291. Inductive and Polarizability Effects of an Exocyclic Diene-Iron Tricarbonyl Group. The Acetolyses of *exo*- and *endo*-Irontricarbonyl Complexes of 5,6-Dimethylidene-2-*exo*-norbornyl and 2,3-Dimethylidene-7-*anti*-norbornyl Parabromobenzenesulfonates[1])

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Summary

The *exo*- and *endo*-irontricarbonyl complexes of 5,6-dimethylidene-2-*exo*-norbornyl alcohols **10x**, **10n**, *p*-bromobenzenesulfonates **11x**, **11n**, acetate **12x** and of the 2,3-dimethylidene-7-*anti*-norbornyl alcohols **17x**, **17n**, *p*-bromobenzenesulfonates **19x**, **19n** and acetates **20x**, **20n** have been prepared. The S_N1 buffered acetolyses of **11x**, **19x** and **19n** gave **12x**, **20x** and **20n**, respectively (retention of configuration). The first-order rate constants of the acetolyses have been evaluated and compared with those of the acetolyses of the uncomplexed 5,6-dimethylidene-2-*exo*-norbornyl (**14**) and 2,3-dimethylidene-7-*anti*-norbornyl *p*-bromobenzenesulfonates (**18**). A rate retardation effect of *ca.* $1.5 \cdot 10^5$ was measured for **11x** → **12x** (65°) compared with the acetolysis of **14**. The retardation effect is larger ($> 5 \cdot 10^7$) with **11n**. Contrastingly, the acetolysis **19x** → **20x** was slightly accelerated with respect to that of the uncomplexed *p*-bromobenzenesulfonate **18**. An unsignificant rate-retardation effect was measured for the acetolysis **19n** → **20n**. The results are interpreted in terms of competitive inductive destabilization and charge-induced dipole stabilizing interaction by the exocyclic diene-iron tricarbonyl fragment. PMO. arguments give a rationale for the difference in polarizability between the diene-Fe(CO)$_3$ group in **19** and that in the *endo*-7-norbornadienyl-iron tricarbonyl system.

Introduction. – Transition metal π-complexes can stabilize an adjacent carbocationic center very efficiently [2]. In 1960, *Fischer* [3] showed that salts of the cyclohexadienyl-iron tricarbonyl cation can be recrystallized from water. The high propensy of the diene-iron tricarbonyl function to stabilize a carbenium ion has been further demonstrated for the molecular skeletons **1** [4], **2** [5] and **3** [6].

[1]) Preliminary communication: [1].

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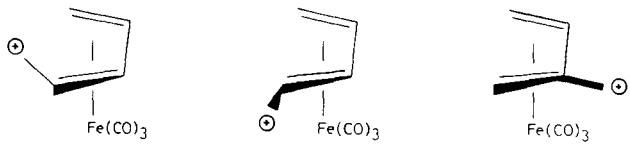

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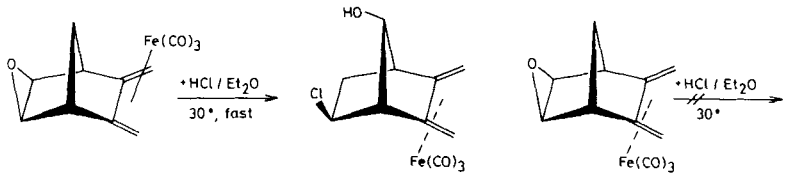
Little is known, however, about the effect of a transition metal complex substituent on the stability of a β-carbenium ion. Depending upon the geometry of the system and the electronic demand of the reaction, an arenechromium tricarbonyl group has been found to accelerate [7] [8] or retard [9] S_N1 solvolyses of π-complexed β-arylalkyl esters. The hydrolysis of 7-norbornadienyl *p*-toluenesulfonates is strongly retarded upon complexation of the 1,4-diene by an *endo*-$Fe(CO)_3$ group

$k_{rel} = (1.0)$ $k_{rel} < 10^{-6}$

[10], eventhough the irontricarbonyl fragment is considered to be an electron-donating group [11]. The dipole moment of the butadiene-iron tricarbonyl complex [12] (the carbonyl groups acting as electron withdrawing substituents) can compete with the high polarizability of this function. The balance between these two effects (that are opposed in the case of cationic species) will be affected by the distance separating the $Fe(CO)_3$-group and the ionized β-carbon-atom as well as by the charge at this centre.



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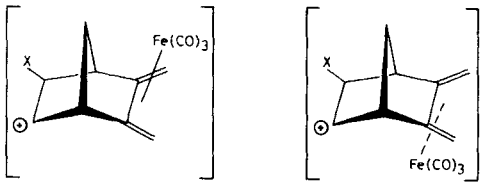
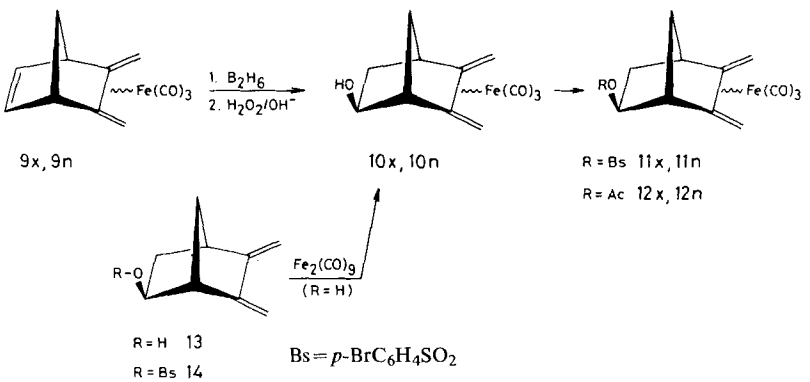


