Journal of Organometallic Chemistry, 113 (1976) 147—156
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTIVITY OF CYCLOHEPTADIENYL-1-ONE IRON TRICARBONYL CATION TOWARDS NUCLEOPHILIC ATTACK

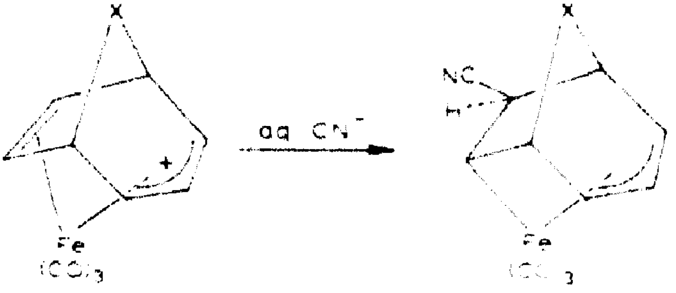
AMIHAI EISENSTADT
Department of Chemistry, Tel-Aviv University, Ramat-Aviv (Israel)
(Received January 16th, 1976)

Summary

Protonated tropone iron tricarbonyl reacts with neutral and anionic nucleophiles to give neutral complexes, some of which contain η-allyl component and metal—carbon σ-bond. The other product contains η-1,3-diene coordinated to the $Fe(CO)_3$ moiety.

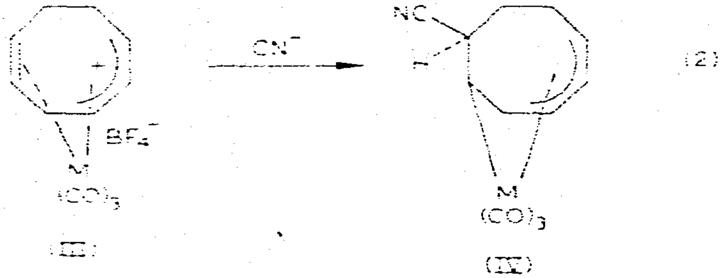
Introduction

It was recently reported that the nucleophilic attack of CN^- or H^- on bicyclic cationic complexes of iron [1] (as well as ruthenium [2]) tricarbonyl (Ia—c) gives neutral compounds in high yields, which contain η-allyl groups and metal—carbon σ-bonds (IIa—c). The configuration of the cyano group was exo [1,2]. Another example of a non-conjugated dienyl grouping coordinated to $M(CO)_3$ which was extensively investigated by Lewis et al. [3] is the cyclooctadienyl complexes of the iron group. These cyclooctadienylium complexes give also on treatment with some nucleophiles similar σ-η allyl compounds [3a—c].

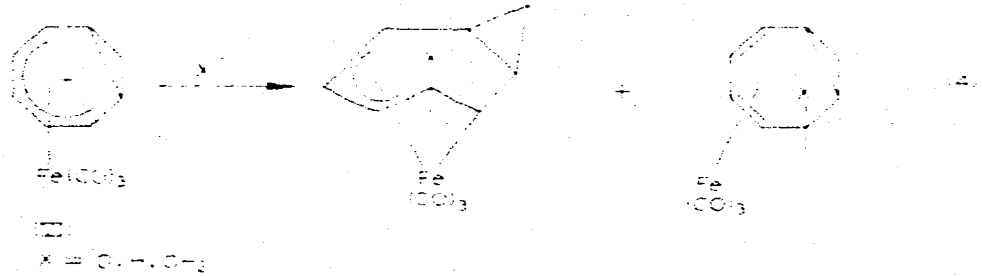


(I a-c) (II a-c) (1)

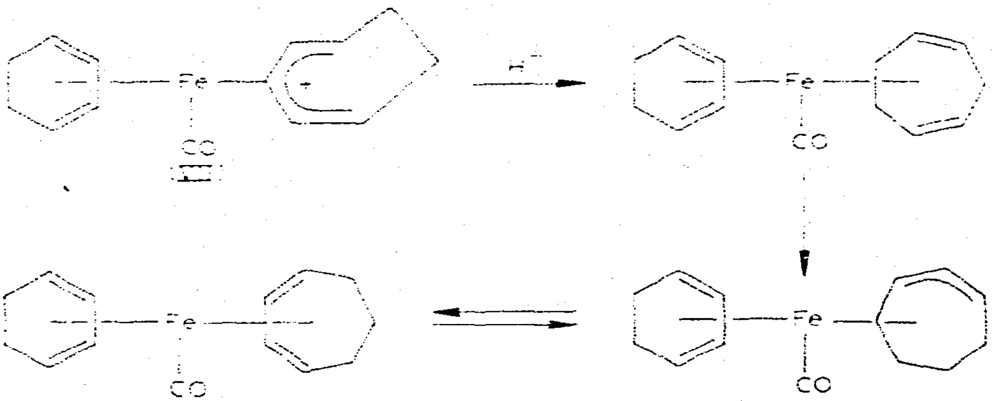
a X = $-CH_2-$, b X = $-CH=CH-$; c X = $o-C_6H_4$



