Journal of Organometallic Chemistry, 56 (1973) 315–321

ORGANOIRON COMPLEXES FORMED IN THE REACTION OF DIIRON ENNEACARBONYL WITH SEMIBULLVALENE

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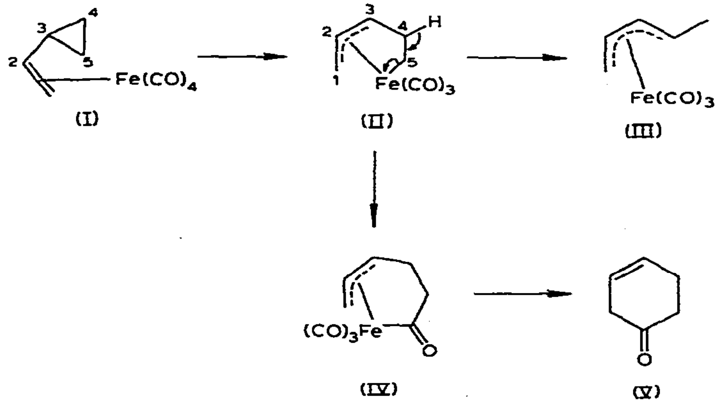
(Received November 28th, 1972)

SUMMARY

Semibullvalene reacts with diiron enneacarbonyl to give four iron carbonyl complexes, $C_8H_8Fe_2(CO)_8$ (XI) possessing an intact semibullvalene skeleton, $C_8H_8Fe(CO)_3$ (XII) and $C_8H_8Fe_2(CO)_7$ (XIII) resulting from a cleavage of the cyclopropane ring, and $C_8H_6Fe_2(CO)_6$, formed by further skeletal rearrangement of XIII.

The reactions of vinylcyclopropanes with palladium[1], nickel[2] and iron[3] complexes have recently been examined. As has been suggested earlier by Sarel[3a], the course of the reaction of vinylcyclopropanes with iron carbonyls may be depicted as proceeding through a non-conjugated *tetrahapto*-iron tricarbonyl complex (II) which subsequently isomerizes through hydrogen shift** to the conjugated system (III), or by carbonyl insertion and decomposition to a cyclohexenone (V)[3b,c,4]. When the rearrangement of intermediate (II) is precluded by the incorporation of C(4) in a bridgehead position, it may be isolated. Several excellent illustrations of this have been provided by Aumann[5] and by Eisenstadt[6] in the reactions of iron enneacarbonyl with bullvalene (VI) and barbaralone (VII), which afford complexes VIII, IX and X.



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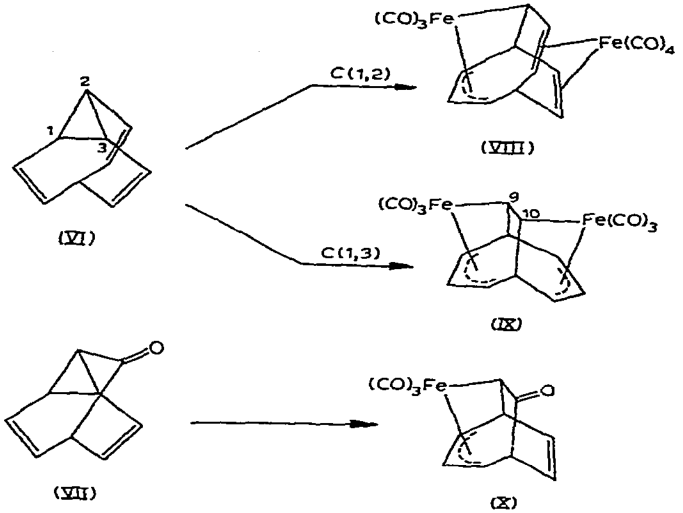
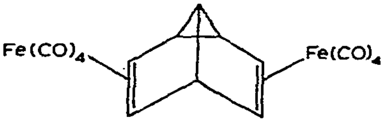
[**] The possibility that an iron hydride species intervenes in these processes cannot be excluded.



A recent brief paper[7] reporting the isolation and characterization of an iron carbonyl complex of similar constitution derived from semibullvalene prompts us to report the results of our own investigation of this reaction.