X=OH: 7x
X= H: 8x

7n
8n

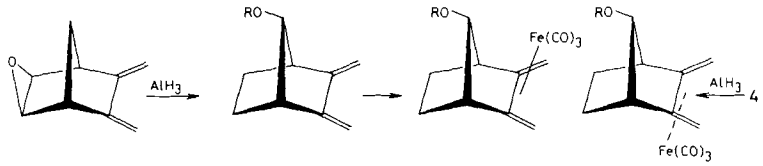
We have shown that the HCl-addition to the epoxide **4** (assumed to undergo *via* the *exo*-3-hydroxy-2-norbornyl cation intermediate **7x**) was a fast and stereospecific process giving the rearranged adduct **5**. In contrast, the *endo*-isomer **6** did not react under the same conditions [13]. This was interpreted as due to a stronger dipole-cation destabilization in the intermediate **7n** than in the *exo*-isomer **7x** because of a shorter C(2), $Fe(CO)_3$-distance in **7n** than in **7x**. We report now on the S_Ni solvolyses of η^4-5,6-dimethylidene-2-*exo*-norbornyl-iron tricarbonyl *p*-bromobenzenesulfonates **11x** (*exo*-$Fe(CO)_3$) and **11n** (*endo*-$Fe(CO)_3$) that are a test for the relative stabilities of the 2-norbornyl cation intermediates **8x** and **8n**, respectively. We have also studied the solvolyses of the η^4-2,3-dimethylidene-7-*anti*-norbornyl-iron tricarbonyl *p*-bromobenzenesulfonates **19x** and **19n**. We shall show that the inductive destabilization of a cationic center homoconjugated with an exocyclic diene-iron tricarbonyl group can be overwhelmed by a stabilization effect due to the polarizability of this function. The greater is the electronic demand (intrinsic instability) of the norbornyl cation intermediate, the larger is the intervention of the latter effect.

Results. – Hydroboration followed by oxidative work-up of a mixture of the *exo*- and *endo*-5,6-dimethylidene-2-norbornene-iron tricarbonyl complexes **9x** and **9n** [14] gave the *exo*-alcohols **10x** (18%) and **10n** (19%) that could be isolated in a pure form by column chromatography. These compounds were transformed readily into the corresponding *p*-bromobenzenesulfonates **11x** and **11n** [15], respectively. The acetate **12x** (Ac_2O, pyridin, 0°, 12 h) was also prepared. The direct reaction of the diene-alcohol **13** [16] and $Fe_2(CO)_9$ in MeOH (50°) gave lower yields of the complexes **10x** (20%) and **10n** (2%). Irradiation (pyrex, THF, −20°) of **13** and $Fe(CO)_5$ led also to very poor yields.



9x, 9n 10x, 10n

Complexation ($Fe_2(CO)_9$, MeOH, 45°, 24 h) of the 7-*anti*-norbornanol **16** obtained by AlH_3-reduction of the epoxy-diene **15** [17] gave the *exo*-complex **17x** in low yield. None of the *endo*-isomer **17n** was observed. The latter was obtained together with **10x** (**10x**/**17n** 2:3) by AlH_3-reduction of the complexed diene-epoxide **4** [13]. The *endo*-complex **17n** was isolated in pure form by column chromatography (13%). The *p*-bromobenzenesulfonates **19x**, **19n** and the acetates **20x**, **20n** were



15 R = H, R = Bs, R = Ac; 16, 18; 17x, 19x, 20x; 17n, 19n, 20n

Bs = *p*-$BrC_6H_4SO_2$

prepared following standard procedures from the alcohols **17x** and **17n**, respectively.

The structures of the new iron tricarbonyl complexes **10–12**, **17–20** were deduced from their mode of formation, their elemental analysis, their spectral data and comparison with those of related systems [13] [14] [18]. The *exo*-position of the hydroxy group in **10** was confirmed by the absence of vicinal coupling constant between the H–C(2) and the bridgehead H–C(1) [19] and by lanthanide ($Eu(dpm)_3$)-induced shifts in the ^{1}H-NMR. spectrum. The *exo- vs. endo*-configuration of the $Fe(CO)_3$-group in the complexes **10–12** was determined unambiguously by chemical correlation with the (+)-(1*S*,2*R*)-5,6-dimethylidene-2-*exo*-norbornyl-*exo*-iron tricarbonyl *p*-bromobenzoate for which a X-ray single crystal structure has been obtained [20]. The *endo*-⇄*exo*-$Fe(CO)_3$ isomerization has never been observed for complexes of exocyclic dienes upon heating or in the presence of large excesses of iron carbonyls [21]. It does not occur either under acidic conditions unless the bicyclic skeleton undergoes a rearrangement as in the case of **4** + HCl → **5** [13]. Analogously, the *endo*-$Fe(CO)_3$ of **17n** was expected for the AlH_3-induced rearrangement-reduction of the epoxide **4** [17]. The stereospecificity of the rearrangement **4** → **5** was established by resolving the single crystal structure of **4** and **5** by X-ray crystallography [13]. The 7-*anti* position of the hydroxy group in **17** was confirmed by $Eu(dpm)_3$-induced shifts in the ^{1}H-NMR. spectrum *(cf. Exper. Part)*.