Recently, it has been shown [4—6] that even a conjugated pentadienyl coordinated grouping [5] may undergo attack in the 2-position by certain nucleophiles and generate η^4-1,3,4,5-M(CO)$_3$ complexes. Thus in both the seven-membered ring complex V [4] and the (1—5-η-bicyclo[5.1.0]octadienyl)-iron tricarbonyl cation VI [6], products of attack on both the 1- and 2-positions are observed.

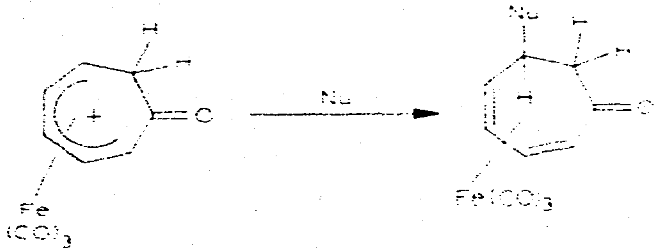


Lewis et al. [6] presented also experimental evidence which suggested involvement of an unstable 1,4-diene complex in a mechanism which led to the σ-η-allyl compound, as presented in the following scheme:



Results and discussion

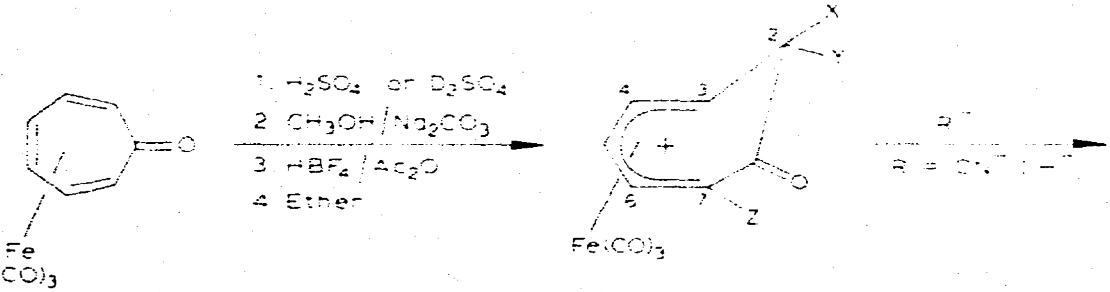
I report below studies of the reaction of the Fe(CO)$_3$ complex of the unsymmetric conjugated dienyl grouping VIII with various nucleophiles, viz. MeOH, RNH$_2$ (R = Ph; Bu^t), N$_3^-$, CN$^-$ and H$^-$. The most interesting feature of this series of reactions is the peculiar behaviour of the last two hard nucleophiles in comparison with the others. The salt VIIIa [7] yielded with each one of the nucleophiles (Nu) CH$_3$OH, PhNH$_2$, t-BuNH$_2$ and N$_3^-$ one corresponding product IX, where attack in position 3 occurred. This was in fact expected on the basis of consideration of charge-density distribution in the pentadienylium system of VIII *. However, the reaction of VIIIa and VIIIb with aqueous cyanide and borohydride ions led to the formation of two products Xa,b and XIa,b in each case, the latter 7-σ-η^3-3,4,5-complex being the major product.



