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THE SYNTHESIS OF BARBARALYL SYSTEMS VIA BICYCLIC[3.2.2] IRONTRICARBONYL CATIONS

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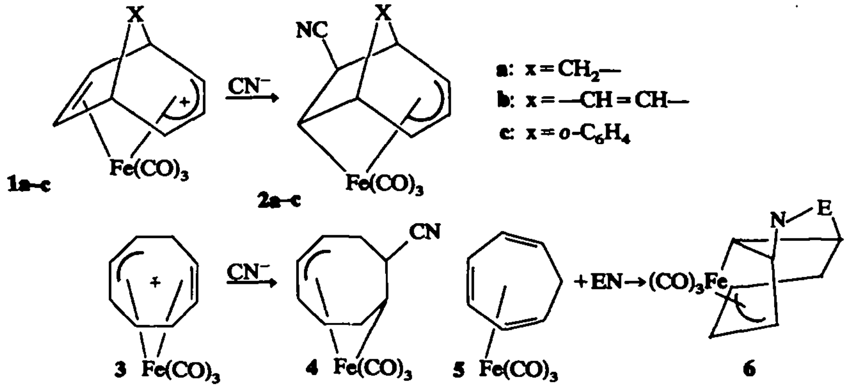
Abstract—Reaction of bicyclo[3.2.2] tertiary alcohols 7b,c and 23b with $Fe_2(CO)_9$ resulted in the corresponding dienyl $Fe(CO)_3$ complexes, which upon HBF_4/Ac_2O treatment yielded the bicyclo[3.2.2] dienyl irontricarbonyl cations. Nucleophilic addition of CN^- to those cations, resulted in the formation of σ,π-bonded complexes, which were degraded with Me_3NO to give substituted tricyclic hydrocarbons (barbaralyl systems) in unusual positions. For purpose of comparison, the trifluoroacetolysis of 2-methyl-*endo*-6,7-benzobicyclo[3.2.2] nonatriene (**22**) has been studied.

Vinylcyclopropanes are known to react with iron carbonyls to give iron complexes resulting from cleavage of a C—C bond in the cyclopropane ring.‡ This type of complex formation was also observed in the reaction of bicyclic and polycyclic hydrocarbons containing VCP systems.[1]

We[2a,b] and others[3a,b] recently reported that reactions of bicyclic (**1**) and mono-cyclic ring (**3**) cations with nucleophiles (such as H^- and CN^-) also lead to the formation of the above type of σ-π-allyl iron complexes (**2** and **4**). In addition, uniparticulate electrophiles (EN) such as TCNE, NPTD, HFA and diphenylketene can enter into cycloaddition reactions with cyclic trieneiron tricarbonyl (**5**) to give 1,3 σ-π-allyl iron tricarbonyl adducts (**6**) by either a stepwise or a concerted mechanism.[4] In order to explore the scope and mechanism of the nucleophic attack (mainly involving CN^-) on coordinated bicyclic dienyl cationic systems, we turned to a study of substituent effects in cations such as **1b,c**. It was also of interest to investigate the oxidative degradation of the latter reaction products, i.e., bicyclo-σ-π-allyl complexes, with trimethylamine-oxide, which led to tricyclic hydrocarbons (the corresponding barbaralyl systems) substituted at unusual positions.

RESULTS AND DISCUSSION

In a previous communication[5] we have described the products which were isolated from the reaction of the secondary bicyclic[3.2.2] alcohol **7a** with $Fe_2(CO)_9$. Both isomeric complexes **8a** and **9a** led on treatment with HBF_4 in acetic anhydride to the *same* cationic species (isolated as stable solid tetrafluoroborate salt), **1b**. The tertiary bicyclo [3.2.2]-trien-2-ols, **7b** and **7c** were prepared from the corresponding ketone with methyllithium and phenyllithium, respectively, in ether solution at −78°.[6] Reaction of **7b,c** and diiron enneacarbonyl in benzene for 2 hr at 45° resulted in formation of a mixture (when R═Me) of two isomeric complexes, where **8b** was the dominant one (**8b**/**9b** ≃ 10 : 1). In **8b** and **8c** the irontricarbonyl moiety is coordinated to 2 vinyl bridges (each involved two carbons), and their H^1-NMR spectra were very similar to that of the parent complex, **8a**[5]: (a) The vinyl protons $H_{6\text{-}9}$ of **8b** and/or **8a** are shifted by ~3 ppm upfield,



1a–c
2a–c

a: x = CH_2—
b: x = —CH = CH—
c: x = *o*-C_6H_4

3 **4** **5** **6**

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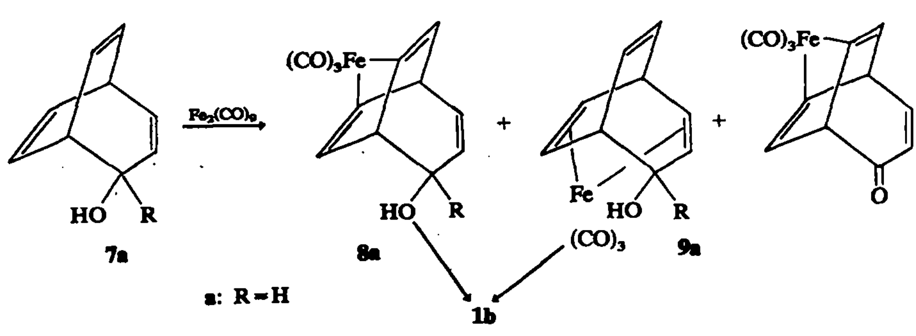
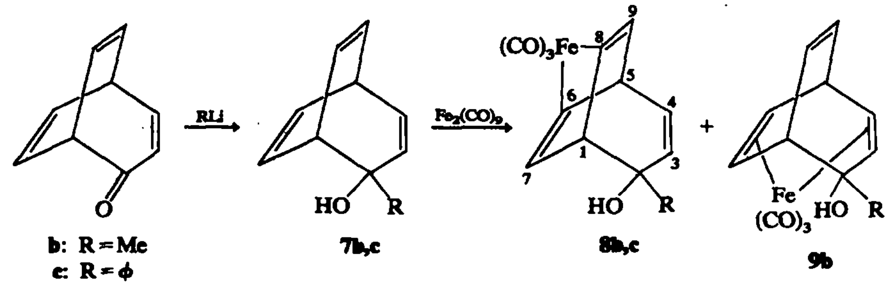
‡ Which involve σ and π-allyl types of bonds between the $Fe(CO)_3$ moiety and the organic ligand.



(1)



(2)

resulting from coordination of the ligand with the metal. (b) $\delta H_{3,4}$ remains unchanged, and the coupling constant between the two protons is not affected by the complexation ($J_{3,4} = 11$ Hz).

Treatment of the complexed alcohols **8b,c** with HBF_4 in acetic anhydride, followed by addition of ether led to the precipitation and isolation of **10b,c** as a fine, yellow powder. The isolated salts involved symmetrically coordinated π-allyl and vinyl-bonded moieties. Use of the appropriate deuterium labeling[5] suggested that deuterium isotope scrambling (determined by H^1-NMR integration) resulted from a 1,2-carbon shift (Wagner–Meerwein process) with ~90% deuterium-incorporation at the bridgehead position, **11a** and the rest ~10% of the total D-content at the vinyl bridge position, **10a**.

