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ETHOXYCYCLOPENTADIENYL-IRON COMPLEXES FROM CYCLOPENTADIENONE DIETHYL KETAL

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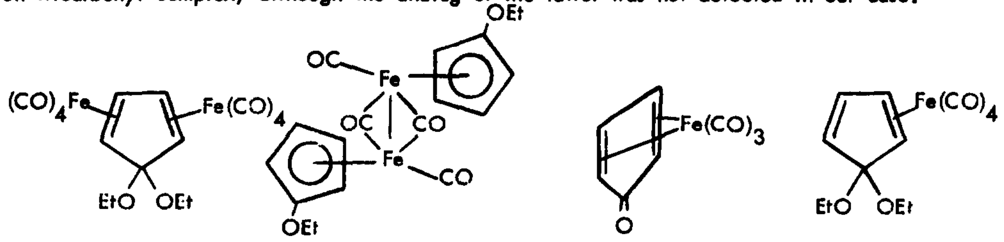
Our interest in the norbornen-and norbornadien-7-one systems[1,2] inevitably led us to pay increased attention to their precursor viz., the cyclopentadienone system. The latter is in itself a richly documented topic[3a] and in that framework one also finds cylcopentadienone-metal-π- complexes to have been quite extensively investigated.[3] However, we could find no reports on corresponding ketal-π-complexes and we took up the subject for reasons that will become obvious in subsequent publications. We present here our first results which provide a novel and convenient entry into alkoxycyclopentadienyl-iron-carbonyl complexes and alkoxy ferrocenes. Both classes of compounds are scarcely documented[4,5] and their chemistry all but unknown.

When a pentane solution of cyclopentadienone diethylketal[6] and diiron enneacarbonyl was refluxed for two hours, four compounds were detected by tlc and three of them were isolated and characterized[7] Chromatographic separation on basic alumina provided *I*,*II* and finally the known cyclopentadienone iron-tricarbonyl *III* m.p. 112°C, (lit.[4,8] m.p. 112°C; identical ir absorptions).

That *II* and *III* were formed in a secondary process was suggested by subsequent experiments. At room temperature, only *I* is obtained in very small yields. On the other hand, heating of pure *I* in refluxing pentane provided a similar mixture to the original one. Furthermore, heating *I* in refluxing methylclohexane resulted only in formation of pure *II*. The fourth, as yet, unidentified product is rather elusive. Attempts to trap it by gently heating *I* in vacuo resulted in minute yields and this, coupled with its instability, precluded a final structural assignment to date. A rapid ir spectral measurement indicated, though, a tetracarbonyl complex making possible the assumption that we deal with compound *IV*. A similar complex has been invoked as an intermediate in the formation of the unsubstituted analog of *II*[9,10] <u>via</u> the iron-tricarbonyl complex, although the analog of the latter was not detected in our case.



I *II* *III* *IV*

The ready formation of the dinuclear compound *II*, even at relatively low temperature, is in accord with the good "leaving-group"-character of EtO^-, the migration and cleavage of which is thus relatively enhanced to give *II*. This provides additional strength to the original mechanism envisaged for formation of this type of carbonyl bridged dinuclear compounds viz., migration of a negatively charged moiety to be followed by cleavage and dimerization[9,10].

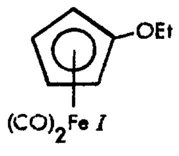
Concerning the intimate structure of *I*, the only available anologies are, to our knowledge, a tentatively assigned spiro [2.4] hepta-4,6-diene complex[11a] and the diphenylfulvene bis(irontetracarbonyl) complex in which the iron nuclei are assigned a trans relationship[11b]. The ABX_3 nmr pattern of the OCH_2CH_3 protons in *I* with no discernible chemical shift between the CH_3 resonances apparently indicate magnetic non-equivalency of the methylene protons. Such a situation would occur in the dissymmetric trans-*I*, with chemically equivalent methyl groups[12]. Turning to the dinuclear complex *II*, an unequivocal assignment is still not possible although a trans geometry seems probable[13]. A variable temperature nmr study down to -100° did not reveal any significant change in the resonances of *II*. Thus the barrier to interconversion between stereoisomers is apparently low relative to the unsubstituted analog ($E_a \sim 13$ kcal)[13].

