190. Chemo- and Stereoselective Coordination of 5,6-Dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene by d^8- and d^6-Metal Carbonyls. *Diels-Alder* Reactivity of Dienes Perturbed by Remote Olefin Complexation

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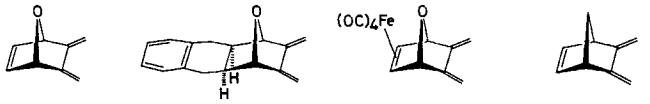
Summary

The endocyclic double bond C(2),C(3) in 5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene (**1**) can be coordinated selectively on its *exo*-face before complexation of the exocyclic s-*cis*-butadiene moiety. Irradiation of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ in the presence of **1** gave tetracarbonyl[(1*R*,2*R*,3*S*,4*S*)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene)]ruthenium (**6**) or -osmium (**8**). Similarly, irradiation of $Cr(CO)_6$ or $W(CO)_6$ in the presence of **1** gave pentacarbonyl[(1*R*,2*R*,3*S*,4*S*)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]chromium (**10**) or -tungsten (**11**). Irradiation of complexes **6** and **11** in the presence of **1** led to further CO substitution giving *bcd*-tricarbonyl-*ae*-bis[(1*R*,2*R*,3*S*,4*S*)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]ruthenium (**7**) and *trans*-tetracarbonyl[(1*R*,2*R*,3*S*,4*S*)-2,3-η-(5,6-dimethylidene-7-oxabicyclo-[2.2.1]hept-2-ene)]tungsten (**12**), respectively. The diosmacyclobutane derivative *cis*-μ-[(1*R*,2*R*,3*S*,4*S*)-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hepta-2,3-diyl)]bis(tetracarbonyl-osmium) (*Os-Os*) (**9**) was also obtained. The *Diels-Alder* reactivity of the exocyclic s-*cis*-butadiene moiety in complexes **7** and **8** was found to be significantly higher than that of the free triene **1**.

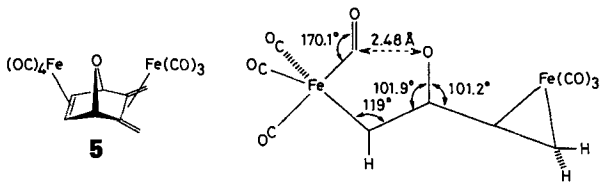
Introduction. – The 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**), readily prepared in three steps from furan and maleic anhydride [1], is a valuable synthetic intermediate. This has been illustrated recently by our discovery of the unique property of **1** in forming the polycyclic derivative **2** when treated with $Fe_2(CO)_9$ in MeOH [2] [3]. Diene **2** is a potential precursor in the synthesis of antitumoral anthracyclinone such as demethoxydaunomycinone [4] [5]. A few years ago, we reported that the endocyclic double bond of **1** reacts faster than the exocyclic diene with iron carbonyls. This allowed the isolation of the relatively stable (η^2-triene)$Fe(CO)_4$ complex **3** in good yield, in which the $Fe(CO)_4$ group sits on the *exo*-face of the ligand [6].

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



1 **2** **3** **4**

No such η^2-complex has ever been observed upon treatment of the hydrocarbon analog **4** under various conditions in the presence of iron carbonyls. The extraordinary ease, and thus chemoselectivity, of the coordination reaction **1**→**3** was earlier attributed to the π-anisotropy of the 7-oxabicyclo[2.2.1]hept-2-ene double bond which was then estimated based on MINDO/3 calculations to be more localized on the *exo*-face in **1** than in **4** [6]. However, recent X-ray data [7], as well as *ab initio* STO 3G calculations on **1** and **4** [8] do not support the above hypothesis [6]. A closer inspection of the X-ray structure of the bimetallic complex **5** suggests the existence of an interaction between one of the axial CO groups of the $Fe(CO)_4$ moiety and the oxa-bridge *(Fig. 1)*. This stabilizing interaction might explain the relative stability of complexes **3** and **5**.



