

29. d⁶ and d⁸ 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

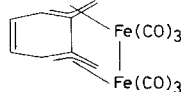
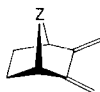
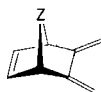
by Jacques Ioset¹⁾ and Raymond Roulet*

Institut de chimie minérale et analytique de l'Université de Lausanne, 3, place du Château, CH-1005 Lausanne

(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/H₂O 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 [Fe₂(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/H₂O, 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 d⁸-metal carbonyls were susceptible of a formal [4 + 2] addition of a diene on the coordinated C,C-double bond, which represents a 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

4

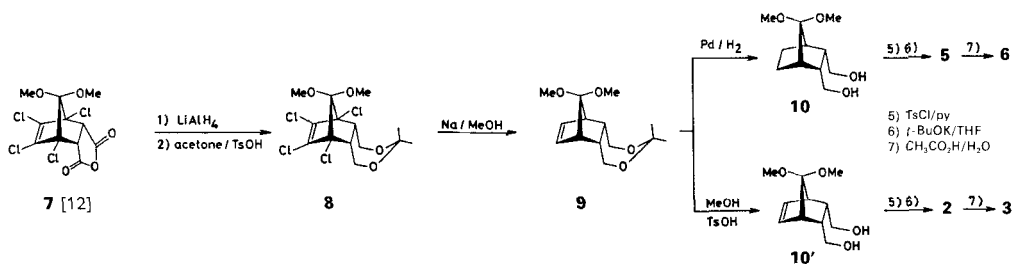
¹⁾ Abstracted in part from the Ph. D. dissertation of J. I., University of Lausanne, 1985.

known that thermal decomposition of substituted norbornadienone acetals takes place with loss of dialkoxycarbenes [4] [5]. Likewise, loss of CO is observed upon gas 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 d⁶ and d⁸ 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*).

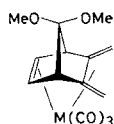
Scheme 1. Preparation of **2**, **3**, **5**, and **6**



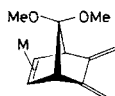
Adduct **7** [12] was first reduced (LiAlH₄/THF) into the corresponding diol whose OH groups were subsequently protected by formation of the cyclic acetonide **8** (80%; acetone/TsOH). Dehalogenation of **3** was achieved using *Paddon-Row*'s procedure (Na/MeOH) [13] giving **9** (49%). Recovery of the OH functions was achieved either by catalytic hydrogenation (H₂/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/H₂O) gave **3** (78%) and **6** (24%), respectively.

2.2. *Synthesis and Characterization of Complexes of 2, 5, and 6.* d⁶ 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(NH₃)₃] [14] in dioxane.

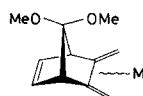
The d⁸ metal carbonyl complexes were obtained in the following ways: the reaction of **2** with [Fe(benzalacetone)(CO)₃] [15] (toluene, 80°C, 1 atm CO) gave **17** (84%) and **21xx** (11%). The reaction of **2** or **5** with [Fe₂(CO)₉] (1:3, MeOH, 45°C) gave **19n** (45%) and



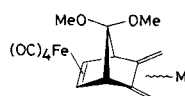
14 M = Cr
15 M = Mo
16 M = W



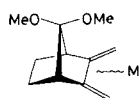
11 M = Cr(CO)₅
12 M = Mo(CO)₅
13 M = W(CO)₅
17 M = Fe(CO)₄
18 M = Ru(CO)₄



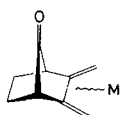
19x M = *exo*-Fe(CO)₃
19n M = *endo*-Fe(CO)₃
20n M = *endo*-Ru(CO)₃



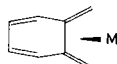
21xn M = *endo*-Fe(CO)₃
21xx M = *exo*-Fe(CO)₃



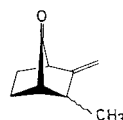
24x M = *exo*-Fe(CO)₃
24n M = *endo*-Fe(CO)₃
25x M = *exo*-Ru(CO)₃
25n M = *endo*-Ru(CO)₃



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



28

21xn (1%), or **24x** (21%) and **24n** (33%), respectively. Further reaction of **17** with $[\text{Fe}_2(\text{CO})_9]$ in hexane or MeOH gave **21xx** or **21xn** as the major product, respectively. Irradiation of **3** in the presence of $[\text{Fe}(\text{CO})_5]$ (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 $[\text{Ru}(\text{CO})_3(1,5\text{-cyclooctadiene})]$ [**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/H₂O 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 $[\text{Ru}(\text{CO})_3(1,5\text{-cyclooctadiene})]$ (benzene, 80°C , 1 atm CO) gave **27** (10%). No complexes of **3** could be isolated. The reaction of **3** with $[\text{Fe}(\text{CO})_3(\text{benzalacetone})]$ (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 $[\text{Ru}(\text{CO})_3(1,5\text{-cyclooctadiene})]$ (benzene, 0°C) gave **23** (20%). Complex **23** was identified as $[\text{Ru}(\text{CO})_3(5,6\text{-dimethylidenecyclohexa-1,3-diene})]$ by comparison with a sample independently prepared by the reaction of $\text{Na}_2[\text{Ru}(\text{CO})_4]$ 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) ($J_{1,2} \leq 1.1$) 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 $\eta^2\text{-Fe}(\text{CO})_4$ 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 $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$ (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.e.* and chromatography on silica gel with petroleum ether gave **22** (1.8 g, 40%) after sublimation ($50^\circ\text{C}/10^{-1}$ 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.

