29. d^6 and d^8 Metal Carbonyl Complexes of 7,7-Dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene. Stereoselective Hydroformylation of an [$Fe(CO)_4$(olefin)] Complex

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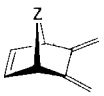
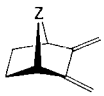
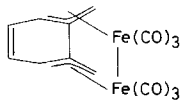
(8.X.84)

Reaction of 7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene (**2**) with various metal carbonyls and their derivatives gave the η^2-$M(CO)_4$ (M = Fe (**17**), Ru (**18**)), η^4-$M(CO)_3$ (M = Fe (**19x**, **19n**), Ru (**20n**)), and η^2-$M(CO)_5$ and η^6-$M(CO)_3$ (M = Cr, Mo, W) complexes. The trigonal bipyramidal η^2-$M(CO)_4$ complexes present an exceptional C_{3v} symmetry at the metal with the C,C-double bond in an axial position. In all the η^2-complexes, this double bond is stereospecifically coordinated by its *exo*-face. The *exo- vs. endo*-η^4-$Fe(CO)_3$ configuration was established by chemical correlation (hydrolysis, hydrogenation) with the corresponding complexes (**24x**, **24n**) of 7,7-dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane (**5**). The relative rates of hydrolysis ($AcOH/H_2O$ 2:1, 50°C) of ligands **2** and **5** and of complexes **19x**, **19n**, **24x**, and **24n** to the corresponding ketones showed an acceleration effect only when the metal is coordinated to the *exo*-face. This was attributed to an F-strain effect on the leaving group of the substrate. Compound **17** was further metallated by [$Fe_2(CO)_9$] giving the bimetallic isomers **21xn** and **21xx**. The endocyclic C,C-double bond of the latter can be stereospecifically hydroformylated (1 atm CO, $AcOH/H_2O$, 25°C) giving **29x** (49%). Hydroformylation of **17** gave the corresponding uncoordinated aldehydes **30x**/**30n** in better yields (76%) but with lower selectivity (3:1). These are the first examples of hydroformylation of an isolated [$Fe(CO)_4$(olefin)] complex.

1. Introduction. – We have reported recently that the endocyclic double bond at C(2),C(3) in 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**) can be selectively coordinated by its *exo*-face in preference to complexation of the exocyclic *s-cis*-butadiene moiety [1]. We have found that η^2-complexes of **1** with d^8-metal carbonyls were susceptible of a formal [4 + 2] addition of a diene on the coordinated C,C-double bond, which represents an unique example of such a reaction [2]. Moreover, the thermal reaction of **1** with [$Fe(CO)_5$] in benzene leads, by O-atom abstraction, to the formation of **4** as minor product [3]. Since the latter reaction may provide a synthetic route to new bimetallic complexes with M–M bonds, we have extended this study to bicyclic trienes and dienes with other Z-bridges. $C(OR)_2$ and CO groups were chosen as Z-bridges since they should be readily eliminated from the complex under suitable conditions. For example, it is







1 Z = O
2 Z = $C(OMe)_2$
2′ Z = $C(OEt)_2$
3 Z = CO

5 Z = $C(OMe)_2$
5′ Z = $C(OEt)_2$
6 Z = CO

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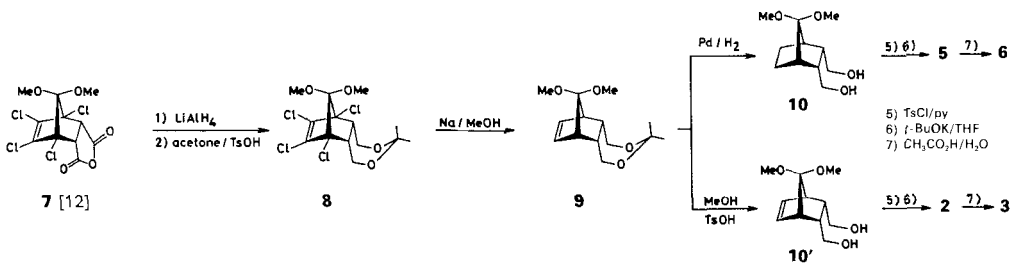
[1]) Abstracted in part from the Ph. D. dissertation of *J. I.*, University of Lausanne, 1985.

known that thermal decomposition of substituted norbornadienone acetals takes place with loss of dialkoxycarbenes [4] [5]. Likewise, loss of CO is observed upon gaz phase photolysis of **3** and **6** giving benzocyclobutene [6] and a diradical [7], respectively. In addition, these groups promote the η_2-coordination of the ligand as evidenced by the Fe and Cr η^2-complexes of 7,7-dimethoxynorborn-2-ene and of *syn*-7-alkoxynorborn-2-enes [8] [9] where the metal is also coordinated to one alkoxy group.

We report in this first communication on the synthesis of ligands **2**, **3**, **5**, and **6**, on the characterization of their d^6 and d^8 metal carbonyl complexes, and on their behaviour towards acid hydrolysis. The latter reaction provides an uncommon example of hydroformylation of a C,C-double bond coordinated to a $Fe(CO)_4$ group. The possibility of obtaining bimetallic complexes with M–M bonds by thermolysis or photolysis of these complexes is under investigation.

2. Results and Discussion. – 2.1. *Synthesis of Ligands* **2**, **3**, **5**, *and* **6**. The reported syntheses of **2′**, **3** [8], **5′** [10], and **6** [9] [10] require as a first step the *Diels-Alder* addition of maleic anhydride to 5,5-diethoxycyclopentadiene in dilute solutions, which is a low-yield reaction. Alternatively, ketone **3** has been obtained in small yields from 2-*exo*,3-*exo*-epoxy-5,6-dimethylidenebicyclo[2.2.1]heptane [11]. We have utilized a different route which provides synthetically viable quantities of **2** and **3** or **5** and **6** in three steps *(Scheme 1)*.

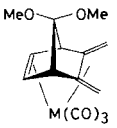
Scheme 1. *Preparation of* **2**, **3**, **5**, *and* **6**



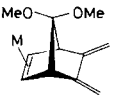
Adduct **7** [12] was first reduced ($LiAlH_4$/THF) into the corresponding diol whose OH groups were subsequently protected by formation of the cyclic acetonide **8** (80%; acetone/TsOH). Dehalogenation of **3** was achieved using *Paddon-Row*'s procedure (Na/MeOH) [13] giving **9** (49%). Recovery of the OH functions was achieved either by catalytic hydrogenation (H_2/Pd) giving **10** (92%) or by transacetalation (MeOH/TsOH) giving 2,2-dimethoxypropane and **10′** (68%). Ligands **2** and **5** were obtained by tosylation (TsCl/pyridine) and elimination (*t*-BuOK/THF) from **10** (47%) and **10′** (26%), respectively, hydrolysis of **2** and **5** (AcOH/H_2O) gave **3** (78%) and **6** (24%), respectively.

2.2. *Synthesis and Characterization of Complexes of* **2**, **5**, *and* **6**. d^6 metal carbonyl η^2-complexes of **2** were obtained by irradiation of **2** with $[M(CO)_6]$ (M = Cr, Mo, W; THF/hexane 1:3) giving **11** (23%), **12** (28%), and **13** (34%), respectively. The corresponding η^6-complexes **14** (16%), **15** (43%), and **16** (31%) were obtained by treatment of **2** with $[M(CO)_3(NH_3)_3]$ [14] in dioxane.

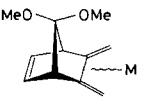
The d^8 metal carbonyl complexes were obtained in the following ways: the reaction of **2** with [Fe(benzalacetone)$(CO)_3$] [15] (toluene, 80°C, 1 atm CO) gave **17** (84%) and **21xx** (11%). The reaction of **2** or **5** with $[Fe_2(CO)_9]$ (1:3, MeOH, 45°C) gave **19n** (45%) and



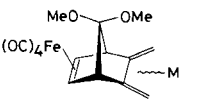
14 M = Cr
15 M = Mo
16 M = W



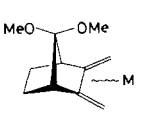
11 M = $Cr(CO)_5$
12 M = $Mo(CO)_5$
13 M = $W(CO)_5$
17 M = $Fe(CO)_4$
18 M = $Ru(CO)_4$



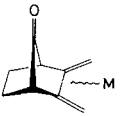
19x M = *exo*-$Fe(CO)_3$
19n M = *endo*-$Fe(CO)_3$
20n M = *endo*-$Ru(CO)_3$



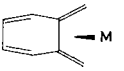
21xn M = *endo*-$Fe(CO)_3$
21xx M = *exo*-$Fe(CO)_3$



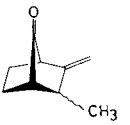
24x M = *exo*-$Fe(CO)_3$
24n M = *endo*-$Fe(CO)_3$
25x M = *exo*-$Ru(CO)_3$
25n M = *endo*-$Ru(CO)_3$



