25°) and activation enthalpy (ΔH) for the solvent exchange reactions of the ions, $Mg(OH_2)_6{}^{2+}$ in aqueous acetone and $Mg(CH_3OH)_6{}^{2+}$ in methanolic acetone, were obtained from the temperature dependence of the coordinated solvent line widths: 1.3×10^5 sec^{-1} and 8.4 kcal; 2.5×10^4 sec^{-1} and 12 kcal, respectively. Accurate solvent exchange parameters for these systems are being obtained *via* a complete analysis of the line shapes.[26,27]

We have attempted to extend the techniques discussed here to the determination of the solvation numbers of a variety of cations in water, aqueous acetone, and methanol. No coordinated solvent pmr signal could be distinguished for the cations Li^+, Ca^{2+}, Zn^{2+}, Hg^{2+}, In^{3+}, Y^{3+}, and La^{3+}. However, the pmr signals of the complex ions $Be(OH_2)_4{}^{2+}$, $Ga(OH_2)_6{}^{3+}$, and $Co(OH_2)_6{}^{2+}$ can be distinguished readily in aqueous acetone and concentrated aqueous solutions at low temperature.[28,30] Details of these studies, including a complete line-shape analysis of the pmr signals, will be the subject of a future report.[30]

Acknowledgment. N. A. M. is grateful to the National Science Foundation for a postdoctoral fellowship, 1963–1964, during the tenure of which most of these studies were initiated.

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[26] Wawro and Swift[27] have completed such a study for the system Mg^{2+}–H_2O–acetone. The other systems are being analyzed in our laboratories.

[27] R. G. Wawro and T. J. Swift, private communication.

[28] While these studies were in progress Schuster and Fratiello[29] reported the detection of the pmr signal of $Al(OH_2)_6{}^{2+}$ in concentrated aqueous solutions of $AlCl_3$ at low temperatures.

[29] R. Schuster and A. Fratiello, *J. Chem. Phys.*, **47**, 1554 (1967).

[30] P. E. Darley and N. A. Matwiyoff, studies in progress.

Iron Carbonyl Complexes of Cyclooctatetraene Dimers

G. N. Schrauzer[1] and P. W. Glockner[2]

Contribution from the Department of Chemistry, University of California, San Diego (Revelle College), La Jolla, California, and The Institute of Inorganic Chemistry, The University, Munich, Germany, *Received November 20, 1967*

Abstract: The prolonged irradiation of a mixture of $Fe(CO)_5$ with excess cyclooctatetraene yields two isomeric complexes $C_{16}H_{16}Fe(CO)_3$ (**1**, mp 118°; **2**, mp 172° dec). Both compounds react with excess of $Fe(CO)_5$ to produce a trinuclear iron carbonyl complex, $C_{16}H_{16}Fe_3(CO)_9$ (**3**, mp 170° dec) which was thermally degraded to two isomeric complexes $C_{16}H_{16}Fe_2(CO)_6$ (**4**, mp 191° dec; **5**, mp 191° dec). Complexes **1**, **3**, **4**, and **5** can also be prepared by the light-induced reaction of $Fe(CO)_5$ with the cyclooctatetraene dimer of mp 73°. With $Fe_2(CO)_9$ under mild conditions this olefin produces an additional complex (**9**) of composition $C_{16}H_{16}Fe(CO)_4$ which readily decarbonylates to produce **1**. Complex **1** in solution undergoes reversible valence isomerization similarly as the parent cyclooctatetraene dimer. Complex **2** does not fluctuate and was shown to be an $Fe(CO)_3$ complex of tetracyclo[$6.0^{1,8}.0^{9,16}.0^{10,15}.4$]hexadeca-2,4,6,11,13-pentaene. Complex **3** appears to be a bis(π-allyl)tricarbonyliron derivative of **2** in which two additional $Fe(CO)_3$ groups are attached to the cyclooctatriene moiety of this $C_{16}H_{16}$-$Fe(CO)_3$ system. Complex **4** is shown to be hexacarbonyl-π-pentacyclo[$4.4.0^{5,16}.0^{6,15}.0^{7,14}.0^{8,13}$] hexadeca-2,4,10,12-tetraenediiron, whereas **5** is probably a derivative of **1** in which an additional $Fe(CO)_3$ group is attached to the two free double bonds of the ligand. The oxidative degradation of all complexes with ferric chloride in acetonitrile was found to yield naphthalene.

