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A NOVEL ROUTE TO BICYCLIC IRON TRICARBONYL COMPLEXES INVOLVING π-ALLYL AND σ-COMPONENTS

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SUMMARY

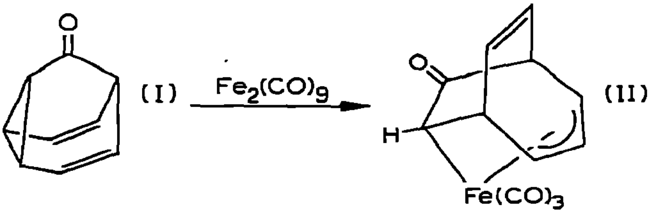
Nucleophilic attack of CN^- on bicyclo[3.2.1]octadienyl-, bicyclo[3.2.2]nonadienyl-, and 6,7-benzobicyclo[3.2.2]nonadienyliron tricarbonyl tetrafluoroborates, results in mixed-type complexes containing both σ and π-allyl bonds. The cyano group in the products is located *exo* to the bicyclic ring.

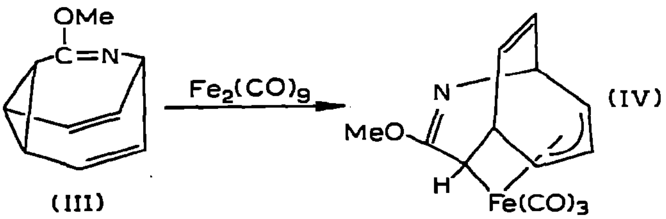
In contrast, the three cations react smoothly with I^-; carbon monoxide is displaced to give iron complexes containing covalently-bound halogen.

INTRODUCTION

Neutral polycyclic olefins containing a cyclopropane group have been recently reported to react with $Fe_2(CO)_9$ to yield complexes containing both π-allyl and σ-components bonded to the $Fe(CO)_3$ unit[1-5]. This type of bonding has been suggested to exist in the bullvalene[1], tetracyclo[$4.4.0.0^{5,7}.0^{2,10}$]deca-3,8-diene[2], isobullvalene[3] and semibullvalene[4] complexes. On the other hand, cyclopropylstyrene upon treatment with $Fe_2(CO)_9$ yields substituted Diene–$Fe(CO)_3$ complexes[5].

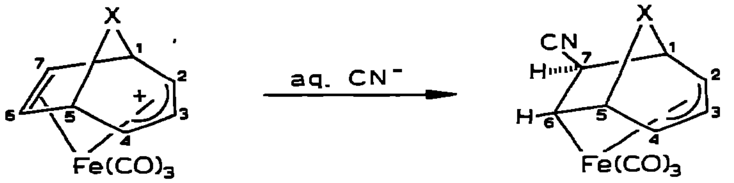
We have recently reported complex formation between barbaralone (I)[6], and its 6,7-benzo derivative[7] as well as azabullvalene (III)[8], and $Fe_2(CO)_9$. Again, since a vinylcyclopropane system forms an integral part of each of these organic





ligands, the latter gave rearranged complexes where the bonding between the $Fe(CO)_3$ moiety and the modified unsaturated hydrocarbon was thought to be of both σ- and π-allyl types.

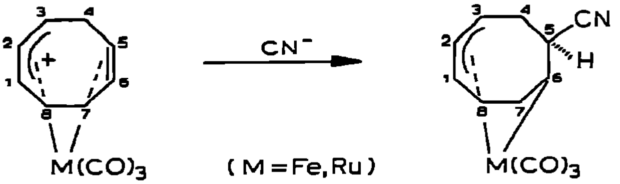
Following these observations, we set out to investigate the reactions of the bicyclic iron tricarbonyl carbonium ions (Va–c) with two nucleophiles, *viz.* CN^- and I^-. Nucleophilic attack of CN^- on either of the three cationic species (Va–c) resulted in nearly quantitative yields of mixed type complexes involving iron–σ- and iron–π-allyl bonds in a bicyclic system (VIa–c), *i.e.*, the iron atom is bonded to the olefinic moiety by a novel 2,3,4,6-*tetrahapto* system.