RESULTS AND DISCUSSION

Treatment of semibullvalene with iron enneacarbonyl at room temperature in hexane solution yielded four products which were separated by chromatography on alumina. The first of these, an unstable yellow oil, could not be characterized due to its high lability and was not investigated further. The second band from the chromatographic column, a low melting yellow substance, yielded a crystalline material, m.p. 88–90°, on fractional crystallization from hexane at low temperature. Its analysis as well as its mass spectrum, showing the successive loss of eight carbonyl groups from a parent peak at m/e 440, establish it as $C_8H_8Fe_2(CO)_8$. Its infrared spectrum, with peaks at 1970, 1995 and 2076 cm^{-1}, is in accord with the formulation of this substance as a bis-iron tetracarbonyl complex*, and its decomposition on heating above 90° to semibullvalene shows that the hydrocarbon skeleton of the complex is not rearranged. Of the three possible geometric isomers, an *endo–endo* structure may be excluded on steric grounds, while the NMR spectrum, which shows in particular a simple two proton doublet and a one proton quartet for the cyclopropyl protons, rules out the less symmetrical *endo–exo* isomer. This substance is accordingly assigned structure (XI).



(XI)

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* Compare for example (1,5-cyclooctadiene)diiron octacarbonyl with $\gamma(CO)$ (in CCl_4) 1965, 1995, 2098 (see ref. 8).

A second, yellow crystalline material, m.p. 66–68°, was also recovered from this fraction. Its analysis and mass spectrum were in accord with the composition $C_8H_8Fe_2(CO)_7$[*].

The final product obtained from the column was a yellow oil. Analytical and spectral data showed it to be identical with the complex $C_8H_8Fe(CO)_3$ reported recently by Moriarty, Yeh and Ramey[7] and shown by them to have the structure XII. The heptacarbonyl complex above was shown, in a separate experiment, to be formed on treatment of XII with iron enneacarbonyl. The close structural relationship between these two complexes is evident from a comparison of their NMR spectra (Table 1). Structure XIII, in which the iron tetracarbonyl group is *endo* to the bicycloheptadienyl ligand, is assigned to this substance, since it is the chemical shift of H(3) rather than that of H(8) in XII which is altered by the introduction of additional complexation.

TABLE 1

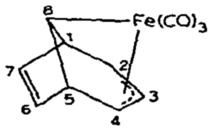
COMPARISON OF THE NMR SPECTRA OF COMPOUNDS XII AND XIII

	Chemical shift, τ^a (ppm)	
	XII	*XIII*
H(1), H(5)	6.95	6.98
H(2), H(4)	5.41	5.36
H(3)	5.82	5.36
H(6), H(7)	3.84	6.39
H(8)	9.61	9.65

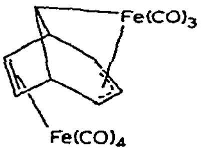
[a] Taken in CS_2 solution, TMS as internal standard.

Attempts to cleave the Fe–C bond in XII with acid were unsuccessful and led either to the recovery of starting material or its destruction.

The chemical shift of H(8) in both XII and XIII is anomalously high. It seems unlikely that this can be ascribed simply to the fact that it is bonded to the carbon bearing the metal atom[7]. Thus, while the methyl protons in h^5-$C_5H_5Fe(CO)_2CH_3$ are highly shielded (τ 9.87 ppm, CS_2), the methylene protons in the corresponding, ethyl, n-propyl, i-butyl and neopentyl derivatives fall within the relatively normal range of τ 8.2–8.7 ppm, but the methine proton in the i-propyl derivative appears abnormally deshielded at τ 7.5 ppm[9]. Similarly the protons at C(9,10) in IX have been reported to



(XII)



(XIII)

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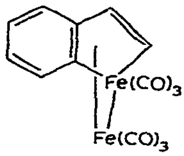
[*] Brief mention of this substance is made in ref. 4, but the manner of its synthesis is not given.

absorb at τ 8.08 ppm[5], although the structural relationship of each such proton is closely analogous to H(8) in XII and XIII, and they are moreover each proximate to the second metal atom. Valence angle distortions at C(8) in XII and XIII may contribute to the unusual shielding of these protons, but magnetic anisotropy effects associated with the metal or the carbonyl groups in these complexes may also play an important role, as they also appear to in deshielding H(9,10) in IX and H(3) in XII.