(VIIIa) (IX)

Nu = CH$_3$OH , N$_3^-$, PhNH$_2$, t-BuNH$_2$

Support for the assigned structures came from 100 MHz ^{1}H NMR spectra and double irradiation experiments (see figs. 1—2 and Tables 1—2). In order to further elucidate the NMR spectra of the cyano derivatives Xa and XIa, we have prepared Xb and XIb, labelled at positions 2 and 7 with three deuterium atoms by using VIIIb as substrate for CN$^-$ and H$^-$ attack. The NMR of Xa reveals also

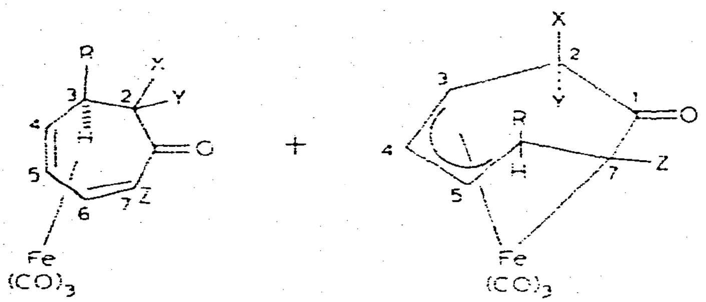


(VIIIa) X = Y = Z = H

(VIIIb) X = Y = Z = D ≡ VIII-d_3

---

[*] Treating VIII with CH$_3$O$^-$/MeOH or PhNH$_2$, converted the cation into the parent compound, tropone iron tricarbonyl, probably via proton removal from the α-position to the carbonyl group.



(Xa)

(XIa)

(Xb) X-d_3

(XIb) XI-d_3

the marked chemical-shifts difference (1.5 ppm) between the α-keto protons on C_2 as compared to those on C_7 which is σ-bound to the metal atom. This is to

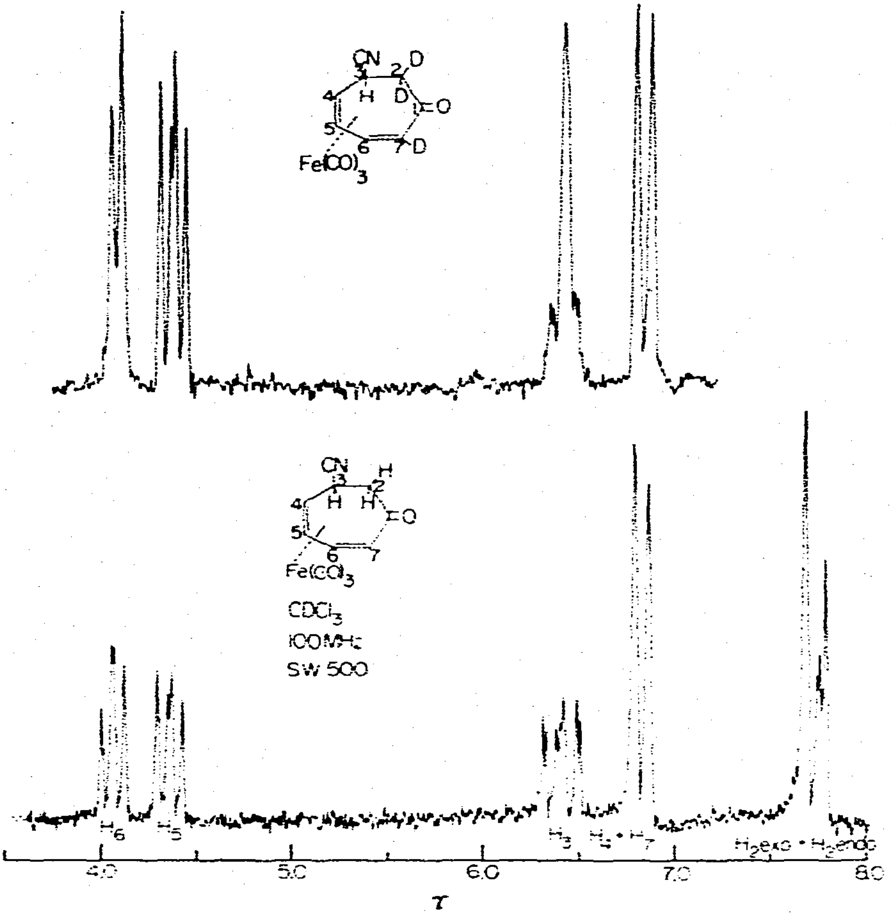


Fig. 1. ^{1}H NMR spectra of compounds Xa and X-d_3.