(V) (VI)

(a) $X = -CH_2-$; (b) $X = -CH{=}CH-$; (c) $X = -o\text{-}C_6H_4-$

While this work was in progress, Cotton *et al.*[9a,b] described the reaction of the 1,2,3,5,6-*pentahapto*cyclooctadienyl–$M(CO)_3$ cations (VII) (M = Fe, Ru) with nucleophiles, such as H^- or CN^-, in which the resulting complexes (VIII) were thought to involve carbon–metal σ- and h^3-allyl bonds.



(VII) (VIII)

Our novel results with the *bicyclic* systems thus complement the findings of Cotton and Lewis *et al.* as regards the eight-membered *monocyclic* ring[9a,b].

RESULTS

Cations (Vb) and (Vc) were prepared as previously described[10,11]. (Va) was first reported by Rosenblum[12] but we used a different and more efficient route to this cation*, thus acid treatment (HBF_4/Ac_2O) of the mixture of epimeric *exo* and *endo*-4-methoxy bicyclo[3.2.1]octadiene–$Fe(CO)_3$ (X)** gave pure (Va) in 83 % yield.

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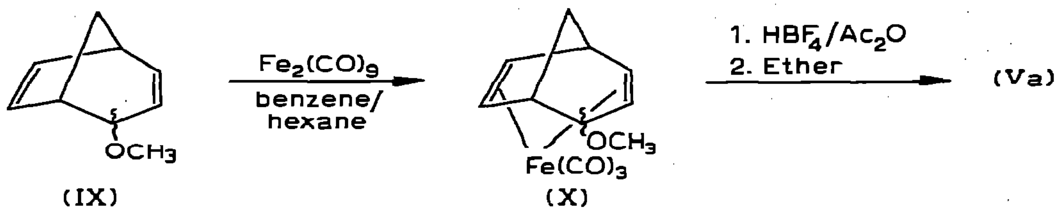
* Preliminary observations on this subject were made while enjoying the kind hospitality of the late Professor S. Winstein at U.C.L.A., California.

** The ligand was prepared according ref. 13.



Addition of the mixed salts to a mixture of aqueous KCN with ether resulted in high yield of the σ-h^3 cyano complexes (VIa–c); we based our structural assignments for (VIa–c) on 100 MHz ^{1}H NMR spectra using double resonance techniques which are most informative (see Figs. 1–3 and Table 1). The proton bonded to carbon

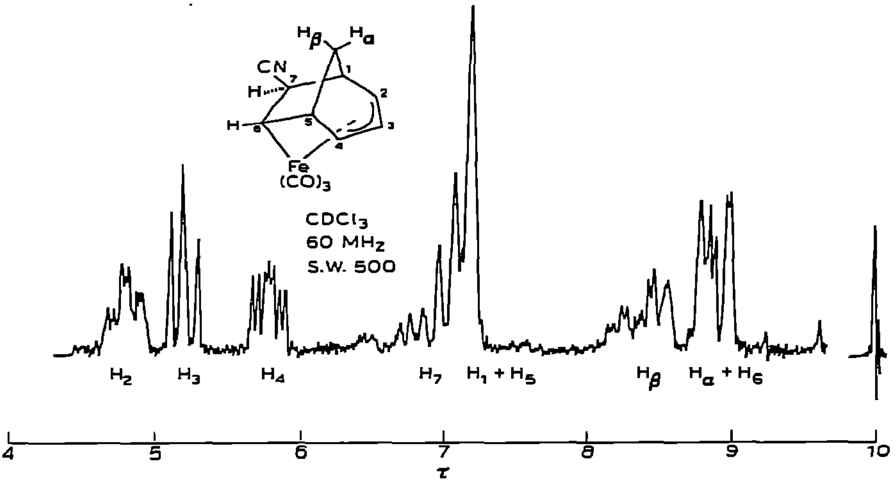


Fig. 1. ^{1}H NMR spectrum of compound (VIa).