The H^1-NMR spectrum of the salt that resulted from HBF_4 treatment of **8b** (after *ca* 30 min) showed the existence of a mixture of cations, **10b** + **11b**, based on the appearance of two Me signals at δ1.8 (d) and at δ1.5 (s), respectively. Stirring this mixture for 24 hr at room temperature led to disappearance of the signal at δ1.5, and indicated the existence of a single cationic product, characterised as **10b** (Fig. 1). The increased relative amounts of cation **11b** resulted from shorter reaction times (in acidic media) and lower temperatures. Under the same conditions only a single cation **10c** was observed when **8c** was treated with HBF_4/Ac_2O.

While formation of cationic species **11a–c** is apparently kinetically controlled via a concerted mechanism, the second ion, **10a–c**, is obtained by a thermodynamically controlled process. A possible principle mechanism involves the rearrangement of the kinetically formed **11a–c** to **10a–c** via **11′**. In addition, one should also consider competitive

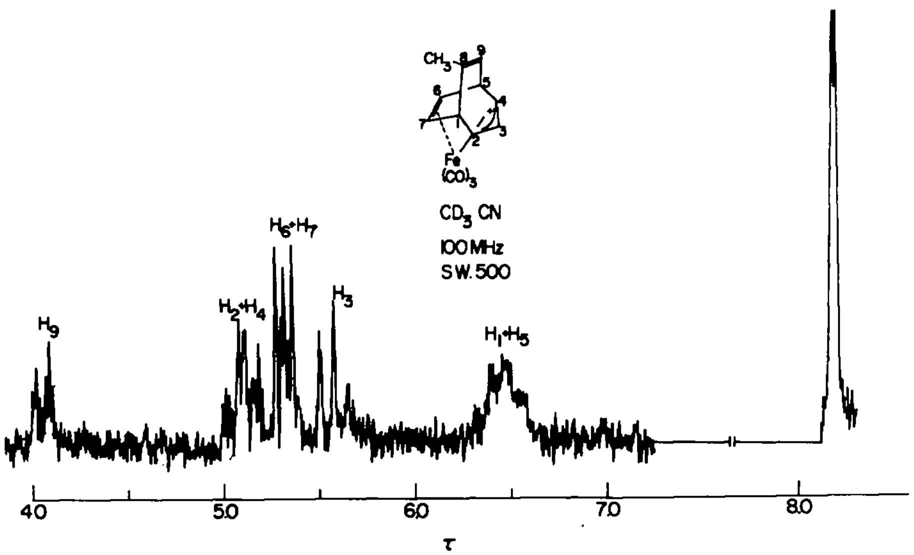
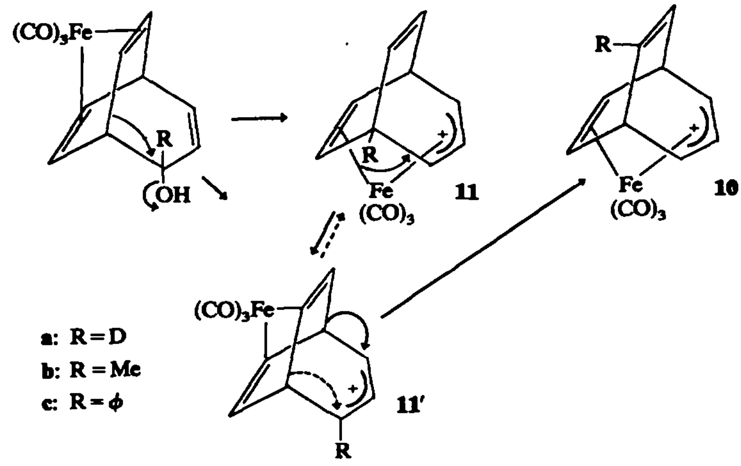


Fig. 1



a: R = D
b: R = Me
c: R = φ

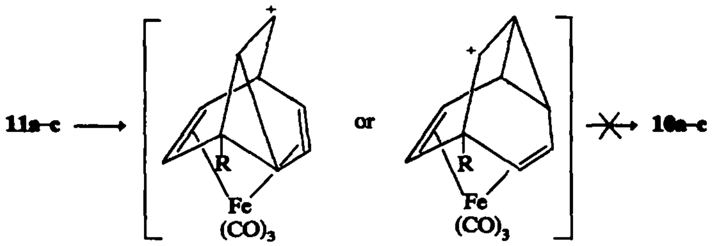
(3)

reaction, where **8a–c** is converted to **10a–c** and **11a–c** via **11′** (Scheme 3). We tend to assume, that **11c** constitutes a labile intermediate, and therefore is rapidly converted to **10c** where a steric hindrance of a bulky substituent such as phenyl group is removed.

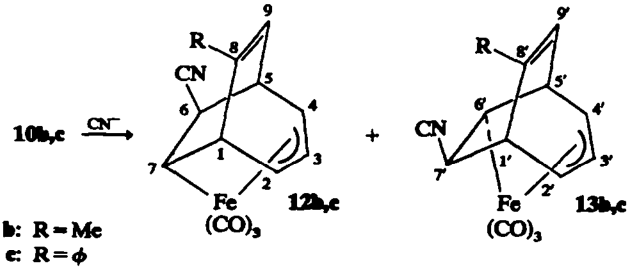
The alternative intermediacy of the barbaralyl cation (in which the metal still remains in its stable coordinative configuration), should be ruled out, since such an intermediate will not lead to cation **10**. Addition of the salts **10b,c** to a mixture of aqueous NaCN and ether resulted in high yields of the observed σ-η^3 allyl-cyano complexes **12b,c** and **13b,c**. A diagnostic spectral feature of the σ-η^3-allyl complexes is the strong shielding of the proton bonded to the carbon bearing the Fe atom. The CN^- nucleophile attacks the cationic species (**10b,c**) at the vinyl carbons from the *exo*-direction (*trans* to the metal-atom), as discussed elsewhere[2a] and confirmed by X-ray structural analysis of the monocyclic-σ-η^3 complex **4**[3b].

The above isomeric σ-η^3 complexes could not be separated by routine methods such as preparative tlc or column chromatography. The H^1-NMR spectrum of mixture (**12b**+**13b**) showed Me doublets of ratio 3:1 (area 3 protons). The same ratio has been found for the following set of protons: H_7/H'_6, H_9/H'_9 and H_4/H'_2. At this stage, we could not say which of the two isomers was the major one. The H^1-NMR spectrum of a mixture of analogous phenyl σ-η^3 isomeric complexes (**12c**+**13c**) exhibited two signals corresponding to one proton total of an uncomplexed double bond at δ6.36 (dd, $H_9+H'_9$) in a ratio of 1:1. Therefore, attack of CN^- on cation **10c** had resulted in equal amounts of the two possible cyano-σ-η^3 complexes. The preference for cyanide ion attack on **10b** is not yet well understood. Oxidative degradation of the above σ-η^3-allyl complexes was carried out with $Me_3N \rightarrow O$ in acetone. Trimethyl-amine-oxide is considered to be a mild $Fe(CO)_3$-"dissengager" which does not cause damage to sensitive organic ligands.[8]