26x M = *exo*-$Fe(CO)_3$
26n M = *endo*-$Fe(CO)_3$
27 M = $Ru(CO)_3$



22 M = $Fe(CO)_3$
23 M = $Ru(CO)_3$



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21xn (1%), or **24x** (21%) and **24n** (33%), respectively. Further reaction of **17** with $[Fe_2(CO)_9]$ in hexane or MeOH gave **21xx** or **21xn** as the major product, respectively. Irradiation of **3** in the presence of $[Fe(CO)_5]$ (pentane, −50°C, pyrex vessel) gave **19n** (22%), **19x** (9%), **17** (3%), and **21xx** (1%) (the η^2- and η^4-coordinations of the ligand occurred in parallel, in contrast with the irradiation of **1** under the same conditions where η^4-coordination follows η^2-coordination). The reaction of **2** or **5** with $[Ru(CO)_3$(1,5-cyclooctadiene)] [16] (benzene, 80°C, 1 atm CO) gave **18** (20%) and **20n** (18%) or **25n** (20%), respectively. The highest yields of the iron complexes of **6** were obtained by hydrolysis of **24x** (65°C, 5 h) or **24n** (65°C, 2 days) in AcOH/H_2O 2:1 giving **26x** (78%) or **26n** (70%), respectively. Unfortunately, hydrolysis of the corresponding Ru complexes **25x** and **25n** led only to demetallation and formation of the hydrogenated ligand **28**. However, the direct reaction of **6** with $[Ru(CO)_3$(1,5-cyclooctadiene)] (benzene, 80°C, 1 atm CO) gave **27** (10%). No complexes of **3** could be isolated. The reaction of **3** with $[Fe(CO)_3$(benzalacetone)] (toluene, 80°C) gave the 5,6-dimethylidenecyclohexa-1,3-diene complex **22** (12%), a known compound obtainable in similar or lower yields by various routes [17] [18][2]). The reaction of **3** with $[Ru(CO)_3$(1,5-cyclooctadiene)] (benzene, 0°C) gave **23** (20%). Complex **23** was identified as $[Ru(CO)_3$(5,6-dimethylidenecyclohexa-1,3-diene)] by comparison with a sample independently prepared by the reaction of $Na_2[Ru(CO)_4]$ and α,α'-dibromo-*ortho*-xylene in NH_3 at −78°C.

The *exo*-coordination of the metal in **11**–**13**, **17**, **18**, and **21** was established by comparison of their proton coupling constants between H–C(1) and H–C(2) ($J_{1,2} \leqslant 1.1$) with that of the free ligand **2** (2.2 Hz). An *exo*-coordination pushes these protons towards the *endo*-face of the endocyclic double bond and hence reduces their mutual coupling relative to that in the free ligand (this effect was ascertained by X-ray analysis in the case of an η^2-$Fe(CO)_4$ complex of **1** [3]). The validity of this method of assignment is further

[2]) We have devised a synthesis of **22** giving better yields than the published procedures: a solution of $(Et_4N)_2[Fe_2(CO)_8]$ (18 mmol) [19] and α,α'-dibromo-*ortho*-xylene (21 mmol) in acetone (70 mmol) was stirred at 0°C for 42 h. Evaporation *i.v.* and chromatography on silica gel with petroleum ether gave **22** (1.8 g, 40%) after sublimation (50°C/10^{-1} Torr).

confirmed by an enhancement of the $J_{1,2}$ coupling constant relative to that in **2** (2.4 (Cr), 3.0 (Mo) and 3.1 Hz (W)) in complexes **14**, **15**, and **16**, respectively, where the *endo*-coordination is unambiguous.

Few [$Cr(CO)_5$(olefin)] complexes have been isolated to date (olefin = *cis*- and *trans*-cyclooctene [20]; tetracyanoethylene [21]; **1** [1] [3]). The new complexes **11–13** are stable in degassed solutions. The stability of the metal-olefin bond in these complexes is probably due in part to a relief of ring strain on complexation [22]. The ^{13}C-NMR coordination shifts ($\Delta\delta$ 56.1 (Cr), 54.9 (Mo), 63.6 ppm (W)) do not vary regularly from Cr to W; it is therefore assumed that factors other than the extent of M-π*(olefin) back-donation are dominant, and the arguments cited in [3] are of limited value.

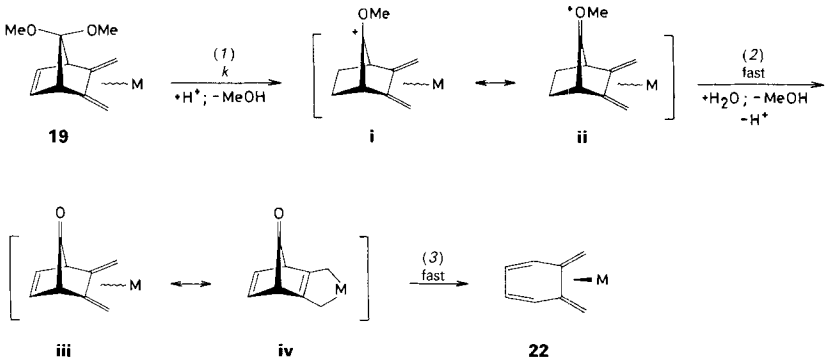
Complex **17** presents 3 IR bands in the ν(CO) region indicating, in the absence of accidental degeneracy, a C_{3v} symmetry at the metal atom. For comparison, the η^2-$Fe(CO)_4$ complex of **1** presents the usual 4 IR bands and has a C_{2v} symmetry (X-ray analysis). The C_{3v} symmetry is confirmed for the parent Ru complex **18** by its ^{13}C-NMR spectrum. Below 0°C, 2 CO resonances (200.8 and 199.3 ppm) are present in a 3:1 integration ratio. These complexes are thus the first examples of trigonal bipyramidal [$M(CO)_4$(olefin)] complexes having a C,C-double bond in an axial rather than an equatorial position [23]. The relative stabilization of the axial isomer is probably due to a steric effect (a molecular model of the equatorial isomer indicates a severe crowding between the methoxy group *syn* to the metal and one axial CO group). Likewise, a C_{3v} symmetry was attributed to the η^2-$Fe(CO)_4$ group in isomers **21xx** and **21xn** since both displayed 6 IR bands in the ν(CO) region rather than 7 (3 of these are due to the $Fe(CO)_3$ group).

Both tetragonal pyramidal isomers **24x** and **24n** are fluxional as they present two ^{13}C-NMR signals in the CO region (1:2 integration ratio) which coalesce upon warming. Coalescence is observed at *ca.* 90 and *ca.* 30°C for **24x** and **24n**, respectively. Line-shape analysis has indicated a large difference in the rates of CO-site exchange (basal *vs.* apical), *e.g.* $k_{333} = 2.68 \cdot 10^3$ (**24x**), $2.00 \cdot 10^4$ s^{-1} (**24n**), and $\Delta G^{\ddagger}_{333} = 14.3 \pm 0.3$ (**24x**), 13.0 ± 0.2 kcal·mol^{-1} (**24n**). Since the methoxy group *syn* to the *s-cis*-butadiene moiety must hinder the CO-site exchange when the $Fe(CO)_3$ group is in the *exo*-position, we attribute the *exo*-configuration to **24x**. The ^{13}C-NMR spectra of the corresponding Ru complexes **25x** and **25n** indicate that the CO exchange is still blocked at 100°C for both isomers (decomposition takes place above 100°C). However, one can tentatively attribute the *endo*-configuration to **25n** from a comparison of the δ_C's of C(7) with those of the Fe isomers (122.0 (**25n**), 122.0 (**24n**); 113.7 (**25x**), 113.6 ppm (**24x**)) and from the similarities in the $\Delta\delta_C$ and $\Delta\delta_H$ coordination shifts of the methoxy group *syn* to the $M(CO)_3$ group (of opposite signs for both pairs of isomers, see *Exper. Part*).

The *exo- vs. endo*-configuration of the $Fe(CO)_3$ group in **19x**, **19n**, **20n**, **21xn** and **21xx** was established by chemical correlation. Catalytic hydrogenation (H_2, Pd/C, AcOEt) of **19x**, **19n**, and **20n** gave **24x**, **24n**, and **25n**, respectively ($\geq 95\%$). Protolysis (AcOH/H_2O 1:2, 25°C) of **21xn** and **21xx** gave **24n** and **24x**, respectively ($> 75\%$).

