), C(10)); 22.5 (t, J = 130, C(3), C(9)). MS (70 eV): 214 (54, M⁺), 200 (21), 196 (23), 186 (29), 119 (64), 94 (100). Anal. calc. for C₁₄H₁₄O₂ (214.27): C 78.48, H 6.59; found: C 78.25, H 6.60.

Octacarbonyl- μ -[1-3- η :4,5,C- η -(5,6-dimethylidene-1,3-cyclohexadiene)]- μ -2-oxo-triangulo-triruthenium (11). Red crystals, m.p. 136° (dec.). IR: 2100, 2042, 2030, 2004, 1962, 1951 (CO). UV (isooctane): 444 (sh, 5416), 336 (17760), 228 (sh, 21500), 255 nm (24380 dm³ mol⁻¹ cm⁻¹). ¹H-NMR (C₆D₆): 4.71, 4.33 (2s, 2H, CH₂=C(6)); 4.40 (d, ³J = 3.9, 1H, H-C(1)); 4.30 (dd, ³J = 5.5, 4.3, 1H, H-C(3)); 3.72 (dt, ³J = 5.5, ⁴J = 0.5, 1H, H-C(4)); 3.71, 2.64 (2 br. s, ²J < 0.5, 2H, CH₂=C(5)); 2.25 (dd, ³J = 4.3, 3.9, 1H, H-C(2)); ¹³C-NMR (CD₂Cl₂): 210.7, 207.6, 205.2, 201.9, 199.4, 198.0, 190.6, 190.3 (8s, CO); 147.0, 100.0 (2s, C(5), C(6)); 106.9 (t, J = 159, CH₂=C(6)); 88.4, 87.3 (2d, J = 166, 160, C(1), C(3)); 60.90, 43.2 (2d, J = 159, 162, C(2), C(4)); 59.5 (t, J = 159, CH₂=C(5)). MS (ZAB-2F spectrometer): 648 (7, M⁺), 620 (6), 592 (16), 564 (38), 536 (22), 508 (100), 480 (40), 452 (62), 424 (97, M⁺ - 8 CO). Anal. calc. for C₁₆H₈O₉Ru₃ (647.45): C 29.68, H 1.25; found: C 30.04, H 1.33.

Tricarbonyl[(1R,2S,3R,4S)-C,2,3,C- η -(2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane)]ruthenium (13). Colourless crystals, m.p. 93-94°. IR: 2080, 1990 (br., CO). ¹H-NMR (CDCl₃): 4.71 (m, 2H, H-C(1), H-C(4)); 2.06, 1.74 (2m, 4H, 2H-C(5), 2H-C(6)); 2.04 (dd, 2H, Htrans to C(2), C(3)); 0.49 (d, 2H, Hcis to C(2), C(3)); ²J(Sexo,5endo) = 12, ³J(Sexo,6exo) = 5, ³J(5endo,6endo) = 4.3, ³J(6exo,1) = 3, ²J(Hcis,Htrans) = 2.8, ⁴J(1,Htrans) = 0.7. ¹³C-NMR (CDCl₃): 195.6 (s, CO); 109.2 (s, C(2), C(3)); 76.8 (d, J = 160, C(1), C(4)); 25.3 (t, J = 160, CH₂=C(2)); 24.3 (t, J = 140, C(5), C(6)). MS (70 eV): 308 (31, M⁺), 280 (38), 252 (38), 224 (100, M⁺ - 3 CO), 204 (100), 194 (47), 167 (31), 122 (12), 102 (25). Anal. calc. for C₁₁H₁₀O₄Ru (307.27): C 42.99, H 3.28; found: C 42.91, H 3.15.