The study of iron carbonyl complexes of cyclooctatetraene has produced numerous new compounds with unexpected structures and properties. Although almost ten years has elapsed since the discovery of the first complexes,[3–5] active research is continuing and has become especially intriguing in view of the structural nonrigidity of some of the complexes and related phenomena of structural and valence isomerization.[6–13]

Cyclooctatetraeneiron tricarbonyl is relatively unreactive toward typical dienophiles but is known to add tetracyanoethylene.[14,15] Recently, reaction of diphenylacetylene with $C_8H_8Fe(CO)_3$ has been reported[16] to

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[1] University of California.

[2] Abstracted, in part, from the dissertation of P. W. Glockner, The University, Munich, 1965.

[3] (a) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960); (b) *Proc. Chem. Soc.*, 90 (1959).

[4] M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).

[5] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[6] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1388 (1965).

[7] R. T. Bailey, E. R. Lippincott, and D. Steele, *ibid.*, **87**, 5346 (1965).

[8] F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966).

[9] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *ibid.*, **88**, 3158 (1966).

[10] C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

[11] C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).

[12] F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *ibid.*, **89**, 2489 (1967).

[13] F. A. L. Anet, *ibid.*, **89**, 2491 (1967).

[14] G. N. Schrauzer and S. Eichler, *Angew. Chem.*, **74**, 585 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 454 (1962).

[15] A. Davison, W. McFarlane, and G. Wilkinson, *Chem. Ind.* (London), 820 (1962).

[16] U. Krüerke, *Angew. Chem.*, **79**, 55 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 79 (1967).

yield "diphenylbullvalene." In the present paper the addition of cyclooctatetraene is described which produces iron tricarbonyl complexes of cyclooctatetraene dimers. The work was initiated in 1961 with S. Eichler and was so far only described in two preliminary communications.[14,17] The structure of one complex (mp 172°) has been determined.[18]

Preparation of the Complexes

In our early work on cyclooctatetraene complexes of iron carbonyl, heating together with light irradiation was used as the means of activation.[4] It was observed that the best yields of $C_8H_8Fe(CO)_3$ were obtained if approximately stoichiometric amounts of cyclooctatetraene and iron pentacarbonyl were irradiated in benzene solution for not longer than 24 hr. On prolonged irradiation the reaction solution attained a brown color, especially in the presence of excess cyclooctatetraene. It was subsequently found that this was due to the formation of two new complexes of composition $C_{16}H_{16}Fe(CO)_3$: complex **1**, mp 118°; complex **2**, mp 172° dec. The ratio between the amounts of **1** and **2** formed is dependent essentially on the wavelength of light used for the irradiation, the uv transparency of the glass vessels, and the concentration of the reaction solution.[19] Complex **1** is formed predominantly if the maximum intensity of the activating light source is in the visible. Complex **2** forms if the light source is rich in the uv region. The complexes are evidently mainly produced *via* $C_8H_8Fe(CO)_3$, since if the latter is heated and irradiated in the presence of C_8H_8, **1** and **2** are obtained after considerably shorter reaction times. The direct reaction of $Fe(CO)_5$ with C_8H_8 is experimentally more convenient, however. If complexes **1** and **2** are heated and irradiated with excess $Fe(CO)_5$, they both produce the same product, a yellow-red compound of composition $C_{16}H_{16}Fe_3(CO)_9$ (dec pt 170°) (**3**).[17] This material can be thermally degraded into two isomeric complexes $C_{16}H_{16}Fe_2(CO)_6$ (**4** and **5**) (both mp 191° dec). In addition small amounts of a third complex, $C_{16}H_{16}Fe(CO)_3$ (**6**), mp 175–180°, are sometimes isolated. The interrelations of the complexes are shown in Scheme I.

Properties and Structure

Complex **1** exhibits temperature-dependent nmr spectra similar to the "fluctuating" $C_{16}H_{16}$ dimer of mp 73° (**7**). It can be prepared directly from this hydrocarbon on reaction with $Fe_3(CO)_{12}$ and hence is likely to have structure **1**. The X-ray structure determination of **1** is not yet completed,[20] but indicates that the complex does not undergo valence isomerization in the solid state, possibly as the result of lattice forces.[21] The nmr spectra at two temperatures are shown together with the proposed assignments in Figure 1.