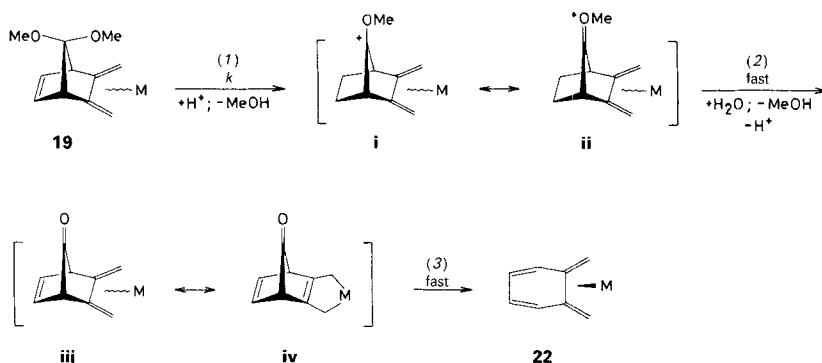
Few $[\text{Cr}(\text{CO})_5(\text{olefin})]$ complexes have been isolated to date (olefin = *cis*- and *trans*-cyclooctene [20]; tetracyanoethylene [21]; **1** [1] [3]). The new complexes **11–13** are stable in degassed solutions. The stability of the metal-olefin bond in these complexes is probably 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 $\text{M}-\pi^*(\text{olefin})$ back-donation are dominant, and the arguments cited in [3] are of limited value.

Complex **17** presents 3 IR bands in the $\nu(\text{CO})$ region indicating, in the absence of accidental degeneracy, a C_{3v} symmetry at the metal atom. For comparison, the $\eta^2\text{-Fe}(\text{CO})_4$ 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 $[\text{M}(\text{CO})_4(\text{olefin})]$ 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 $\eta^2\text{-Fe}(\text{CO})_4$ group in isomers **21xx** and **21xn** since both displayed 6 IR bands in the $\nu(\text{CO})$ region rather than 7 (3 of these are due to the $\text{Fe}(\text{CO})_3$ 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**), $2.00 \cdot 10^4 \text{ s}^{-1}$ (**24n**), and $\Delta G_{333}^\ddagger = 14.3 \pm 0.3$ (**24x**), $13.0 \pm 0.2 \text{ kcal} \cdot \text{mol}^{-1}$ (**24n**). Since the methoxy group *syn* to the *s-cis*-butadiene moiety must hinder the CO-site exchange when the $\text{Fe}(\text{CO})_3$ 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 $\text{M}(\text{CO})_3$ group (of opposite signs for both pairs of isomers, see *Exper. Part*).

The *exo- vs. endo*-configuration of the $\text{Fe}(\text{CO})_3$ 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 ($\text{AcOH}/\text{H}_2\text{O}$ 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 $\text{AcOH}/\text{H}_2\text{O}$ 2:1 giving **26x** in better yields (78%) than the direct reaction of **6** with $\text{Fe}_2(\text{CO})_9$. We have extended this reaction to other complexes of **2** and **5**, and a kinetic study (see *Exper. Part*) under pseudo-first order conditions ($\text{AcOH}/\text{H}_2\text{O}$ 2:1, $50.0 \pm 0.1^\circ\text{C}$) 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 $(5.5 \pm 0.5) \cdot 10^{-6} \text{ s}^{-1}$ (**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** → **22³**) 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** → **22³**) 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 Å⁴) and as 4.1 Å⁵) in **24n**).

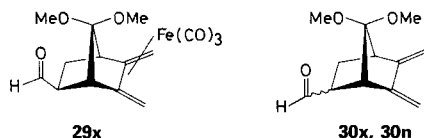
2.4. Hydroformylation of Iron-Carbonyl Complexes of 2. Reactions of aliphatic halides and sulfonates with Na₂[Fe(CO)₄] under CO lead to acyliron(0) intermediate [30] which have also been obtained from *Grignard* reagents or lithio alkanes and [Fe(CO)₅] [31]. Subsequent treatment with H₂O, alcohols, alkyl 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/H₂O 2:1 at room temperature (giving **24x** as major product).

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].



The reaction of **21xx** with CO (1 atm) in AcOH/H₂O 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 ($\tilde{\nu}(\text{C}=\text{O}) = 1730 \text{ cm}^{-1}$) and by NMR spectroscopy (δ_{H} 9.81 (s); δ_{CO} 201.3 ppm (d, $J_{\text{C,H}} = 181 \text{ Hz}$)). 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) ($J_{3,4} = 3.3 \text{ Hz}$). 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 $[\text{Fe}(\text{CO})_4(\text{olefin})]$ complex has been reported to date.