Tricarbonyl[(1R,2S,3R,4S)-C,2,3,C- η -(2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane)]iron (14). Yellow crystals, m.p. 88-89°. IR: 2060, 1980 (br. CO). ¹H-NMR (CDCl₃): 4.88 (m, 2H, H-C(1), H-C(4)); 2.09 (dd, 2H, Htrans to C(2), C(3)); 1.97 (m, 4H, 2H-C(5), 2H-C(6)); 0.38 (d, 2H, Hcis to C(2), C(3)); ²J_{gem} = 3, ⁴J(1,Htrans) = 0.8. ¹³C-NMR (CDCl₃): 210.7 (s, CO); 109.9 (s, C(2), C(3)); 77.1 (d, J = 160, C(1), C(4)); 32.1 (t, J = 160, CH₂=C(2), CH₂=C(3)); 26.2 (t, J = 140, C(5), C(6)). MS (70 eV): 262 (9, M⁺), 234 (33), 206 (46), 178 (100, M⁺ - 3 CO), 160 (37), 152 (11), 148 (17), 134 (9), 122 (43), 56 (26). Anal. calc. for C₁₁H₁₀FeO₄ (262.048): C 50.42, H 3.85; found: C 50.46, H 3.98.

Tricarbonyl[(1R,2R,3S,4S)-C,2,3,C- η -(2,3-dimethylidene-7-oxabicyclo[2.2.2]heptane)]iron (14'). Yellow needles, m.p. 72-73°. IR: 2062, 1982, 1964 (CO). ¹H-NMR (CDCl₃): 5.20 (m, 2H, H-C(1), H-C(4)); 2.05 (m, 4H, 2H-C(5), 2H-C(6)); 1.96 (d, 2H, Htrans to C(2), C(3)); 0.40 (d, 2H, Hcis to C(2), C(3)); ²J(Htrans,Hcis) = 3.5, ⁴J(1,Htrans) \approx 0. ¹³C-NMR (CDCl₃): 210.0 (s, CO); 123.0 (s, C(2), C(3)); 79.9 (d, J = 161, C(1), C(4)); 31.0 (t, J = 161, CH₂=C(2), CH₂=C(3)); 30.4 (t, J = 136, C(5), C(6)). MS (70 eV): 262 (3, M⁺), 234 (33), 206 (58), 178 (100, M⁺ - 3 CO), 176 (4), 161 (31), 152 (27), 150 (55), 148 (28), 134 (33), 132 (31), 122 (82). Anal. calc. for C₁₁H₁₀FeO₄ (262.048): C 50.42, H 3.85; found: C 50.19, H 3.76.

4. Reactions with Osmium Carbonyls. - 4.1. *Catalytic Reactions.* a) A solution of **1** (1.5 g, 12.5 mmol) and Os₃(CO)₁₂ (100 mg, 0.11 mmol) in MeOH (100 ml) was heated to 65° for 11 days. Evaporation *i.v.* and column chromatography on Florisil (80 \times 1 cm) with hexane/CH₂Cl₂ 4:1 gave **15** (0.4 g, 25%) and α,α' -dimethoxy-*o*-xylene (0.6 g, 30%). b) A suspension of **1** (1.5 g, 12.5 mmol) and Os₃(CO)₁₂ (2 g, 2.2 mmol) in THF (100 ml) was heated to 65° for 15 days. Os₃(CO)₁₂ (1.5 g) was recovered by filtration. Evaporation *i.v.* and column chromatography on silica gel (80 \times 1.5 cm) with hexane/Et₂O 95:5 gave **16** (100 mg, 7% relative to **1**) and **17** (80 mg, 14.5% relative to Os).

4.2. *Preparation of 17*. Me_3NO was added portionwise to a suspension of $\text{Os}_3(\text{CO})_{12}$ (0.7 g, 0.77 mmol) in CH_2Cl_2 (300 ml) and MeCN (10 ml) which was vigorously stirred at 35° until all the cluster was dissolved (giving $\text{Os}_3(\text{CO})_{11}(\text{MeCN})$). Then **1** (0.6 g, 5 mmol) was added, and the solution was stirred at 20° for 5 h. After evaporation *i.v.*, the residue was taken up in CH_2Cl_2 , filtered, and column chromatographed on *Florisil* (30×1.5 cm) with CH_2Cl_2 . Recrystallization from hexane at -25° gave **17** (0.25 g, 36% relative to Os).