The buffered acetolyses of **11x**, **19x** and **19n** gave the acetates **12x**, **20x** and **20n**, respectively. No other product could be detected (beside some uncomplexed diene formed slowly upon heating), thus demonstrating the high stereoselectivity of these S_N1 solvolyses. The acetolysis of the *endo*-complex **11n** was too slow to

Table. *First-order rate constants of the buffered* (CH_3CO_2K) *acetolyses* (CD_3CO_2D) *of the* p-*bromobenzenesulfonates* **11x**, **11n**, **14**, **18**, **19x** *and* **19n** *at 65°* ([*p*-bromobenzenesulfonate] ≃ $2.3 \cdot 10^{-4}$ M)

Starting material	k [s^{-1}][a]	k_{rel}	Starting material	k [s^{-1}][a]	k_{rel}
14	$5.5 \cdot 10^{-3}$[b]	(1.0)	**18**	$1.1 \cdot 10^{-7}$[d]	(1.0)
11x	$4.8 \cdot 10^{-8}$	$8.7 \cdot 10^{-6}$	**19x**	$4.2 \cdot 10^{-6}$	38
11n	$< 10^{-10}$[c]	$< 2 \cdot 10^{-8}$	**19n**	$2.9 \cdot 10^{-8}$	0.26

[a]) Slope of ln[unreacted complex] *vs.* time; least-squares bb′ > 0.98. [b]) Extrapolated from [16]. [c]) Too slow to be detected beside the thermal decomposition of the complex. [d]) Extrapolated from [22].

be detected beside decomposition of the complex, followed by acetolysis of the free ligand [16]. The retention of configuration can be explained in terms of steric effects in the acetolyses of **11x** and **19x**, but not for **19n**→**20n**. In the latter case, participation of the *endo*-diene-Fe(CO)$_3$ group must be invoked, as suggested also by the comparison of the rate constants measured at 65° (see *Table*).

Discussion. – The acetolysis of the *exo*-complex **11x** was found to be retarded by a factor of *ca.* 10^5 compared with that of the uncomplexed *p*-bromobenzenesulfonate **14**. This can be attributed to the inductive effect of the Fe(CO)$_3$-group. The retardation effect is somewhat smaller than in the case of the hydrolysis of the 7-nonbornadienyl-iron tricarbonyl tosylate [10]. A rate retardation effect larger than $5 \cdot 10^7$ is observed for the acetolysis of the *endo*-complexed *p*-bromobenzenesulfonate **11n** compared with that of **14**. This is expected since the distance between C(2) and the Fe-atom is shorter in **11n** (3.4 Å[3])) than in **11x** (4.4 Å[4])). In contrast, the acetolysis of the Fe(CO)$_3$ complexed *p*-bromobenzenesulfonate **19x** is accelerated when compared with those of the *endo*-isomer **19n** and the uncomplexed *p*-bromobenzenesulfonate **18** (see *Table*). The C(7), Fe-distance in **19x** is evaluated to 3.3 Å[4]) and to 4.1 Å[3]) in **19n**. If only a charge C(7), dipole (diene-Fe(CO)$_3$) interaction (V_C [23]) should dominate the stability of the carbocationic intermediate, we would have the expected rate retardation effects for the solvolyses of **19x** and **19n** (*vs.* **18**) comparable to those observed for the acetolyses of **11n** and **11x** (*vs.* **14**), respectively.

$$V_C = \pm q\mu \cos\theta/\varepsilon r^2$$

$$V_I = -q^2\alpha/2\varepsilon r^4$$

The 7-norbornyl cation is much less stable than its 2-norbornyl isomer [24]. Thus, the electronic demand of the cationic intermediates generated in the S_N1 solvolyses of **19x** and **19n** is greater than that in the 2-norbornyl cation intermediates **8x** and **8n**. If one considers a charge C(7), induced dipole (diene-Fe(CO)$_3$) interaction V_I (stabilizing effect [23]) to be competitive, one sees for a given distance r that its contribution can overide that of V_C (a destabilization interaction because of the sign of the dipole moment μ) if the charge q at the ionizing center is large enough. This must be so because V_C is a function of q whereas V_I depends upon q^2 [5]).

According to the simple Electrostatic Field Model [23], the dramatic rate retardation observed in the hydrolysis of the 7-norbornadienyl *p*-toluenesulfonate upon complexation by an *endo*-Fe(CO)$_3$ group is unexpected unless one assumes a much smaller polarizability α for the *endo*-1,4-diene-Fe(CO)$_3$ function in the latter system than for the *endo*- and *exo*-exocyclic diene-Fe(CO)$_3$ groups in **19n**

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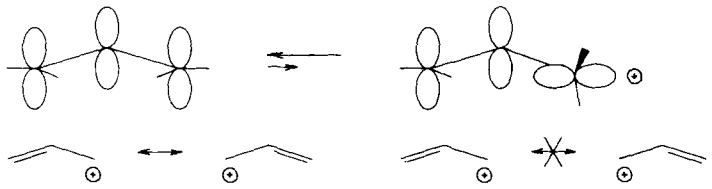
[3]) From the single crystal structure of 5,6-dimethylidene-7-*syn*-hydroxy-2-*exo*-methoxynorbornane-*endo*-iron tricarbonyl [13].

[4]) From the single crystal structure of (+)-(1*S*,2*R*)-5,6-dimethylidene-2-*exo*-norbornyl-*exo*-iron tricarbonyl *p*-bromobenzoate [20].