2.3. *Hydrolysis of Metal-Carbonyl Complexes of* **2** *and* **5**. Hydrolysis of the acetal group of **24x** proceeds cleanly in AcOH/H_2O 2:1 giving **26x** in better yields (78%) than the direct reaction of **6** with $Fe_2(CO)_9$. We have extended this reaction to other complexes of **2** and **5**, and a kinetic study (see *Exper. Part*) under pseudo-first order conditions (AcOH/H_2O 2:1, 50.0 ± 0.1°C) gave the following rate constants k: $(1.9 \pm 0.1) \cdot 10^{-5}$ (**2**→**3**), $(5.7 \pm 0.2) \cdot 10^{-4}$ (**19x**→**22**), $(7.7 \pm 0.3) \cdot 10^{-5}$ (**19n**→**22**), $(7.0 \pm 0.7) \cdot 10^{-6}$ (**5**→**6**),

Scheme 2. *Hydrolysis of* **19**



$(2.4 \pm 0.1) \cdot 10^{-4}$ (**24x**→**26x**), and $(5.5 \pm 0.5) \cdot 10^{-6}$ s^{-1} (**24n**→**26n**). Under the same conditions, all other complexes were demetallated, and **25x** (or **25n**) gave the diastereoisomers of the hydrogenated ketone **28** in 1:1 molar ratio.

The rate-determining step in the hydrolysis of acetals is the formation of an alkoxy carbocation [24]. In the present case, the charge of the carbocation must be delocalized (*Scheme 2,* limiting structures **i**↔**ii**) since the relative-rate constants of reactions **2**→**3** (2.7) and **5**→**6** (1) are comparable (an acceleration effect of *ca.* 10^5 is expected upon introducing an endocyclic double bond in such systems if the positive charge is localized at C(2) [25]). The weak electronic demand on the surroundings caused by the delocalization of charge in the carbocationic intermediate and the resulting weak polarization effect of a remote *endo*-$Fe(CO)_3$ group is reflected in the similar relative-rate constants of reactions **19n**→**22**[3]) and **2**→**3** (4:1) and of reactions **24n**→**26n** and **5**→**6** (0.8:1). In contrast, an *exo*-$Fe(CO)_3$ coordination has a marked acceleration effect as shown by the relative rate constants of reactions **19x**→**22**[3]) and **24x**→**26x** compared with those of the corresponding free ligands (30:1 and 34:1, respectively). We attribute this to an F-strain effect [26] due to the proximity of an *exo*-$Fe(CO)_3$ group which should destabilize the substrate with respect to the cationic intermediate (the C(7),Fe-distance in **24x** is evaluated as 3.3 Å[4]) and as 4.1 Å[5]) in **24n**).

2.4. *Hydroformylation of Iron-Carbonyl Complexes of* **2**. Reactions of aliphatic halides and sulfonates with $Na_2[Fe(CO)_4]$ under CO lead to acyliron(0) intermediate [30] which have also been obtained from *Grignard* reagents or lithio alkanes and $[Fe(CO)_5]$ [31]. Subsequent treatment with H_2O, alcohols, alkyl halides, and AcOH gives the corresponding carboxylic acids, esters, ketones, and aldehydes.

We had noted the formation of an aldehyde as a minor product (10%) during the hydrolysis of **21xx** in $AcOH/H_2O$ 2:1 at room temperature (giving **24x** as major product).

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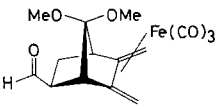
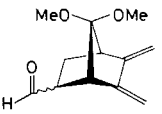
[3]) *Step 3* in *Scheme 2* must be fast compared to *Step 1* as it corresponds to a chelotropic elimination of CO from limiting structure **iv** which resembles that from norbornadienone (known to be fast [27]) and which is favoured by the aromaticity of product **22**.

[4]) From the single-crystal structure of (+)-tricarbonyl[((1*S*,2*R*)-5,6-dimethylidene-2-*exo*-norbornyl *p*-bromobenzoate)]iron [28].

[5]) From the single-crystal structure of tricarbonyl[(2-*exo*-methoxy-5,6-dimethylidenenorbornan-7-*syn*-ol)]iron [29].



29x



30x, 30n

The reaction of **21xx** with CO (1 atm) in $AcOH/H_2O$ 2:1 is complete after 10 min at room temperature giving **24x** (40%) and the stereospecifically hydroformylated product **29x** (49%). The presence of the 2-formyl substituent was evidenced by IR ($\tilde{\nu}$(C=O) = 1730 cm^{-1}) and by NMR spectroscopy (δ_H 9.81 (*s*); δ_{CO} 201.3 ppm (*d*, $J_{C,H}$ = 181 Hz)). Its *exo*-configuration was ascertained by comparison of the proton-coupling constants between H–C(2) and H–C(1) ($J_{1,2} \approx 0$) and between H_{exo}–C(3) and H–C(4) ($J_{3,4}$ = 3.3 Hz). Adding aqueous HCl to a solution of **17** in MeOH/AcONa under CO (1 atm) at room temperature gave a higher yield of hydroformylation (76%) but with lower stereoselectivity since a 3:1 ratio of **30x/30n** was obtained. Iron carbonyls are known to be hydroformylation catalysts [32], however, no other example of direct hydroformylation of an $[Fe(CO)_4$(olefin)] complex has been reported to date.

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Experimental Part

1. General Remarks. – See [32]. IR: *Bruker IFS-113c* spectrometer. Compound **7** was prepared following the published procedure [12].

2. Preparation of Ligands. – 2.1. *7,7-Dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene* (**2**). A solution of **7** (144.8 g, 0.4 mol) in THF (700 ml) was added dropwise to a suspension of $LiAlH_4$ (30.4 g, 0.8 mol) in THF (1300 ml). The mixture was refluxed for 12 h, then hydrolyzed with 10% aq. $(NH_4)_2SO_4$ (250 ml) at 0°. Coagulation of insoluble salts was obtained by heating under reflux for 1 h. Filtration and evaporation *i.v.* gave a brown oil which was dried *i.v.* over P_4O_{10}. TsOH · H_2O (1 g) was added to the oil dissolved in acetone (400 ml)/$CHCl_3$ (600 ml), and H_2O was removed under reflux with *Linde 4A* molecular sieves (3 × 100 ml) in a *Soxhlet* apparatus for 3 days. TsOH was neutralized by NH_3, and the formed ammonium salt was filtered over *Celite*. Evaporation *i.v.* gave *1,9,10,11-tetrachloro-12,12-dimethoxy-5,5-dimethyl-4,6-dioxatricyclo[7.2.1.0^{2,8}]dodec-10-ene* (**8**) as a brown oil (125 g, 80%) which crystallized from MeOH at –25°. M.p. 69–70°. IR (KBr): 2990, 2950, 2885, 2850, 1602, 1485, 1450, 1380, 1370, 1280, 1235, 1190, 1160, 1115, 1090, 1050, 930, 910, 890, 840. ^{1}H-NMR ($CDCl_3$): 4.2–3.6 (*m*, 4H); 3.57, 3.52 (2*s*, 6H); 3.2–2.9 (*m*, 2H); 1.33 (*s*, 6H). MS: 375(2), 355(3), 299(34), 253(100). Anal. calc. for $C_{14}H_{18}Cl_4O_4$ (392.10): C 42.95, H 4.63; found: C 42.88, H 4.63.

Na pellets (368 g, 16 mol) were added portionwise to a soln. of **8** (125 g, 0.32 mol) in MeOH (1400 ml) and refluxed for 3 h. Excess Na was filtered, and the filtrate was poured into ice/H_2O (3000 ml). The precipitate was filtered, washed with H_2O, and redissolved in CH_2Cl_2. Drying over $MgSO_4$, filtration, evaporation *i.v.*, and recrystallization from MeOH at –25° gave *12,12-dimethoxy-5,5-dimethyl-4,6-dioxatricyclo[7.2.1.0^{2,8}]dodec-10-ene* (**9**) as colourless crystals (40 g, 49%). M.p. 136°. IR (KBr): 2990, 2975, 2960, 2940, 2830, 1480, 1440, 1385, 1360, 1280, 1235, 1220, 1195, 1180, 1165, 1140, 1125, 1105, 1080, 1060, 1040, 1020, 1005, 970, 950, 930, 890, 845, 835. ^{1}H-NMR ($CDCl_3$): 6.15 (*dd*, 2H); 3.9–3.5 (*m*, 4H); 3.22–3.12 (2*s*, 6H); 3.0–2.7 (*m*, 4H); 1.35 (*s*, 6H). MS: 254 (6), 196 (53) 165 (100), 151 (45). Anal. calc. for $C_{14}H_{22}O_4$ (254.32): C 66.10, H 8.61; found: C 66.11, H 8.71.