We thank the *Swiss National Science Foundation* for financial support, Prof. *P. Vogel* (Institute of Organic Chemistry, University of Lausanne) for helpful discussions, and Mr. *D. Grandjean* for technical assistance.

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 LiAlH₄ (30.4 g, 0.8 mol) in THF (1300 ml). The mixture was refluxed for 12 h, then hydrolyzed with 10% aq. (NH₄)₂SO₄ (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 P₄O₁₀. TsOH · H₂O (1 g) was added to the oil dissolved in acetone (400 ml)/CHCl₃ (600 ml), and H₂O was removed under reflux with *Linde 4A* molecular sieves (3 × 100 ml) in a *Soxhlet* apparatus for 3 days. TsOH was neutralized by NH₃, 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. ¹H-NMR (CDCl₃): 4.2–3.6 (m, 4H); 3.57, 3.52 (2s, 6H); 3.2–2.9 (m, 2H); 1.33 (s, 6H). MS: 375(2), 355(3), 299(34), 253(100). Anal. calc. for C₁₄H₁₈Cl₄O₄ (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/H₂O (3000 ml). The precipitate was filtered, washed with H₂O, and redissolved in CH₂Cl₂. Drying over MgSO₄, 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. ¹H-NMR (CDCl₃): 6.15 (dd, 2H); 3.9–3.5 (m, 4H); 3.22–3.12 (2s, 6H); 3.0–2.7 (m, 4H); 1.35 (s, 6H). MS: 254 (6), 196 (53), 165 (100), 151 (45). Anal. calc. for C₁₄H₂₂O₄ (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 NH₃ in MeOH (50 ml) and evaporation *i.v.* gave a residue which was taken up in Et₂O (500 ml)/H₂O (50 ml) and extracted with Et₂O (3 × 200 ml). The org. extracts were dried over MgSO₄ and evaporated *i.v.* giving the corresponding diol **10'** (22 g, 68%) as a yellow oil. The oil was dissolved in anhyd. 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 H₂O (1500 ml) at 0°. The precipitate was decanted, washed with H₂O, and dissolved in Et₂O (500 ml). The soln. was washed with H₂O (4 × 500 ml), dried over MgSO₄, 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/H₂O (3000 ml) and extracted with petroleum ether (3 × 500 ml). The extracts were washed with H₂O, dried over MgSO₄, and evaporated *i.v.* Sublimation at 45°/5 · 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. ¹H-NMR (CDCl₃, 360 MHz): 6.24 (*dd*, *J*_{1,2} ≈ *J*_{1,3} = 2.2, H–C(2), H–C(3)); 5.44, 5.10 (2*s*, CH₂=C(5), CH₂=C(6)); 3.44 (*dd*, H–C(1), H–C(4)); 3.28, 3.21 (2*s*, 2 CH₃O). ¹³C-NMR (CDCl₃, 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, CH₂=); 54.8 (*br. d.*, *J* = 149, C(1), C(4)); 51.7, 50.3 (2*q*, *J* = 142, CH₃O). MS: 178 (64, *M*⁺), 163 (55), 147 (73), 135 (53), 131 (51), 104 (100). Anal. calc. for C₁₁H₁₄O₂ (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/H₂O 2:1 (200 ml) was heated under Ar at 65° for 3 h, then extracted with CH₂Cl₂ (3 × 200 ml). The extracts were washed with aq. sat. NaHCO₃ (3 × 200 ml), then H₂O (2 × 100 ml), dried over MgSO₄, and evaporated *i.v.* Chromatography on silica gel with pentane/CH₂Cl₂ 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]. ¹H-NMR (CDCl₃): 6.65 (*dd*, *J*_{2,1} ≈ *J*_{3,1} = 2.4, H–C(2), H–C(3)); 5.38, 5.09 (2*s*, CH₂=C(5), CH₂=C(6)); 3.56 (*dd*, H–C(1), H–C(4)). ¹³C-NMR (CDCl₃): 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, CH₂=); 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 H₂ (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. ¹H-NMR (CDCl₃): 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 C₁₁H₂₀O₄ (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. ¹H-NMR (CDCl₃): 5.23, 4.83 (2*s*, CH₂=C(2), CH₂=C(3)); 3.25, 3.23 (2*s*, 2 CH₃O); 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*(*S*_{exo}, *S*_{endo}) = 14.5, *J*(1, *S*_{exo}) = 2.6, *J*(*S*_{exo}, *S*_{endo}) = 4.2, *J*(1, *S*_{exo}) = 1.8. ¹³C-NMR (CDCl₃): 149.8 (*s*, C(2), C(3)); 112.0 (*s*, C(7)); 101.4 (*t*, *J* = 159, CH₂=); 50.8, 49.7 (2*q*, *J* = 142, CH₃O); 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]. ¹H-NMR (CDCl₃): 5.39, 4.95 (2*s*, CH₂=C(2), CH₂=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*(*S*_{exo}, *S*_{endo}) = 12.0, *J*(1, *S*_{exo}) = 2.1, *J*(*S*_{exo}, *S*_{endo}) = 5.1, *J*(1, *S*_{exo}) = 2.1. ¹³C-NMR (CDCl₃): 204.1 (*s*, C=O); 145.6 (*s*, C(2), C(3)); 103.3 (*t*, *J* = 159, CH₂=); 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 CH₂Cl₂/hexane 3:1. Recrystallization from hexane/CH₂Cl₂ at –25° gave **11** (0.48 g, 23%), **12** (0.64 g, 28%), and **13** (0.92 g, 34%), resp.