Treatment of **12c**+**13c** ($R{=}\phi$) with

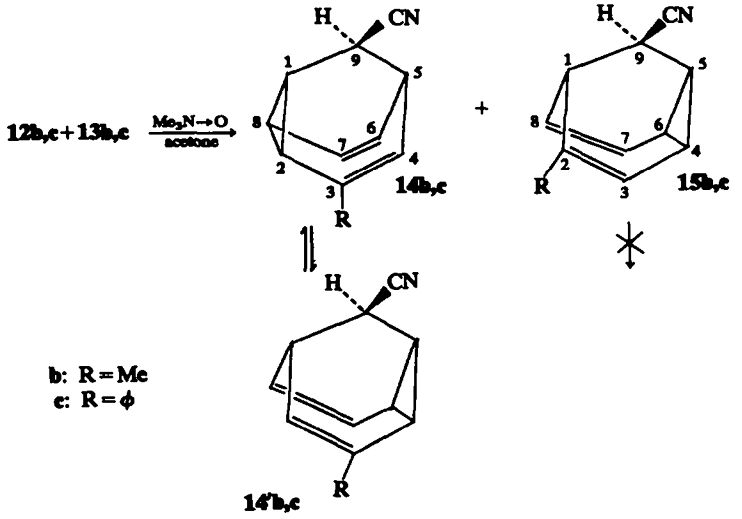


(4)



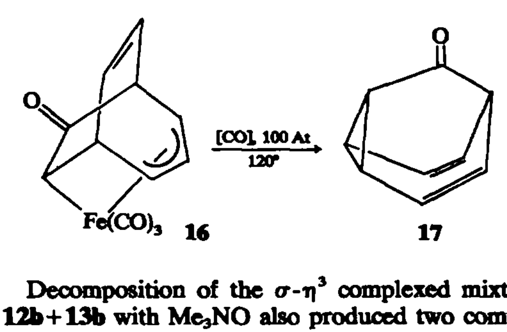
b: R = Me
c: R = φ

(5)



(6)

Me$_3$NO/acetone at room temperature resulted, as expected, in two products. One of them appeared as a cyrstalline white material, **14c**,† and was identified as a rarely known fluxional 3,9-disubstituted barbaralyl system. The NMR of **14c** reveals at room temperature a fast valence isomerization of **14c**⇄**14c** (Fig. 2). The second product **15c**, was very labile and air sensitive, and its H^1-NMR spectrum seems to indicate a non-fluxional system such as **15c**. Hence, the oxidative degradation of σ-η^3-iron bicyclo complexes opened a convenient route to the generation of tricyclo vinylcyclopropane systems (a novel synthesis of substituted barbaralyl molecules). Lewis[9] described recently the reaction of 16[10] (a σ-η^3-bicyclo iron complex) with CO under very severe conditions (120°, 100 ats), which liberated barbaralone, **17** (90%), a tricyclo vinylcyclopropane ketône.‡



Decomposition of the σ-η^3 complexed mixture **12b**+**13b** with Me$_3$NO also produced two components, **14b**+**15b**, in 39% yield. These compounds could not be separated by crystallisation or by column chromatography. Integration of H^1-NMR spectrum of the mixture showed a ratio of 1:5 between the two components (based on relative areas of the Me signals at δ1.88 and δ1.75 respectively). Hence, the isomer with fluxional behavior appears to be a minor product in the oxidative degradation of **12b**+**13b**. It seems obvious that complex **13b** (which is the precursor for **15b**) was the major component in the parent mixture of cyano-σ-η^3 complexes (**13b**/**12b**=3:1). The reason for this isomer preference is not well understood.

THE SOLVOLYTIC BEHAVIOUR OF 6,7-BENZOBICYCLO[3.2.2]NONATRIENYL SYSTEMS

The interesting behavior of coordinated 2-t-bicyclo[3.2.2]nonatrienyl alcohols prompted us to examine also the related benzo-fused system. It has been reported recently[11] that the solvolysis of epimeric 6,7-benzobicyclo[3.2.2]nona-2,6,8-trien-4-yl-ODNB's, **18**, showed similar rates, via the intermediacy of the corresponding cation, benzobicyclo[3.2.2]nonatrienyl, **19** and benzobarbaralyl **19'**. The solvolysis gives mainly 9-hydroxy- or 9-*p*-nitro-benzoate barbaralyl systems, **20**, with some (up to 10%) unrearranged alcohol.

We wish to report the behaviour of 2-methyl-benzobicyclo[3.2.2]nonatrien-2-ol in acidic media (CF$_3$COOH), and to compare it with the behavior of its irontricarbonyl complex in similar media.

The epimeric 2-methyl-6,7-benzobicyclo[3.2.2]-nona-3,6,8-trien-2-ols **22** (*endo*) and **23** (*exo*) were obtained by methyllithium treatment of the corresponding ketone **21**[12a,b].

Since structural assignments, based on paramagnetic shift reagent Eu$^{\text{III}}$ studies, were ambiguous, other arguments were used:

(a) Epimeric distribution of reduction of ketone **21**:

	R	**22** (*endo*)	**22** (*exo*)
a[11]	H	63	29
b	CH$_3$	87	13
c	φ	78	Not produced

The minor epimer (*exo*) is apparently obtained as a result of nucleophilic attack by (R$^-$) from the more hindered side of ketone **21**.

(b) Comparison of the chemical shifts of the vinyl bridge (H$_{8,9}$) protons of isomer **22** and **23** shows

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† We do not have a straight forward proof for the config. at C$_9$, but from the discussion of the second part of this work, one tends to assign a *syn* (*cis*) relationship between the φ and the CN groups.

‡ Treatment of **16** with Me$_3$NO/acetone for 24 hr at room temp also liberated barbaralone in reasonable yield.

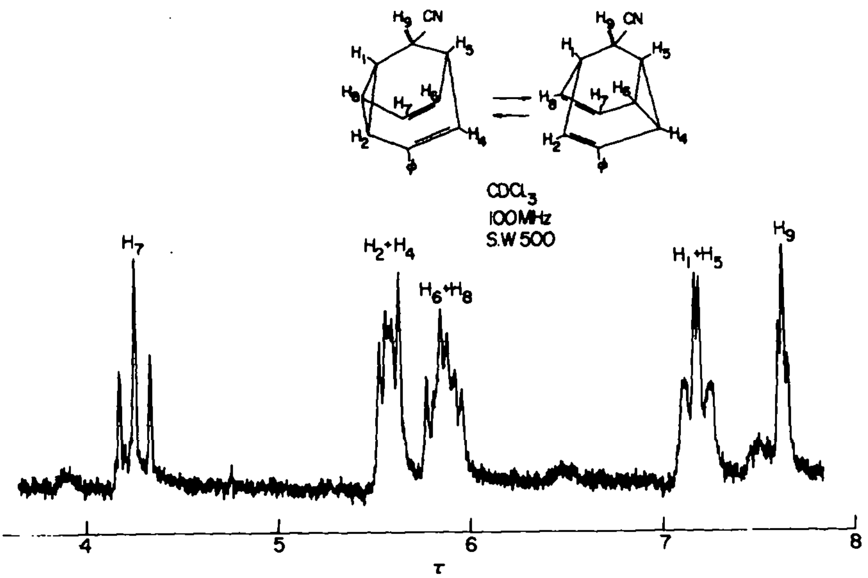
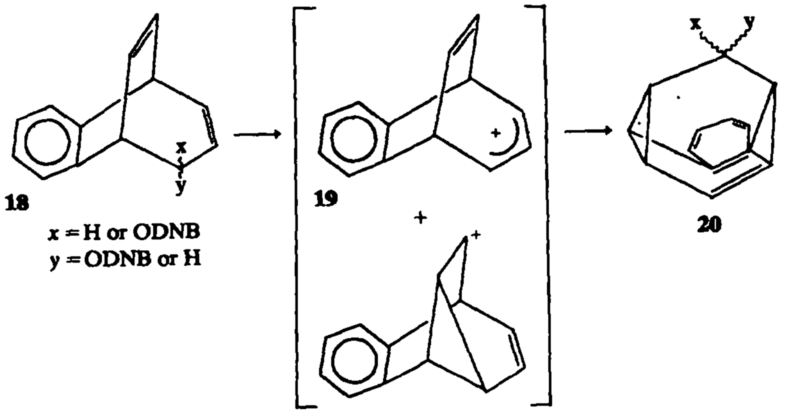