A soln. of **9** (38.1 g, 0.15 mol) and TsOH (1.9 g, 10 mmol) in MeOH (1600 ml) was heated, and the azeotropic dimethoxypropane/MeOH was distilled until complete disappearance of **9** (TLC). Addition of a sat. soln. of NH_3 in MeOH (50 ml) and evaporation *i.v.* gave a residue which was taken up in Et_2O (500 ml)/H_2O (50 ml) and extracted with Et_2O (3 × 200 ml). The org. extracts were dried over $MgSO_4$ and evaporated *i.v.* giving the corresponding diol **10′** (22 g, 68%) as a yellow oil. The oil was dissolved in anh. pyridine (100 ml) and added

dropwise to a soln. of TsCl (190 g, 1 mol) in pyridine (600 ml) at 0°. After standing at −25° for 3 days, the mixture was poured under vigorous stirring into H_2O (1500 ml) at 0°. The precipitate was decanted, washed with H_2O, and dissolved in Et_2O (500 ml). The soln. was washed with H_2O (4 × 500 ml), dried over $MgSO_4$, and evaporated *i.v.* The crude bis(*p*-toluenesulfonate) (containing *ca.* 10% of TsCl) was dissolved in THF (200 ml), and the soln. was divided into 2 equal portions. Each portion was separately added portionwise to a soln. of *t*-BuOK (22.4 g, 0.2 mol) in THF (200 ml) at 0°. After heating at 45° for 12 h, the solns. were poured into ice/H_2O (3000 ml) and extracted with petroleum ether (3 × 500 ml). The extracts were washed with H_2O, dried over $MgSO_4$, and evaporated *i.v.* Sublimation at 45°/$5 \cdot 10^{-2}$ Torr on a cold finger (−40°) gave **2** as colourless crystals (4.8 g, 26%). M.p. 47–48°. IR (KBr): 3060, 2990,2930, 2830, 1275, 1195, 1100, 1070, 1040, 880, 810, 790. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.24 (*dd*, $J_{1,2} \approx J_{1,3} = 2.2$, H–C(2), H–C(3)); 5.44, 5.10 (2*s*, CH_2=C(5), CH_2=C(6)); 3.44 (*dd*, H–C(1), H–C(4)); 3.28, 3.21 (2*s*, 2 CH_3O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 114.2 (*s*, C(5), C(6)); 133.8 (*d*, $J = 174$, C(2), C(3)); 119.6 (*s*, C(7)); 102.8 (*t*, $J = 158$, CH_2=): 54.8 (br. *d*, $J = 149$, C(1), C(4)); 51.7, 50.3 (2*q*, $J = 142$, CH_3O). MS: 178 (64, M^+), 163 (55), 147 (73), 135 (53), 131 (51), 104 (100). Anal. calc. for $C_{11}H_{14}O_2$ (178.23): C 74.13, H 7.92; found: C 74.08, H 7.87.

2.2. *5,6-Dimethylidenebicyclo[2.2.1]hept-2-en-7-one* (**3**). *Roth*'s method starting with **2′** [17] was modified in the following way: A soln. of **2** (1.78 g, 10 mmol) in AcOH/H_2O 2:1 (200 ml) was heated under Ar at 65° for 3 h, then extracted with CH_2Cl_2 (3 × 200 ml). The extracts were washed with aq. sat. $NaHCO_3$ (3 × 200 ml), then H_2O (2 × 100 ml), dried over $MgSO_4$, and evaporated *i.v.* Chromatography on silica gel with pentane/CH_2Cl_2 1:1 and evaporation *i.v.* below 30° gave **3** as a colourless liquid (625 mg, 47%) and **2** (712 mg) which can be recycled. IR, MS: see [17]. ^{1}H-NMR ($CDCl_3$): 6.65 (*dd*, $J_{2,1} \approx J_{3,1} = 2.4$, H–C(2), H–C(3)); 5.38, 5.09 (2*s*, CH_2=C(5), CH_2=C(6)); 3.56 (*dd*, H–C(1), H–C(4)). ^{13}C-NMR ($CDCl_3$): 198.9 (*s*, C=O); 141.7 (*s*, C(5), C(6)); 133.1 (*d*, $J = 177$, C(2), C(3)); 104.3 (*t*, $J = 160$, CH_2=); 57.4 (br. *d*, $J = 156$, C(1), C(4)).

2.3. *7,7-Dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane* (**5**) *and 2,3-Dimethylidenebicyclo[2.2.1]heptan-7-one* (**6**). A suspension of **9** (40.7 g, 0.16 mol) and 10% Pd/C (1.5 g) in MeOH (500 ml) was stirred under H_2 (3.5 atm) for 3 days, then filtered, and evaporated *i.v.* Toluene was added to eliminate residual MeOH by azeotropic distillation giving *7,7-dimethoxybicyclo[2.2.1]heptane-2,3-bismethanol* (**10**) as colourless crystals (31.8 g, 93%). M.p. 92°. IR (Nujol): 3260, 3150, 1325, 1310, 1295, 1250, 1230, 1200, 1160, 1145, 1130, 1095, 1065, 1025, 1020, 990, 800. ^{1}H-NMR ($CDCl_3$): 4.05, 3.66 (2*m*, 4H); 3.31, 3.26 (2*s*, 6H); 2.52 (*m*, 2H); 2.10 (br. *s*, 2 OH); 1.60 (*m*, 2H); 1.36 (*dd*, 2H). MS: 216 (8), 199 (9), 198 (3), 186 (14), 185 (100). Anal. calc. for $C_{11}H_{20}O_4$ (216.28): C 61.11, H 9.23; found: C 61.09, H 9.26.

Tosylation and elimination as above (*2.1*) starting with **10** gave **5** (12.3 g, 47%) as a colourless deliquescent solid. M.p. 43–45°. IR (KBr): 2960, 2860, 2830, 1485, 1470, 1460, 1370, 1320, 1300, 1260, 1230, 1200, 1190, 1140, 1090, 1080, 1040, 1020, 1000, 940, 910, 820. ^{1}H-NMR ($CDCl_3$): 5.23, 4.83 (2*s*, CH_2=C(2), CH_2=C(3)); 3.25, 3.23 (2*s*, 2 CH_3O); 2.73 (*m*, H–C(1), H–C(4)); 1.94 (*m*, H_{exo}–C(5), H_{exo}–C(6)); 1.37 (*m*, H_{endo}–C(5), H_{endo}–C(6)); $J(5_{exo},5_{endo}) = 14.5$, $J(1,6_{exo}) = 2.6$, $J(5_{exo},6_{endo}) = 4.2$, $J(1,5_{exo}) = 1.8$. ^{13}C-NMR ($CDCl_3$): 149.8 (*s*, C(2), C(3)); 112.0 (*s*, C(7)); 101.4 (*t*, $J = 159$, CH_2=); 50.8, 49.7 (2*q*, $J = 142$, CH_3O); 48.1 (br. *d*, $J = 144$, C(1), C(4)); 26.7 (*t*, $J = 134$, C(5), C(6)). MS: 180 (100, M^+), 165 (15), 149 (15).

Hydrolysis of **5** (60°, 2 days) as above (*2.1*) gave **6** (0.32 g, 24%) as a colourless liquid. IR, MS: see [17]. ^{1}H-NMR ($CDCl_3$): 5.39, 4.95 (2*s*, CH_2=C(2), CH_2=C(3)); 2.69 (*dd*, H–C(1), H–C(4)); 2.08 (*m*, H_{exo}–C(5), H_{exo}–C(6)); 1.73 (*dd*, H_{endo}–C(5), H_{endo}–C(6)); $J(5_{exo},5_{endo}) = 12.0$, $J(1,6_{exo}) = 2.1$, $J(5_{exo},6_{endo}) = 5.1$, $J(1,5_{exo}) = 2.1$. ^{13}C-NMR ($CDCl_3$): 204.1 (*s*, C=O); 145.6 (*s*, C(2), C(3)); 103.3 (*t*, $J = 159$, CH_2=); 49.8 (*d*, $J = 152$, C(1), C(4)); 23.9 (*t*, $J = 137$, C(5), C(6)).

3. Preparation of Complexes. – 3.1. *Preparation of* **11**–**13**. A soln. of **2** (1.08 g, 5.6 mmol) and $Cr(CO)_6$ (1.45 g), $Mo(CO)_6$ (1.77 g) or $W(CO)_6$ (2.36 g), resp., in THF/hexane 1:3 (200 ml) was irradiated (high-pressure Hg lamp *Philips HPK-125, Pyrex* vessel) under Ar at −20° for 8 h. Evaporation *i.v.* left a residue which was chromatographed on silica gel with CH_2Cl_2/hexane 3:1. Recrystallization from hexane/CH_2Cl_2 at −25° gave **11** (0.48 g, 23%), **12** (0.64 g, 28%), and **13** (0.92 g, 34%), resp.