Pentacarbonyl[(1*R*,2*S*,3*R*,4*S*)-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). ¹H-NMR (C₆D₆, 360 MHz): 5.34, 4.91 (2*s*, CH₂=C(5), CH₂=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 CH₃O). ¹³C-NMR (CDCl₃, 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, CH₂=); 77.7 (*d*, *J* = 180, C(2), C(3)); 60.7, 52.0 (2*q*, *J* = 146, 143, CH₃O); 52.5 (*br. d.*, *J* = 151, C(1), C(4)). MS (⁵²Cr): 342 (10, *M*⁺ – CO), 314 (7), 286 (13), 258 (71), 230 (100, *M*⁺ – 5CO). Anal. calc. for C₁₆H₁₄CrO₇ (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). ¹H-NMR (C₆D₆): 5.32, 4.89 (2s, 4H); 4.39 (dd, $J_{1,2} \approx J_{1,3} = 1.1$, 2H); 2.95 (dd, 2H); 2.69, 2.58 (2s, 6H). ¹³C-NMR (CDCl₃): 219.9, 218.2, 216.0, 210.8 (4s, ratios 1:1:1:2, CO); 145.7, 114.5 (2s); 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 (⁸⁶Mo): 414 (< 5, M^+), 386 (96), 358 (10), 330 (< 5), 302 (< 5), 274 (41), 178 (63), 104 (100). Anal. calc. for C₁₆H₁₄MoO₇ (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). ¹H-NMR (C₆D₆): 5.33, 4.87 (2s, 4H); 4.01 (br. s, $J_{1,2} \approx J_{1,3} < 0.5$, 2H); 2.87 (br. s, 2H); 2.81, 2.57 (2s, 6H). ¹³C-NMR (CDCl₃): 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 (2s); 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 (¹⁸⁴W): 474 (34, $M^+ - CO$), 390 (7), 362 (90), 178 (100). Anal. calc. for C₁₆H₁₄O₇W (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(NH₃)₃(CO)₃] (748 mg, 4 mmol), [Mo(NH₃)₃(CO)₃] (924 mg) or [W(NH₃)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/CH₂Cl₂ 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). ¹H-NMR (CDCl₃): 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 (2s, 2 CH₃O); 3.10, 1.27 (2*d*, $J_{gem} = 1.9$, CH₂=C(5), CH₂=C(6)). ¹³C-NMR (CDCl₃): 240.8, 234.1 (2s, ratio 2:1, CO); 124.3 (s, C(7)); 77.0 (s, C(5), C(6)); 63.5 (*t*, $J = 163$, CH₂=); 51.9, 51.1 (2*q*, $J = 143$, CH₃O); 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 C₁₄H₁₄CrO₅ (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). ¹H-NMR (CDCl₃): 3.46, 3.35 (2*dd*, $J_{1,2} = 3.0$, $J_{1,3} = 2.1$, 4H); 3.33, 3.32 (2s, 6H); 3.47, 1.74 (2*d*, $J_{gem} = 1.8$, 4H). ¹³C-NMR (CDCl₃): 227.9, 219.3 (2s, ratio 2:1); 124.3, 80.7 (2s); 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 C₁₄H₁₄MoO₅ (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). ¹H-NMR (CDCl₃): 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 (2s, $J_{gem} = 2.3$, 4H). ¹³C-NMR (CDCl₃): 220.7, 210.4 (2*t*, $J_{C,W} = 171$, 156, ratio 2:1); 126.4, 73.8 (2s); 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 C₁₄H₁₄O₅W (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 [Fe₂(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/H₂O 2:1 was stirred at 65° under Ar for 5 h, then was poured into H₂O (500 ml) and extracted with CH₂Cl₂ (3 × 50 ml). The org. extracts were washed with aq. sat. NaHCO₃ (3 × 50 ml) and dried over MgSO₄. Evaporation *i.v.* and crystallization from hexane/CH₂Cl₂ 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). ¹H-NMR (CDCl₃): 5.40, 5.06 (2s, CH₂=C(5), CH₂=C(6)); 3.51 (s, $J_{1,2} < 0.5$, H–C(2), H–C(3)); 3.06 (s, 2 CH₃O); 2.85 (s, H–C(1), H–C(4)). ¹³C-NMR