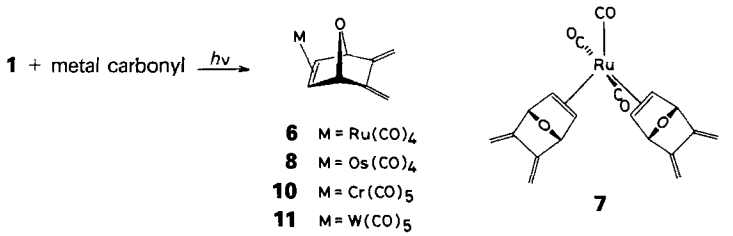
5

Fig. 1. *X-ray characteristics of* **5** [6]

We report now on the photochemical complexations of **1** with ruthenium, osmium, chromium and tungsten carbonyls which are also chemo- and stereoselective. We report also preliminary kinetic data on the cycloadditions of these complexes to dimethyl acetylenedicarboxylate (DMAD) showing that the *Diels-Alder* reactivity of the exocyclic diene moiety at C(5),C(6) in **1** can be significantly enhanced upon coordination of the homoconjugated, endocyclic double bond at C(2),C(3) with low-valent d^8-metals.

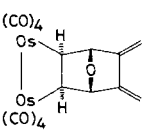
Results and Discussion. – Irradiation of a mixture of **1** and $Ru_3(CO)_{12}$ (1:5.5) using *Grevels* technique [9] (hexane, 20°C, $\lambda > 370$ nm) gave the η^2-$Ru(CO)_4$ complex **6** (11%) together with polymeric, organic material. Further CO substitution in **6** occurred when using pyrex-filtered UV light giving **7** (56%).

Irradiation of **1** and $Os_3(CO)_{12}$ (hexane, 10°C, $\lambda > 370$ nm) gave **8** (27.5%) and a smaller amount (6.5%) of the diosmacyclobutane derivative **9.** The CO substitution in **9** could not be achieved upon irradiation with pyrex-filtered UV light even though some (η^2-olefin)$_2$Os(CO)$_3$ complexes have been found to be significantly more stable

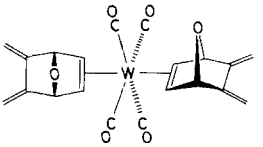


6 M = $Ru(CO)_4$
8 M = $Os(CO)_4$
10 M = $Cr(CO)_5$
11 M = $W(CO)_5$

7



9



12

than the Fe and Ru analogs [10]. Irradiation of **1** and $M(CO)_6$ (M = Cr, W; hexane, −20°C, pyrex) gave the (η^2-olefin)$M(CO)_5$ complexes **10** (18%) and **11** (11%). Only in the case of tungsten, a further CO substitution took place giving **12** (9%).

The *exo*-configuration of the metal atoms in **6**–**12** was confirmed by ^{1}H-NMR spectroscopy, and more specifically by the relatively weak vicinal coupling constants between the protons at C(2),C(3) (of the coordinated endocyclic double bond) and the bridgehead protons ($^3J_{H,H}$ = 0.3–0.5 Hz; compare also with **3** and **5** [6]). The validity of this NMR criterion has been discussed earlier [6], and was assumed for the octahedral complexes **10**–**12** (in agreement with the *exo*-configuration given for (7,7-dimethoxybenzonorbornadiene)$Cr(CO)_4$ [11] where $^3J_{H,H}$ = 1.0 and 2.5 Hz for the complex and the free ligand, respectively).

Complex **7** is nonfluxional between −80 and 80°C, and olefin rotation appears to be a slow process on the ^{1}H-NMR-time scale since the *AA'XX'* pattern of the protons at C(2) and C(3) remains unchanged in this temperature range. It most probably has the trigonal bipyramidal geometry common to the great majority of known $Ru(CO)_3L_2$ complexes [12], with one equatorial CO (δ_C 188.5 ppm). The slightly different δ_C's of the two axial CO groups (194.74 and 194.68 ppm) indicate a symmetry lower than C_{2v} probably due to the oxa-bridges pointing towards the same apex. Unlike the ruthenium complex **6**, **7** is surprisingly inert towards CO substitution and insertion (toluene, 60°C, 60 atm CO) and towards cyclodimerization (MeOH, 70°C; see following paper).

The η^2-complexes **3**, **5**, **6**, and **8**, however, are fluxional. They displayed only one single peak for the carbonyls in their ^{13}C-NMR spectra below (Fe, Ru) or above room temperature (Os). This is typical for d^8-$M(CO)_4L$ complexes [10]. The ^{1}H- and ^{13}C-NMR spectra of **3**, **6**, and **8** show an increasing shielding of the protons at C(2) and C(3) and of the carbon nuclei C(2) and C(3) (δ_H 3.35 (Fe), 2.86 (Ru), 2.48 (Os); δ_C 54.9 (Fe), 45.7 (Ru), 32.0 ppm (Os)), and of the carbonyl groups (δ_{CO} 210.3 (Fe), 197.1 (Ru), 177.3 ppm (Os)). This indicates an increase in M→π*(olefin) back-donation along the sequence Fe < Ru < Os as expected for olefinic d^8-complexes.