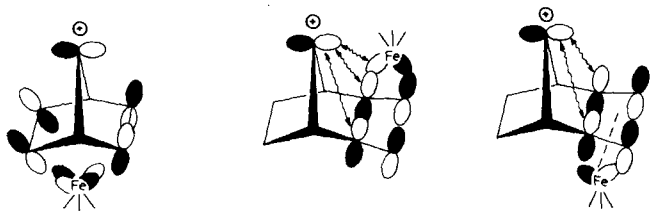
[5]) The effects of one, two and three fluoro or methoxy substituents ((–*I*)-effect (dipole), +*M*-effect (polarizability)) on the stability of the methyl cation illustrate this fact [25].

and **19x**, respectively. This is possible because of symmetry differences between these systems.

The polarizability of the vinyl substituent in an allyl cation is not the same for a planar cation (stable) or a perpendicular (unstable) species [26].

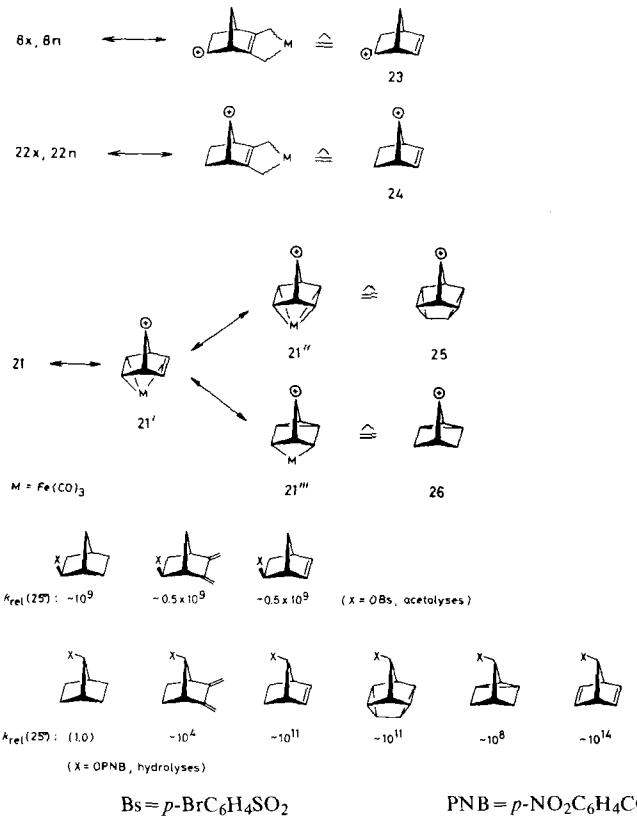


The Perturbational Molecular Orbital (PMO) theory [27] can rationalize these facts easily. It invokes different overlaps between the substituent localized HOMO and the carbenium ion localized LUMO. The valence bond theory can also rationalize the difference in stability between the parallel and perpendicular allyl cations. Upon complexation by a $Fe(CO)_3$-fragment, the electron density in the HOMO of the diene is decreased. Back-donation from the transition metal populates the former LUMO of the π-system [28]. In the case of the 7-norbornadienyl cation **21**, complexation by the *endo*-$Fe(CO)_3$ group leads to a decreased overlap between the olefin HOMO's and C(7) empty orbital. No stability can be gained by a 'filled' LUMO (olefin) – empty p (C(7)) interaction, the overlap being zero for reasons of symmetry. In the case of the 2,3-dimethylidene-7-norbornyl cation intermediates **22x** and **22n**, the HOMO(diene-$Fe(CO)_3$), empty p (C(7)) interaction is possible. It is expected to be larger in **22x** than in **22n** (see below). These interactions can be viewed as a participation of the homoconjugated diene-iron tricarbonyl group to the S_N1 solvolyses of the 7-*anti*-norbornyl esters, thus explaining the retention of configuration observed in the acetolyses of **19x** and **19n** and the greater S_N1 reactivity of **19x** compared with that of **19n**.



21 22x 22n

If one assumes the usual limiting structures implying σ-bonded $Fe(CO)_3$ to describe the properties of the diene complexes [29], one can also rationalize the differences in stability between the 2- and 7-norbornyl cationic species **8** and **22**, respectively, by comparing them with the 2- and 7-norbornenyl cations **23** and **24**, respectively [30]. The electronic demand of the cation at C(7) in **24** being larger than that of the cation at C(2) in **23**, a significantly larger participation of the exocyclic double bond was evidenced for **24** than for **23** [24] [30].



Bs = *p*-$BrC_6H_4SO_2$ PNB = *p*-$NO_2C_6H_4CO$

If **21'**, **21''** and **21'''** are limiting structures of **21**, one expects this intermediate to be less stable than the 7-norbornadienyl cation. One estimates a S_N1 rate-retardation effect $\geqslant 10^3$ by analogy with the *Coates'* cation **25** [31] and the 3-nortricyclyl cation **26** [32]. If one considers now the inductive effect $< 10^{-5}$ of the *endo*-$Fe(CO)_3$ group, as evaluated by the comparison of the acetolyses rate constants for **11x** *vs.* **14**, one calculates a rate-retardation effect larger than 10^8 for the solvolysis of 7-norbornadienyl esters upon *endo*-complexation by the $Fe(CO)_3$-group. This is in agreement with the observations [10]. The same crude treatment applied to the solvolysis of **19n** leads to a predicted rate acceleration $< 10^7$ when going from **18** to an *anti*-7-norborn-2-enyl ester. Considering the same inductive effect ($< 10^{-5}$) due to complexation with an *endo*-$Fe(CO)_3$ group, one calculates a rate ratio < 100 for the acetolyses of **19n** *vs.* **18**. This is not far off our observations.