(CDCl₃): 213.5 (s, CO); 147.8 (s, C(5), C(6)); 114.7 (s, C(7)); 103.5 (t, $J = 159$, CH₂=); 61.0, 52.1 (2q, $J = 147$, 144, CH₃O); 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 C₁₅H₁₄FeO₇ (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). ¹H-NMR (CDCl₃): 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 (2s, 2 CH₃O); 1.75, 0.18 (2d, $J_{\text{gem}} = 2.7$, CH₂=C(5), CH₂=C(6)). ¹³C-NMR (CDCl₃): 215.4, 209.6 (2s, ratio 1:2, CO); 142.3 (d, $J = 180$, C(2), C(3)); 123.6, 116.4 (2s, C(7), C(5), C(6)); 53.4 (br. d, $J = 148$, C(1), C(4)); 51.3, 50.2 (2q, $J = 142$, 143, CH₃O); 31.3 (t, $J = 160$, CH₂=). MS: 318 (< 5, M^+), 290 (37), 262 (92), 234 (47), 178 (100). Anal. calc. for C₁₄H₁₄FeO₅ (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). ¹H-NMR (CDCl₃): 6.62, 3.63 (2dd, $J_{1,2} \approx J_{1,3} = 2.5$, 4H); 3.27, 3.24 (2s, 6H); 2.18, 0.90 (2d, $J_{\text{gem}} = 2.6$, 4H). ¹³C-NMR (CDCl₃): 211.0 (br. s, CO); 138.7 (d, $J = 176$); 133.2, 113.8 (2s); 52.4 (br. d, $J = 150$); 51.6, 51.1 (2q, $J = 143$); 38.8 (t, $J = 160$). MS: 290 (36, M^+ - CO), 262 (80), 234 (100), 178 (97), 160 (69), 104 (39). Anal. calc. for C₁₄H₁₄FeO₅ (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). ¹H-NMR (CDCl₃): 3.84 (s, $J_{1,2} < 0.5$, H-C(2), H-C(3)); 3.22, 3.03 (2s, 2 CH₃O); 2.75 (s, H-C(1), H-C(4)); 1.56, 0.46 (2d, $J_{\text{gem}} = 2.8$, CH₂=C(5), CH₂=C(6)). ¹³C-NMR (CDCl₃): 211 (br. s, CO); 211.7, 211.4 (2s, CO); 118.5 (s, C(7)); 111.4 (s, C(5), C(6)); 61.8, 51.6 (2q, $J = 147$, 144, CH₃O); 56.1 (d, $J = 173$, C(2), C(3)); 47.4 (d, $J = 156$, C(1), C(4)); 31.7 (t, $J = 161$, CH₂=). MS: 430 (33, M^+ - 2 CO), 402 (100), 374 (41), 346 (43), 318 (65), 290 (54). Anal. calc. for C₁₈H₁₄Fe₂O₉ (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). ¹H-NMR (CDCl₃): 3.68 (s, $J_{1,2} < 0.5$, 2H); 3.15, 3.12 (2s, 6H); 2.99 (s, 2H); 2.07, 0.65 (2d, $J_{\text{gem}} = 2.6$, 4H). ¹³C-NMR (CDCl₃): 213.0 (s), 211.0 (br. s); 123.6, 116.8 (2s); 61.8, 53.2 (2q, $J = 147$, 144); 56.7, 48.9 (2d, $J = 180$, 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 C₁₈H₁₄Fe₂O₉ (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). ¹H-NMR (CDCl₃): 3.26, 3.12 (2s, 2 CH₃O); 2.81 (dd, $J(1,6_{\text{exo}}) = 2.0$, $J(1,5_{\text{exo}}) = 1.4$, H-C(1), H-C(4)); 2.22 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 11.6$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 3.9$, H_{exo}-C(5), H_{exo}-C(6)); 1.41 (m, H_{endo}-C(5), H_{endo}-C(6)); 1.70, 0.05 (2d, $J_{\text{gem}} = 2.5$, CH₂=C(2), CH₂=C(3)). ¹³C-NMR (CDCl₃): 215.7, 209.8 (2s, ratio 1:2, CO); 113.6 (s, C(7)); 108.2 (s, C(2), C(3)); 50.6, 49.4 (2q, $J = 143$, CH₃O); 44.5 (d, $J = 149$, C(1), C(4)); 30.1 (t, $J = 159$, CH₂=); 26.4 (t, $J = 137$, C(5), C(6)). MS: 320 (< 1, M^+); 292 (14), 264 (84), 236 (100), 180 (6). Anal. calc. for C₁₄H₁₆FeO₅ (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). ¹H-NMR (CDCl₃): 3.33, 3.29 (2s, 6H); 2.93 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 2.0$, H-C(1), H-C(4)); 2.24 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 12.3$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 4.6$); 1.30 (dd, 2H); 1.87, 0.47 (2d, $J_{\text{gem}} = 2.8$, 4H). ¹³C-NMR (CDCl₃): 211.0 (br. s, CO); 122.0, 119.7 (2s); 