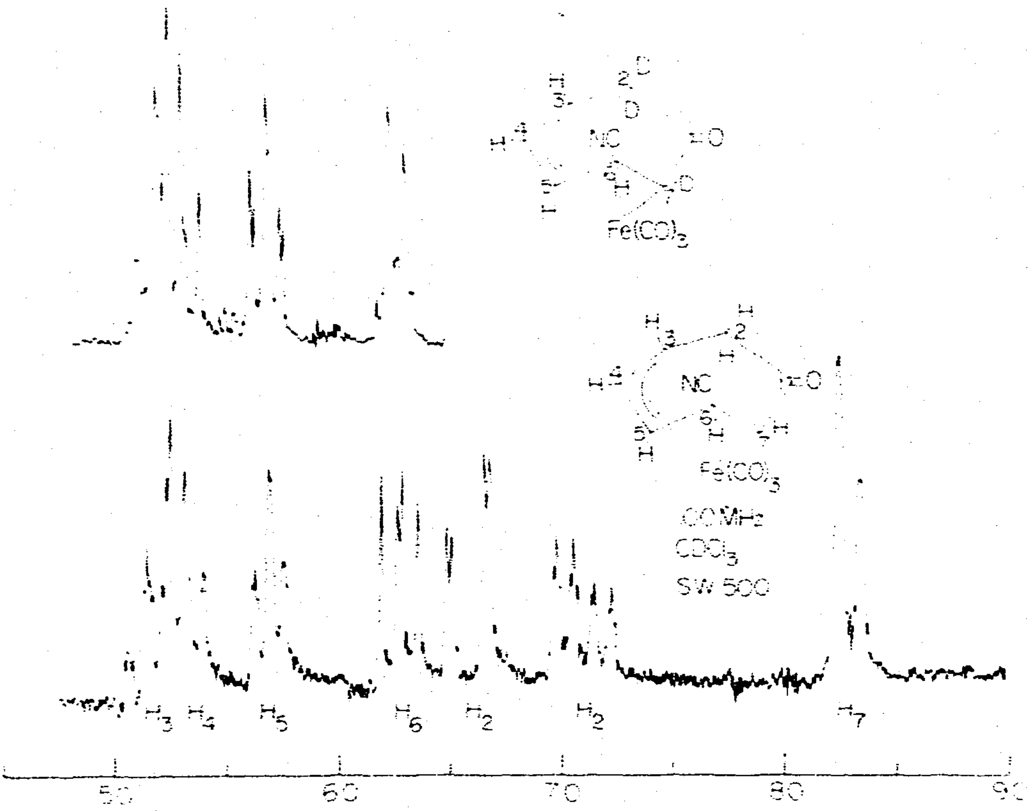
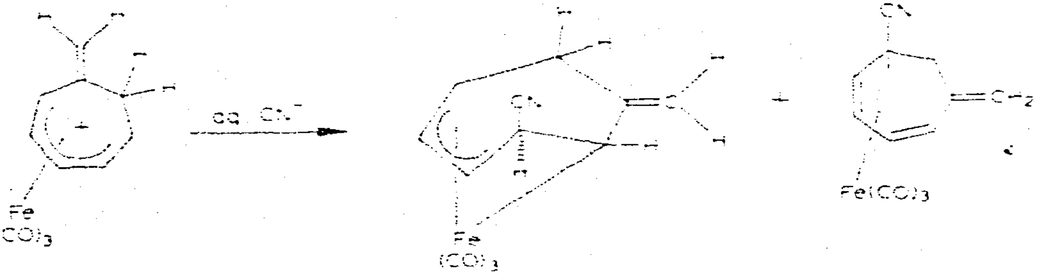


Fig. 2. ¹H NMR spectra of compounds XIa and XI-d_3.

our knowledge, the first instance where two such protons are incorporated in the same molecular structure.

In order to check the generality of the cyanide attack on unsymmetric coordinated cationic species, I also used as a substrate complex XII, which was previously reported by Lewis et al. [9]. When XII was treated with aq. solution of NaCN, the isomeric compounds XIII and XIV were produced together with minor amounts of the dimer of heptafuluene-Fe(CO)$_3$ [10].