Fig. 2


18

x = H or ODNB
y = ODNB or H

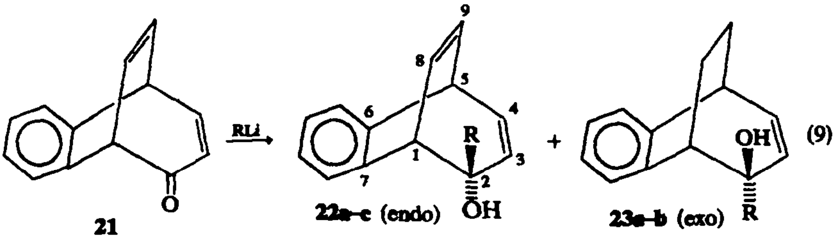
19

+

19'

20

(8)



21

22a–c (endo)

23a–b (exo)

(9)

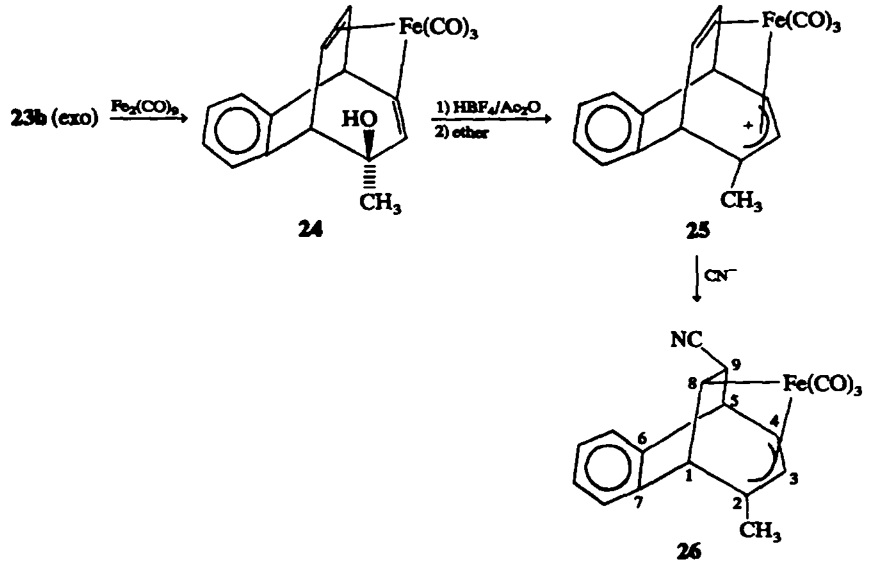
a: R = H
b: R = Me
c: R = ϕ

the following (δ units):

	H_9	H_8		H_9	H_8
22a	6.28	6.70	**23a**	6.28	6.78
22b	6.33	6.71	**23b**	6.35	6.85

The chemical shift of H_9 remains unchanged in the two pairs of isomers while the shift of H_8 to lower field in the *exo* isomers can be attributed to the deshielding effect of the nearby OH group.

(c) Both parent alcohols **22a** and **23a** can react with $Fe_2(CO)_9$ to yield the corresponding complexes. On the other hand, only the minor component of the **22b**+**23b** epimeric mixture formed an iron-tricarbonyl complex. The single tertiary phenyl analog **22c** (isolated from the reaction of ϕLi and **21**) was found to be inert to $Fe_2(CO)_9$ under the above conditions, probably for steric reasons. Treatment of **23b** (the *exo*-isomer) with $Fe_2(CO)_9$ in benzene solution afforded **24** in fair yield (62%). On dissolving the latter complex in HBF_4/Ac_2O, followed by dilution with ether, the 2-methylbenzobicyclo[3.2.2]nonatrienyl cation precipitated as a bright yellow fluoroborate salt. Again in **25**,



(10)

the ligand is attached to the metal atom by a π-olefinic and π-allylic bonds.

Unlike the case of the parent 2-methyl-bicyclo-[3.2.2]nonatrien-2-ol complex (**8b**), the dehydration of carbinol **24** in acidic conditions *is not* accompanied by 1,2-alkyl shift and allylic rearrangement, since alcohol **24** lacks a free uncomplexed double bond (in contrast to **8b** structure) in addition to the coordinated π-olefins fragments. Therefore, cation **25**, represents an unusual bicyclic dienyl-cationic system with unsymmetrical π-allyl moiety included in the cyclic system.

Reaction of **25** with CN$^-$ gave a mixture of two products;† the predominant component (64%), was determined as **26**, and its structure was deduced from its mass spectrum and its H^1-NMR spectrum (Fig. 3). The coupling constants, $J_{5,9} = 5.5$ Hz, $J_{8,9} = 1.5$ Hz, enabled us to assign *trans*-geometry to the CN group relative to the metal atom. Decoupling of H_8 caused the collapse of the bridge-head proton H_1 into a singlet, indicating a Fe-C_8 σ-bonding interaction rather than the alternate M—C_9. NMR analysis of the major product (**26**) indicated that cyanide attack favoured the vinyl position away from the Me substituent. In terms of previously suggested possible intermediates[2a], it is reasonable to propose **27** or **28** as the intermediate in the course of CN$^-$ attack on cation **25**.

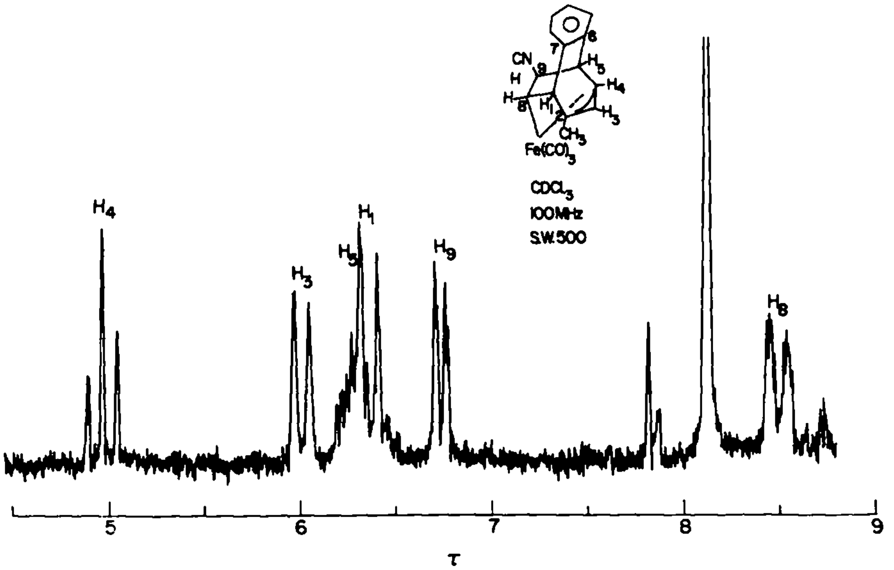


Fig. 3

According to Schleyer,[13] an intermediate with structure of **28** should be more stable than **27**; therefore, the nucleophilic addition of the CN$^-$ to cation **25** proceeds via the intermediate **27**, and should result in the *kinetic* product, i.e. **26**.