Pentacarbonyl[(1R,2S,3R,4S)-2,3-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]chromium (**11**). Orange crystals, m.p. 155°. IR (hexane): 2040, 1945, 1925, 1890 (CO). ^{1}H-NMR (C_6D_6, 360 MHz): 5.34, 4.91 (2*s*, CH_2=C(5), CH_2=C(6)); 4.29 (*dd*, $J_{1,2} = J_{1,3} = 1.0$, H–C(2), H–C(3)); 2.93 (*dd*, H–C(1), H–C(4)); 2.49 (*s*, 2 CH_3O). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 228.9, 225.0, 222.8 (3*s*, CO); 145.5 (*s*, C(5), C(6)); 113.3 (*s*, C(7)); 105.8 (*t*, $J = 159$, CH_2=); 77.7 (*d*, $J = 180$, C(2), C(3)); 60.7, 52.0 (2*q*, $J = 146$, 143, CH_3O); 52.5 (br. *d*, $J = 151$, C(1), C(4)). MS (^{52}Cr): 342 (10, $M^+ - CO$), 314 (7), 286 (13), 258 (71), 230 (100, $M^+ - 5CO$). Anal. calc. for $C_{16}H_{14}CrO_7$ (370.27): C 51.90, H 3.81; found: C 51.55, H 4.08.

Pentacarbonyl[(1R,2S,3R,4S)-2,3-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]molybdenum (**12**). Yellow crystals, m.p. 165° (dec.). IR (hexane): 2040, 1942, 1932, 1885 (CO). ^{1}H-NMR (C_6D_6): 5.32, 4.89 (2*s*, 4H); 4.39 (*dd*, $J_{1,2} \approx J_{1,3}$ = 1.1, 2H); 2.95 (*dd*, 2H); 2.69, 2.58 (2*s* 6H). ^{13}C-NMR ($CDCl_3$): 219.9, 218.2, 216.0, 210.8 (4*s*, ratios 1:1:1:2, CO); 145.7, 114.5 (2*s*); 105.7 (*t*, *J* = 159); 78.9 (*d*, *J* = 180); 61.9, 52.0 (2*q*, *J* = 146, 144); 53.3 (*d*, *J* = 151). MS (^{96}Mo): 414 (< 5, M^+), 386 (96), 358 (10), 330 (< 5), 302 (< 5), 274 (41), 178 (63), 104 (100). Anal. calc. for $C_{16}H_{14}MoO_7$ (414.22): C 46.39, H 3.42; found: C 46.21, H 3.47.

Pentacarbonyl[(1R,2S,3R,4S)-2,3-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]tungsten (**13**). Yellow crystals, m.p. 160° (dec.). IR (hexane): 2035, 1940, 1930, 1885 (CO). ^{1}H-NMR (C_6D_6): 5.33, 4.87 (2*s*, 4H); 4.01 (br. *s*, $J_{1,2} \approx J_{1,3}$ < 0.5, 2H); 2.87 (br. *s*, 2H); 2.81, 2.57 (2*s*, 6H). ^{13}C-NMR ($CDCl_3$): 213.8, 208.7, 205.0, 191.2 (4*t*, $J_{C,W}$ = 154, 185, 122, 127, ratios 1:1:2:1, CO); 146.2, 116.2 (2*s*); 105.8 (*t*, *J* = 159); 70.2 (*d*, *J* = 181); 63.6, 52.4 (2*q*, *J* = 147, 144); 53.0 (br. *d*, *J* = 151). MS (^{184}W): 474 (34, M^+ – CO), 390 (7), 362 (90), 178 (100). Anal. calc. for $C_{16}H_{14}O_7W$ (502.13): C 38.27, H 2.81; found: C 37.65, H 2.95.

3.2. *Preparation of* **14–16**. A soln. of **2** (540 mg, 3 mmol) and $[Cr(NH_3)_3(CO)_3]$ (748 mg, 4 mmol), $[Mo(NH_3)_3(CO)_3]$ (924 mg) or $[W(NH_3)_3(CO)_3]$ (1.28 g), resp., in anh. peroxide-free dioxane (40 ml) was heated under Ar at 100° for 8 h. The solvent was evaporated *i.v.*, and the residue was chromatographed on degassed silica gel with hexane/AcOEt 9:1. Recrystallization from hexane/CH_2Cl_2 at −25° gave **14** (240 mg, 25%), **15** (460 mg, 43%) or **16** (410 mg, 31%), resp. Small amounts of complexes **11–13** were obtained in yields depending on flow-rate of Ar (5–15%).

Tricarbonyl[(1R,2R,3S,4S,5S,6R)-2,3-η:C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]chromium (**14**). Orange crystals, m.p. 130–132°. IR (hexane): 2060, 1980, 1950 (CO). ^{1}H-NMR ($CDCl_3$): 3.45, 3.37 (2*dd*, $J_{1,2} \approx J_{1,3}$ = 2.4, H–C(1), H–C(2), H–C(3), H–C(4)); 3.33, 3.32 (2*s*, 2 CH_3O); 3.10, 1.27 (2*d*, J_{gem} = 1.9, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 240.8, 234.1 (2*s*, ratio 2:1, CO); 124.3 (*s*, C(7)); 77.0 (*s*, C(5), C(6)); 63.5 (*t*, *J* = 163, CH_2=); 51.9, 51.1 (2*q*, *J* = 143, CH_3O); 47.8 (br. *d*, *J* = 150, C(1), C(4)); 46.2 (*d*, *J* = 183, C(2), C(3)). MS: 314 (23, M^+), 286 (51), 258 (34), 230 (100), 178 (16), 104 (42). Anal. calc. for $C_{14}H_{14}CrO_5$ (314.25): C 53.50, H 4.49; found: C 53.89, H 4.88.

Tricarbonyl[(1R,2R,3S,4S,5S,6R)-2,3-η:C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]molybdenum (**15**). Orange crystals, m.p. 130° (dec.). IR (hexane): 1992, 1932, 1910 (CO). ^{1}H-NMR ($CDCl_3$): 3.46, 3.35 (2*dd*, $J_{1,2}$ = 3.0, $J_{1,3}$ = 2.1, 4H); 3.33, 3.32 (2*s*, 6H); 3.47, 1.74 (2*d*, J_{gem} = 1.8, 4H). ^{13}C-NMR ($CDCl_3$): 227.9, 219.3 (2*s*, ratio 2:1); 124.3, 80.7 (2*s*); 61.1 (*t*, *J* = 163), 51.9, 51.0 (2*q*, *J* = 143); 48.7 (br. *d*, *J* = 154); 47.8 (*d*, *J* = 182). MS: 358 (37, M^+), 350 (30), 302 (37), 274 (100), 178 (10), 104 (24). Anal. calc. for $C_{14}H_{14}MoO_5$ (358.20): C 46.94, H 3.94; found: C 46.81, H 3.97.

Tricarbonyl[(1R,2R,3S,4S,5S,6R)-2,3-η:C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]tungsten (**16**). Red crystals, m.p. 139°. IR (hexane): 1990, 1930, 1900 (CO). ^{1}H-NMR ($CDCl_3$): 3.46, 3.10 (2*dd*, $J_{1,2}$ = 3.1, $J_{1,3}$ = 1.9, 4H); 3.33 (*s*, 6H); 3.37, 1.46 (2*s*, J_{gem} = 2.3, 4H). ^{13}C-NMR ($CDCl_3$): 220.7, 210.4 (2*t*, $J_{C,W}$ = 171, 156, ratio 2:1); 126.4, 73.8 (2*s*); 54.2 (*t*, *J* = 163); 51.8, 51.0 (2*q*, *J* = 142, 143); 47.4, 33.9 (2 br. *d*, *J* = 154, 180). MS: 446 (100, M^+), 418 (20), 362 (36), 178 (10), 104 (15). Anal. calc. for $C_{14}H_{14}O_5W$ (446.11): C 37.69, H 3.16; found: C 37.68, H 3.25.