4.3. *Data of 15–18*. (*1R,4S,4aS,9aR*)-1,4-Epoxy-6-methoxy-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene (**15**). Colourless crystals, m.p. $123\text{--}125^\circ$. $^1\text{H-NMR}$ (CDCl_3): 7.03, 6.69 (2m, 2H, H–C(7), H–C(8)); 6.71 (d, 1H, H–C(5)); 5.23, 5.00 (2s, 4H, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$); 4.69 (s, 2H, H–C(1), H–C(4)); 3.79 (s, 3H, CH_3O); 2.84, 2.54, 2.14 (3m, 6H, $\text{CH}_2(9)$, $\text{CH}_2(10)$, H–C(4a), H–C(9a)); $J(5,8) = 2$, $J(7,8) = 8$, $^2J(\text{endo,9exo}) = 13$, $^3J(\text{endo,9a}) = 6$, $^3J(\text{9exo,9a}) = 10$. $^{13}\text{C-NMR}$ (CDCl_3): 158.2, 149.5, 147.9 (3s); 130.4, 113.2 (2d, $J = 156$, C(6), C(7)); 127.5, 111.0 (2d, $J = 159$, 156, C(5), C(8)); 101.0, 100.9 (2t, $J = 159$, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$); 87.0 (d, $J = 159$, C(1), C(4)); 55.3 (q, $J = 144$, CH_3O); 45.0, 44.6 (2d, $J = 136$, 134, C(4a), C(9a)); 32.6, 31.4 (2 t, $J = 128$, C(9), C(10)). MS (70 eV): 254 (100, M^+), 239 (17), 223 (16), 94 (42). Anal. calc. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ (254.332): C 80.28, H 7.13; found: C 79.88, H 6.86.

(*1R,4S,4aS,5S,8R,9aR*)-1,4,5,8-Diepoxy-2,3-dimethylidene-1,2,3,4,4a,5,6,7,8,9,9a,10-dodecahydroanthracene (**16**). Colourless crystals, m.p. $117\text{--}119^\circ$. $^1\text{H-NMR}$ (CDCl_3): 5.19, 4.95 (2s, 4H, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$); 4.85 (m, 2H, H–C(5), H–C(8)); 4.49 (s, 2H, H–C(1), H–C(4)); 2.51, 2.13, 1.97, 1.76, 1.02 (5m, 10H); $^2J(\text{6exo,6endo}) = 12$, $^3J(\text{6exo,5}) = 3$, $^2J(\text{9exo,9endo}) = 13.5$, $^3J(\text{9endo,4a}) = 5$, $^3J(\text{9exo,4a}) = 9$. $^{13}\text{C-NMR}$ (CDCl_3): 148.0, 140.5 (2s); 100.7 (t, $J = 160$, $=\text{CH}_2$); 87.5, 80.3 (2d, $J = 159$, 162, C(1), C(4), C(5), C(8)); 44.9 (d, $J = 135$, C(4a), C(9a)); 24.9 (2t, $J = 136$, 128). MS (70 eV): 242 (6, M^+), 224 (4), 214 (22), 196 (8), 185 (11), 129 (22), 128 (17), 119 (21), 115 (13), 105 (12), 95 (19), 94 (100), 91 (28), 77 (21), 66 (15), 65 (20). Anal. calc. for $\text{C}_{16}\text{H}_{18}\text{O}_2$ (242.32): C 79.32, H 7.49; found: C 78.80, H 7.30.