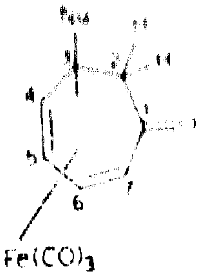
(continued on p. 154)



(XII) (XIII) (XIV)

TABLE 1

NMR SPECTRAL DATA (τ, ppm) FOR COMPOUNDS IX



Compound IX	$H_{2,exo}$	$H_{2,endo}$	H_3	H_4	H_5	H_6	H_7	Nu
Nu								
OCH_3[a]	8.1 (t)	7.6 (m)	6.09 (ddd)	6.72	4.4	4.13	6.82	6.65 (s)
PhNH-[a]	8.1 (t)	7.6 (m)	5.73	6.67	4.59	4.22	6.67	
–N–Bu-t[a]	8.17 (t)	7.76 (m)	6.22	6.9	4.53	4.2	6.22–6.9	8.82 (s)
$-N_3$[b]	8.0 (t) $J_{exo,endo}$ 12.0 Hz $J_{exo,3}$ 12.0 Hz	7.64 (m) (12 lines) $J_{endo,3}$ 5.5 Hz $J_{endo,7}$ 2.0 Hz	5.9 (ddd) $J_{3,4}$ 2.0 Hz	6.76 $J_{4,5}$ 6.0 Hz	4.58	4.34	6.76	
CN	7.6		6.32 $J_{3,exo}$ 10.5 Hz $J_{3,endo}$ 7.5 Hz	6.73 (d) $J_{4,6}$ 1.1 Hz $J_{4,3}$ 2.0 Hz $J_{4,5}$ 7.5 Hz	4.2 (m) $J_{5,6}$ 5.5 Hz	3.97 (t)	6.73 d	
CN, IX-d_1			(bs)	(dt)	(dd)	(dd)		

[a] Measured in $CDCl_3$ with TMS as internal standard at 60 MHz. [b] Measured in $CDCl_3$ with TMS as internal standard at 100 MHz.

TABLE 2

NMR SPECTRAL DATA (τ, ppm) OF COMPOUNDS XIII AND XIa

	X	$H_{2\,endo}$	$H_{2\,exo}$	H_3	H_4	H_5	H_6	H_7
X = O[a] R = CN		6.58 $J_{2endo,2exo}$ 16.5 Hz $J_{2,3}$ 2.5 Hz	7.09 $J_{2,3}$ 6.0 Hz $J_{2,8}$ 2.0 Hz	5.15 $J_{3,4}$ 9.5 Hz	5.31 $J_{4,5}$ 6.5 Hz	5.7	5.27 $J_{6,7}$ 7.0 Hz	8.28 $J_{7,8}$ 2.0 Hz $J_{7,9}$ 9.0
X = CH$_2$[a] R = CN	5.85 5.67	7.05		4.9	5.15	5.78	6.21	8.27
				(All coupling constants as above)				
R = H[b] X = O		6.77 $J_{2endo,2exo}$ 15.7 Hz $J_{2,3}$ 3.0 Hz	7.32	5.52	5.55	5.8	7.32 (2H)	8.61 (m)

[a] Measured in CDCl$_3$ at 100 MHz. [b] Measured in CDCl$_3$ at 60 MHz.

Experimental

All m.p.'s are uncorrected. IR spectra were recorded on Perkin–Elmer 257 and 337 spectrometers using polystyrene film as calibrant. Mass spectra were obtained on a Du Pont Model 21-491B. ^1H NMR spectra were recorded on Jeol-60 Hz and Varian-Associates HA100 spectrometers.

Reaction of VIII with azide

The salt was added in small amounts to aqueous solution of sodium azide covered with ether at room temperature. After 20 min two layers separated. The water layer was extracted with diethyl ether and the combined extracts were washed with water, and dried over $MgSO_4$ and the ether was removed. The residue was crystallized from hexane to give IX (Nu = N_3) as yellow crystals. (80%), m.p. 61–62°C. $\nu_{max}(CHCl_3)$: 2090 (N_3), 1660 (C=O); ν_{max}(hexane): 2060, 2005, 1996 (C≡O) and 1680 (C=O) cm^{-1}.

Reaction of VIII with aniline and methanol

To excess of aniline in ether (20 ml) was added in small portions 330 mg of salt VIII. After the addition was completed, the solution was stirred for another 20 min, and then poured into 60 ml water. The aq. layer was extracted with 20 ml ether, and the combined extracts washed with water, dried and evaporated to give crude solid, which crystallized from hexane to give 245 mg (IX, Nu = PhNH), m.p. 138–140°C; $\nu_{max}(CHCl_3)$: 1668 (C=O), 3440 (NH); ν_{max} (hexane): 2070, 2010 and 1998 cm^{-1}; mass spectrum: *m/e* 339 (M^+); 283 ($M^+ - 2CO$); 255 ($M^+ - 3CO$); 247 (M^+ − PhNH); 218 ($M^+ - PhNH_2 - CO$).