3.3. *Preparation of Iron Complexes.* a) A soln. of **2** (1.07 g, 6 mmol) and [Fe(benzalacetone)$(CO)_3$] [15] (3.42 g, 12 mmol) in toluene (250 ml) was stirred at 80° under CO (1 atm) for 24 h. Evaporation *i.v.* and chromatography on degassed silica gel with petroleum ether/AcOEt 9:1 gave **21xx** (0.32 g, 11%) and **17** (1.75 g, 84%) after recrystallization from MeOH at −25°.

b) A suspension of **2** (1.78 g, 10 mmol) and $[Fe_2(CO)_9]$ (10.8 g, 30 mmol; added portionwise) in MeOH (50 ml) was stirred at 45° under Ar for 5 days. Evaporation *i.v.* and chromatography on degassed silica gel with petroleum ether/AcOEt 9:1 gave **21xn** (60 mg, 1%) and **19n** (1.5 g, 48%) after recrystallization from MeOH at −25°. The same procedure as for **19n** starting with **5** (1.8 g, 10 mmol) gave **24x** (0.66 g, 21%) and **24n** (1.05 g, 33%).

c) Irradiation (high pressure Hg lamp *Philips HPK-125*, −60°, 8 h, *Pyrex*) of a soln. of **2** (1.07 g, 6 mmol) and $[Fe(CO)_5]$ (14.1 g, 72 mmol; added portionwise) in pentane (250 ml), then evaporation *i.v.*, and chromatography on silica gel with petroleum ether/AcOEt 9:1 gave **21xx** (45 mg, 1%), **17** (68 mg, 3%), **19x** (0.18 g, 9%), and **19n** (0.42 g, 22%).

d) A solution of **24x** (0.8 g, 2.5 mmol) in AcOH/H_2O 2:1 was stirred at 65° under Ar for 5 h, then was poured into H_2O (500 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The org. extracts were washed with aq. sat. $NaHCO_3$ (3 × 50 ml) and dried over $MgSO_4$. Evaporation *i.v.* and crystallization from hexane/CH_2Cl_2 at −25° gave **26x** (0.54 g, 78%). The same procedure as for **26x** starting with **24n** (60°, 2 days) gave **26n** (0.48 g, 70%).

Tetracarbonyl[(1R,2S,3R,4S)-2,3-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron (**17**). Red crystals, m.p. 47–49°. IR (hexane): 2040, 1963, 1955 (CO). ^{1}H-NMR ($CDCl_3$): 5.40, 5.06 (2*s*, CH_2=C(5), CH_2=C(6)); 3.51 (*s*, $J_{1,2}$ < 0.5, H–C(2), H–C(3)); 3.06 (*s*, 2 CH_3O); 2.85 (*s*, H–C(1), H–C(4)). ^{13}C-NMR

($CDCl_3$): 213.5 (*s*, CO); 147.8 (*s*, C(5), C(6)); 114.7 (*s*, C(7)); 103.5 (*t*, J = 159, CH_2=); 61.0, 52.1 (2*q*, J = 147, 144, CH_3O); 51.6 (*d*, J = 173, C(2), C(3)); 51.1 (*d*, J = 149, C(1), C(4)). MS: 346 (29, M^+), 318 (23), 290 (52), 262 (100), 234 (50), 178 (70). Anal. calc. for $C_{15}H_{14}FeO_7$ (346.12): C 52.05, H 4.08; found: C 51.91, H 3.99.

Tricarbonyl[(1R,4S,5S,6R)-C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron (**19x**). Yellow oil. IR (hexane): 2055, 1980, 1965 (CO). ^{1}H-NMR ($CDCl_3$): 6.97 (*dd*, $J_{1,2} \approx J_{1,3}$ = 2.2, H–C(2), H–C(3)); 3.55 (*dd*, H–C(1), H–C(4)); 3.18, 3.15 (2*s*, 2 CH_3O); 1.75, 0.18 (2*d*, J_{gem} = 2.7, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 215.4, 209.6 (2*s*, ratio 1:2, CO); 142.3 (*d*, J = 180, C(2), C(3)); 123.6, 116.4 (2*s*, C(7), C(5), C(6)); 53.4 (br. *d*, J = 148, C(1), C(4)); 51.3, 50.2 (2*q*, J = 142, 143, CH_3O); 31.3 (*t*, J = 160, CH_2=). MS: 318 (< 5, M^+), 290 (37), 262 (92), 234 (47), 178 (100). Anal. calc. for $C_{14}H_{14}FeO_5$ (318.11): C 52.86, H 4.44; found: C 52.73, H 4.49.

Tricarbonyl[(1R,4S,5R,6S)-C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron (**19n**). Yellow crystals, m.p. 85°. IR (hexane): 2060, 1978, 1967 (CO). ^{1}H-NMR ($CDCl_3$): 6.62, 3.63 (2*dd*, $J_{1,2} \approx J_{1,3}$ = 2.5, 4H); 3.27, 3.24 (2*s*, 6H); 2.18, 0.90 (2*d*, J_{gem} = 2.6, 4H). ^{13}C-NMR ($CDCl_3$): 211.0 (br. *s*, CO); 138.7 (*d*, J = 176); 133.2, 113.8 (2*s*); 52.4 (br. *d*, J = 150); 51.6, 51.1 (2*q*, J = 143); 38.8 (*t*, J = 160). MS: 290 (36, $M^+ - CO$), 262 (80), 234 (100), 178 (97), 160 (69), 104 (39). Anal. calc. for $C_{14}H_{14}FeO_5$ (318.11): C 52.86, H 4.44; found: C 52.56, H 4.44.

*Heptacarbonyl-*cis*-μ-[(1R,2S,3R,4S,5R,6S)-2,3-η:C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo-[2.2.1]hept-2-ene)]-diiron* (**21xx**). Orange crystals, m.p. 150°. IR (hexane): 2053, 2041, 1985, 1972, 1968, 1963 (CO). ^{1}H-NMR ($CDCl_3$): 3.84 (*s*, $J_{1,2}$ < 0.5, H–C(2), H–C(3)); 3.22, 3.03 (2*s*, 2 CH_3O); 2.75 (*s*, H–C(1), H–C(4)); 1.56, 0.46 (2*d*, J_{gem} = 2.8, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 211 (br. *s*, CO); 211.7, 211.4 (2*s*, CO); 118.5 (*s*, C(7)); 111.4 (*s*, C(5), C(6)); 61.8, 51.6 (2*q*, J = 147, 144, CH_3O); 56.1 (*d*, J = 173, C(2), C(3)); 47.4 (*d*, J = 156, C(1), C(4)); 31.7 (*t*, J = 161, CH_2=). MS: 430 (33, $M^+ - 2$ CO), 402 (100), 374 (41), 346 (43), 318 (65), 290 (54). Anal. calc. for $C_{18}H_{14}Fe_2O_9$ (486.00): C 44.49, H 2.90; found: C 44.58, H 3.05.

*Heptacarbonyl-*trans*-μ-[(1R,2S,3R,4S,5S,6R)-2,3-η:C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo-[2.2.1]hept-2-ene)]diiron* (**21xn**). Red crystals, m.p. 97–99°. IR (hexane): 2053, 2040, 1986, 1975, 1968, 1958 (CO). ^{1}H-NMR ($CDCl_3$): 3.68 (*s*, $J_{1,2}$ < 0.5, 2H); 3.15, 3.12 (2*s*, 6H); 2.99 (*s*, 2H); 2.07, 0.65 (2*d*, J_{gem} = 2.6, 4H). ^{13}C-NMR ($CDCl_3$): 213.0 (*s*), 211.0 (br. *s*); 123.6, 116.8 (2*s*); 61.8, 53.2 (2*q*, J = 147, 144); 56.7, 48.9 (2*d*, J = 180, 152); 35.7 (*t*, J = 160). MS: 458 (7, $M^+ - CO$), 430 (33), 402 (48), 374 (14), 346 (36), 318 (55), 290 (98), 234 (100), 178 (58), 104 (19). Anal. calc. for $C_{18}H_{14}Fe_2O_9$ (486.00): C 44.49, H 2.90; found: C 44.15, H 3.11.

Tricarbonyl[(1R,2R,3S,4S)-C,2,3,C-η-(7,7-dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane)]iron (**24x**). Yellow oil. IR (hexane): 2060, 1975, 1963 (CO). ^{1}H-NMR ($CDCl_3$): 3.26, 3.12 (2*s*, 2 CH_3O); 2.81 (*dd*, $J(1,6_{exo})$ = 2.0, $J(1,5_{exo})$ = 1.4, H–C(1), H–C(4)); 2.22 (*m*, $J(5_{exo},5_{endo})$ = 11.6, $J(5_{exo},6_{endo})$ = 3.9, H_{exo}–C(5), H_{exo}–C(6)); 1.41 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 1.70, 0.05 (2*d*, J_{gem} = 2.5, CH_2=C(2), CH_2=C(3)). ^{13}C-NMR ($CDCl_3$): 215.7, 209.8 (2*s*, ratio 1:2, CO); 113.6 (*s*, C(7)); 108.2 (*s*, C(2), C(3)); 50.6, 49.4 (2*q*, J = 143, CH_3O); 44.5 (*d*, J = 149, C(1), C(4)); 30.1 (*t*, J = 159, CH_2=); 26.4 (*t*, J = 137, C(5), C(6)). MS: 320 (< 1, M^+); 292 (14), 264 (84), 236 (100), 180 (6). Anal. calc. for $C_{14}H_{16}FeO_5$ (320.12): C 52.53, H 5.04; found: C 52.58, H 5.13.