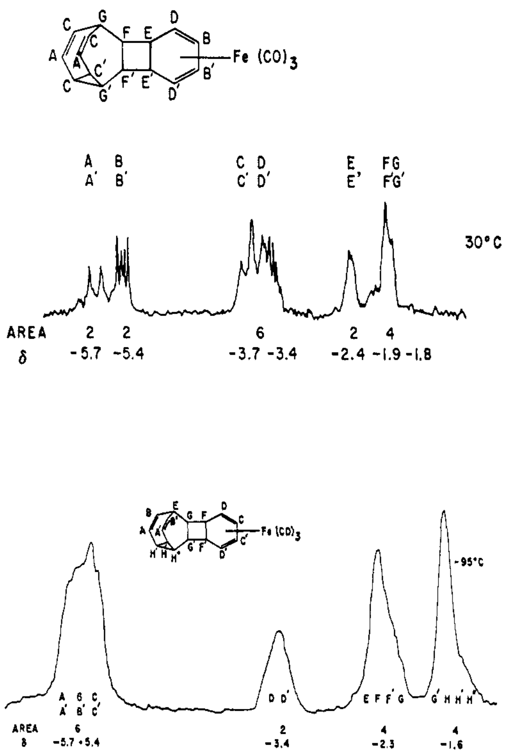
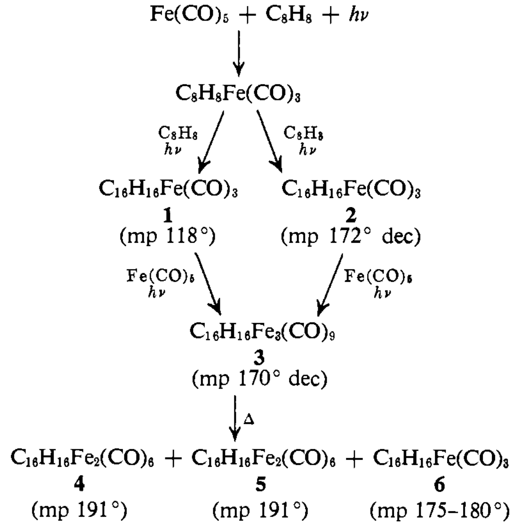


Figure 1. Structure of complex **1**, nmr spectra at 30 and −95° (in CS_2), and assignments.

Scheme I. Products of the Reaction of $Fe(CO)_5$ with Excess Cyclooctatetraene



Complex **1** does not produce well-recognizable monomeric hydrocarbon products on thermal decomposition. During the catalytic hydrogenation with Pd–C (5%) the $Fe(CO)_3$ group is cleaved off and a mixture of olefins (mainly $C_{16}H_{20}$ and $C_{16}H_{22}$ with small amounts of $C_{16}H_{18}$) is obtained whose structures have not been elucidated. With ferric chloride solution in acetonitrile,

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(17) G. N. Schrauzer, P. W. Glockner, and R. Merenyi, *Angew. Chem.*, **76**, 498 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 509 (1964).

(18) A. Robson and M. R. Truter, *Tetrahedron Letters*, **41**, 3079 (1964). In this preliminary communication the structure was described as that of the 118° isomer. It was subsequently shown to be in fact that of the 172° compound.

(19) This fact was not known in 1961, when crystals of 1 were sent to Professor Truter. One sample of 1 was obtained from the reaction in a vessel with greater uv transparency, and therefore contained a small amount of 2. Crystals of 2 from this sample were selected for the X-ray analysis, however, causing the temporary confusion concerning the structure of 1.[18]

(20) M. R. Truter, private communication.

(21) The $AgNO_3$ complex of bullvalene similarly seems to contain a "frozen" valence tautomer of the ligand. See M. G. Newton and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 3161 (1966).

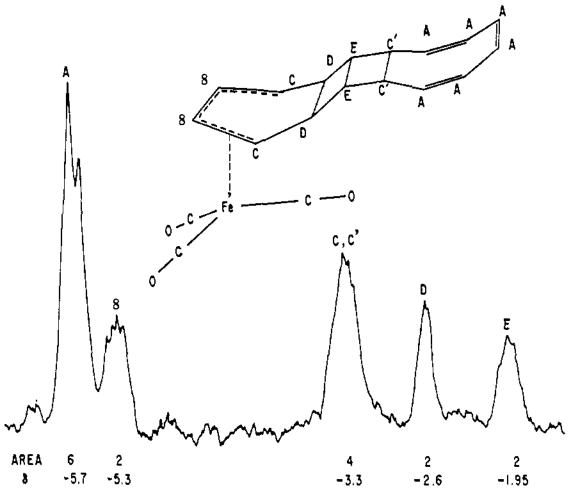
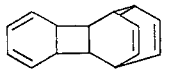


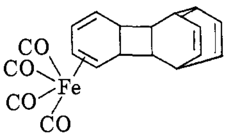
Figure 2. Structure[18] of complex **2** ($C_{16}H_{16}Fe(CO)_3$, mp 172°), nmr spectrum at 30° (in $CDCl_3$), and assignments.