Oxidative degradation of the σ-η^3-allyl complexes **26** and **29**[2a] led to the corresponding substi-

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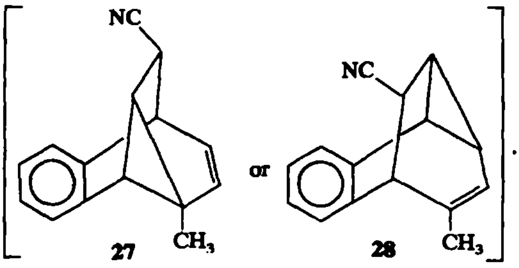
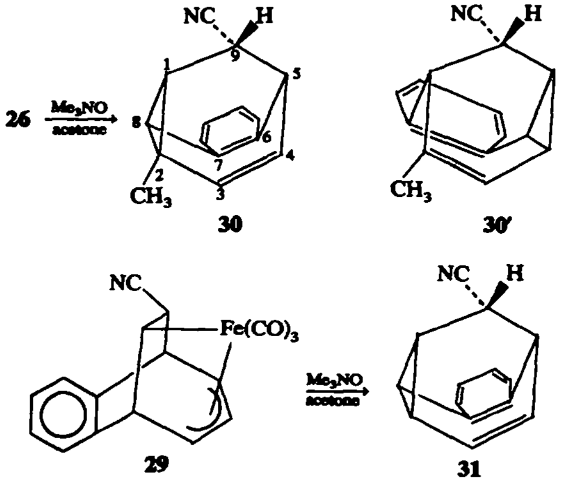
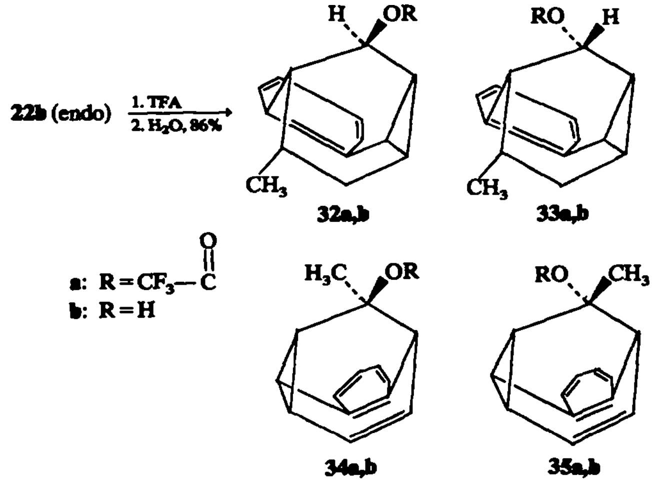
† We are not able to characterize the minor product.



(11)



(12)



a: $R = CF_3{-}\overset{\overset{\displaystyle O}{\|}}{C}$
b: $R = H$

(13)

tuted benzobarbaralyl systems, **30** and **31**, respectively.

The structures of the products **30** and **31** were determined on the basis of the NMR data (Fig. 4). The location of the Me group in the oxidative-degradation product **30** is dictated by its location in the parent-compound (σ-η^3). Decomposition of **26** led to **30**, which is thermodynamically less stable than the alternative structure **30'**. A direct isomerisation of the type: **14**$\rightleftharpoons$**14'** may be excluded, since in benzobarbarlyl systems the aromatic ring precludes double bond shifting (as occurring in divinylcyclopropane systems).

Quite different behavior was observed when the uncomplexed tertiary alcohol **22b**† was dissolved in trifluoracetic acid, quenched in ice water, and the resulting trifluoroesters hydrolysed on a basic alumina column. Compound **22b** reacts differently with a proton-acid than its analogous complex alcohol **24**, as can be judged from the different types of products generated in reaction **13** (Fig. 5). We have already reported[12b] that trifluoroacetolysis of **18** (x = H or OH; y = H or OH) resulted in an epimeric mixture of **20**. Structural assignments for the epimeric pair of isomers **34b** and **35b** were made on the basis of their NMR spectra (Fig. 5). The more diagnostic spectral feature of both structures was the difference in the chemical shifts of H_3, $\Delta\delta \simeq 0.3$ ppm. In the case of **34b**, the OH group is closer to H_3, and therefore the latter is shifted to lower field than in **35b**. The same should

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† We have used the *endo*-epimer, **22b**, for the trifluoroacetolysis since it constituted a predominant component of reaction (9) and in strong acidic media should give rise to the same carbonium ion as its epimer, *exo*-**23b**, (as described also for the solvolysis of **18**).

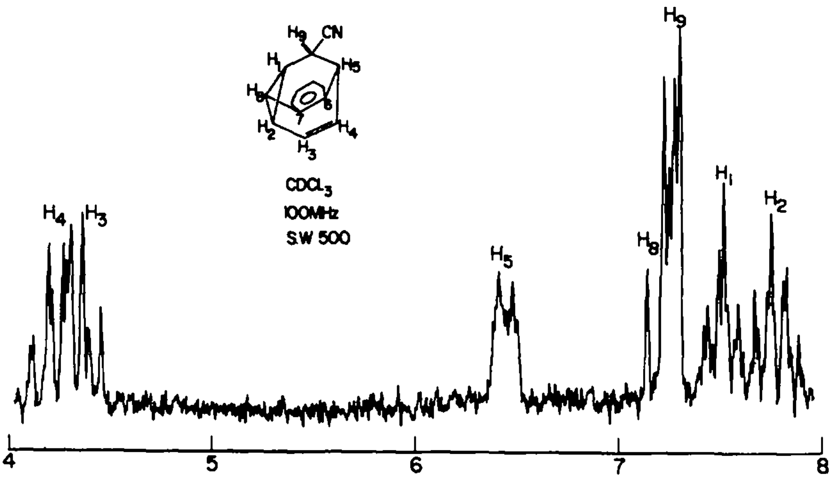
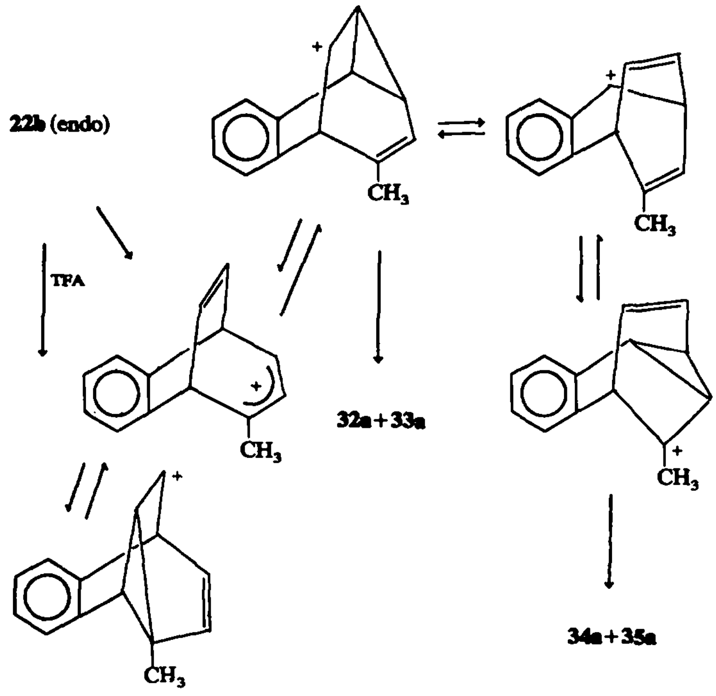


Fig. 4



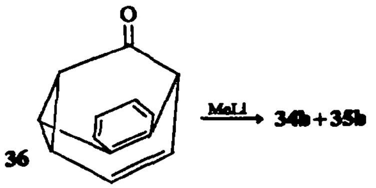
(14)

be true for the other pair of the solvolysis products, **32b** and **33b**.