Preparation of IX (Nu = t-butylamine)

The reaction of VIII with t-butylamine was carried out according to the method used above. 600 mg of the salt VIIIa were treated with excess of t-butylamine to give IX (Nu = t-BuNH) as orange crystals (442 mg), m.p. 142–144°C; mass spectrum: *m/e* 263 ($M^+ - 2CO$); 235 ($M^+ - 3CO$); 247 (M^+ − BuNH); 179 ($M^+ - Fe(CO)_3$); (Found: C, 53.22; H, 5.33; N, 4;05. $C_{14}H_{17}FeNO_4$ calcd.: C, 52.66; H, 5.36; N, 4.4%) $\nu_{max}(CHCl_3)$: 3580 (NH), 1650 (C=O) ν_{max} (hexane): 2060, 1998, 1988 (C≡O); 1775 (C=O) cm^{-1}.

The tetrafluoroborate salt of VIIIa and VIII-d_3 were prepared according to ref. 10.

Reaction of VIII with $NaBH_4$

The salt VIII (610 mg) was added to a suspension of $NaBH_4$ in water in small portions at 0°C, and covered with an ether layer. After 10 min the ether layer was removed and the aqueous solution was extracted once again with ether. The combined extracts were dried, and evaporated to give a yellow paste. Separation of the residue on silica gave 124 mg Xa (R = H), m.p. 108–109°C (lit. [8] 104–105°C); and 110 mg XIa (R = H) m.p. 116°C; mass spectrum: *m/e* 220 ($M^+ - 28$), 192 ($M^+ - 2CO$), 164 ($M^+ - 3CO$), 108 ($M^+ - 3CO - Fe$).

Reaction of VIIIb with cyanide

The tetrafluoroborate salt, VIIIb, (1.05 g) was added to a vigorously stirred

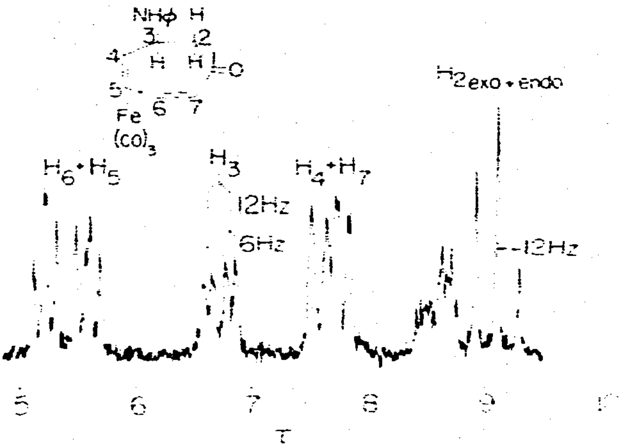


Fig. 3. ¹H NMR spectrum of compound IX (Nu = PhNH—).

mixture of aq. solution of sodium cyanide covered with ether at 0°C. After 30 min, the two layers were separated and the aq. solution extracted with ether. The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed to give an oil which was chromatographed on silica. Two products were obtained: The first compound to leave the column, using CH_2Cl_2 as eluent was found to be Xa (234 mg), m.p. 155—157°C (crystallization from ethanol). Mass spectrum *m/e* M^+ = 273, 245 (M^+ — CO), 217 (M^+ — 2CO), 189 (M^+ — 3CO),