smooth oxidative degradation was observed yielding naphthalene as the main organic product. It is conceivable that the complex is at first cleaved into benzene and bullvalene which undergoes secondary $FeCl_3$-catalyzed degradation to naphthalene. The thermal conversion to the latter hydrocarbon is well known.[22]

Complex **1** readily adds tetracyanoethylene to produce a sparingly soluble 1:1 adduct (**8**) which lacks free olefinic double bounds as evidenced by ir and nmr measurements. In the search for possible precursors of **1**, the dimer **7** in methylene chloride was allowed to react with $Fe_2(CO)_9$ at 30°. A yellow complex (**9**) was obtained; the formula $C_{16}H_{16}Fe(CO)_4$ was indicated by analysis. Complex **9** is light sensitive. On standing in solution, even in the dark it slowly decomposes into **1** and CO. The nmr spectrum could not be determined satisfactorily because of this instability in solution. In liquid SO_2 decomposition into the dimer hydrocarbon took place, leaving no doubt that the compound still contained the unrearranged **7**.



7



(and valence isomer)

9

The structure of complex **2** was determined by Robson and Truter[18] and is shown in Figure 2. The compound, tricarbonyl-π-tetracyclo[$6.0^{1,8}.0^{9,16}.0^{10,15}.4$]hexadeca-2,4,6,11,13-pentaeneiron, can be regarded as a derivative of Jones' dimer[23a] of cyclooctatetraene of mp 53° which is now known[23b] to have structure **10** rather than **11**. The nmr spectrum on this basis can be assigned as shown in Figure 2. Dimer **10** reacts with $Fe(CO)_5$ on heating and irradiating. Initial experiments indicate that complexes **1** and **2** are formed. In view of the tendency of **10** to rearrange into **7**, the reaction has not been studied in detail.

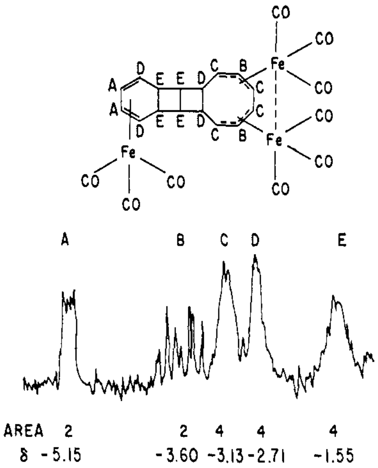
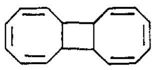
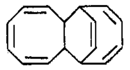


Figure 3. Proposed structure of complex **3** ($C_{16}H_{16}Fe_3(CO)_9$), nmr spectrum (in $CDCl_3$), and suggested assignments.



10



11

Complex **2** does not react with TCNE because of the absence of a planar 1,3-diene system in the molecule. The free dimer hydrocarbon forms Diels–Alder adducts only with the more dienophilic acetylenedicarboxylate.[23b] Degradation with $FeCl_3$ produces naphthalene as the main product.

For $C_{16}H_{16}Fe_3(CO)_9$, a bis-π-allylic type of interaction is assumed leading to the proposal of structure **3** for this complex. This would be in accord with Mössbauer measurements[24] which indicate that two of the three iron atoms must be in an identical environment. The nmr spectrum furthermore strongly suggests that one $Fe(CO)_3$ group must be attached to a 1,3-cyclohexadiene moiety. The appearance of a group of additional signals would be in accord with the presence of two allylic π-complexed protons. The nmr spectrum is temperature independent between −60 and +100°, indicating that the structure does not fluctuate. The suggested assignment is summarized in Figure 3.

The assumed structure is supported by the result of the thermal degradation which produces the isomeric complexes $C_{16}H_{16}Fe_2(CO)_6$ (**4** and **5**). Complex **4** has a very simple nmr spectrum, indicating that both iron atoms must be equivalent and attached to 1,3-cyclohexadiene moieties. Absence of additional signals in the olefinic region is in accord with formulation **4** of the complex as a derivative of tetracyclo-[4.4′.0.0.0′.0′]hexadecatetraene (Figure 4).

Complex **5** must be regarded as a derivative of the cyclooctatetraene dimer **7** in which all of the double bonds are π-bonded to $Fe(CO)_3$ groups. The nmr spectrum exhibits four signal groups centered around δ −5.44, −3.34, +2.66, and −1.67 with the intensity ratios of 2:4:7:3. The suggested assignment of the signals is shown in Figure 5. The structure of **5** does

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[22] G. Schröder, *Angew. Chem.*, **75**, 722 (2963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963).

[23] (a) W. O. Jones, *Chem. Ind.* (London), 16 (1955); (b) G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem.*, **77**, 774 (1965).