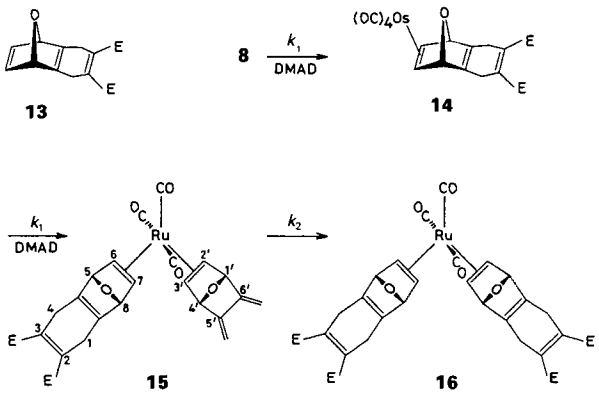
We propose a true metallacycle structure for **9** since its ^{13}C-NMR spectrum shows a signal for C(2) and C(3) (δ_C 0.1 ppm) that is shifted by more than 30 ppm relative to that measured in **8**, and furthermore shows a coupling constant ($J_{C,H}$ = 140 Hz) typical of substituted sp^3-hybridized C-atoms (compare with **8** where $J_{C,H}$ = 170 Hz). To our knowledge there are only three reported examples of disomacarbocycles [13].

The CO groups are more shielded in **11** than in **10** (δ_{CO} 197.0 and 218.1 ppm, resp.). This trend has been observed by *Grevels* [10] for d^6-carbonyl complexes of cyclooctene.

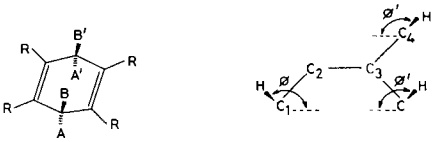
Complex **12** must be the *trans*-$W(CO)_4L_2$ isomer since a single ^{13}C-NMR resonance (δ_C 198.6 ppm, $J_{C,W}$ = 119 Hz) is observed in the CO region (the IR spectrum cannot be used as a geometrical test in this case [14]). The ground-state configuration of **12** must lack a center of symmetry since its ^{1}H-NMR spectrum (25°C) displays four pairs of signals (instead of four signals). Thus, the two endocyclic double bonds are not parallel

but rather perpendicular. The latter arrangement corresponds to maximum d-π* (olefin) overlap and has been ascertained by X-ray analysis in the case of *trans*-(η^2-methyl acrylate)$_2$W(CO)$_4$ [14]. The ^{1}H-NMR spectrum of **12** is temperature-dependent, *e.g.* the 2 *t* at 3.02 and 3.01 ppm ($J_{H,W}$ = 12.5 Hz) for H–C(2) and H–C(3) coalesce at *ca.* 50°C without loss of coupling. This observation is attributed to olefin rotation for which the activation parameters, $\Delta H^{\neq} = 13.8 \pm 0.9$ kcal·mol^{-1} and $\Delta S^{\neq} = -7 \pm 3$ cal·mol^{-1}·K^{-1}, were obtained by line shape analysis of the signals of the bridgehead protons (2 *s* at 4.82 and 4.72 ppm) in the range $20 < T < 90$°C. The activation parameters obtained for **12** are quite comparable with those obtained for *trans*-(η^2-methyl acrylate)$_2$W(CO)$_4$ [14]. The observed negative $\Delta S^{\neq}$ is in accordance with a transition state of higher symmetry (probably parallel arrangement of the two endocyclic double bonds) than that of the proposed ground-state structure.

***Diels-Alder* Reactivity.** – The attempted addition of dimethyl acetylenedicarboxylate (DMAD), maleic anhydride, ethylenetetracarbonitrile (TCE) or *N*-phenylpyrazolindione to **3, 6, 10,** and **11** in various solvents led only to ligand substitution and decomposition of the complexes. However, in the presence of an excess of DMAD, **1, 8,** and **7** underwent *Diels-Alder* additions in $CHCl_3$ at 60°C giving adducts **13** [15] (95%), **14** (75%), and **16** (90%), respectively. The adducts were characterized by ^{1}H- and ^{13}C-NMR (see *Exper. Part*).

