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THE REACTION BETWEEN BARBARALONE AND DIIRON NONACARBONYL

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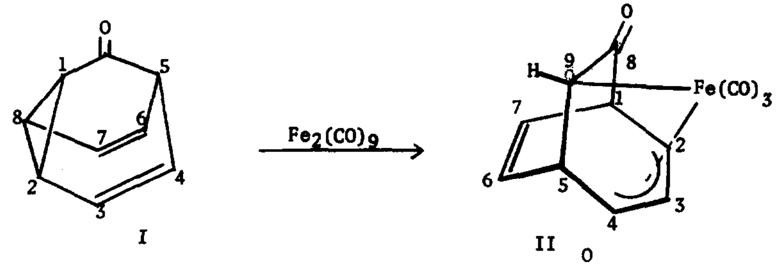
It has recently been reported that the reaction of some polycyclic olefins containing a cyclopropane group with $Fe_2(CO)_9$ gave complexes where the bonding was proposed to involve π-allyl and σ-components to the $Fe(CO)_3$ unit. This type of bonding has been suggested to exist in the bullvalene complex[1], tetracyclo[4.4.0.0^{5,7} .0^{2,10}] deca-3,8-diene complex[2], isobullvalene complex[3] and, very recently, in the semibullvalene complex[4]. On the other hand, cyclopropylstyrene treatment with $Fe_2(CO)_9$ produced substituted diene-$Fe(CO)_3$ complexes[5].

We report the first example of such a C_9H_8 complex, where the organic ligand exists in bicyclo[3.2.2]nonatrienyl form.

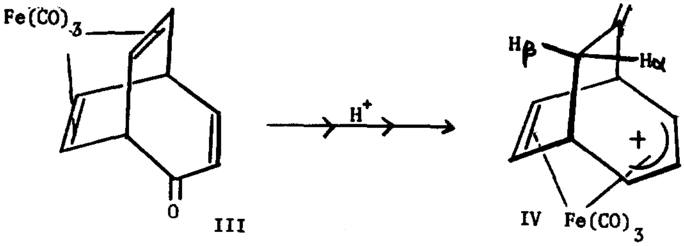
The reaction of the barbaralone I[6] and $Fe_2(CO)_9$ gave the complex II as the only product in 70% yield which could be purified by basic alumina chromatography and crystallization from hexane, m.p. 132-133°C, ir (hexane) 2058, 2000, 1922 cm^{-1} (coordinated CO), 1670 cm^{-1} (carbonyl CO); mass spectrum (70eV): m/e 272(M^+), 244(M-CO), 216(M-2CO), 188(M-3CO), 160(M-4CO), 134(160-C_2H_2). The CH skeleton of II was determined by H^1-nmr analysis (Figure 1) which included double resonance irradiation experiments. The spectra at 60 and 100 MHz were in good agreement with the proposed structure of the neutral complex II, showing no element of symmetry within the molecule. Each of the eight protons exhibits separate and well resolved absorptions which enables the determination of the exact chemical shifts and coupling constants (Table).

It is instructive to compare the structure of II with that of the C_9H_9-cationic complex generated by protonation of bicyclo[3.2.2]nonatrienone-$Fe(CO)_3$, IV[9] (Figure 2). The significant differences between II and IV are charge of the cation and type and site of bonding to the metal. It is worth mentioning the reverse order of chemical shifts of the allylic protons in II and IV.[9]



I

II



III

IV

Table: Nmr parameters for II

Chemical Shift[a] τ	Coupling Constants[b] Hz
H_7 = 3.75	$J_{6,7}$ = 8.5
H_6 = 3.93	$J_{6,5}$ = 2.5
H_2 = 4.84	$J_{1,7}$ = 5.5
	$J_{1,2}$ = 7.5
H_3 = 5.55	$J_{2,3}$ = 8.0
H_4 = 5.85	$J_{2,4}$ = 1.5
H_1 = 6.89	$J_{3,4}$ = 6.0
	$J_{4,5}$ = 7.0
H_5 = 7.12	$J_{5,9}$ = 8.5
H_9 = 8.04[c]	$J_{1,9}$ = 2.5

a. Determined at 100 MHz on a Varian H-100 and at 60 MHz on a Jeol C-60 HZ instrument.

b. Coupling constants were determined by spin decoupling at 100 MHz.

c. The H_9 proton bonded to the carbon bearing the iron is expected to be shielded but occurs at a lower field compared with the same proton in similar complexes (ref. 1-4) as the result of its location α to the electron withdrawing carbonyl group.