All four products of the solvolysis in TFA had the Me substituent at position 4 and 9 at the ratio 1/1.2 between the two pairs of isomers **34a**+**35a**/**32a**+**33a**.

In contrast to the solvolysis of **18**, there were not detected benzo[3.2.2]-trienyl derivatives in the above trifluoroacetolysis; the Me scrambling in positions 4 and 9 could be interpreted in terms of benzo[3.2.2]trienyl cation intermediacy (Scheme 14).

In conclusion, solvolysis of the benzo-substrates lead to the most stable benzobarbaralyl system, and in the same time, the corresponding irontrienyl complexes precursors (where the σ-η^3-allyl moiety dictate the substituent location), can be transformed to a "kinetic" product.



Finally, we have carried out two additional reactions in order to verify the structural assignments of the above trifluoroacetolysis products:

(1) Both isomers **34b** and **35b** were independently obtained by action of MeLi on benzobarbaralone, **36**, in a ratio of ~1:1.

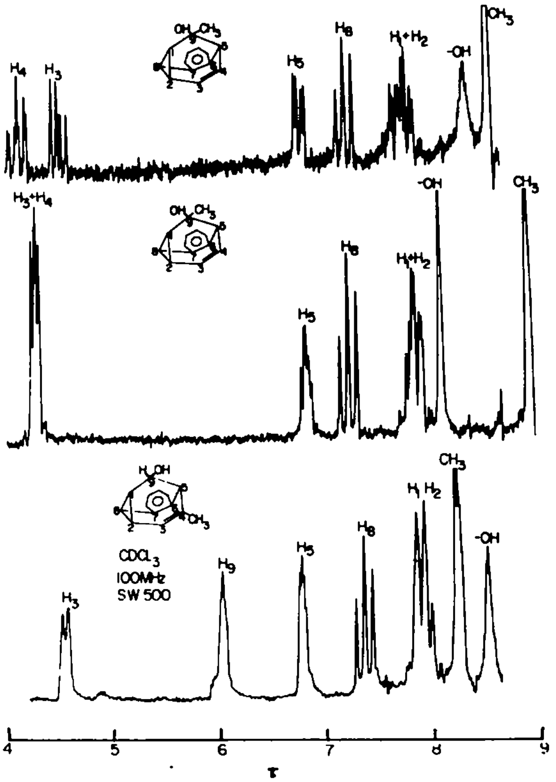
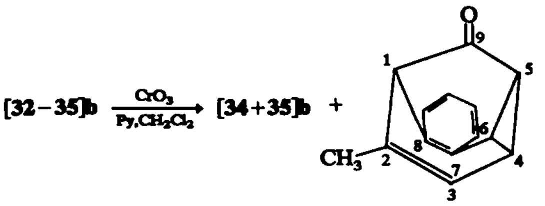


Fig. 5

(2) Oxidation of the mixture of alcohols (**32–35b**) with CrO_3 in pyridine left the tertiary substrates quantitatively unreacted, together with 2-methyl-7,8-benzobarbaralone, **38**.

LAH reduction of **38** regenerated the parent epimeric alcohols, **32b** and **33b**.



38

EXPERIMENTAL

IR spectra were recorded on Perkin-Elmer 257 and 177 Spectrometers. PMR spectra were measured with a Jeol HNM-C-60 HL and Varian HA-100 spectrometers with TMS as internal reference standard.† Mass spectra were obtained using a Du-Pont 21-491B spectrometer and with a direct inlet system and ionization potential of 70 eV. All reactions involving Fe-complexes were carried out under nitrogen. All m.ps. were determined with Thomas and Hoover apparatus and are uncorrected.

Bicyclo[3.2.2]*nona*-3,6,8-*trien*-2-*one* was obtained according to Grutzner and Winstein[7] in 80% yield.

2-*Methyl-bicyclo*[3.2.2]*nona*-3,6,8-*triene*-2-*ol* (**7b**) prepared from the corresponding ketone with MeLi in ether soln at −78°.[6]

2-*Phenyl-bicyclo*[3.2.2]*nona*-3,6,8-*triene*-2-*ol* (**7c**). To a soln of 1.75 g above bicyclo[3.2.2]ketone (80% pure) in 30 ml dry ether, a soln of 2.6 g (32 mmol) PhLi in 25 ml dry ether was added dropwise at −78°. After 1 hr, the mixture was allowed to warm up to r.t., ice-water was added to destroy the Li-complex, and the aqueous layer acidified to pH-6. Separation of the organic layer was followed by (2×15) ml more extractions.

The combined etheral extracts were dried over $MgSO_4$ and evaporated under reduced pressure. Chromatography of the residue on 3% basic alumina gave 2.3 g of alcohol (83%) as yellow crystals, m.p. 84–85°; IR ($CHCl_3$): 3570 (OH); MS: 210 (M^+); NMR ($CDCl_3$, 60 MHz): 2.2 (s, 1H, OH), 3.1–3.65 (m, 2H, H_1+H_5), 4.99 (dd, 1H, H_3), 5.68 (ddd, 1H), 6.1–6.65 (m, 4H), 6.33 (dd, 1H, H_4). (Found: C, 84.14; H, 6.55. Calc. for $C_{15}H_{14}O$: C, 85.71; H, 6.67%).

Reaction of **7b** *with* $Fe_2(CO)_9$. A mixture of 1.5 g (10 mmol) of **7b** and 8.0 g (22 mmol) $Fe_2(CO)_9$ in 70 ml benzene was stirred for 2 hr at 47° under N_2. The mixture was filtered and evaporated. Separation of the residue on basic alumina (5%) column gave, in order of elution, 130 mg of **9b** and 1.28 g (44%) of **8b** as yellow needles, m.p. 65° (from pt. ether); IR (hexane): 2030, 1967: (Fe—C≡O) MS: 228 (M^+), 232 (M^+-2CO), 204 (M^+-3CO); NMR ($CDCl_3$, 100 MHz): 1.24 (s, 3H, CH_3), 1.76 (s, 1H, OH), 2.95–3.95 (m, 6H, $H_{1,5-9}$), 5.40 (dd, 1H, H_3), 5.86 (dd, 1H, H_4); (Found: C, 54.16; H, 4.39; Fe, 19.27 Calc. for $C_{13}H_{12}FeO_4$: C, 54.17; H, 4.17; Fe, 19.44%).

Reaction of **7c** *with* $Fe_2(CO)_9$. The reaction and isolation of products were carried out as described for **7b**; **8c** was obtained (91%) as yellow prisms, m.p. 88–89° (Hexane); IR ($CHCl_3$): 2020, 1960 (Fe—C≡O); NMR (C_6D_6, 60 MHz): 1.63 (s, 1H, OH), 2.31 (dd, 1H, H_1), 2.50–3.20 (m, 4H, H_6—H_9), 3.40 (m, 1H, H_5), 5.08 (dd, 1H, H_3), 5.47 (dd, 1H, H_4); [($CDCl_3$): 2.08 (s, 1H, OH), 2.75 (ddd, 1H, H_1), 3.1–4.0 (m, 5H, H_5—H_9), 5.47 (d, 1H, H_3), 6.10 (dd, 1H, H_4)]. (Found: C, 61.80; H, 4.00, Fe, 16.03. Calc. for $C_{18}H_{14}FeO_4$ C, 61.77; H, 4.01; Fe, 15.94%).