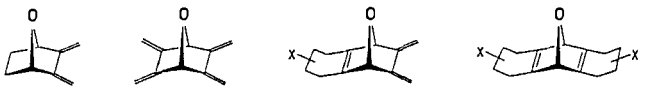


In the case of **14,** simulation of the ^{1}H-NMR signals of CH_2(1) and CH_2(4) as an *AA'BB'*-spin system (δ_H 3.15 ppm) gave $J^{gem}_{A,B} = -23.0$, $^5J^{cis}_{A,A'} = 9.6$, $^5J^{cis}_{B,B'} = 9.3$, and 1/2 ($^5J^{trans}_{A,B'} + {}^5J^{trans}_{A',B}$) = $^5J^{trans}_{av.} = 9.1$ Hz and $^5J^{cis}_{av.} = 9.45$ Hz. A VB model [16] has shown that the angular dependence of a homoallylic coupling is given by $^5J^{\pi}_{H,H} = 4.00 \cdot \sin^2\Phi\sin^2\Phi'$. The ratio $J^{cis}_{av.}/J^{trans}_{av.}$ may then be used to calculate angle Φ which is related to the coplanarity of the carbocycle (*e.g.* for 1,4-dihydronaphtalene $J^{cis}_{av.}/J^{trans}_{av.} = 1.19$, thus giving $\Phi \approx 115°$ and indicating an average planar conformation in solution [17]). For **14,** $J^{cis}_{av.}/J^{trans}_{av.} = 1.04$, thus corresponding to an angle $\Phi \approx 127°$. This indicates a tilt of the carbocycle of *ca.* 5° towards the *endo*-face of the bicyclic system in agreement with the values (3–10°) found by *Mahaim et al.* [18] for other cyclohexadienes grafted onto bicyclo[2.2.1]hept-2-ene systems.



The kinetics of the addition of DMAD to **1, 8,** and **7** were followed by ^{1}H-NMR spectroscopy under second-order conditions in $CDCl_3$ at 60°C (see *Exper. Part*), and the following rate constants were obtained: $2.3 \cdot 10^{-4}$ (**1**→**13**), $2.6 \cdot 10^{-3}$ (**8**→**14**), $5.8 \cdot 10^{-2}$ (**7**→**15**), and $5.8 \cdot 10^{-2}$ $dm^3 \cdot mol^{-1} \cdot min^{-1}$ (**15**→**16**). Monoadduct **15** could not be isolated but was characterized by its ^{1}H-NMR spectrum.

The *Diels-Alder* reactivity of the exocyclic diene moiety at C(5),C(6) in **1** can thus be significantly enhanced upon coordination of the homoconjugated, endocyclic double bond at C(2),C(3) with a low-valent d^8-metal. This striking result is at variance with the retarding effect caused by coordination of one diene moiety by an η^4-$M(CO)_3$ group in the *Diels-Alder* reactivity of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane [19] and [2.2.2]hericene [20].



17 **18** **19** **20**

The addition of DMAD to **1** was found to be *ca.* 150 times slower than the addition of DMAD to 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane (**17**) (25°C, CCl_4 [21]). The latter diene had about the same *Diels-Alder* reactivity as that of the tetraene **18** [22]; that of the monoadduct **19** was similar to that of triene **1** [22] [23]. In agreement with the *Dimroth* [24] or *Bell-Evans-Polanyi* principle [25], the more exothermic a reaction, the faster it is. Cycloadditions **19**→**20** (and **1**→**13**) are slower than reactions **18**→**19** (and *Diels-Alder* additions of diene **17**) because the former are less exothermic than the latter. Bicyclo[2.2.1]hepta-2,5-diene is known to be about 10 kcal·mol^{-1} more strained than bicyclo[2.2.1]hept-2-ene [26]. The increase of strain between monoadduct **19** and bis-adducts **20** was attributed to an olefin-oxabridge repulsion effect [23]. X-ray structures of 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene derivatives show that the C(7) or O(7) bridges are repelled by the endocyclic double bond (angle α is larger than angle β, see *Fig. 2*) [7]. Since there is an attractive interaction between the oxa-bridge and one of

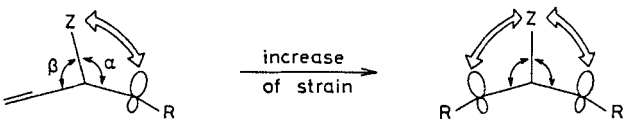


Fig. 2. *Representation of the strain increase when going from mono adducts* **19** (Z = O, CH_2) *to bis-adducts* **20**

the carbonyl groups in **5** (see *Fig. 1*), the extra strain due to 'enhanced' olefin-bridge repulsion in adducts **14**–**16** must be reduced by coordination of one double bond of the 7-oxabicyclo[2.2.1]hepta-2,5-diene systems with low-valent transition-metal carbonyls. Thus, one expects the cycloadditions **8**→**14**, **7**→**15** and **15**→**16** to be more exothermic and consequently faster than the cycloaddition **1**→**13** of the uncomplexed triene.