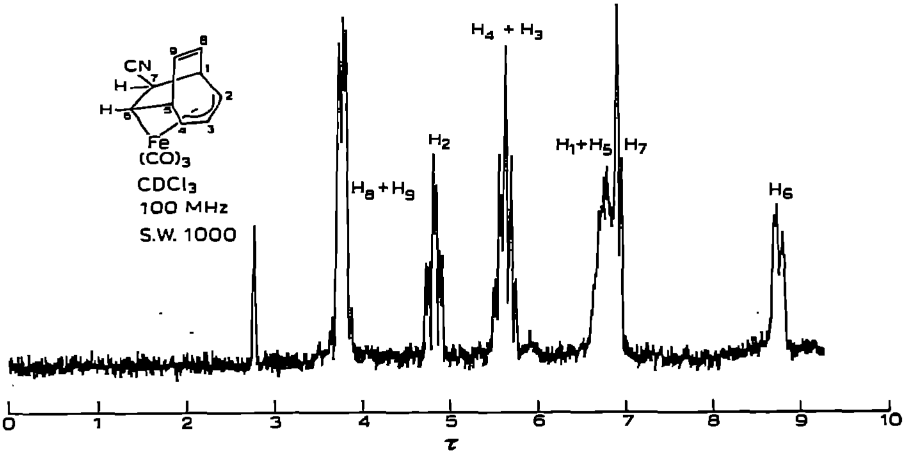


Fig. 2. ^{1}H NMR spectrum of compound (VIb).

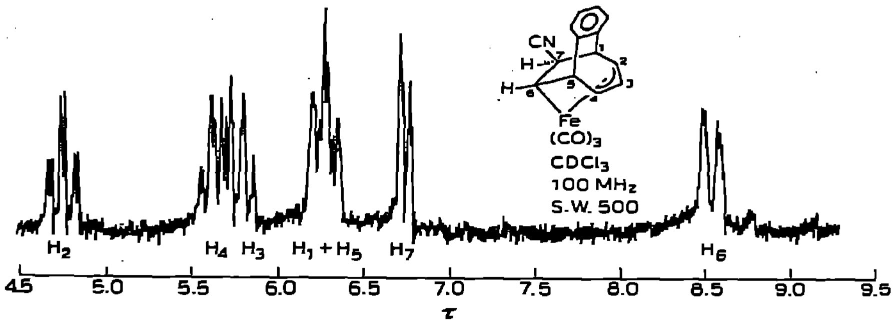
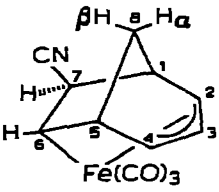
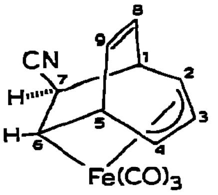
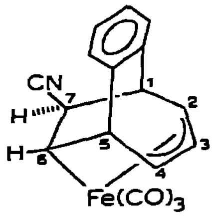


Fig. 3. ^1H NMR spectrum of compound (VIc) (Aromatic signals are not shown).

TABLE I

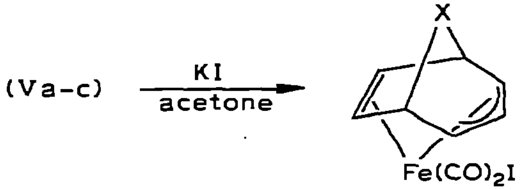
PARAMETERS OF NMR SPECTRA OF (VIa–c) (τ UNITS)

Structure	*Compound*	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{8,9}$	$H_{8\alpha}$
	(VIa)[a]	7.20	4.81	5.22	5.8	7.20	8.78 −9.3 ($+H_{8\beta}$)	7.03		8.38
	(VIb)[b]	6.76	4.82	5.69	5.57	6.76	8.75	6.93	3.77	
	(VIc)[b]	6.23	4.72	5.75	5.58	6.23	8.48	6.69		

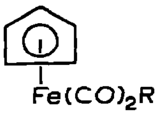
[a] Chemical shifts have been taken downfield from TMS as internal reference at 60 Mc, $CDCl_3$.
[b] At 100 MHz, $CDCl_3$.

bearing the iron atom is strongly shielded and absorbs at τ ca. 9 ppm [1–4,6–8]. The disposition of CN *trans* to the metal in (VIb–c) is concluded from the vicinal coupling constants $J_{6,7}$ and $J_{1,7}$ [1.4 Hz and 5.5 Hz respectively in (VIc)] as well as from examination of models. Thus, it appears that the cyanide nucleophile attacks the cationic species (Va–c) at the vinyl carbons from the *exo* direction.