Conclusion. – The 2-norbornyl cation intermediates homoconjugated to an exocyclic diene-iron tricarbonyl group are destabilized under the conditions of the S_N1 acetolysis because of the dominating charge(cation), dipole(diene-$Fe(CO)_3$) interaction. This effect is larger for the *endo*-complex **11n** than for the *exo*-isomer **11x**. In the case of the intrinsically less stable 7-norbornyl derivatives **19x** and **19n**, the stabilizing charge C(7), induced dipole(diene-$Fe(CO)_3$) interaction becomes

competitive. The latter effect can be explained in simple PMO terms that invoke the overlap between the empty p orbital localized at the cationic center and the HOMO of the remote diene-iron tricarbonyl substituent.

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Experimental Part

General Remarks. All reactions were carried out under Ar and the solvents were dried and degassed by standard methods [33]. Melting points (m.p.) (not corrected), *Tottoli* apparatus. IR. spectra ($\tilde{\nu}$ [cm^{-1}]), *Perkin-Elmer* 577 spectrophotometer. UV. spectra, *Beckman Acta V* spectrophotometer (λ_{max} [nm] (ε [M^{-1} cm^{-1}])). Mass spectra (MS.) at 70 eV, *Hewlett-Packard* GC-MS 5980 spectrometer (*m/z* [amu] (% base peak)). ^{1}H-NMR. spectra, *Bruker WH-360* spectrometer (360 MHz): δ [ppm] (multiplicity, number of protons, tentative attribution [LIS: relative shift induced by addition of Eu(dpm)$_3$]), coupling constants *J* [Hz]. ^{13}C-NMR. spectra, *Bruker WH-360* spectrometer (90.55 MHz, deuterium signal of $CDCl_3$ as lock signal, δ_C of $CDCl_3$ as internal reference (76.91 ppm)): δ [ppm] (multiplicity, ^1J(C,H) coupling constant ($\pm$ 1 Hz), tentative attribution). Separations by HPLC. were made on a *Dupont 830* liquid chromatograph (Kieselgel preparative column, 100 psi, hexane/ethyl acetate 4:1). *E. Manser* (Mikrolabor, ETH, Zürich) carried out the microanalyses.

*Preparation of (η⁴-5,6-dimethylidene-2-*exo*-norbornanol)irontricarbonyl* (**10x** *and* **10n**). $BF_3 \cdot Et_2O$ (15 ml) and $NaBH_4$ (3.2 g, 84.5 mmol) in THF were added dropwise to a 1:1 solution of **9x/9n** ([14] (0.774 g, 3 mmol) in ether (20 ml) at 0°, and the mixture stirred at RT. for 2 h. Water was added, then 3 M KOH in water and 30% H_2O_2-solution (1 ml). The suspension was filtered, reduced to a small volume, and chromatographed on neutral alumina (activity grade II). Elution with hexane/ethyl acetate 4:1 brought down two fractions. Recrystallization at −20° from hexane/ether 4:1 gave **10x** (18%) and **10n** (19%) as yellow microcrystals. The direct reaction of **13** (22 mmol) and $Fe_2(CO)_9$ (28 mmol) in methanol at 50° followed by chromatography on silica gel with hexane/dichloromethane gave **10n** in lower yield (2%) and **10x** (20%). Extensive decomposition was observed with $Fe_2(CO)_9$ in hexane, whereas irradiation of **13** and $Fe(CO)_5$ in THF at −20° gave a negligible yield of products. **10x**: m.p. 99–100°. **10n**: m.p. 90–91°. The spectral data of **10x** and **10n** are identical with those of the corresponding optically pure isomers which were prepared by a different route [20].

$C_{12}H_{12}FeO_4$	Calc.	C 52.21	H 4.38%			
(276.08)	Found	„ 52.29	„ 4.49% (**10x**)	C 52.68	H 4.49% (**10n**)	

*Preparation of (η⁴-2,3-dimethylidene-7-*anti-*norbornanol)-*exo*-irontricarbonyl* (**17x**). A solution of **15** (7 g, 52 mmol) and AlH_3 [17] (60 mmol) in THF (250 ml) was heated under reflux for 5 h. After addition of water, the mixture was extracted with CH_2Cl_2 and the combined extracts dried over $MgSO_4$, filtered and reduced to a small volume. The liquid containing **13**, **15** and **16** was taken up in MeOH (100 ml) containing $Fe_2(CO)_9$ (3 g) and stirred at 45° for 24 h. After filtration and reduction to a small volume, the residue was chromatographed on *Florisil* using first hexane to eliminate $Fe_3(CO)_{12}$. Elution with hexane/ether (50 *v/v* %) brought down complex **17x** containing **10x** as an impurity. Purification by HPLC. followed by recrystallization from hexane/ether 1:1 at −25° gave complex **17x** (0.6 g; 4% with respect to **15**). Yellow crystals, m.p. 116°. – IR. (CCl_4): 2060, 1980, 1965 (CO); 3620 (OH). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 4.05 (*m*, 1 H, H*syn*–C(7)); 2.52 (*m*, 2 H, H–C(1,4)); 2.19 (*m*, 2 H, H*endo*–C(5,6)); 1.76 (*d*, 2 H, H(*E*)–C(8,9)); 1.57 (*m*, 2 H, H*exo*–C(5,6)); 0.23 (*d*, 2 H, H(*Z*)–C(8,9)); $J(1,7) = 1.7$, $J(1,6x) = 3.8$, $J(1,6n) < 1$, $J(5x,5n) = 12$, $J(5n,6x) = 3$, $J(5x,6x) = 5$, $J(E,Z) = 2.6$ Hz. – ^{13}C-NMR. (90.55 MHz, $CDCl_3$): 209.6 (*s*, CO), 109.7 (*s*, C(2,3)); 80.3 (*d*, 154, C(7)); 44.2 (*d*, $J = 148$, C(1,4)); 32.3 (*t*, $J = 160$, C(8,9)); 24.3 (*t*, $J = 136$, C(5,6)). – MS.: 276 (10, M^+), 248 (51), 220 (85), 192 (100, $M^+ - 3$ CO), 91 (85), 56 (90).