[24] Measurements performed by Dr. A. Bearden, University of California at San Diego.

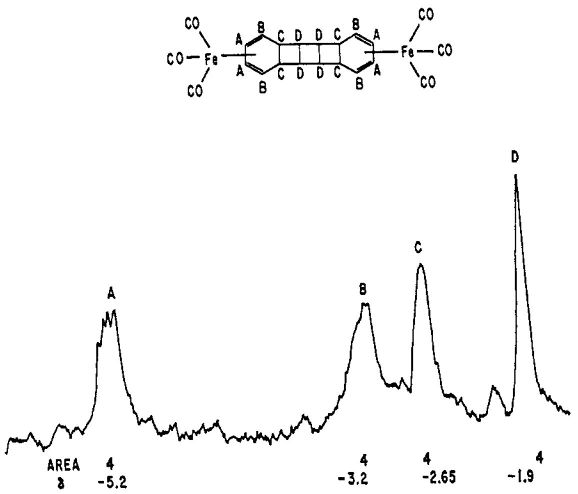
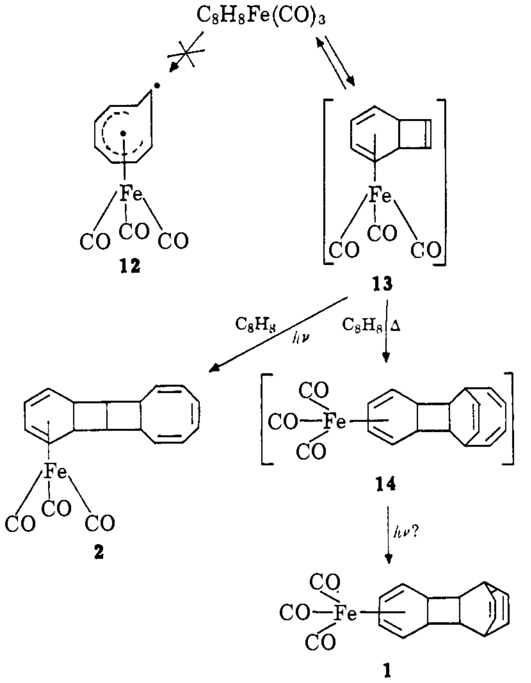


Figure 4. Proposed structure of complex **4** ($C_{16}H_{16}Fe_2(CO)_6$, mp 191°), nmr spectrum (in CS_2), and assignments.

not fluctuate. Complexes **4**, **5**, and traces of **6** were also obtained by the reaction of $Fe(CO)_5$ with the cyclooctatetraene dimer **7**. The structure of complex **6**, which has only been accessible in trace amounts, is not known.

Discussion

The mechanism of the thermal dimerization of cyclooctatetraene to **7** and **10** is unknown. Dimer **10** is formed first, probably *via* biradical intermediates, as its concerted formation is symmetry forbidden. In the presence of iron carbonyl fragments, radical intermediates could become stabilized through π-complex formation. In view of the photochemical stability of solutions of $C_8H_8Fe(CO)_3$ in the absence of cyclooctatetraene, it appears, however, that a species such as **12** is not formed. A more plausible activated form of $C_8H_8Fe(CO)_3$ would seem to be **13**, whose subsequent addition to cyclooctatetraene could either proceed thermally to yield complex **1** or photochemically to produce complex **2**. The fact that the yield of **2** increases at the expense of that of **1** if light of shorter wavelength is used to activate the reaction suggests that **2** is formed in a concerted photochemical reaction, in accordance to the Woodward–Hoffman rules. Formation of **1** probably occurs *via* a multistep mechanism involving a Diels–Alder addition of C_8H_8 to **13** as the first event. The conversion of **14** into **1** could possibly be light induced. The isomerization of the bicyclo[4.2.2]-deca-2,4,7-triene to bullvalene is known to proceed photochemically.[25]



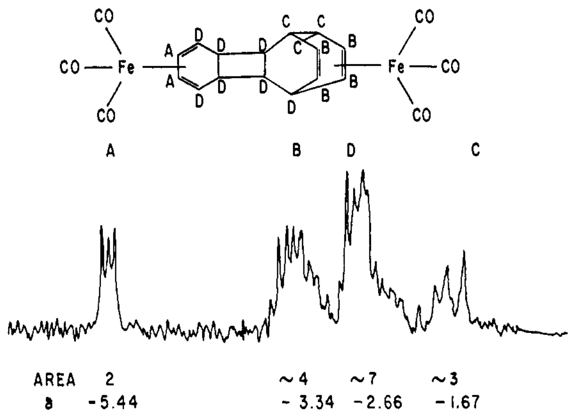
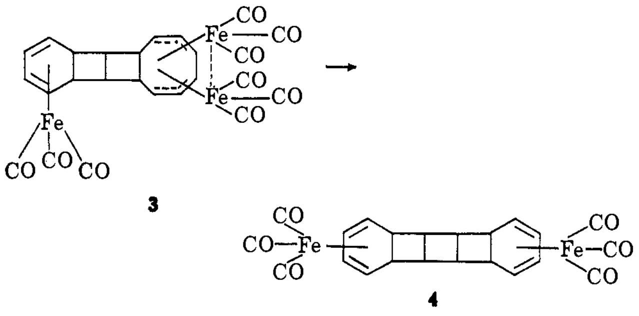