On the other hand, when cations (Va–c) were subjected to nucleophilic attack by iodide (KI in acetone), the corresponding iron dicarbonyl iodide complexes XII(a–c) were obtained. This is clearly analogous to the reaction of cyclopentadienyliron iodide dicarbonyl, well known for its aromatic character[14,15].



(XII a-c)

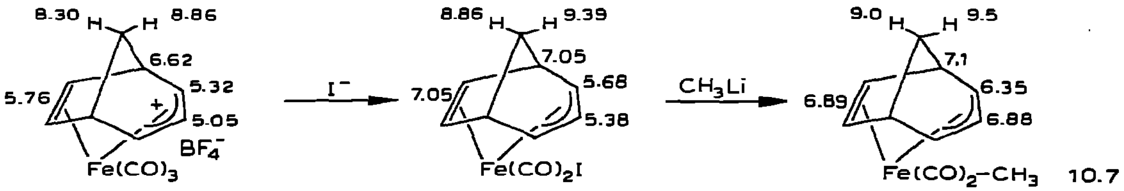


(XIII) R = I
(XIV) R = CH_3
(XVI) R = CO (cation)

A spectral comparison (UV, IR and Mössbauer parameters) of (XIII) with our bicyclo[3.2.1]octadienyliron dicarbonyl (XIIa) shows conclusive similarities.

IR $\nu(C{\equiv}O)$ (cm^{-1}) (*hexane*)		*UV* nm_{max} (*hexane*)		*Mössbauer parameters*[a]		
(*XIIa*)	(*XIII*)	(*XIIa*)	(*XIII*)		*I.S.*	*Q.S.*
2033	2046	214	218	(XIIa)	0.32	1.48
1992	2006	240	243	(XIII)	0.48	1.94
		264	264	(Va)	0.39	1.56
		355	348	(XVI)	0.53	1.91

[a] The Mössbauer spectra were kindly recorded by Professor R. Herber, Rutgers University, N.J., to whom we are greatly indebted.



(Va) (in CD_3CN) (XII a) (in $CDCl_3$) (XV)

The Mössbauer measurements establish the similar chemical environment for iron in the cations and iodides. Furthermore, when (XIIa) (Fig. 4) was reacted with MeLi at −78° in ether, the σ-methyl complex (XV) was obtained (*cf.* XIII→XIV[15]).

The most significant difference between (XV) and (XIV) lies in the varying extent of methyl-proton shielding in the ^1H NMR spectra: *i.e.*, in the former the methyl singlet is shifted +0.8 ppm to higher field than in the latter[14,15] (τ 10.7 and 9.9 ppm respectively). One possible explanation is to ascribe some bishomoaromaticity behavior to the ligand in complex (XV). We can offer no other plausible explanation for this phenomenon.