The preparation of the fluoroborate salts, **10b** *and* **10c**. To a cold (0°) soln of 1 g (3.5 mmol) of **8b** in 3 ml Ac_2O, was added 5.5 ml HBF_4/Ac_2O (1.5:4 by volume), and the soln was stirred for 30 min. Adding 25 ml ether caused precipitation of the yellow powder, which was filtered and washed with (2×10) ml ether to yield the mixture, 0.9 g (75%), of **10b**+**11b** (identified as such by NMR spectrum). Stirring this mixture again in acetonitrile under N_2 for 24 hr, followed by ether addition, led to the precipitation of 0.87 g salt **10b**, m.p. 132°; IR (KBr): 2100, 2040 (Fe—C≡O), 1060 (BF_4^-); NMR (CD_3CN, 100 MHz): See Fig. 1 (Found: C, 43.50; H, 3.23; Fe, 15.84. Calc. for $C_{13}H_{11}BF_4FeO_3$: C, 43.57; H, 3.35, Fe, 15.65%).

Fluoroborate salt **10c**. The isolation of the salt was carried out as described for **10b**; 3 g (8.6 mml) of **8c** yielded in the acid treatment 3 g (83%) of **10c** as yellow powder, m.p. 157–158°; IR (KBr): 2090, 2030, (Fe—C≡O), 1060 (BF_4^-); NMR (CD_3CN, 60 MHz): 3.4–5.2 (m, 7H), 6.45 (dd, 1H, H_9).

The reaction of **10b** *with cyanide.* 0.8 g (2.1 mmol) of the solid Salt **10b** was added in small portions to a vigorously stirred mixture of 5 ml of sat s of NaCNaq and 60 ml ether. After 30 min the two layers were separated and the aqueous soln extracted with ether (2×20) ml. The combined etheral extracts were washed with water and NaClaq, dried over $MgSO_4$ and concentrated to leave a residue, which was crystallised from petroleum ether, to give yellow crystals of **12b**+**13b**, 0.6 g (87%), m.p. 53°. The two isomers show one spot by tlc and could not be separated on a neutral alumina column. IR (hexane): 2224 (C≡N), 2050, 1995 (Fe—C≡O); MS: 297 (M^+), 269, 241, 213, (*m/e* values

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† In experimental section all chemical shifts are cited in ppm units. Phenyl signals are omitted as well as in Figs. 1–5.

corresponding to the successive loss of 3 CO ligands); NMR ($CDCl_3$, 100 MHz): 1.20 (dm, 1H, $H_{7+6'}$), {[1.73 (d), 1.87 (d)], 3H, CH_3} 3.08 (m, 3H), 4.30 (m, 2H), {[5.21 (ddd), 5.14 (ddd)], 1H, $H_{4+2'}$}, 5.83 (dm, 1H, $H_{9+9'}$).

The reaction of **10c** *with cyanide.* 1.40 g (3.3 mmol), of **10c** yielded 1.0 g (83%) of the unseparable isomeric mixture (**12c**+**13c**), m.p. 127°; IR (hexane): 2220 ($C\equiv N$), 2050, 1995 ($Fe{-}C\equiv O$); MS: 359 (M^+), 331 (M^+—CO), 303 (M^+—2CO), 275 (M^+—3CO); NMR ($CDCl_3$, 100 MHz): 1.35 (dm, 1H, $H_{7,6'}$), 3.24 (m, 2H), 3.75 (m, 1H), 4.24 (m, 2H), 5.22 (ddd, 1H), 5.35 (dd+dd, 1/2H each, $H_{9+9'}$). (Found: C, 63.21; H, 3.55; Fe, 16.02. Calc. for $C_{19}H_{13}FeNO_3$: C, 63.51; H, 3.61; Fe, 15.50%).

Degradation of cyano-iron complexes (**12c**+**13c**) *with trimethylamine-oxide.* To a soln of 450 mg (1.3 mmol) of the mixture of **12c**+**13c** in 40 ml dry acetone, 0.68 g (9 mmol) Me_3NO was added, and the suspension was stirred for 24 hr at room temp. The residue was chromatographed on neutral alumina (4%) to give 110 mg (40%) of a colorless oil, from which **14c** could be crystallised from petroleum ether as pale yellow needles, m.p. 146°; (The second component, **15c**, is very air-sensitive, and tends to decompose on standing). Compound **14c**: IR ($CHCl_3$): 2235 ($C\equiv N$); MS: 219 (M^+); NMR ($CDCl_3$, 100 MHz) see Fig. 2. (Found: C, 87.43; H, 6.40; N, 6.07. Calc. for $C_{16}H_{13}N$: C, 87.70; H, 6.40; N, 5.94%). Compound **15c**: NMR ($CDCl_3$, 60 MHz): 2.4 (m, 4H), 3.45 (m, 1H, H_5). 5.7 (AB, 2H, H_{7+8}), 6.0 (dd, 1H, H_3).

Degradation of cyano-iron complexes (**12b**+**13b**) *with trimethylamine oxide.* A mixture of 0.54 g (1.8 mmol) of **12b**+**13b** was stirred with 0.68 g Me_3NO (9 mmol) in 50 ml acetone for 24 hr at room temp. After filtration and evaporation of the solvent, the residue (one spot by tlc) purified on 4% neutral alumina column. The H^1-NMR shows **15b**/**14b** = 5 : 1 (based on integration of the Me signals of the two isomers) **15b** (85% pure) IR ($CHCl_3$): 2230 ($C\equiv N$); MS: 157 (M^+); NMR ($CDCl_3$, 100 MHz), under irradiation decoupling of δ 5.4—5.9 region: 1.88 (d, 3H, CH_3), 2.0–2.6 (m, 4H, $H_{1,9,4,6}$), 2.75 (m, 1H, H_5), 5.4–5.9 (m, 3H, $H_{3,7,8}$). On substraction the NMR spectrum of **15b** a reasonable spectrum of **14b** could be obtained: ($CDCl_3$, 60 MHz) 1.75 (d, 3H, CH_3), [2.0–3.0] (3H, H_{1+5+9}), [3.7–4.2] (4H, $H_{2+8+4+6}$), [5.4–5.9] (1H, H_7).

2-*Methyl*-6,7-*benzo*-*bicyclo*[3.2.2]-*Nona*-3,8-*diene*-2-*ol*, **22b** (endo) *and* **23b** (exo). To a soln of 4.72 g (26 mmol) of 21 in 60 ml dry ether was added from a dropping funnel 32 ml of ~2M—MeLi in ether at −78°. After stirring for 1 hr and work up as described for the preparation of **7b**, the residue was chromatographed on 4% basic alumina to give 4.0 g (78%) endo isomer **22b** and 0.66 (12%) **23b** (*exo*) as white crystals.

Compound **22b** (*endo*): m.p. 58°, IR ($CHCl_3$): 3570 (OH-free), 3430 (bonded OH); MS: 198 (M^+); NMR ($CDCl_3$, 60 MHz): 1.30 (s, 3H, CH_3), 1.72 (s, 1H, OH), 3.4–3.9 (m, 2H, H_{1+5}), 4.78 (dd, 1H, H_3), 6.08 (dd, 1H, H_4), 6.33 (ddd, 1H, H_9), 6.71 (ddd, 1H, H_8); (Found: C, 83.86; H, 7.00; Calc. for $C_{14}H_{14}O$: C, 84.85; H, 7.07%).