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Experimental Part

1. *General Remarks.* See [20]. The preparations of **1** [1], **3, 5** [2], and **13** [15] have been reported previously. The procedures reported below have not been optimalized.

2. *Preparation of Complexes.* a) *Ruthenium Complexes.* A stirred suspension of **1** (1 g, 8.3 mmol) and $Ru_3(CO)_{12}$ (3 g, 46 mmol) in hexane (250 ml) was irradiated (high-pressure Hg lamp *Philips HPK-125,* pyrex vessel, $\lambda > 370$ nm [9]) at 25° for 6 h. Evaporation *in vacuo,* chromatography on *Florisil* (50 × 1 cm column) with hexane/Et_2O 9:1, and recrystallization from hexane at −25° gave **6** (0.3 g, 11%). Irradiation without filter (pyrex; 1.5 g of **1**, 3.5 g of $Ru_3(CO)_{12}$, 450 ml of hexane, 20°, 15 h) gave **6** (0.4 g, 11%) and **7** (1.5 g, 56%).

Tetracarbonyl[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]ruthenium (**6**). Thermally unstable, colourless crystals, m.p. 30–31° (dec.). IR: 2120, 2050, 2040, 1995 (CO). ^{1}H-NMR ($CDCl_3$): 5.31, 5.10 (2 *d,* 4H, 2 =CH_2); 4.67 (*s,* 2H, H–C(1), H–C(4)); 2.86 (*s,* 2H, H–C(2), H–C(3)); $J_{1,2} = J_{4,5} < 0.5$ Hz. ^{13}C-NMR ($CDCl_3$): 197.1 (*s,* CO); 146.6 (*s,*C(5), C(6)); 102.3 (*t, J* = 160, =CH_2); 83.4 (*dd, J* = 160, ^3J = 6, C(1), C(4)); 45.7 (*d, J* = 169, C(2), C(3)). MS: 334 (< 1, M^+), 318 (5, $M^+ - O$), 306 (20, $M^+ - CO$), 290 (25, $M^+ - O - CO$), 278 (100, $M^+ - 2\,CO$), 262 (90, $M^+ - O - 2\,CO$), 250 (55, $M^+ - 3\,CO$), 234 (20, $M^+ - O - 3\,CO$), 222 (30, $M^+ - 4\,CO$), 206 (35, $M^+ - O - 4\,CO$).

bcd-*Tricarbonyl*-ae-*bis[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxybicyclo[2.2.1]hept-2-ene)]ruthenium* (**7**). Colourless crystals, m.p. 140–2° (dec.). IR: 2140, 2068, 2038 (CO). ^{1}H-NMR ($CDCl_3$, 25°): 5.23, 5.09, 5.01, 4.81 (4 *s,* 8H, =CH_2); 4.66, 4.51 (2 *s,* 4H, H–C(1), H–C(4)); 2.81, 2.56 (2 *m,* 4H, H–C(2), H–C(3); simulation as an *AA'XX'* system gave $J_{A,A'} = 5.2$, $J_{X,X'} = 0$, $J_{A,X} = J_{A',X'} = 9$, $J_{A,X'} = J_{A',X} = -0.9$). ^{13}C-NMR ($CDCl_3$, 25°): 194.74, 194.68 (2 *s,* apical CO's); 188.5 (*s,* equatorial CO); 151.0, 148.0 (2 *s,*C(5), C(6)); 101.3, 98.4 (2 *t, J* = 159, =CH_2); 90.4, 89.6 (2 *d, J* = 160, C(1), C(4)); 63.4, 41.9 (2 *d, J* = 133, 134, C(2), C(3)). MS (70 eV, ^{102}Ru): 426 (1, M^+), 398 (16), 370 (100), 342 (80, $M^+ - 3\,CO$), 283 (90), 192 (100), 149 (95). Anal. calc. for $C_{19}H_{16}O_5Ru$ (426.41): C 53.64, H 3.79; found: C 53.26, H 3.72.

b) *Osmium Complexes.* A suspension of **1** (2 g, 17 mmol) and $Os_3(CO)_{12}$ (1.3 g, 1.43 mmol) in hexane (40 ml) was irradiated (*Philips HPK-125,* $\lambda > 370$ nm, pyrex) at 25° for 48 h. After filtration and evaporation *in vacuo,* the residue was chromatographed on *Florisil* (80 × 1.5 cm column) with hexane. Recrystallization from hexane at −25° gave **8** (0.5 g, 27.5%) and **9** (0.1 g, 6.4% relative to Os).