Tricarbonyl[(1R,2S,3R,4S)-C,2,3,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]heptane)]iron (**24n**). Yellow crystals, m.p. 76°. IR (hexane): 2050, 1973, 1958 (CO). ^{1}H-NMR ($CDCl_3$): 3.33, 3.29 (2*s*, 6H); 2.93 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 2.0, H–C(1), H–C(4)); 2.24 (*m*, $J(5_{exo},5_{endo})$ = 12.3, $J(5_{exo},6_{endo})$ = 4.6); 1.30 (*dd*, 2H); 1.87, 0.47 (2*d*, J_{gem} = 2.8, 4H). ^{13}C-NMR ($CDCl_3$): 211.0 (br. *s*, CO); 122.0, 119.7 (2*s*); 51.8, 49.5 (2*q*, J = 143); 45.6 (*d*, J = 146); 33.5, 30.4 (2*t*, J = 157, 134). MS: 320 (5, M^+), 292 (32), 264 (100), 236 (69), 180 (11). Anal. calc. for $C_{14}H_{16}FeO_5$ (320.12): C 52.53, H 5.04; found: C 52.47, H 5.05.

Tricarbonyl[(1R,2R,3S,4S)-C,2,3,C-η-(2,3-dimethylidenebicyclo[2.2.1]heptan-7-one)]iron (**26x**). Yellow crystals, m.p. 138°. IR (hexane): 2060, 1982, 1979 (CO), 1785 (C=O). ^{1}H-NMR ($CDCl_3$): 2.87 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 1.8, H–C(1), H–C(4)); 2.32 (*m*, $J(5_{exo},5_{endo})$ = 12.3, $J(5_{exo},6_{endo})$ = 5.1, H_{exo}–C(5), H_{exo}–C(6)); 1.82 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 2.09, 0.43 (2 *d*, J_{gem} = 3.1, CH_2=C(2), CH_2=C(3)). ^{13}C-NMR ($CDCl_3$): 215.0 (br. *s*, CO); 201.4 (*s*, C(7)); 106.5 (*s*, C(2), C(3)); 47.8 (*d*, J = 156, C(1), C(4)); 35.4 (*t*, J = 161, CH_2=); 23.0 (*t*, J = 138, C(5), C(6)). MS: 274 (14, M^+), 246 (42), 218 (58), 190 (57), 162 (100), 134 (12). Anal. calc. for $C_{12}H_{10}FeO_4$ (274.06): C 52.59, H 3.67; found: C 52.76, H 3.63.

Tricarbonyl[(1R,2S,3R,4S)-C,2,3,C-η-(2,3-dimethylidenebicyclo[2.2.1]heptan-7-one)]iron (**26n**). Yellow crystals, m.p. 106°. IR (hexane): 2060, 1982, 1970 (CO), 1800 (C=O). ^{1}H-NMR ($CDCl_3$): 3.03 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 2.0, 2H); 2.31 (*m*, $J(5_{exo},5_{endo})$ = 12.0, $J(5_{exo},6_{endo})$ = 5.1, 2H); 1.25 (*m*, 2H); 2.06, 0.60 (2*d*, J_{gem} = 3.0, 4H). ^{13}C-NMR ($CDCl_3$): 208.9, 201.0, 115.1 (3*s*); 47.3 (*d*, J = 155); 34.4, 27.8 (2*t*, J = 160, 138). MS: 274 (17, M^+), 246 (85), 218 (93), 190 (78), 162 (100), 134 (11). Anal. calc. for $C_{12}H_{10}FeO_4$ (274.06): C 52.59, H 3.67; found: C 52.62, H 3.77.

3.4. *Preparation of Ru Complexes.* A soln. of **2** (1.07 g, 6 mmol) and [Ru(CO_3)(1,5-cyclooctadiene)] [16] (2.35 g, 8 mmol) in benzene (10 ml) was stirred at 80° under CO (1 atm) for 15 h. Evaporation *i.v.* and chromatography on

silica gel with petroleum ether/AcOEt 9:1 gave **18** (0.46 g, 20%) and **20n** (0.40 g, 18%) after recrystallization from hexane or MeOH at −25°, resp.

The same procedure as for **18** starting with **3** (6 mmol, 4 h) or **6** (6 mmol, 15 h) gave **23** (0.35 g, 20%) and **27** (0.192 g, 10%) after sublimation (50°/5·10^{-2} Torr).

Starting with **5** (6 mmol, 15 h) gave **25x** (0.75 g, 34%) and **25n** (0.44 g, 20%) after recrystallization from MeOH at −25°.

Tetracarbonyl[(1R,2S,3R,4S)-2,3-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]ruthenium (**18**). Yellow crystals, m.p. 76–77°. IR (hexane): 2053, 1976, 1970 (CO). ^{1}H-NMR ($CDCl_3$): 5.35, 5.00 (2*s*, CH_2=C(5), CH_2=C(6)); 3.39, 3.15 (2*s*, 2 CH_3O); 2.99 (*s*, $J_{1,2}$ < 0.5, H–C(2), H–C(3)); 2.79 (*s*, H–C(1), H–C(4)). ^{13}C-NMR ($CDCl_3$): 200.5 (*s*, CO); 149.1 (*s*, C(5), C(6)); 116.2 (*s*, C(7)); 102.9 (*t*, *J* = 158, CH_2=); 62.3, 52.3 (2*q*, *J* = 147, 144, CH_3O); 51.4 (br. *d*, *J* = 148, C(1), C(4)); 42.3 (*d*, *J* = 171, C(2), C(3)). MS (^{102}Ru): 364 (16, M^+ − CO), 336 (83), 308 (88), 262 (7), 234 (69), 206 (100), 178 (26). Anal. calc. for $C_{15}H_{14}O_6Ru$ (391.34): C 46.04, H 3.61; found: C 46.38, H 3.94.

Tricarbonyl[(1R,4S,5R,6S)-C,5,6,C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]ruthenium (**20n**). Colourless crystals, m.p. 78°. IR (hexane): 2070, 1990, 1980 (CO). ^{1}H-NMR ($CDCl_3$): 6.51 (*dd*, $J_{1,2} \approx J_{1,3}$ = 2.4, H–C(2), H–C(3)); 3.54 (*dd*, H–C(1), H–C(4)); 3.27, 3.22 (2*s*, 2 CH_3O); 2.17, 1.12 (2*d*, J_{gem} = 2.7, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 201.5, 195.2 (2*s*, ratio 1:2, CO); 139.8 (*d*, *J* = 179, C(2), C(3)); 134.0 (*s*, C(7)); 117.6 (*s*, C(5), C(6)); 52.6 (*d*, *J* = 150, C(1), C(4)); 51.4, 51.1 (2*q*, *J* = 143, CH_3O); 32.0 (*t*, *J* = 158, CH_2=). MS: 364 (< 5, M^+), 336 (100), 308 (43), 280 (49), 234 (41), 206 (97), 178 (32), 104 (25). Anal. calc. for $C_{14}H_{14}O_5Ru$ (363.37): C 46.28, H 3.88; found: C 46.42, H 3.89.

Tricarbonyl[(C,5,6,C-η-(5,6-dimethylidenecyclohexa-1,3-diene)]ruthenium (**23**). Colourless crystals, m.p. 37–38°. IR (hexane): 2080, 1995 (CO). ^{1}H-NMR (CD_2Cl_2): 7.5–7.2 (*m*, H–C(1), H–C(2), H–C(3), H–C(4)); 2.46, 0.56 (2*d*, J_{gem} = 4.0, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 201.8, 193.4 (2*s*, ratio 1:2, CO); 131.8, 128.4 (2*d*, *J* = 163, 161, C(1), C(2), C(3), C(4)); 104.2 (*s*, C(5), C(6)); 28.8 (*t*, *J* = 156, CH_2=). MS: 290 (25, M^+), 262 (36), 234 (31), 206 (100, M^+ − 3 CO).

Tricarbonyl[(1R,2R,3S,4S)-C,2,3,C-η-(7,7-dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane)]ruthenium (**25x**). Colourless crystals, m.p. 55–56°. IR (hexane): 2070, 1990, 1980 (CO). ^{1}H-NMR ($CDCl_3$): 3.22, 3.04 (2*s*, 2 CH_3O); 2.78 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 2.0, H–C(1), H–C(4)); 2.20 (*m*, $J(5_{exo},5_{endo})$ = 11.0, $J(5_{exo},6_{endo})$ = 3.4, H_{exo}–C(5), H_{exo}–C(6)); 1.38 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 1.73, 0.26 (2*d*, J_{gem} = 3.0, CH_2=C(2), CH_2=C(3)). ^{13}C-NMR ($CDCl_3$): 201.9, 195.8 (2*s*, ratio 1:2, CO); 113.7, 111.0 (2*s*); 50.2, 49.4 (2*q*, *J* = 142, CH_3O); 44.9 (*d*, *J* = 149, C(1), C(4)); 25.9, 22.8 (2*t*, *J* = 136, 157, C(5), C(6), CH_2=). MS: 338 (100, M^+ − CO), 310 (60), 282 (46), 264 (25), 236 (85), 180 (30). Anal. calc. for $C_{14}H_{16}O_5Ru$ (365.35): C 46.02, H 4.41; found: C 45.73, H 4.33.