When *II* was subjected to oxidative cleavage with iodine it readily gave ethoxycyclopentadienyl dicarbonyl iodide V. Treatment of the latter with silver fluoroborate yielded ethoxycyclopentadienyl iron dicarbonyl fluoroborate *VI*, which on sodium borohydride reduction yielded back *II* instead of the expected iron hydride[9].

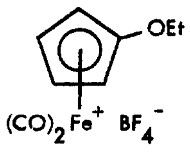
The iodide V was of obvious interest to us as a possible precursor to the σ-cyclopentadienyl iron complex *VII*. The latter would fill a gap in the investigation of the fluxional behaviour of such σ-complexes[14], since the parent complex (π-C_5H_5)Fe(CO)$_2$ (σ-C_5H_5)[15] and its acetyl derivative[16] have been scrutinized and shown to be subject to a temperature dependent succession of Fe-C sigmatropic shifts. However, treatment of V and *VI* with sodium cyclopentadienide at various temperatures, invariably led to ethyoxyferrocene *VIII* accompanied by small amounts of ferrocene. When V was reacted with RLi (R=Me, Ph) the corresponding σ-complexes *IX* were obtained but were found to be rather unstable.

Finally, thermolysis of *II* (at $\sim 250^\circ$)gave diethoxyferrocene X.

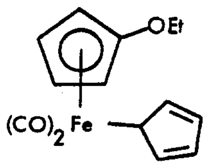
The electron releasing character of the ethoxy group towards the iron nucleus in these complexes appears to be established both by their chemical behaviour and spectroscopic data secured so far. Moreover, we regard the approach to the synthesis and transformations of these classes of compounds as being of preparative as well as of mechanistic interest. These and other aspects are now being pursued in our laboratary.



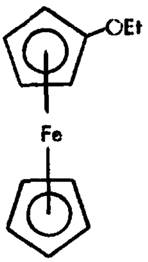
V



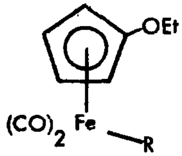
VI



VII



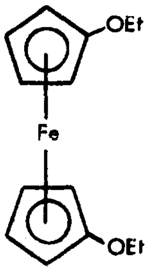
VIII



IX

a) R = Me

b) R = Ph



X

TABLE

Properties of the ethoxycyclopentadienyl-iron complexes.

Compound	m.p., C°	$\nu_{max,}^{CO}$ cm^{-1}	τ [a]
I	86-88(d)	2080, 2022 2011, 1990[b]	5.55(AB, 4, H_α H_β); 5.5(<u>AB</u>X_3, 4, OCH_2) 8.9 (t, 6, CH_3)
II	112	1990, 1950 1755[b]	5.43 (t, 4, H_α); 5.75 (t, 4, H_β); 5.95(q, 4, OCH_2); 8.63 (t, 6, CH_3).
III	63	2025, 1980[c]	5.32 (t, 2, H_α); 5.38 (t, 2, H_β); 6.06 (q, 2, OCH_2); 8.63 (t, 3, CH_3).
VI	129-131(d)	2050, 2000[c]	4.6 (2, H_α); 4.85 (2, H_β); 5.8 (q, 2, OCH_2); 8.6 (t, 3, CH_3).
VIII	oil		5.83 (s, 5, C_5H_5); 5.94(m, 2, H_α); 6.2 (m, 2, H_β); 6.17 (q, 2, OCH_2); 8.67 (t, 3, CH_3).
*IX*a	oil	1990, 1940[b]	5.56 (t, 2, H_α); 5.74 (t, 2, H_β); 6.26 (q, 2, OCH_2); 8.7 (t, 3, C-CH_3); 9.9 (s, 3, Fe-CH_3).
*IX*b	oil	2010, 1960[b]	2.5;3.05 (m, 5, C_6H_5); 5.42 (t, 2, H_α); 5.62 (t, 2, H_β); 6.60 (q, 2, OCH_2); 8.98 (t, 3, CH_3).
X	oil		5.93 (t, 4, H_α); 6.18 (t, 4, H_β); 6.16 (q, 4, OCH_2); 8.67 (t, 6, CH_3).

a) All nmr spectra but those of *I* and VI were taken in $CDCl_3$/TMS. *I* was measured in benzene and VI in acetone-d_6/TMS. Multiplets are centered at their respective τ values. H_α and H_β are the corresponding cyclopentadienyl protons.

b) Hexane

c) KBr

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