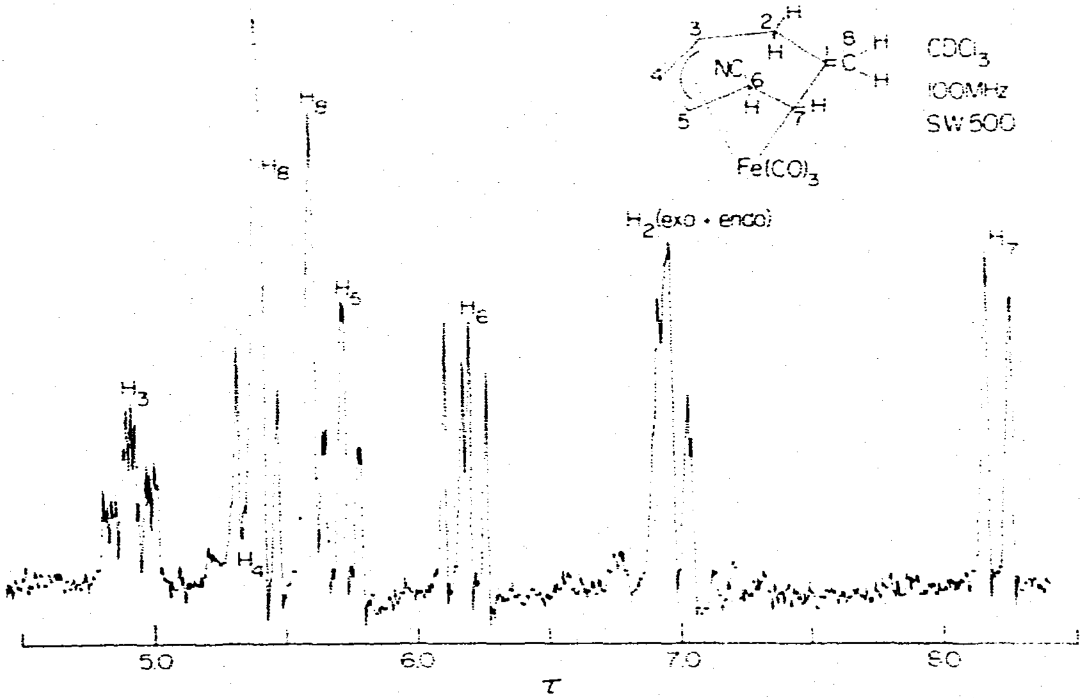


Fig. 4. ¹H NMR spectrum of compound XIII.

162 (189 − HCN), 134 (162 − CO); ν_{max}($CHCl_3$): 2230 (C≡N), 1665 (C=O), 2080, 2000b (C≡O) cm^{-1}; (Found: C, 48.60; H, 2.77. $C_{11}H_4D_3FeNO_4$ calcd. C, 47.86; H, 3.6%). The second band eluted with CH_2Cl_2 yielded XI-d (316 mg) m.p. 166–170°C decomp. (after crystallization from ethyl acetate). Mass spectrum m/e 273 (M^+), 246 (M^+ − HCN) and successive loss of CO units. ν_{max}($CHCl_3$): 2220 (C≡N), 2080 and 2000 (C≡O), 1670 (C=O) cm^{-1} (Found: C, 48.21; H, 2.86; Fe, 20.38. $C_{11}H_4D_3FeNO_4$ calcd.: C, 47.86; H, 3.6; Fe, [illegible]%). NMR data for X and IX, see Table 1 and Figs. 1 and 3.

6-Cyano iron tricarbonyl XIII

Using the above method for making the cyano derivatives of IX and X, the salt XII (707 mg) afforded after chromatography on silica and recrystallization from hexane, yellow crystals 114 mg (XIII), m.p. 100–104°C decomp. IR ν_{max}($CHCl_3$): 2220 (C≡N), 1630 (C=C) cm^{-1}, ν_{max}(hexane) 1991, 1999, [illegible] (C≡O) cm^{-1}; Mass spectrum m/e 243 (M^+ − CO), 215 (M^+ − 2CO), 187 (M^+ − 3CO), 160 (187 − HCN), 105 (187 − CN − Fe), 131 (160 − [illegible]) [illegible] NMR spectrum see Fig. 4.) The second compound was identified as XIV ([illegible] mg).

Acknowledgements

The author wishes to thank Prof. B.Z. Fuchs for his interest and Mrs. [illegible] (NMR determinations), and S. Hauptman (mass spectra determinations) for technical assistance.

References

1 [illegible], J. Organometal. Chem., 60 (1973) 335.
2 [illegible] B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, [illegible]
3 [illegible] J. Lewis et al., J. Amer. Chem. Soc., [illegible] 94 (1972) 4626. (c) J. Lewis et al., J. Chem. Soc., Dalton, [illegible]
4 [illegible], J. Organometal. Chem., 47 (1973) C29.
5 [illegible], Angew. Chem. Int. Ed., 12 (1973) 574.
6 B.F.G. Johnson, J. Lewis, J.W. Matheson, I.F. Ryder and M.J. [illegible]
7 [illegible] and S. Winstein, Tetrahedron Lett. (1971) [illegible]
8 [illegible], G.C. Farrant and G.T. Rodeheaver, J. Organometal. Chem., [illegible]
9 J. Lewis et al., J. Chem. Soc. Chem. Commun., 273 (1969).
10 [illegible], R. Mason and J.M. Gass, J. Organometal. Chem., [illegible]