A better yield of the tricarbonyl complex (XII) could be obtained by heating semibullvalene in hexane solution with iron enneacarbonyl for 14 hours. In addition, another complex, a red crystalline material, m.p. 121°, was isolated in low yield from this reaction. The heptacarbonyl complex (XIII) is probably its precursor since XIII is formed from XII, and treatment of an equimolar mixture of these two complexes with iron enneacarbonyl at 60° for 1.5 hours gave the new substance in moderate yield.

The mass spectrum of this material and its elemental analysis are in accord with its formulation as $C_8H_6Fe(CO)_6$. The appearance of a prominent peak (52% of base peak) for Fe_2 at *m/e* 112 suggests the presence of an Fe–Fe bond in the molecule. However the iron carbonyl groups are not structurally equivalent as is indicated by the complexity of the carbonyl stretching absorptions near 2000 cm^{-1} (5 bands). The NMR spectrum of this substance exhibited complex absorption in the region of τ 2–3.5 ppm but no absorption at higher field. These data are in accord with structure XIV for the complex. Similar diiron hexacarbonyl complexes, possessing either a ferracyclopentadiene or ferraindene nucleus and prepared by the reaction of acetylenes or thiophene with iron carbonyls are reported to exhibit 4-5 carbonyl stretching absorptions[10]. Of greater diagnostic significance is the fact that olefinic protons in these complexes, unlike those in 1,3-butadiene or styreneiron[11] tricarbonyls, are highly deshielded, showing typical absorption near τ 3.5 ppm[10b–e].

Shortly after the isolation of the complex, Victor, Ben-Shoshan and Sarel[12] reported the isolation of an iron hexacarbonyl complex of the same constitution from the photolysis of *o*-bromostyrene in the presence of iron pentacarbonyl, to which they assigned structure XIV. A comparison of these substances established their identity*.



(XIV)

The detailed mechanism by which the heptacarbonyl (XIII) is transformed to the hexacarbonyl (XIV) cannot be specified, but sufficient precedent exists for the general processes of metal insertion into C–H bonds and aromatization which must occur in this change. It is of interest to note that a plausible mechanism which preserves the 18-electron configuration of the intermediates may be written. Such a pathway, involving organometallic radicals as intermediates, is depicted below:

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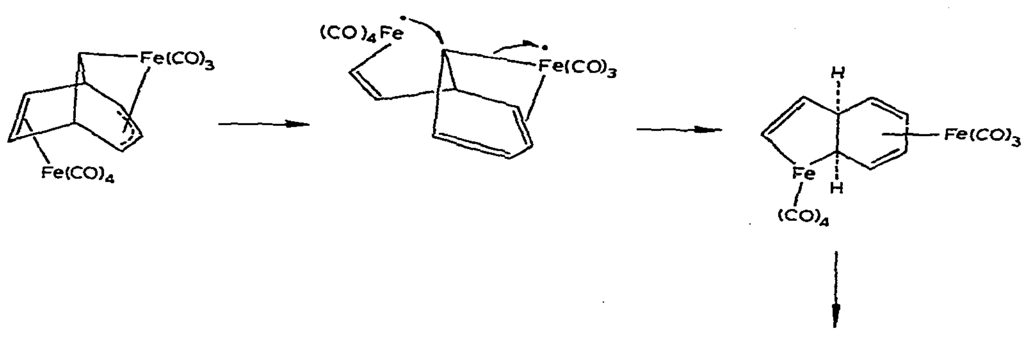
* We are indebted to Professor Sarel for providing us with a sample of the complex for comparison of its NMR spectra with our own.



(XIV)

EXPERIMENTAL

IR spectra were measured on a Perkin–Elmer Model 457 spectrophotometer, and proton magnetic resonance spectra on a Varian A-60A. Mass spectra were obtained on an MS 12, purchased with NSF Grant 3644, mass spectrometer operating at 75 eV. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. All melting points are uncorrected.