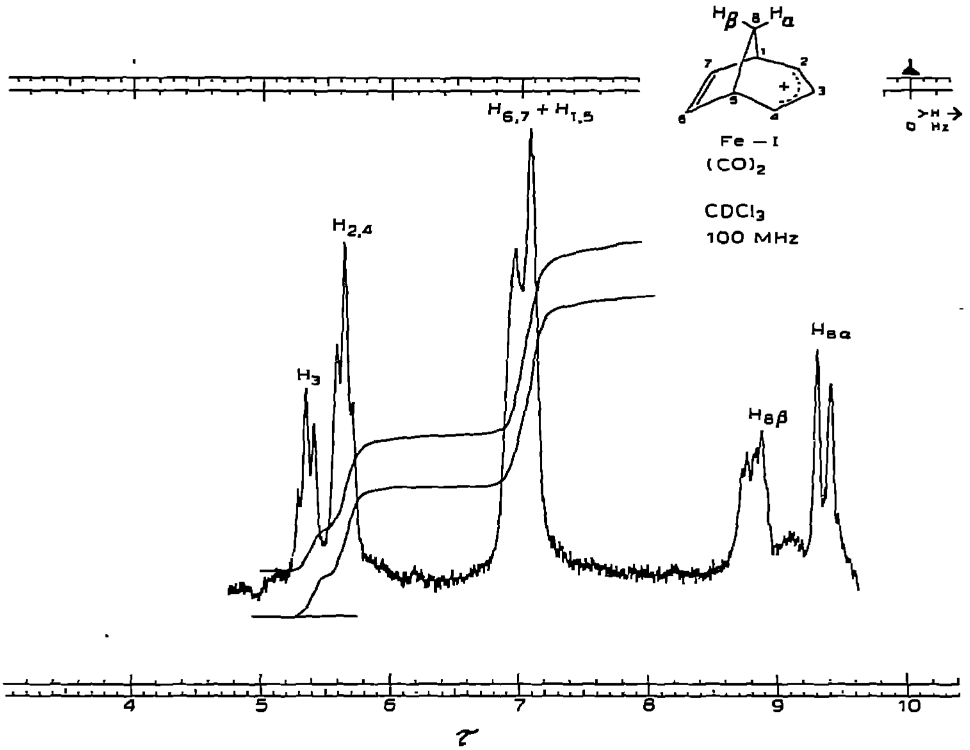
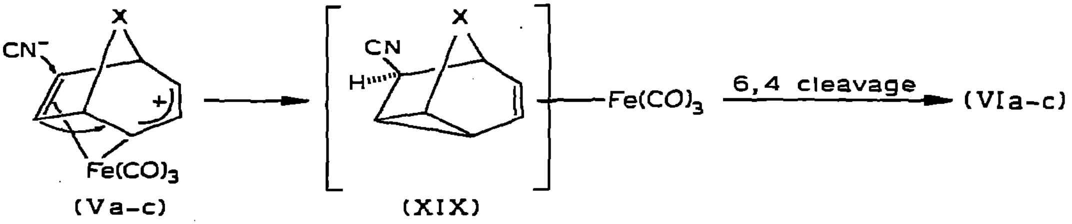


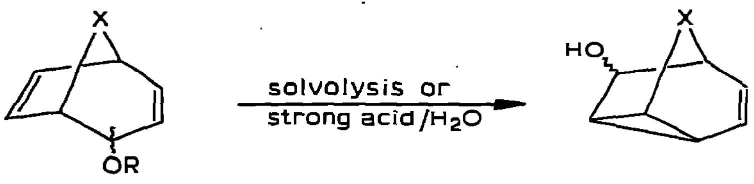
Fig. 4. ¹H NMR spectrum of bicyclo[3.2.1]octadienyliron dicarbonyl iodide (XIIa).

DISCUSSION

A tentative rationalization for the mode of formation of the σ,h^3-allyl complexes (VIa–c) via a tricyclic intermediate (XIX) is given below. (The ligand-to-metal bonding in (XIX) is, however, uncertain and might alternatively involve diradical species.)



This is strengthened by the findings[16] that the solvolyses of *exo*- and *endo*-bicyclooctadienyl *p*-nitrobenzoates (XVIIa) results in small amounts of tricyclic alcohols (XVIIIa). In addition, bicyclo[3.2.2]nonatrienyl *p*-nitrobenzoate[17] and benzobicyclo-[3.2.2]nonadien-4-ol[10] undergo very similar rearrangements to those found in the corresponding barbaralyl systems, and upon quenching of the cations in water, the tricyclic alcohols (XVIIb–c) are formed in quantitative yields.