Tetracarbonyl[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]osmium (**8**). Colourless crystals, m.p. 52–3°. IR: 2128, 2048, 2038, 1988 (CO). ^{1}H-NMR ($CDCl_3$): 5.30 (*d,* $^4J_{H,H} \approx 0.6$, 2H, $2H_{cis}$ to C(5),C(6)); 5.07 (*s,* 2H, 2H *trans* to C(5),C(6)); 4.66 (*d,* $J_{H,H} \approx 0.6$, 2H, H–C(1), H–C(4)); 2.48 (*s,* 2H, H–C(2), H–C(3)); $^3J_{1,2} < 0.5$ Hz. ^{13}C-NMR ($CDCl_3$): 177.3 (*s,* CO); 147.0 (*s,* C(5), C(6)); 101.9 (*t, J* = 161, =CH_2); 83.5 (*d, J* = 162, C(1), C(4)); 32.0 (*d, J* = 170, C(2), C(3)). MS (70 eV, ^{192}Os): 422 (11, M^+), 394 (32), 366 (55), 338 (51), 310 (100, $M^+ - 4\,CO$), 270 (70), 252 (29). Anal. calc. for $C_{12}H_8O_5Os$ (422.4): C 34.12, H 1.90; found: C 34.30, H 1.98.

cis-*μ-[(1R,2R,3S,4S)-(5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,3-diyl)]bis(tetracarbonylosmium)*-(Os-Os) (**9**). Colourless crystals, m.p. 113 –5°. IR: 2138, 2092, 2058, 2048, 2038, 2005, 1998 (CO). ^{13}H-NMR ($CDCl_3$): 5.07, 4.81 (2 *s,* 4H, 2 =CH_2); 4.68 (*s,* 2H, H–C(1), H–C(4)); 1.99 (*s,* 2H, H–C(2), H–C(3)); $^3J_{1,2} < 0.5$ Hz, ^{13}C-NMR ($CDCl_3$): 179.5, 178.2, 172.0, 168.2 (4 *s,* ratios 1:1:1:1, CO); 150.3 (*s,* C(5), C(6)); 99.3 (*t, J* = 159, =CH_2); 92.6 (*d, J* = 160, C(1), C(4)); 0.1 (*d, J* = 140, C(2), C(3)). MS (*ZAB-2F* spectrometer, ^{192}Os): 724 (M^+), 696 ($M^+ - CO$), 668 ($M^+ - 2\,CO$), 640 ($M^+ - 3\,CO$), 612 ($M^+ - 4\,CO$), 604 ($Os_2(CO)_8^+$), 584 ($M^+ - 5\,CO$), 576 ($Os_2(CO)_7^+$), 556 ($M^+ - 6\,CO$), 548 ($Os_2(CO)_6^+$), 528 ($M^+ - 7\,CO$), 520 ($Os_2(CO)_5^+$), 500 ($M^+ - 8\,CO$); 492 ($Os_2(CO)_4^+$), 464 ($Os_2(CO)_3^+$), 436 ($Os_2(CO)_2^+$), 408 (Os_2CO^+), 380 (Os_2^+), 302 ($Os(CO)_4^+$), 274 ($Os(CO)_3^+$), 246 ($Os(CO)_2^+$), 218 ($OsCO^+$), 192 (Os^+), 120 (1^+); isotopic distribution of peaks envelope centered at 380: 386 (1), 385 (12), 384 (71), 383 (17), 382 (199), 381 (68), 380 (84), 379 (48), 378 (48), 377 (22), 376 (9), 375 (3), 374 (1). No satisfactory elemental analyses could be obtained.

c) *Chromium and Tungsten Complexes.* A solution of **1** (1.35 g, 11 mmol) and $Cr(CO)_6$ (5 g, 22 mmol) in hexane (500 ml) was irradiated (*Philips HPK-125,* pyrex) at −20° for 15 h. After filtration and evaporation *in vacuo* at 20°, the residue was taken up in benzene and chromatographed on *Florisil* (50 × 1.5 cm column) with benzene. Evaporation *in vacuo* gave a yellow oil which crystallized from hexane at −70° giving **10** (0.6 g, 18%). Irradiation of **1** (11 mmol) and $W(CO)_6$ (15 mmol) in hexane (250 ml) at −20° for 6 h followed by the same workup as for **10** gave **11** (0.55 g, 11%) and **12** (0.55 g, 9%).