Figure 5. Complex **5** ($C_{16}H_{16}Fe_2(CO)_6$, mp 191°), suggested structure, nmr spectrum (in $CDCl_3$), and assignments.

The alternative possibility that **1** and **2** are formed at least in part through the addition of $Fe(CO)_3$ groups to the corresponding C_8H_8 dimers produced by the iron carbonyl independent light or thermal reaction cannot be ruled out completely. Whereas the conversion of **2** into **3** is readily understood, the demonstrated formation of **3** out of **1** merits further consideration. In the metal-free system this reaction would correspond to the conversion of **7** to **10**, a reaction which is only known in the opposite direction and regarded to be essentially irreversible. However, it is conceivable that the formation of the π-allyl-$Fe(CO)_3$ systems provides the necessary driving force for the reverse rearrangement.



The thermal degradation of **3** into **4** supports the assumed structure of **3**. It is of interest that **10** undergoes a similar Diels–Alder addition with acetylenedicarboxylate to procure **15** and **16**.[23b] The $Fe(CO)_3$ group in this case appears to have a comparable effect onto the carbon atom skeleton.

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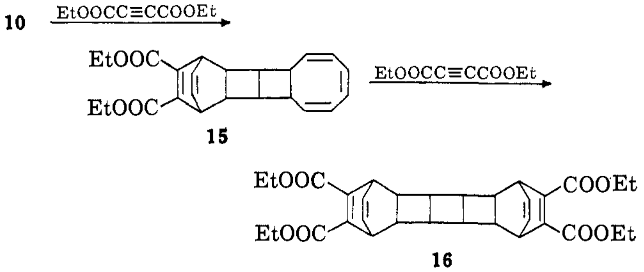
(25) M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967).



The formation of **5**, on the other hand, parallels the reactions of the metal-free system. It thus appears that the chemistry of the cyclooctatetraene dimers is not fundamentally altered by the presence of the iron carbonyl fragments. Their main effect, at least under the conditions of this study, appears to be a change in the activation energies for certain of the rearrangement processes which is evidently brought about by π-bonding interactions. The isomerization of bullvalene into 9,10-dihydronaphthalene similarly occurs at much lower temperatures in the presence of π-bonded iron carbonyl.[17] The oxidative degradation of the complexes to naphthalene (with $FeCl_3$ in acetonitrile) is of interest in view of related recent observations on metal-ion-catalyzed cyclobutene–butadiene and benzocyclobutene–*o*-xylylene isomerizations.[26]

Experimental Section

Complex 1 ($C_{16}H_{16}Fe(CO)_3$, Mp 118°) from Cyclooctatetraene and $Fe(CO)_5$. To a solution of 45 ml of freshly distilled cyclooctatetraene in 20 ml of benzene, iron pentacarbonyl (10 ml) was added. The solution was heated and irradiated in a Pyrex vessel equipped with a reflux condenser in an atmosphere of nitrogen. A 500-W G.E. projector spot lamp was used as the source of heat and light. After 96 hr the solvent and unreacted starting materials were removed at reduced pressure on a steam bath. The dark brown, oily residue was heated with 200 ml of ethanol to the boiling point. Activated carbon was added to absorb impurities. After filtration the complex was precipitated and at the same time freed from iron-containing impurities by adding 3 ml of 2 *N* HCl. Recrystallization of the product from ethanol yielded 16 g of complex **1**, mp 118–120° (Kofler melting point apparatus).

Anal. Calcd for $C_{19}H_{16}FeO_3$: C, 65.54; H, 4.63; Fe, 16.04; mol wt, 348.2. Found: C, 65.32; H, 4.79; Fe, 16.05; mol wt 335 (osmometry in benzene).