51.8, 49.5 (2q, $J = 143$); 45.6 (d, $J = 146$); 33.5, 30.4 (2t, $J = 157$, 134). MS: 320 (5, M^+), 292 (32), 264 (100), 236 (69), 180 (11). Anal. calc. for C₁₄H₁₆FeO₅ (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). ¹H-NMR (CDCl₃): 2.87 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 1.8$, H-C(1), H-C(4)); 2.32 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 12.3$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 5.1$, H_{exo}-C(5), H_{exo}-C(6)); 1.82 (m, H_{endo}-C(5), H_{endo}-C(6)); 2.09, 0.43 (2d, $J_{\text{gem}} = 3.1$, CH₂=C(2), CH₂=C(3)). ¹³C-NMR (CDCl₃): 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, $J = 161$, CH₂=); 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 C₁₂H₁₀FeO₄ (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). ¹H-NMR (CDCl₃): 3.03 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 2.0$, 2H); 2.31 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 12.0$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 5.1$, 2H); 1.25 (m, 2H); 2.06, 0.60 (2d, $J_{\text{gem}} = 3.0$, 4H). ¹³C-NMR (CDCl₃): 208.9, 201.0, 115.1 (3s); 47.3 (d, $J = 155$); 34.4, 27.8 (2t, $J = 160$, 138). MS: 274 (17, M^+), 246 (85), 218 (93), 190 (78), 162 (100), 134 (11). Anal. calc. for C₁₂H₁₀FeO₄ (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 ($50^\circ/5 \cdot 10^{-2}$ 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. $76\text{--}77^\circ$. IR (hexane): 2053, 1976, 1970 (CO). $^1\text{H-NMR}$ (CDCl_3): 5.35, 5.00 (2s, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$); 3.39, 3.15 (2s, 2 CH_3O); 2.99 (s, $J_{1,2} < 0.5$, $\text{H-C}(2)$, $\text{H-C}(3)$); 2.79 (s, $\text{H-C}(1)$, $\text{H-C}(4)$). $^{13}\text{C-NMR}$ (CDCl_3): 200.5 (s, CO); 149.1 (s, C(5), C(6)); 116.2 (s, C(7)); 102.9 (t, $J = 158$, $\text{CH}_2=$); 62.3, 52.3 (2q, $J = 147$, 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, $M^+ - \text{CO}$), 336 (83), 308 (88), 262 (7), 234 (69), 206 (100), 178 (26). Anal. calc. for $\text{C}_{15}\text{H}_{14}\text{O}_6\text{Ru}$ (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). $^1\text{H-NMR}$ (CDCl_3): 6.51 (dd, $J_{1,2} \approx J_{1,3} = 2.4$, $\text{H-C}(2)$, $\text{H-C}(3)$); 3.54 (dd, $\text{H-C}(1)$, $\text{H-C}(4)$); 3.27, 3.22 (2s, 2 CH_3O); 2.17, 1.12 (2d, $J_{\text{gem}} = 2.7$, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$). $^{13}\text{C-NMR}$ (CDCl_3): 201.5, 195.2 (2s, 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 (2q, $J = 143$, CH_3O); 32.0 (t, $J = 158$, $\text{CH}_2=$). MS: 364 (< 5 , M^+), 336 (100), 308 (43), 280 (49), 234 (41), 206 (97), 178 (32), 104 (25). Anal. calc. for $\text{C}_{14}\text{H}_{14}\text{O}_5\text{Ru}$ (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. $37\text{--}38^\circ$. IR (hexane): 2080, 1995 (CO). $^1\text{H-NMR}$ (CD_2Cl_2): 7.5–7.2 (m, $\text{H-C}(1)$, $\text{H-C}(2)$, $\text{H-C}(3)$, $\text{H-C}(4)$); 2.46, 0.56 (2d, $J_{\text{gem}} = 4.0$, $\text{CH}_2=\text{C}(5)$, $\text{CH}_2=\text{C}(6)$). $^{13}\text{C-NMR}$ (CDCl_3): 201.8, 193.4 (2s, ratio 1:2, CO); 131.8, 128.4 (2d, $J = 163$, 161, C(1), C(2), C(3), C(4)); 104.2 (s, C(5), C(6)); 28.8 (t, $J = 156$, $\text{CH}_2=$). MS: 290 (25, M^+), 262 (36), 234 (31), 206 (100, $M^+ - 3 \text{ CO}$).