Preparation of $C_8H_8Fe_2(CO)_8$, $C_8H_8Fe(CO)_3$ and $C_8H_8Fe_2(CO)_7$ from semibullvalene

Semibullvalene[13] (0.70 g, 6.7 mmole) was dissolved in 90 ml of hexane, $Fe_2(CO)_9$ (20 g, 55 mmole) was added, and the resulting suspension was stirred at room temperature in a nitrogen atmosphere for 18 hours. The solution was then filtered through infusorial earth, and the solvent removed on a rotary evaporator. The residue was chromatographed on 50 g of neutral alumina (activity II) in Skelly B, to give three yellow bands:

(1) a very unstable yellow oil (0.2 g) which decomposed rapidly at room temperature or on exposure to air; IR (film): 1972, 1996, 2083 cm^{-1}.

(2) a very air-sensitive yellow oil (0.34 g) which crystallized on standing.

(3) A yellow oil (30 mg, ~2%) with spectral characteristics identical to those of the $C_8H_8Fe(CO)_3$ complex described below.

Recrystallization of fraction (2) from hexanes at −78° gave yellow crystals, m.p. 55–57° (dec.) consisting of an approximately 1/1 mixture of XI and XIII.

Anal. Found: C, 43.86; H, 1.83; Fe, 24.98. $C_{16}H_8Fe_2O_8$ calcd.: C, 43.68; H, 1.83; Fe, 25.39%. $C_{15}H_8Fe_2O_7$ calcd.: C, 43.69; H, 1.94; Fe, 27.18%. Repeated fractional crystallization from hexanes at −20° gave two different complexes. The less soluble $C_8H_8Fe_2(CO)_8$ complex, crystallized first; m.p. 88–90°; IR (CS_2) 1970, 1995 and 2076 cm^{-1} (CO), NMR (acetone-d_6, 0°) τ 6.19 (m, 5H), 7.29 (d, 2H, J 5.5 Hz), 8.45 ppm (q, 1H, J 5.5 Hz). *Anal.* Found: C, 42.76; H, 1.87%. The mass spectrum exhibited peaks at m/e 440 (P), and those expected for $P-(CO)_x$, ($x=1$–8).

The more soluble $C_8H_8Fe_2(CO)_7$ complex, was obtained from the later fractions; m.p. 66–68°; IR (CS_2): 1978, 1988 and 2055 cm^{-1}; NMR (acetone-d_6, 0°) τ 5.18 (m, 3H), 6.20 (s, 2H), 6.92 (m, 2H), 9.60 (m, 1H) ppm. *Anal.* Found: C, 43.51; H, 2.08; Fe, 26.21%. The mass spectrum exhibited peaks at m/e 412 (P), and those expected for $P-(CO)_x$, ($x=1$–7).

Both complexes were found to be air and heat sensitive but could be stored at 0° in a nitrogen atmosphere without appreciable decomposition.

Preparation of $C_8H_8Fe(CO)_3$ and $C_8H_6Fe_2(CO)_6$ from semibullvalene

Semibullvalene (2.4 g, 23 mmole) was dissolved in 100 ml of hexane, $Fe_2(CO)_9$ (29 g, 80 mmole) was added, and the solution was stirred under nitrogen in a 70° oil bath for 14 hours. It was then filtered through infusorial earth, and solvent removed on a rotary evaporator. The resulting oil was chromatographed on 125 g of neutral alumina (activity II) to give two bands:

(1) A yellow band, which eluted with Skelly B and contained an air-sensitive yellow oil, was further purified by distillation (30–35°/0.04 mm) to yield 0.6 g (10%) of the $C_8H_8Fe(CO)_3$ complex; IR (hexanes) 1967, 2000, 2070 cm^{-1} (CO); NMR (CS_2) τ 3.84 (t, 2H, J 1.4 Hz), 5.41 (t, 2H, J 5.5 Hz), 5.82 (t, 1H, J 6 Hz), 6.95 (t, 2H, J 5.5 Hz), 9.61 ppm (t, 1H, J 6 Hz). The spectrum of this substance was unchanged on heating to 125° in nitrobenzene.