Compound **23b** (*exo*): m.p. 115°; IR: 3580 (free OH), 3430 (bonded OH); MS: 198 (M^+); NMR ($CDCl_3$, 60 MHz); 1.16 (s, 3H, CH_3), 2.02 (s, 1H, OH), 3.35–3.85 (m, 2H, H_{1+5}), 4.82 (dd, 1H, H_3), 6.20 (dd, 1H, H_4), 6.33 (ddd, 1H, H_9), 6.85 (ddd, 1H, H_8).

2-endo-*Phenyl*-6,7-*benzobicyclo*[3.2.2]*Nona*-3,8-*diene*-2-*ol* (**22c**). 1.5 g (8.2 mmol) of **21** was treated with PhLi as above to yield 1.67 g (78%) of **22c**, colorless crystals m.p. 107°; IR ($CHCl_3$): 3560 (free OH); MS: 260 (M^+); NMR ($CDCl_3$, 60 MHz): 2.00 (s, 1H, OH), 3.80 (m, 2H, H_{1+5}), 5.02 (dd, 1H, H_3), 5.88 (ddd, 1H), 6.43 (dd, 1H, H_4), 6.75 (ddd, 1H).

Reaction of **23b** (exo) *with* $Fe_2(CO)_9$. A mixture of 0.21 g (1.1 mmol) of **23b** (*exo*) and 1.0 g (2.7 mmol) of $Fe_2(CO)_9$ in 20 ml THF was stirred for 2 hr at 45° under N_2. the mixture was filtered and evaporated, and the residue was chromatographed on 5% basic alumina to give 0.23 g (62%) of **24**, a yellow complex, m.p. 82–84°. (When this reaction was carried out in benzene as solvent, the yield of **24** dropped down to 18%). IR (hexane): 2030, 1975 ($Fe{-}C\equiv O$); MS: 310 (M^+—CO), 282 (M^+—2CO), 254 (M^+—3CO); NMR ($CDCl_3$, 60 MHz): 0.85 (s, 3H, CH_3), 1.25 (s, 1H, OH), 2.9–3.7 (m, 4H), 3.8–4.2 (m, 2H); (Found: C, 59.84; H, 4.19. Calc. for $C_{17}H_{14}FeO_4$; C, 60.36; H, 4.14%).

Preparation of the tetrafluoroborate salt **25**. 0.36 g (1.0 mmol) of **24** was dissolved in 2 ml Ac_2O at 0°, followed by the addition of 1 mmol HBF_4 in Ac_2O. The usual work up (see for **10b**) gave 0.35 g (80%) of **25** as a yellow powder, m.p. 205–207°; IR (KBr): 2100, 2040 ($Fe{-}C\equiv O$), 1060 (BF_4^-); NMR (CD_3CN, 100 MHz): 2.22 (s, 3H, CH_3), 3.9–4.3 (m, 3H), 3.5–3.8 (m, 3H).

The reaction of **25** *with cyanide.* (For a typical procedure see above for **10b**) 0.32 g (0.8 mmol) of **26** gave 0.25 g (92%) of a yellow oily product, which after crystallisation from petroleum ether gave yellow needles (**26**), 0.16 g (64%). m.p. 104–106°; IR (hexane): 2235 ($C\equiv N$), 2050, 1980 ($Fe{-}C\equiv O$); MS: 347 (M^+), followed by 3 values of *m*/*e*, corresponding to successive loss of 3 CO's. NMR ($CDCl_3$, 100 MHz): See Fig. 3. $J_{4,3} = J_{4,5} =$ 8.0 Hz; $J_{5,9} =$ 5.5 Hz; $J_{8,9} =$ 1.5 Hz.

Degradation of cyano-iron complex **26** *with trimethylamine oxide.* A mixture of 0.24 g (0.7 mmol) of **26** and 0.38 g (5 mmol) of Me_3NO in 40 ml dry acetone was stirred for 24 hr at room temp. The residue after work up (as for **12c**) was purified on 4% neutral alumina to give 36 mg (24%) of **30** as a colorless oil. IR ($CHCl_3$): 2230 ($C\equiv N$); MS: 207 (M^+); NMR ($CDCl_3$, 60 MHz): 1.52 (s, 3H, CH_3), 2.28 (ddd, 1H, H_1), 2.58 (d, 1H, H_8), 2.82 (dd, 1H, H_9), 3.63 (dm, 1H, H_5), 5.50 (d, 1H, H_3), 5.87 (dd, 1H, H_4). $J_{1,5} =$ 2 Hz; $J_{1,9} = J_{5,9} =$ 2.5 Hz; $J_{1,8} =$ 7.5 Hz; $J_{3,4} =$ 9 Hz; $J_{4,5} =$ 7.5 Hz.

Degradation of cyano-iron complex **29** *with trimethylamine oxide.* 0.4 g (1.2 mmol) of **29** with 0.45 g (6 mmol) of Me_3NO in 40 ml dry acetone gave (after the same work up as above) 120 mg (51%) colorless crystals of **31** m.p. 123°; IR ($CHCl_3$): 2230 ($C\equiv N$); MS: 193 (M^+); NMR ($CDCl_3$, 100 MHz): See Fig. 4. $J_{1,8} = J_{1,2} = J_{2,8} =$ 7.5 Hz $J_{5,9} = J_{1,9} =$ 2.5 Hz; $J_{1,5} =$ 2 Hz; $J_{2,3} =$ 6 Hz.

Solvolysis of **22b** (endo) *in trifluoroacetic acid.* 2.9 g (15 mmol) of **22b** (*endo*) in 12 ml CH_2Cl_2 was cooled to 0° and 1.9 g (15 mmol) TFA was added. The mixture was stirred for 2 hr, 50 ml of 5% $NaHCO_3$aq was added to destroy excess acid, and aqueous layer was further extracted with 3 × 10 ml CH_2Cl_2. The combined organic solvents were removed under vacuum. As detected by the NMR spectrum of the crude, **32a**+**33a**/**34a**+**35a** = 1.2/1. The oily residue was passed through 5% basic alumina column in order to hyolrolyse the resulting trifluoroesters. 2.5 g (86%) of a mixture of four isomers was obtained. **32b**, m.p. 142–43°; **34b**, m.p. 119°; All the alcohols products gave MS parent ions *m*/*e* 198 (M^+); NMR ($CDCl_3$, 100 MHz): See Fig. 5.

Oxidation of **32b** *with* CrO_3/Py. To a soln of 0.5 g (2.5 mmol) of **32b** in 8 ml dry CH_2Cl_2 was added 1.5 ml pyridine in 6 ml CH_2Cl_2 and 1.0 g CrO_3. The mixture was stirred for 24 hr at room temp after the work up, chromatography of the residue on 5% neutral alumina gave 0.43 g (86%) of **38** as colorless crystals, m.p. 110°; IR ($CHCl_3$): 1700 ($C{=}O$); MS: 196 (M^+); NMR ($CDCl_3$, 60 MHz): 1.75 (d, 3H, CH_3), 2.2–2.8 (m, 2H, H_{4+5}), 3.07 (dd, 1H, H_6), 3.47 (bs, 1H, H_1), 5.32 (dm, 1H, H_3).

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