$C_{12}H_{12}FeO_4$ (276.08) Calc. C 52.21 H 4.38% Found C 52.11 H 4.41%

*Preparation of (η⁴-2,3-dimethylidene-7-*anti-*norbornanol)-*endo*-irontricarbonyl* (**17n**) *and (η⁴-5-*exo*-deuterio-2,3-dimethylidene-7-*anti-*norbornanol)-*endo*-irontricarbonyl* (**17n(D)**). A solution of AlH_3 (14.1 mmol hydride) in THF (8 ml) was added dropwise to a solution of **4** (1 g, 3.65 mmol) in ether

(50 ml). After stirring for 24 h at room temperature, water (10 ml) was added, and the cooled mixture extracted with ether. The combined extracts were dried over $MgSO_4$ and evaporated to dryness. The crude product was taken up in CH_2Cl_2 and chromatographed on a 40×2 cm column packed with *Florisil*. Elution with hexane/CH_2Cl_2 1:1 brought down a 3:2 mixture of **17n** and **10x** (30% yield). The two isomers were separated by chromatography with hexane/ether 95:5. Recrystallization from hexane/ether 4:1 at −25° gave yellow crystals of **17n** (0.14 g, 18%). Other reducing agents gave lower yields ($LiAlH_4$) or decomposed the starting complex (Et_3BLiH or vitride). Reduction of **4** by AlD_3 in THF followed by the same work-up gave **17n(D)** as yellow crystals. Yield 18%.

Data of **17n**. M.p. 123–124°. – UV. (heptane): 305 (2198), 220 (21300). – IR. (CCl_4): 2060, 1980, 1965; 3620. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 4.34 (br. *d*, 1H (29%), H–C(7)); 2.78 (*m*, 2H (13%), H–C(1,4)); 2.32 (*d*, 1H (100%), OH); 2.27 (*m*, 2H (17%), H*exo*–C(5,6)); 1.92 (*d*, 2H (4%), H(*E*)–C(8,9)); 1.30 (*m*, 2H (9%), H*endo*–C(5,6)); 0.40 (*d*, 2H (3%), H(*Z*)–C(8,9)); $J(1,7)=1.5$, $J(1,6x)=3.5$, $J(5x,5n)=12$, $J(5x,6x)=5$, $J(5n,6x)\simeq 2$, $J(7,OH)=5$, $J(E,Z)=2.7$. – ^{13}C-NMR. (90.55 MHz, $CDCl_3$): 211.1 (*s*, CO); 118.8 (*s*, C(2,3)); 84.4 (*d*, $J=156$, C(7)); 46.7 (*d*, $J=146$, C(1,4)); 33.7 (*t*, $J=159$, C(8,9)); 29.1 (*t*, $J=136$, C(5,6)). – MS.: 276 (2, M^+), 248 (16), 220 (31), 192 (48), 174 (7), 164 (100), 148 (6), 91 (54), 56 (90).

$C_{12}H_{12}FeO_4$ (276.08) Calc. C 52.21 H 4.38% Found C 52.03 H 4.31%

Data of **17n(D)**. M.p. 123–124°. – IR. and UV.: same as **17n**. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 4.33 (br. *d*, 1H (13%), H–C(7)); 2.77 (*m*, 2H (8%), H–C(1,4)); 2.28 (*d*, 1H (100%), OH); 2.23 (*m*, 1H (20%), H*exo*–C(6)); 1.86 (*d*, 2H (3%), H(*E*)–C(8,9)); 1.30 (*m*, 2H (10%), H*endo*–C(5,6)); 0.40 (*d*, 2H (3%), H(*Z*)–C(8,9)). – ^{13}C-NMR. (90.55 MHz, $CDCl_3$): 211.1 (*s*, CO); 119.1 (*s*, C(2,3)); 84.8 (*d*, $J=156$, C(7)); 47.1 (*d*, $J=146$, C(1,4)); 33.7 (*t*, $J=159$, C(8,9)); 29.0 (*t*, $J=135$, C(6)); 28.9 (*d*×*d*, $J=135$, $J(C,D)=41.2$, C(5)). – MS.: 277 (3, M^+), 249 (17), 221 (39), 143 (50), 193 (50), 164 (100), 91 (50), 56 (90).