Complex 9 ($C_{16}H_{16}Fe(CO)_4$) and Complex 1 from Dimeric Cyclooctatetraene. The cyclooctatetraene dimer of mp 73° (prepared according to Schröder[27] (4.5 g, 21.6 mmoles) was dissolved in 100 ml of pure methylene chloride, and 5 g (13.7 mmoles) of $Fe_2(CO)_9$ was added. The suspension was stirred for 2 hr at 30° under nitrogen. After filtration and evaporation of the green reaction solution to about 30 ml, an equal volume of methanol was added. Yellow crystals of the complex precipitated and were collected by filtration. For further purification (the crude product was contaminated with $Fe_3(CO)_{12}$ formed during the reaction), the complex was recrystallized three times from methylene chloride by adding methanol to the concentrated solution, yield 1.2 g, mp 112–114° dec. The compound was found to be sensitive to light and air.

Anal. Calcd for $C_{20}H_{16}FeO_4$: C, 63.86; H, 4.29; Fe, 14.85. Found: C, 63.62; H, 4.41; Fe, 15.48.

Complex **9** (0.8 g, 2.13 mmoles) was refluxed in 50 ml of toluene. The carbon monoxide evolved during the reaction was measured. After 20 min the degradation of **9** to **1** was essentially complete (CO calcd: 2.13 mmoles; found, 2.08 mmoles). Evaporation of the clear toluene solution under reduced pressure and recrystallization of the product from methanol afforded complex **1**, identical with the product prepared from cyclooctatetraene and $Fe(CO)_5$ by comparison of the ir and nmr spectra and by the melting point and mixture melting point. Complex **1** was also isolated directly as the reaction product of the cyclooctatetraene dimer with $Fe_3(CO)_{12}$ in refluxing toluene.

Complex 8 (Tetracyanoethylene Adduct of 1). Complex **1** (11 g) was refluxed with 4.0 g of freshly sublimed tetracyanoethylene in 70 ml of benzene under nitrogen for 45 min. A yellow precipitate formed which was filtered off and purified by extraction with 200 ml of hot acetonitrile. The yellow needles had mp 250° dec.

Anal. Calcd for $C_{25}H_{16}N_4O_3Fe$: C, 63.04; H, 3.39; Fe, 11.72; N, 11.76. Found: C, 62.82; H, 3.40; Fe, 11.0; N, 11.45.

Catalytic Hydrogenation of Complex 1. Complex **1** (2.5 g) dissolved in 100 ml of methanol was catalytically hydrogenated using 200 mg of 5% palladium on carbon at 80° and 50 atm of hydrogen. After filtration and evaporation of the solvent, a yellow oil was obtained which was vacuum distilled. Analysis by glpc indicated the presence of three main components in the ratio of 91:7:1%. Mass spectrographic analysis of the mixture showed the presence of masses of molecular weight 212, 214, and 210.

Complex 2 ($C_{16}H_{16}Fe(CO)_3$, Mp 172°). A mixture of 45 ml of freshly distilled cyclooctatetraene and 10 ml of $Fe(CO)_5$ in 20 ml of benzene was heated and irradiated in an atmosphere of nitrogen using a quartz irradiation vessel and a mercury vapor light source. Work-up after 96 hr of irradiation afforded 7.4 g of complex **2**, mp 172°, after treatment with 2 *N* HCl and recrystallization from benzene–methanol as described in the preparation of complex **1**.

Anal. Calcd for $C_{19}H_{16}FeO_3$: C, 65.54; H, 4.63; Fe, 16.04. Found: C, 65.52; H, 4.69; Fe, 16.33.

Complex 3 ($C_{16}H_{16}Fe_3(CO)_9$). Complex **1** (2.0 g), or the identical amount of complex **2**, was dissolved in 6 ml of benzene. After adding 2.9 ml of $Fe(CO)_5$, the reaction solution was heated and irradiated under nitrogen for 24 hr. Evaporation of the filtered reaction solution at reduced pressure (bath temperature 80°) yielded a brown-red, oily residue which was dissolved in 15 ml of acetone. Addition of 5 ml of 2 *N* HCl produced an oily, brown-red precipitate which was isolated. The product was again dissolved in acetone and treated with dilute HCl until a crystalline product was obtained. This was recrystallized from toluene, affording yellow-red crystals, mp 170° dec.

Anal. Calcd for $C_{25}H_{16}Fe_3O_9$: C, 47.82; H, 2.57; Fe, 22.90; O, 26.71; mol wt, 627.9. Found: C, 47.51; H, 2.42; Fe, 22.90; O, 26.72, mol wt, 649 (osmometry in benzene).

The complexes obtained from either complex **1** or **2** were shown to be identical in every respect by comparing the infrared and nmr spectra and by chemical analysis.