Tricarbonyl[(1R,2S,3R,4S)-C,2,3,C-η-(7,7-dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane)]ruthenium (**25n**). Colourless crystals, m.p. 57–58°. IR (hexane): 2055, 1980, 1965 (CO). ^{1}H-NMR ($CDCl_3$): 3.33, 3.29 (2*s*, 6H); 2.93 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 2.1, 2H); 2.24 (*m*, $J(5_{exo},5_{endo})$ = 12.0, $J(5_{exo},6_{endo})$ = 4.8, 2H); 1.31 (*m*, 2H); 1.88, 0.47 (2*d*, J_{gem} = 2.8, 4H). ^{13}C-NMR ($CDCl_3$): 201.2, 195.5 (2*s*, ratio 1:2, CO); 122.0, 119.7 (2*s*); 51.9, 49.6 (2*q*, *J* = 142, 143); 45.8 (*d*, *J* = 149); 33.6, 30.5 (2*t*, *J* = 160, 135). MS: 292 (31, M^+ − $C(OMe)_2$), 264 (98), 236 (81), 180 (100). Anal. calc. for $C_{14}H_{16}O_5Ru$ (365.35): C 46.02, H 4.41; found: C 46.11, H 4.50.

Tricarbonyl[C,2,3,C-η-(2,3-dimethylidenebicyclo[2.2.1]heptan-7-one)]ruthenium (**27**). Colourless crystals, m.p. 135–136°. IR (hexane): 2070, 1990, 1985 (CO), 1785 (C=O). ^{1}H-NMR ($CDCl_3$): 2.84 (*dd*, $J(1,6_{exo}) \approx J(1,5_{exo})$ = 1.9, H–C(1), H–C(4)); 2.28 (*m*, $J(5_{exo},5_{endo})$ = 11.7, $J(5_{exo},6_{endo})$ = 4.4, H_{exo}–C(5), H_{exo}–C(6)); 1.75 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 2.08, 0.61 (2*d*, J_{gem} = 3.4, CH_2=C(2), CH_2=C(3)). ^{13}C-NMR ($CDCl_3$): 202.5, 200.3 (2*s*, ratio 1:2, CO); 194.2, 109.1 (2*s*); 48.1 (*d*, *J* = 156); 27.8, 23.0 (2*t*, *J* = 159, 139). MS: 320 (7, M^+), 292 (32), 236 (23), 208 (100). Anal. calc. for $C_{12}H_{10}O_4Ru$ (319.28): C 45.14, H 3.16; found: C 45.03, H 3.25.

4. Kinetic Measurements. – Solns. of **2**, **5**, **19x**, **19n**, **24x** or **24n** in AcOH/H_2O 2:1 (initial concentrations: c_o = 3.33·10^{-2}M) were thermostatted at 50°. Aliquots of each soln. were sampled until 50–80% conversion and extracted as described for **26x** (*cf. 3.3*). The molar ratios for reactions **2**→**3**, **5**→**6**, **19x**→**22**, **19n**→**22**, **24x**→**26x** and **24n**→**26n** were determined by ^{1}H-NMR and the corresponding pseudo-first order rate constants $k[s^{-1}]$ were calculated by linear regression of equation $\ln(c/c_o) = -kt$ (all correlation coefficients were equal to or greater than 0.991). Hydrolysis of the Ru complexes **25x** and **25n** under the same conditions provoked rapid demetallation and hydrogenation giving in both cases a 1:1 mixture (GC) of *exo*- and *endo*-isomers **28x** and **28n** (*2-methyl-3-methylidenebicyclo[2.2.1]heptan-7-one*; 90%), resp. IR: 1780 (C=O). ^{1}H-NMR ($CDCl_3$): 4.95, 4.94, 4.83, 4.82 (4*s*, 4H); 2.86, 2.50 (*m*, 4H); 2.0–1.5 (*m*, 10H); 1.22, 1.20 (2*d*, 4H). ^{13}C-NMR ($CDCl_3$): 213.0 (2*s*); 152.5 (2*s*); 104.9 (2*t*, *J* = 158); 49.8 (2*d*, *J* = 159); 46.1 (2*d*, *J* = 149); 37.5 (2*d*, *J* = 130); 25.6 (*t*, *J* = 136); 15.9 (2*t*, *J* = 138); 13.9 (2*q*, *J* = 127). GC/MS: 136 (86, M^+), 121 (36), 108 (100).

5. Hydroformylation Reactions. – a) A soln. of **21xx** (0.243 g, 0.5 mmol) in AcOH (30 ml) sat. with CO was stirred for 2 min, H_2O (10 ml) sat. with CO was added dropwise and stirring was continued for 10 min. The mixture was poured into H_2O (50 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The org. extracts were washed with aq. $NaHCO_3$, dried over $MgSO_4$, and evaporated *i.v.* Chromatography on silica gel with petroleum ether/AcOEt 9:1 gave **29x** (85 mg, 49%) after recrystallization from hexane at −75° and **24x** (64 mg, 40%).

b) Aq. 25% HCl was added dropwise under CO (1 atm) to a soln. of **17** (0.138 g, 0.4 mmol) and AcONa (0.8 g) in MeOH (30 ml)/H_2O (10 ml) sat. with CO until disappearance of the red color. The solution was extracted as for **29x**. Chromatography on silica gel with petroleum ether/AcOEt 8.5:1.5 gave a 1:3 mixture of **30n**/**30x** (63 mg, 76%). Only **30x** could be separated as a pure colourless liquid by HPLC (*Waters Associates 6000A*, 0.8 × 30-cm column packed with μ-*Porasil* (10 μm), same eluent, 4 ml/min).

Tricarbonyl[(1RS,2SR,4SR,5SR,6RS)-C,5,6,C-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]heptane-2-carbaldehyde)]iron (**29x**). Yellow crystals, m.p. 54°. IR (hexane): 2060, 1985, 1972 (CO), 1730 (C=O). ^{1}H-NMR ($CDCl_3$): 9.81 (*s*, CHO); 3.34 (*s*, H–C(1)); 3.18, 3.14 (2*s*, 2 CH_3O); 2.88 (*d*, H–C(4)); 2.53 (*m*, H_{exo}–C(3)); 2.52 (*m*, H–C(2)); 1.83 (*dd*, H_{endo}–C(3)); 1.76, 1.72, 0.15, 0.07 (4*d*, $J_{gem} \approx 3.0$, CH_2=C(5), CH_2=C(6)); $J(1,2) \approx 0$, $J(2,3_{endo}) = 8.0$, $J(2,3_{exo}) = 3.0$, $J(3_{exo},3_{endo}) = 13.4$, $J(3_{exo},4) = 3.3$. ^{13}C-NMR ($CDCl_3$): 209.5, 208.6 (2*s*, ratio 1:2, CO); 201.3 (*d*, J = 181, CHO); 113.3, 110.1, 106.2 (3*s*, C(5), C(6), C(7)); 53.0 (*dd*, J = 133, ^2J = 27, C(2)); 51.0, 49.4 (2*q*, J = 143, CH_3O); 47.9, 45.3 (2*d*, J = 154, 150, C(1), C(4)); 30.6, 29.6 (2*dd*, J = 157, 161, CH_2=); 28.9 (*t*, J = 138, C(3)). MS: 320 (20, M^+ − CO), 292 (100), 264 (31), 236 (< 5), 180 (16), 179 (98). Anal. calc. for $C_{15}H_{16}FeO_6$ (348.14): C 51.75, H 4.63; found: C 51.90, H 4.63.

(1RS,2SR,4SR)-7,7-Dimethoxy-5,6-dimethylidenebicyclo[2.2.1]heptane-2-carbaldehyde (**30x**). IR (hexane): 1730 (C=O). ^{1}H-NMR ($CDCl_3$): 9.64 (*s*, CHO); 5.33, 5.30, 5.00, 4.94 (4*s*, CH_2=C(5), CH_2=C(6)); 3.27 (*s*, H–C(1)); 3.24, 3.16 (2*s*, 2 CH_3O); 2.89 (*dd*, H–C(4)); 2.38 (*dd*, H–C(2)); 2.30 (*m*, H_{exo}–C(3)); 1.70 (*dd*, H_{endo}–C(3)); $J(2,3_{endo}) = 9.8$, $J(2,3_{exo}) = 4.6$, $J(3_{exo},3_{endo}) = 12.1$, $J(3_{exo},4) = 4.8$. MS: 108 (27, M^+), 180 (17), 179 (100).

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