$C_{12}DH_{11}FeO_4$ (277.09) Calc. C 52.02 H + D 4.73% Found C 52.15 H + D 4.44%

*Preparation of (η⁴-5,6-dimethylidene-2-*exo*-norbornyl)irontricarbonyl* p*-bromobenzenesulfonate* (**11x** *and* **11n**), *η⁴-2,3-dimethylidene-7-*anti*-norbornyl-irontricarbonyl brosylate* (**19x** *and* **19n**). A solution of **17n** (0.18 g, 0.65 mmol) and 4-bromobenzenesulfonyl chloride (0.25 g, 0.97 mmol) in pyridin (16 ml) was stirred for 3 days at RT., then extracted with 60 ml ether/ice water 5:1. The combined ether extracts were washed with 5% HCl-solution, then with saturated $NaHCO_3$-solution, finally with water, and dried over $MgSO_4$. Column chromatography on *Florisil* with hexane/CH_2Cl_2 4:1 gave two yellow bands containing **19n** and unreacted **17n** (30%). Recrystallization from hexane/ether 3:1 at −25° gave complex **19n** (0.2 g, 62%). The same reaction starting with **10x**, **10n**, and **17x** gave **11x** (88%), **11n** (85%) and **19x** (65%), respectively.

Data of **11x**. Yellow crystals, m.p. 132–133°. – UV. (isooctane): 285 (3090), 230 (29900). – IR. (CCl_4): 2060, 1985, 1970. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.81 and 7.73 (2 *d*, each 2H, $J(H,H)=9$); 4.91 (*m*, H–C(2)); 2.92 (br. *m*, 1H, H–C(1)); 2.75 (br. *m*, 1H, H–C(4)); 2.11 (*m*, 1H, H*endo*–C(3)); 1.96 (*m*, 1H, H*exo*–C(3)); 1.85 (*m*, 1H, H*syn*–C(7)); 1.83 (*d*, 2H, H(*E*)–C(8,9)); 1.82 (*m*, 1H, H*anti*–C(7)); 0.31 and 0.27 (2 *d*, each 1H, H(*Z*)–C(8,9)); $J(1,2)\simeq J(4,3n)<1$, $J(1,7s)\simeq J(4,7s)\simeq J(1,7a)\simeq J(4,7a)=1.5$, $J(2,7a)\simeq J(3n,7a)=2.5$, $J(2,3n)=6.5$, $J(2,3x)=3$, $J(3x,3n)=13.0$, $J(3x,4)=3.6$, $J(7a,7s)=8.5$, $J(E,Z)=2.1$. – MS. (^{56}Fe, ^{81}Br, ^{79}Br): 468, 466 (1, M^+-CO), 440, 438 (4), 412, 410 (14, $M^+-3\,CO$), 91 (100).

Data of **11n**. M.p. 133–134°. – IR. (CCl_4): 2060, 1980, 1960. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 7.83 and 7.75 (2 *d*, each 2H, $J(H,H)=9$); 5.10 (*m*, 1H, H–C(2)); 3.00 (br. *m*, 1H, H–C(4)); 2.90 (*m*, 1H, H–C(1)); 2.15–1.70 (*m*, 4H); 1.80 (*d*, 2H, H(*E*)–C(8,9)); 0.52 and 0.42 (2 *d*, each 2H, H(*Z*)–C(8,9)). – MS.: 468, 466 (1), 440, 438 (10), 412, 410 (21), 91 (100).

$C_{18}H_{15}BrO_6SFe$ (495.13) Calc. C 43.66 H 3.05%
Found „ 43.70 „ 3.13% (**11x**) C 43.72 H 3.17% (**11n**)

Data of **19x**. Yellow crystals, m.p. 149–150°. – IR. (CCl_4): 2060, 1980, 1970. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.74 and 7.70 (2 *d*, $J(H,H)=8$, each 2H); 4.42 (br. *m*, 1H, H–C(7)); 2.64 (*m*, 2H, H–C(1,4)); 2.16 (*m*, 2H, H*exo*–C(5,6)); 1.75 (*d*, 2H, H(*E*)–C(8,9)); 1.61 (*m*, 2H, H*endo*–C(5,6)); 0.23 (*d*, 2H, H(*Z*)–C(8,9)); $J(1,7)=1.5$, $J(1,6x)=3.5$, $J(1,6n)<1$, $J(5x,5n)=12$, $J(5x,6x)\simeq J(5n,6n)=5$, $J(E,Z)=2.7$. – ^{13}C-NMR. (90.55 MHz, $CDCl_3$): 208.5 (*s*, CO), 132.7 and 129.4 (2 *d*,

J = 170), 135.6 and 129.3 (2 *s*), 107.5 (*s*, C(2,3)); 86.1 (*d*, J = 154, C(7)); 43.1 (*d*, J = 148, C(1,4)); 32.6 (*t*, J = 160, C(8,9)); 24.8 (*t*, J = 136, C(5,6)). – MS.: 468, 466 (10), 440, 438 (41), 412, 410 (56), 384, 382 (100).

Data of **19n**. M.p. 137°. – UV. (heptane): 300 (1800), 230 (28500). – IR. (CCl_4): 2060, 1980, 1970. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.87 and 7.78 (2 *d*, J(H,H) = 9, each 2 H); 4.78 (*m*, 1 H, H–C(7)); 2.92 (*m*, 2 H, H–C(1,4)); 2.19 (*m*, 2 H, H–C(5x,6x)); 1.89 (*d*, 2 H, H(*E*)–C(8,9)); 1.32 (*m*, 2 H, H–C(5n,6n)); 0.39 (*d*, 2 H, H(*E*)–C(8,9)); J(1,7) = 1.5, J(1,6x) = 3.5, J(5x,5n) = 12, J(5x,6x) = 5, J(5n,6x) = 2, J(*E*,*Z*) = 2.8. – MS.: 468, 466 (5), 440, 438 (19), 412, 410 (27), 382 (100).