Pentacarbonyl[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]chromium (**10**). Air sensitive, yellow crystals, m.p. 80°. IR: 2085, 2000, 1970, 1960, 1955 (CO). ^{1}H-NMR (C_6D_6): 5.24, 4.89 (2 *s,* 4H, 2 =CH_2); 4.48 (*s,* 2H, H–C(1), H–C(4)); 3.76 (*s,* 2H, H–C(2), H–C(3)); $J_{1,2} < 0.5$ Hz. ^{13}C-NMR (C_6D_6): 224.3, 216.6 (2 *s,* ratio 1:4, CO); 143.8 (*s,* C(5), C(6)); 104.9 (*t, J* = 160, =CH_2); 82.1 (*d, J* = 170, C(1), C(4));

81.1 (*d*, J = 178, C(2), C(3)). MS (70 eV, ^{52}Cr): 312 (12, M^+), 284 (10), 256 (12), 228 (30), 220 (100), 200 (60), 172 (12, $M^+ - 5$ CO), 120 (38).

Pentacarbonyl[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)]tungsten (**11**). Pale yellow crystals, m.p. 94–5°. IR: 2099, 2000, 1970, 1968, 1950 (CO). ^{1}H-NMR (C_6D_6): 5.25, 4.89 (2 *s*, 4H, 2 =CH_2); 4.51 (*s*, 2H, H–C(1), H–C(4)); 3.78 (*s*, 2H, H–C(2), H–C(3)); $J_{1,2} < 0.4$ Hz. ^{13}C-NMR (C_6D_6): 201.5, 195.9 (2 *t*, ratio 1:4, $J_{W,CO}$ = 125 *(cis)* and 144 *(trans)*); 143.8 (*s*, C(5), C(6)); 104.6 (*t*, J = 160, =CH_2); 82.6 (*d*, J = 176, C(1), C(4)): 73.8 (*d*, J = 178, C(2), C(3)). MS (70 eV, ^{184}W): 444 (53), 416 (27), 399 (13), 388 (100), 379 (20), 360 (40), 351 (20), 332 (40), 320 (40), 304 (26), 279 (26). Anal. calc. for $C_{13}H_8O_6W$ (444.06): C 35.16, H 1.82; found: C 35.29, H 1.99.

trans-*Tetracarbonylbis[(1R,2R,3S,4S)-2,3-η-(5,6-dimethylidene-7-oxabicyclo[2.2.1.]hept-2-ene)]tungsten* (**12**). Colourless crystals, m.p. 130–40° (dec.). IR: 2020, 1972, 1966 (CO). ^{1}H-NMR (C_6D_6, 25°): 5.36 (*s*, 4H, H_{cis} to C(2),C(3)); 5.01, 4.99 (2 *s*, 4H, H_{trans} to C(2),C(3)); 4.82, 4.72 (2 *s*, 4H, H–C(1), H–C(4)); 3.02, 3.01 (2 *t*, 4H, $J_{H,W}$ = 12.5, H–C(2), H–C(3)); $J_{1,2} < 0.5$ Hz. ^{13}C-NMR (C_6D_6, 25°): 198.6 (*t*, $J_{W,CO}$ = 119); 147.1 (*s*, C(5), C(6)); 102.6, 102.5 (2 *t*, J = 159, =CH_2); 83.4, 83.3 (2 *d*, J = 167, C(1), C(4)); 49.5, 49.2 (2*d*, J = 170, C(2), C(3)). MS (70 eV, ^{184}W): 536 (10, M^+), 508 (20), 480 (1), 452 (28), 424 (100, $M^+ - 4$ CO). Anal. calc. for $C_{20}H_{16}O_6W$ (536.20): C 44.80, H 3.01; found: C 44.98, H 3.17.

3. *Cycloaddition Experiments.* A solution of **8** (0.94 mmol) and DMAD (1.9 mmol) in $CHCl_3$ (20 ml) was heatead to 60° for 4 h. After evaporation *in vacuo* and filtration, recrystallization from hexane/Et_2O at –25° gave **14** as colourless microcrystals (181 mg, 90%). The same procedure as for **14** starting with **7** (0.5 mmol; 1.55 mmol DMAD) gave **16** (75%).