Anal. Found: C, 53.97; H, 3.29; Fe, 22.74. $C_{11}H_8FeO_3$ calcd.: C, 54.10; H, 3.28; Fe, 22.95%. A mass spectrum displayed peaks at m/e 244 (P) and $P-(CO)_x$, ($x=1$–3).

(2) A red band which eluted slowly in benzene and which gave red crystals on evaporation of solvent. These were recrystallized from hexanes at −20° to give 54 mg (0.6%) of a complex, m.p. 121–122°; IR (KBr) 1920, 1960, 1990, 2020 and 2065 cm^{-1}(CO), NMR (CS_2) τ 2.11–2.40 (m, 2H), 2.60–3.42 (m, 4H) ppm.

Anal. Found: C, 43.86; H, 2.03. $C_8H_6Fe_2(CO)_6$ calcd.: C, 43.98; H, 1.57%. The mass spectrum exhibits peaks at m/e 382 (P) and $P-(CO)_x$, ($x=1$–6).

Attempted protonation of $C_8H_8Fe(CO)_3$

A solution of 1 ml of 48% aqueous HBF_4 (0.27 mmole) in 1 ml of acetic anhydride was added dropwise to a solution of the $C_8H_8Fe(CO)_3$ complex (66 mg, 0.27 mmole) in 3 ml of diethyl ether at 0°. No immediate reaction was observed, and an additional 0.8 ml of 48% HBF_4 was added. At this point, a vigorous evolution of gas commenced; no products or starting material could be isolated.

A solution of 48% aqueous HBr (83 mg, 0.5 mmole) in 1.2 ml of diethyl ether was added dropwise to a solution of the $C_8H_8Fe(CO)_3$ complex (120 mg, 0.5 mmole) in 3 ml of diethyl ether stirred at 0° under nitrogen. After 10 minutes at 0°, the solution was filtered through $MgSO_4$ and the solvent was removed by a stream of nitrogen. The oily residue was dissolved in CS_2, and an NMR spectrum showed only unchanged $C_8H_8Fe(CO)_3$ complex.

Preparation of $C_8H_8Fe_2(CO)_7$ from $C_8H_8Fe(CO)_3$ and $Fe_2(CO)_9$

The complex $C_8H_8Fe(CO)_3$ (100 mg, 0.41 mmole) was dissolved in 50 ml of hexane and $Fe_2(CO)_9$ (10 g, 27.5 mmole) was added. The mixture was stirred at room temperature under nitrogen for 17.5 hours. It was then filtered through infusorial earth and the solvent removed under reduced pressure. The residue was chromatographed on 15 g of neutral alumina with hexanes (activity III) to give 64 mg of a 1/3 mixture of $C_8H_8Fe(CO)_3$ and $C_8H_8Fe_2(CO)_7$, as determined by NMR. (38% based on $C_8H_8Fe(CO)_3$ consumed.)

Isolation of $C_8H_6Fe_2(CO)_6$ from the reaction between a $C_8H_8Fe_2(CO)_7/C_8H_8Fe(CO)_3$ mixture and $Fe_2(CO)_9$

A 1/1 mixture of $C_8H_8Fe_2(CO)_7$ (0.065 mmole) and $C_8H_8Fe(CO)_3$ (0.065

mmole) (total 40 mg) was dissolved in 20 ml of hexane and $Fe_2(CO)_9$ (1.5 g) was added. The mixture was stirred at 62° for 1.5 hours, and an additional 0.5 g of $Fe_2(CO)_9$ was added. The reaction mixture was then let cool to room temperature, filtered through infusorial earth, and evaporated under reduced pressure. Chromatography on 15 g of neutral alumina (activity III) in hexane yielded 16 mg (0.042 mmole) of $C_8H_6Fe_2(CO)_6$, identified by its NMR and IR spectra.

ACKNOWLEDGEMENT

This work was supported by grants from the U.S. Army Research Office, Durham. The award of an N.S.F. traineeship to A.R. is also gratefully acknowledged.

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