Undecacarbonyl[*(1R,2R,3S,4S)*-2,3- η -(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]-triangulo-triosmium (**17**). Yellow microcrystals, m.p. $136\text{--}138^\circ$. IR: 2128, 2075, 2060, 2040, 2000, 1988, 1978 (CO). $^1\text{H-NMR}$ (CDCl_3): 5.39, 5.19 (2s, 4H, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$); 4.77 (s, 2H, H–C(1), H–C(4)); 3.22 (s, 2H, H–C(2), H–C(3)); $^3J(1,2) < 0.5$. $^{13}\text{C-NMR}$ (CDCl_3): 184.1, 182.9, 181.5, 175.5, 173.9, 172.0, 169.9, 169.6 (8s, ratios 2:2:2:1:1:1:1:1, CO); 145.0 (s, C(5), C(6)); 83.3 (d, $J = 161$, C(1), C(4)); 39.9 (d, $J = 173$, C(2), C(3)). MS (*ZAB-2F* spectrometer, ^{192}Os): 1004 (1, M^+), 884 (9, $M^+ - \text{L}$), 856 (11, $M^+ - \text{L} - \text{CO}$), 828 (8), 772 (19), 744 (9), 716 (8), 688 (9), 660 (9), 632 (3), 604 (3, $M^+ - \text{L} - 10 \text{ CO}$), 576 (6, Os_3^+), 360 (2, $\text{Os}(\text{CO})_4^+$), 332 (25, $\text{Os}(\text{CO})_5^+$), 304 (47, $\text{Os}(\text{CO})_4^+$), 276 (27, $\text{Os}(\text{CO})_3^+$), 248 (100, $\text{Os}(\text{CO})_2^+$), 220 (56, OsCO^+), 192 (36, Os^+), 120 (100, L^+); isotopic distribution of molecular envelope: 1005 (8), 1004 (39), 1003 (16), 1002 (84), 1001 (66), 1000 (100), 999 (81), 998 (90), 997 (64), 996 (55), 995 (34), 994 (23), 993 (11), 992 (5). Anal. calc. for $\text{C}_{19}\text{H}_8\text{O}_{12}\text{Os}_3$ (998.9): C 22.85, H 0.81; found: C 22.95, H 0.82.

5. *Reaction of 1 with Chromium and Tungsten Carbonyls. Thermal Reactions*. A solution of **1** (0.96 g, 8 mmol) and $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ [17] (24 mmol) in hexane/ Et_2O /THF 2:2:1 (100 ml) was stirred at 30° for 16 h, then evaporated *i.v.* The orange residue was taken up in Et_2O , filtered, and column chromatographed on *Florisil* (50×1.5 cm) first with benzene which brought down a single orange band. Evaporation *i.v.* and recrystallization from hexane at -25° gave **18** (1.2 g, 51%). Then, elution with AcOEt , evaporation *i.v.*, chromatography on silica gel (30×1 cm) with benzene, and recrystallization from hexane at -25° gave **2** (50 mg, 5%) and **16** (25 mg, 2.5%). The same reaction with $\text{W}(\text{CO})_3(\text{MeCN})_3$ failed to give any isolable complex. The reaction of $\text{W}(\text{CO})_3(\text{MeCN})_3$ (20 mmol) and **1** (8 mmol) in Et_2O /hexane 2:1 (40° , 3 days) gave **2** (3%).

Tricarbonyl[*(1R,2R,3S,4S,5S,6R)*-2,3- η -C,5,6-C- η -(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]-chromium (**18**). Orange crystals, m.p. $118\text{--}120^\circ$. IR: 1997, 1946, 1920 (CO). $^1\text{H-NMR}$ (C_6D_6): 4.46 (dd, 2H, H–C(1), H–C(4)); 3.06 (dd, 2H, H–C(2), H–C(3)); 2.97 (d, 2H, *Htrans* to C(5), C(6)); 1.25 (d, 2H, *Hcis* to C(5), C(6)); $^3J(1,2) = 1.6$, $^4J(1,3) = 1.6$, $^2J(\text{Hcis,Htrans}) = 2.2$. $^{13}\text{C-NMR}$ (C_6D_6): 237.3, 235.2 (2s, ratio 2:1, CO); 75.6 (d, $J = 176$, C(1), C(4)); 81.4 (s); 60.2 (t, $J = 164$, $=\text{CH}_2$); 48.7 (d, $J = 186$, C(2), C(3)). MS (70 eV): 256 (30, M^+), 228 (25), 200 (35), 172 (60, $M^+ - 3 \text{ CO}$), 142 (40), 91 (12), 52 (100). Anal. calc. for $\text{C}_{11}\text{H}_8\text{CrO}_4$ (256.181): C 51.57, H 3.15; found: C 51.33, H 3.22.

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