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. $55\text{--}56^\circ$. IR (hexane): 2070, 1990, 1980 (CO). $^1\text{H-NMR}$ (CDCl_3): 3.22, 3.04 (2s, 2 CH_3O); 2.78 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 2.0$, $\text{H-C}(1)$, $\text{H-C}(4)$); 2.20 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 11.0$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 3.4$, $\text{H}_{\text{exo}}-\text{C}(5)$, $\text{H}_{\text{exo}}-\text{C}(6)$); 1.38 (m, $\text{H}_{\text{endo}}-\text{C}(5)$, $\text{H}_{\text{endo}}-\text{C}(6)$); 1.73, 0.26 (2d, $J_{\text{gem}} = 3.0$, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$). $^{13}\text{C-NMR}$ (CDCl_3): 201.9, 195.8 (2s, ratio 1:2, CO); 113.7, 111.0 (2s); 50.2, 49.4 (2q, $J = 142$, CH_3O); 44.9 (d, $J = 149$, C(1), C(4)); 25.9, 22.8 (2t, $J = 136$, 157, C(5), C(6), $\text{CH}_2=$). MS: 338 (100, $M^+ - \text{CO}$), 310 (60), 282 (46), 264 (25), 236 (85), 180 (30). Anal. calc. for $\text{C}_{14}\text{H}_{16}\text{O}_5\text{Ru}$ (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. $57\text{--}58^\circ$. IR (hexane): 2055, 1980, 1965 (CO). $^1\text{H-NMR}$ (CDCl_3): 3.33, 3.29 (2s, 6H); 2.93 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 2.1$, 2H); 2.24 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 12.0$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 4.8$, 2H); 1.31 (m, 2H); 1.88, 0.47 (2d, $J_{\text{gem}} = 2.8$, 4H). $^{13}\text{C-NMR}$ (CDCl_3): 201.2, 195.5 (2s, ratio 1:2, CO); 122.0, 119.7 (2s); 51.9, 49.6 (2q, $J = 142$, 143); 45.8 (d, $J = 149$); 33.6, 30.5 (2t, $J = 160$, 135). MS: 292 (31, $M^+ - \text{C}(\text{OMe})_2$), 264 (98), 236 (81), 180 (100). Anal. calc. for $\text{C}_{14}\text{H}_{16}\text{O}_5\text{Ru}$ (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. $135\text{--}136^\circ$. IR (hexane): 2070, 1990, 1985 (CO), 1785 ($\text{C}=\text{O}$). $^1\text{H-NMR}$ (CDCl_3): 2.84 (dd, $J(1,6_{\text{exo}}) \approx J(1,5_{\text{exo}}) = 1.9$, $\text{H-C}(1)$, $\text{H-C}(4)$); 2.28 (m, $J(5_{\text{exo}}, 5_{\text{endo}}) = 11.7$, $J(5_{\text{exo}}, 6_{\text{endo}}) = 4.4$, $\text{H}_{\text{exo}}-\text{C}(5)$, $\text{H}_{\text{exo}}-\text{C}(6)$); 1.75 (m, $\text{H}_{\text{endo}}-\text{C}(5)$, $\text{H}_{\text{endo}}-\text{C}(6)$); 2.08, 0.61 (2d, $J_{\text{gem}} = 3.4$, $\text{CH}_2=\text{C}(2)$, $\text{CH}_2=\text{C}(3)$). $^{13}\text{C-NMR}$ (CDCl_3): 202.5, 200.3 (2s, ratio 1:2, CO); 194.2, 109.1 (2s); 48.1 (d, $J = 156$); 27.8, 23.0 (2t, $J = 159$, 139). MS: 320 (7, M^+), 292 (32), 236 (23), 208 (100). Anal. calc. for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Ru}$ (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 $\text{AcOH}/\text{H}_2\text{O}$ 2:1 (initial concentrations: $c_0 = 3.33 \cdot 10^{-2}\text{M}$) 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** $\rightarrow$ **3**, **5** $\rightarrow$ **6**, **19x** $\rightarrow$ **22**, **19n** $\rightarrow$ **22**, **24x** $\rightarrow$ **26x** and **24n** $\rightarrow$ **26n** were determined by $^1\text{H-NMR}$ and the corresponding pseudo-first order rate constants $k[\text{s}^{-1}]$ were calculated by linear regression of equation $\ln(c/c_0) = -kt$ (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 ($\text{C}=\text{O}$). $^1\text{H-NMR}$ (CDCl_3): 4.95, 4.94, 4.83, 4.82 (4s, 4H); 2.86, 2.50 (m, 4H); 2.0–1.5 (m, 10H); 1.22, 1.20 (2d, 4H). $^{13}\text{C-NMR}$ (CDCl_3): 213.0 (2s); 152.5 (2s); 104.9 (2t, $J = 158$); 49.8 (2d, $J = 159$); 46.1 (2d, $J = 149$); 37.5 (2d, $J = 130$); 25.6 (t, $J = 136$); 15.9 (2t, $J = 138$); 13.9 (2q, $J = 127$). 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, H₂O (10 ml) sat. with CO was added dropwise and stirring was continued for 10 min. The mixture was poured into H₂O (50 ml) and extracted with CH₂Cl₂ (3 × 20 ml). The org. extracts were washed with aq. NaHCO₃, dried over MgSO₄, 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)/H₂O (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 μ m), 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). ¹H-NMR (CDCl₃): 9.81 (s, CHO); 3.34 (s, H-C(1)); 3.18, 3.14 (2s, 2 CH₃O); 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 (4d, $J_{gem} \approx 3.0$, CH₂=C(5), CH₂=C(6)); $J(1,2) \approx 0$, $J(2,3_{endo}) = 8.0$, $J(2,3_{exo}) = 3.0$, $J(3_{exo},3_{endo}) = 13.4$, $J(3_{exo},4) = 3.3$. ¹³C-NMR (CDCl₃): 209.5, 208.6 (2s, ratio 1:2, CO); 201.3 (d, $J = 181$, CHO); 113.3, 110.1, 106.2 (3s, C(5), C(6), C(7)); 53.0 (dd, $J = 133$, ² $J = 27$, C(2)); 51.0, 49.4 (2q, $J = 143$, CH₃O); 47.9, 45.3 (2d, $J = 154$, 150, C(1), C(4)); 30.6, 29.6 (2dd, $J = 157$, 161, CH₂=); 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 C₁₅H₁₆FeO₆ (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). ¹H-NMR (CDCl₃): 9.64 (s, CHO); 5.33, 5.30, 5.00, 4.94 (4s, CH₂=C(5), CH₂=C(6)); 3.27 (s, H-C(1)); 3.24, 3.16 (2s, 2 CH₃O); 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).