A tentative mechanism for complex II formation is oxidative cleavage of one of the lateral equivalent cyclopropane bonds C_1-C_2 or C_1-C_8 in I. The alternative cleavage of the

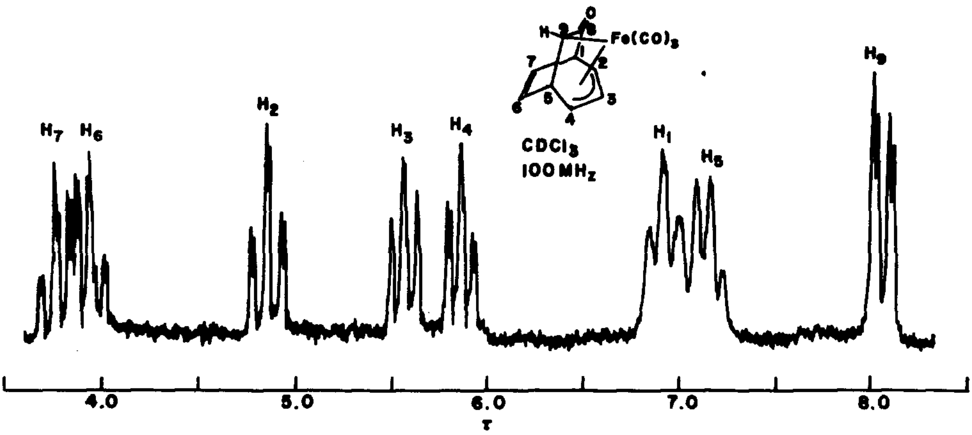


Fig. 1: 100 MHz nmr spectrum of $C_9H_8Fe(CO)_3$(II) in $CDCl_3$ solution, sweep width 500MHz

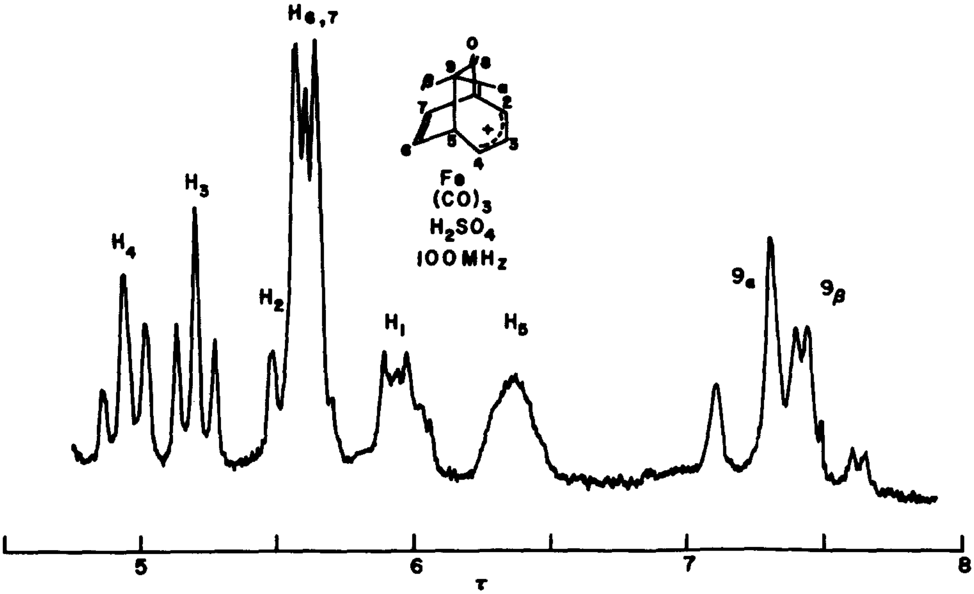
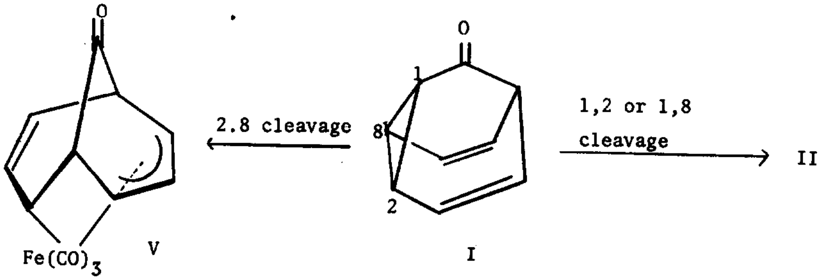


Fig. 2: 100 MHz nmr spectrum of tricarbonyliron 8-keto-bicyclo-[3.2.2]nonatrienyl IV in H_2SO_4 (ambient temp., sweep width 500 Hz).

central bond C_2-C_8 is rejected since it should lead to V which is excluded from the physical data given above.



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