(XVII a-c) R=H, PNB (XVIII a-c)

a. $X = -CH_2-$
b. $X = -CH{=}CH-$
c. $X = -o-C_6H_4-$

The results support the concept that lack of conjugation between the unsaturated moieties in the cation ligands [in (Va–c)] is essential for their transformation to σ,h^3-allyl complexes when CN^- is used as a nucleophile.

EXPERIMENTAL

IR spectra were measured on Perkin–Elmer Model 257 and Beckman AR-4 spectrophotometers; PMR spectra on Varian A-60, HA-100 and Jeol-60 Hz instruments. All m.p.'s are uncorrected.

5-*Cyano iron tricarbonyl complexes* (*VIa–c*)

The solid tetrafluoroborate salts (Va–c) (1.2 mmoles) were added in small portions to a vigorously stirred mixture of 5 ml of a saturated aqueous solution of potassium cyanide and 20 ml ether. After 30 min, the two layers were separated and the aqueous solution extracted with ether; the ethereal extracts were washed with water and saturated NaCl solution, dried over $MgSO_4$ and concentrated to leave a residue which was crystallized from n-hexane, to give in each case yellow crystalline (VIa–c) in greater than 70% (0.84 mmole) yield.

Compound	*M.p.*	*IR* (*hexane*)		*m/e*, M^+ (*mass. spec.*)
(VIa)	65°	2063, 1955, 1993 (CO)	2210 (CN)	271
(VIb)	99–105°	2062, 1996 (CO)	2208 (CN)	283
(VIc)	134–135°	2060, 1994 (CO)	2210 (CN)	333

Each of the mass spectra showed the parent molecular ion and fragment ions at *m/e* values corresponding to the successive loss of 3 CO ligands. (VIb) (Found: C, 56.01; H, 3.27. $C_{13}H_9FeNO_3$ calcd.: C, 55.19; H, 3.20 %); (VIc) (Found: C, 61.32; H, 3.59; N, 4.14. $C_{17}H_{11}FeNO_3$ calcd.: C, 61.26; H, 3.33; N, 4.24 %.)

Treatment of the bicyclic iron tetrafluoroborates (*Va–c*) *with potassium iodide*

The salt (1.5 g of *e.g.* Va) in 50 ml acetone was stirred with 1.5 g KI for 2 h at room temperature. After filtering off the insoluble products, the solvent was removed under reduced pressure, and the residue taken up in 30 ml $CHCl_3$; filtration followed by concentration to ca. 10 ml and subsequent chromatography on silica, gave elegant maroon crystals (1.0 g, 62%).

Compound	*M.p.*	*IR (hexane)*	*m/e, M^+ (mass spec.)*
(XIIa)	110–112°	2033, 1992 (CO)	344
(XIIb)	127–129°	2033, 1992 (CO)	356
(XIIc)	190 decomp.	2033, 1992 (CO)	406

(XIIa) (Found: C, 35.07; H, 2.61. $C_{10}H_9FeIO_2$ calcd.: C, 34.92; H, 2.64 %.);(XIIb) (Found: C, 37.26; H, 2.61. $C_{11}H_9FeIO_2$ calcd.: C, 37.12; H, 2.55%.)

Dicarbonyl(bicyclo[3.2.1]octadienyl)methyliron (XV)

An ethereal solution of methyllithium (2 *M*) (2 ml) were added in one portion to 740 mg of (XIIa) dissolved in 30 ml ether and stirred at −78° under nitrogen. The reaction was stirred for 20 min, then warmed to room temperature, and poured into cold dilute HCl. The ether layer was combined with the ether extract of the aqueous layer, washed with $NaHCO_3$ solution, water, and dried over $MgSO_4$, filtered and concentrated.

The oily residue was chromatographed on silica and eluted with hexane to give 0.4 g (90%) of a yellow crystalline complex, (XV), which after sublimation had m.p. 59°; IR (hexane) 2007, 1954 cm^{-1} (CO). The mass spectrum showed a molecular peak at *m/e* 232 and successive loss of 2 CO's and one methyl group. (Found: C, 57.12; H, 5.05. $C_{11}H_{12}FeO_2$ calcd.: C, 56.93; H, 5.21 %.)

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