Tetracarbonyl[(5R,6R,7S,8S)-6,7-η-(dimethyl 5,8-epoxy-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylate)]-osmium (**14**). M.p. 75 – 8° (dec.). IR: 2125, 2045, 2035 (CO), 1730 (C=O). ^{1}H-NMR ($CDCl_3$): 4.79 (*s*, 2H, H–C(5), H–C(8)); 3.79 (*s*, 6H, 2 CH_3O); 3.15 (*m*, 4H, CH_2(1), CH_2(4)); 2.58 (*s*, 2H, H–C(6), H–C(7)); $J_{5,6} \leqslant 0.4$ Hz. ^{13}C-NMR ($CDCl_3$): 176.9, 176.5 (2 *s*, CO); 168.3 (*s*, C=O); 138.3, 133.2 (2 *s*, C(2), C(3), C(4a), C(8a)); 83.4 (*m*, J = 166, C(5), C(8)); 52.2 (*q*, J = 148, CH_3O); 32.8 (*d*, J = 164, C(6), C(7)); 25.8 (*t*, J = 133, C(1), C(4)). MS (70 eV, ^{192}Os): 564 (13, M^+), 536 (100), 508 (81), 490 (32), 480 (24), 452 (16, $M^+ - 4$ CO). Anal. calc. for $C_{18}H_{14}O_9Os$ (564.51): C 38.31, H 2.50; found: C 38.35, H 2.52.

Tricarbonylbis[(5R,6R,7S,8S)-6,7-η-(dimethyl 5,8-epoxy-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylate)]-ruthenium (**16**). M.p. 155 – 8° (dec.). IR: 2135, 2068, 2028 (CO), 1760 (C=O). ^{1}H-NMR ($CDCl_3$): 4.59, 4.53 (2 *s*, 4H, H–C(5), H–C(8)); 3.77, 3.71 (2 *s*, 12H, CH_3O); 3.17, 2.91 (2 *m*, 8H, H–C(1), H–C(4), same pattern as for **14**); 2.26, 1.97 (2 *m*, 4H, H–C(6), H–C(7), $J_{A,A'} \approx 5$, $J_{A,X} \approx 9$, $J_{A,X'} \approx 1$); $J_{5,6} < 0.4$ Hz. ^{13}C-NMR ($CDCl_3$): 193.4, 193.3 (2 *s*, axial CO's); 188.4 (*s*, equatorial CO); 168.5, 164.4 (2 *s*, C=O); 138,5, 133.6, 133.3, 132.2 (4 *s*, C(2), C(3), C(4a), C(8a)); 86.6 (*d*, J = 160, C(5), C(8)); 52.3 (*q*, J = 148, CH_3O); 54.5, 36.1 (2 *d*, J = 164, C(6), C(7)); 25.3, 25.1 (2 *t*, J = 130, C(1), C(4)). Anal. calc. for $C_{31}H_{28}O_{13}Ru$ (709.64): C 52.47, H 3.98; found: C 52.32, H 3.98.

4. *Kinetic Measurements.* The ^{1}H-NMR spectra of a *ca.* 0.1M solution of **1, 8,** and **7,** resp., in $CDCl_3$ containing a stoechiometric amount of DMAD were recorded (*Bruker-WH-360* spectrometer) at 60.0 ± 0.5° until 70–75% completion of the reaction **1**→**13, 8**→**14,** and **7**→**16,** resp. (2nd order conditions). The course of the reactions was followed by integrating characteristic signals and checking the constancy of the integration sum of corresponding signals. For **1**→**13** and **8**→**14,** the rate constants were calculated by linear regression of the equation $1/(a-x) - (1/a) = kt$ (> 7 measurements, correlation coefficients > 0.992). In the case of **7** ($[7]_0 = 0.1174$M; $[DMAD]_0 = 0.2348$M), additional signals appeared in the first stage of the reaction reaching a maximum after *ca.* 80 min due to the formation of intermediate monoadduct **15** [^{1}H-NMR: 5.22, 5.09, 4.99, 4.88 (4 *s*, 4H, 2 =CH_2); 4.66, 4.65, 4.55, 4.54 (4 *s*, 4 bridgehead H); 3.77, 3.71 (2 *s*, 6H, 2CH_3O); 3.27, 2.89 (2 *m*, 4H, CH_2(1), CH_2(4)); 2.77, 2.35 (2 *d*, 2H, $^3J_{H,H}$ = 8.5, H–C(6), H–C(7)); 2.42, 2.11 (2 *m*, 2H, H–C(2'), H–C(3')). The ratio $k_2/k_1 = r = 1.00 \pm 0.06$ was calculated from equation $(r-1)[\mathbf{16}]/[7] + ([7]/[7]_0)^{r-1} - 1 = 0$ [27] and the rate constant k_1 was calculated from the equation $[7]_0 k_1 t = (1/e^2)\int_2^x (e^x/x)dx$ with $x = 2 - \ln([7]/[7]_0)$ [28].

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