$C_{18}H_{15}BrFeO_6$	Calc.	C 43.66	H 3.05%			
(495.13)	Found	,, 43.74	,, 3.05% (**19x**)	C 44.00	H 3.25% (**19n**)	

*Preparation of (η^4-5,6-Dimethylidene-2-*exo*-norbornyl)irontricarbonyl acetate* (**12x**). *(η^4-2,3-dimethylidene-7-*anti*-norbornyl)irontricarbonyl acetate* (**20x** *and* **20n**). A solution of **17n** (0.2 g, 0.725 mmol) and acetic anhydride (1 ml) in pyridine (1 ml) was stirred for 12 h at 0°. The same work-up as for **19n** gave complex **20n** (90%). Starting with **10x** and **17x** gave **12x** (91%) and **20x** (90%), respectively. The same reaction with **10n** failed to give any reasonable yield of **12n**. Complex **12n** was observed only in solution (by ^{1}H-NMR.) and in small quantity during the kinetic runs of the acetolysis of **11n**. Replacing acetic anhydride by acetyl chloride gave lower yields of complexes (*ca.* 70%).

Data of **12x**. Yellow crystals, m.p. 66–67°. – IR. (CCl_4): 2060, 1980, 1965 (CO)); 1745 (COO). – ^{1}H-NMR. (80 MHz, $CDCl_3$): 5.07 (*m*, 1 H, H–C(2)); 2.85 (*m*, 2 H, H–C(1,4)); 2.10 (*s*, 3 H, CH_3); 2.1–1.8 (*m*, 4 H, H_2C(3,7)); 1.83 (*d*, 2 H, H(*E*)–C(8,9)); 0.37 (*d*, 2 H, H(*Z*)–C(8,9)); J(*E*,*Z*) = 2.2. – MS.: 318 (3, M^+), 290 (33), 262 (40), 234 (100, $M^+ - 3$ CO), 175 (44).

Data of **20x**. M.p. 77–78°. – IR. (Et_2O): 2060, 1980, 1970, 1740. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 4.72 (*m*, 1 H, H–C(7)); 2.77 (*m*, 2 H, H–C(1,4)); 2.20 (*m*, 2 H, H*exo*–C(5,6)); 2.18 (*s*, 3 H, CH_3); 1.87 (*d*, 2 H, H(*E*)–C(8,9)); 1.76 (*m*, 2 H, H*endo*–C(5,6)); 0.32 (*d*, 2 H, H(*Z*)–C(8,9)). – ^{13}C-NMR. (90.55, $CDCl_3$): 209.5 (*s*, CO); 170.2 (*s*, C=O); 108.3 (*s*, C(2,3)); 81.2 (*d*, J = 162, C(7)); 42.3 (*d*, J = 151, C(1,4)); 32.3 (*t*, J = 160, C(8,9)); 24.5 (*t*, J = 136, C(5,6)); 20.9 (*qa*, J = 130, CH_3). – MS.: 318 (5), 290 (47), 262 (50), 234 (100), 206 (70), 91 (100).

Data of **20n**. M.p. 83–84°. – UV. (hexane): 306 (1990), 220 (17500). – IR. (CCl_4): 2060, 1975, 1965, 1740. – ^{1}H-NMR. (80 MHz, $CDCl_3$): 4.95 (br. *s*, 1 H (100%), H–C(7)); 2.75 (*m*, 2 H (46%), H–C(1,4)); 2.07 (*m*, 2 H (46%), H*exo*–C(5,6)); 1.70 (*s*, 3 H (79%), CH_3); 1.65 (*d*, 2 H (6%), J(*E*,*Z*) = 2.8, H(*E*)–C(8,9)); 1.32 (*m*, 2 H (23%) H*endo*–C(5,6)); 0.15 (*d*, 2 H (6%), H(*Z*)–C(8,9)). – MS.: 318 (1, M^+), 290 (13), 262 (29), 234 (26, $M^+ - 3$ CO), 206 (98), 91 (100).

$C_{14}H_{14}FeO_5$	Calc.	C 52.86	H 4.44%	C 53.79	H 4.69% (**20x**)
(318.11)	Found	,, 52.92	,, 4.44% (**12x**)	,, 53.01	,, 4.45% (**20n**)

Kinetics measurements. A typical procedure is given for the reaction **19n** → **20n**. To a NMR. tube containing **19n** (0.057 mmol) in C_6D_6 (0.1 ml) was added CD_3CO_2D (0.4 ml), two drops of freshly distilled acetic anhydride and anhydrous CH_3CO_2K (0.062 mmol). The tube was degassed and sealed *in vacuo*. The acetolysis was carried out at 65° and monitored by ^{1}H-NMR. (80 MHz). The resulting spectra were compared to that of an authentic sample of **20n** and showed a shift from 4.8 ppm in **19n** to 5.1 ppm in **20n** for the H–C(7) signal. Integration of the corresponding resonances for the unreacted *p*-bromobenzenesulfonate and the formed acetate gave the percent of product at time t. About 50% of the reaction was followed. Other products and/or decomposition began to appear for longer times, and at higher temperatures than 65°. The initial rate for the first few percents of reaction was faster than that reported in the *Table*, which corresponds to the slope of ln[unreacted *p*-bromobenzenesulfonate] *vs.* t. A similar observation has been reported for **18** [22]. For the ligands, the rate constants at 65° were extrapolated from the literature data ([16] for **14**, [22] for **18**) using the equation $\ln(k/T) = \ln(k_B/h) + (\Delta S^*/R) - (\Delta H^*/RT)$.

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