REFERENCES

- [1] Ph. Vioget, M. Bonivento, R. Roulet, P. Vogel, *Helv. Chim. Acta* **1984**, 67, 1630.
- [2] Ph. Vioget, P. Vogel, R. Roulet, *Angew. Chem.* **1982**, 94, 454.
- [3] A. A. Pinkerton, P.-A. Carrupt, P. Vogel, T. Boschi, N. N. Thuy, R. Roulet, *Inorg. Chim. Acta* **1978**, 28, 123.
- [4] D. M. Lemal, E. P. Gosselink, A. Ault, *Tetrahedron Lett.* **1964**, 579.
- [5] R. W. Hoffmann, H. Häuser, *Tetrahedron Lett.* **1964**, 197.
- [6] W. R. Roth, B. P. Scholz, *Chem. Ber.* **1981**, 114, 3741.
- [7] W. Grimm, H.-J. Rother, *Angew. Chem.* **1973**, 85, 512; W. R. Roth, M. Biermann, G. Erker, K. Jelić, W. Gerhartz, H. Görner, *Chem. Ber.* **1980**, 113, 586.
- [8] P. Laszlo, A. Stockis, *J. Organomet. Chem.* **1976**, 117, C41.
- [9] D. Wege, S. P. Wilkinson, *J. Chem. Soc., Chem. Commun.* **1972**, 1335.
- [10] T. Tsuji, H. Ishitobi, H. Tanida, *Tetrahedron Lett.* **1972**, 3083.
- [11] A. Chollet, J.-P. Hagenbuch, P. Vogel, *Helv. Chim. Acta* **1979**, 62, 511.
- [12] J. S. Newcomer, E. T. McBee, *J. Am. Chem. Soc.* **1949**, 71, 946.
- [13] B. V. Lap, M. N. Paddon-Row, *J. Org. Chem.* **1979**, 44, 4979.
- [14] J. Vebrel, R. Mercier, J. Belleney, *J. Organomet. Chem.* **1982**, 235, 197.
- [15] J. A. S. Howell, B. F. G. Johnson, P. L. Josty, J. Lewis, *J. Organomet. Chem.* **1972**, 39, 329.
- [16] A. J. P. Domingos, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1975**, 2288.
- [17] W. R. Roth, J. D. Meier, *Tetrahedron Lett.* **1967**, 2053.
- [18] B. F. G. Johnson, J. Lewis, D. J. Thompson, *Tetrahedron Lett.* **1974**, 3789.
- [19] C. E. Sumner Jr., J. A. Collier, R. Pettit, *Organometallics* **1982**, 1, 1351.
- [20] F.-W. Grevels, V. Skibbe, *J. Chem. Soc., Chem. Commun.*, in press.
- [21] M. Herberhold, *Angew. Chem.* **1968**, 80, 314.
- [22] M. von Büren, H.-J. Hansen, *Helv. Chim. Acta* **1977**, 60, 2717; M. von Büren, M. Cosandey, H.-J. Hansen, *ibid.* **1980**, 63, 892.
- [23] 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, Vol. 4, p. 386.
- [24] M. M. Kreevoy, R. W. Taft, Jr., *J. Am. Chem. Soc.* **1955**, 77, 3146, 5590.

- [25] S. Winstein, E. T. Stafford, *J. Am. Chem. Soc.* **1957**, *79*, 505; S. Winstein, in 'Carbonium Ions', Eds. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1972, Vol. 3, p. 965.
- [26] T. T. Tidwell, *J. Org. Chem.* **1974**, *39*, 3533; J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, H. C. Brown, *J. Am. Chem. Soc.* **1974**, *96*, 1969.
- [27] J. M. Landensberg, J. Sieczkowski, *J. Am. Chem. Soc.* **1971**, *93*, 972.
- [28] Ch. Barras, R. Roulet, E. Vieira, P. Vogel, G. Chapuis, *Helv. Chim. Acta* **981**, *64*, 2328.
- [29] J. Wenger, N. N. Thuy, T. Boschi, R. Roulet, A. Chollet, P. Vogel, A. A. Pinkerton, D. Schwarzenbach, *J. Organomet. Chem.* **1974**, *174*, 89.
- [30] J. P. Collman, *Acc. Chem. Res.* **1975**, *8*, 342.
- [31] M. Yamashita, R. Suemitsu, *Tetrahedron Lett.* **1978**, 761; C. S. Giam, K. Ueno, *J. Am. Chem. Soc.* **1977**, *99*, 3166.
- [32] 'Organic Synthesis via Metal Carbonyls', Eds. I. Wender and P. Pino, Wiley, New York, 1977, Vol. 2, p. 199.