Complexes 4 and 5 from Complex 3. A toluene solution (8 ml) containing 1.4 g of **3** was heated in an autoclave for 4 hr at 185°. The pressure in the vessel increased to 8 atm and remained constant for the rest of the heating period. After cooling the autoclave, the contents was at first diluted with 5 ml of toluene and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in 5 ml of warm benzene. To this solution three drops of 2 *N* HCl was added to dissolve ferric impurities. Subsequent addition of 10 ml of petroleum ether (boiling point range 60–80°) afforded 180 mg of a fraction of crystals melting at 191° which were recrystallized from benzene–methanol (fraction A). The combined filtrates were evaporated to dryness under reduced pressure, affording a residue which was dissolved in 3 ml of benzene. Precipitation with 10 ml of petroleum ether afforded a second fraction of crystals (85 mg) which after recrystallization from benzene–methanol melted at 191° (fraction B). Fraction A was identified as "complex **4**;" fraction B was "complex **5**."

Anal. Calcd for $C_{22}H_{16}Fe_2O_6$: C, 54.14; H, 3.30; O, 19.67; Fe, 22.89. Found (**4**): C, 54.22; H, 3.22; O, 20.15; Fe, 21.0. Found (**5**): C, 54.30; H, 3.21; O, 20.35; Fe, 22.85.

It was noted during this work that the sequence of the appearance of the complexes **4** and **5** was sometimes reversed; that is, complex **5** precipitated as the first fraction and complex **4** as the second. This is due to the similar solubilities of the two compounds. Similar observations were also made during the work-up of mixtures containing complexes **1** and **2**.

Preparation of Complexes 4, 5, and 6. A solution of 2 g of complex **1** and 2 ml of $Fe(CO)_5$ in 8 ml of toluene was heated in an autoclave for 5 hr at 185°. Work-up as described in the last experiment afforded 1.4 g of complex **4** and 0.9 g of complex **5**. The two complexes were also obtained in moderate yield from the reaction of the cyclooctatetraene dimer of mp 73° (**7**). A solution containing 3 g of **7** in 10 ml of benzene was heated together with 5 ml of $Fe(CO)_5$ in an autoclave for 2 hr at 185°. Work-up as described for the isolation of complexes **4** and **5** afforded 0.3 g of **4**

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and 0.2 g of **5**. From the mother liquors small amounts of an additional complex, mp 175–180°, were isolated (complex **6**).

Anal. Calcd for $C_{19}H_{16}FeO_3$: C, 65.54; H, 4.63; O, 13.79; Fe, 16.04; mol wt, 348.2. Found: C, 65.30; H, 4.82; O, 13.41; Fe, 17.05; mol wt, 330 (osmometry in $CHCl_3$).

Oxidative Degradation with $FeCl_3$. To a solution of 25 g of anhydrous $FeCl_3$ in 100 ml of acetonitrile, a concentrated acetonitrile solution of 5 g of complex **1** was added over a period of 30 min at room temperature. The CO evolved during this time amounted to 41.7 mmoles (97% of the theoretical amount). The acetonitrile solution was evaporated to dryness at 20° and reduced pressure. The residue was extracted with 150 ml of cold methylene chloride. Vacuum evaporation of the methylene chloride solution afforded 0.32 g (25%) of colorless crystals which were sublimed and identified as naphthalene by comparison of the infrared spectrum and the determination of the mixture melting point with an authentic sample. Similar yields of naphthalene were obtained from the degradation of complex **2**. Naphthalene was also isolated from complexes **3**, **4**, and **5**, albeit in smaller yields.

Characteristic infrared bands of complexes **1–5**, **8**, and **10** (KBr, in cm^{-1}; CO = metal carbonyl) follow.

1. 3040, 2940, 2918, 2045 (CO), 1976 (CO), 1960 (CO), 1930 (sh), 1649, 1450, 1399, 1376, 1349, 1252, 1238, 1227, 1180,...

2. 3130, 2951, 2045 (CO), 1977 (CO), 1960 (CO), 1630, 1450, 1346, 1300, 1250, 1166, 1130,...

3. 2941, 2067 (CO), 2044 (CO), 2025 (CO), 1989 (CO), 1720, 1637, 1450, 1404, 1349, 1312, 1296, 1269, 1230,...

4. 2950, 2045 (CO), 1980 (CO), 1980 (CO), 1955 (CO), 1465, 1450, 1401, 1370, 1339,....

5. 2941, 2057 (CO), 2041 (CO), 1984 (CO), 1960, 1950, 1450,....

8 (TCNE adduct of **1**). 3020, 2940, 2370, 2265, 2181, 2125 (CO), 2046 (CO), 1972 (CO), 1459, 1399, 1379, 1350, 1330, 1288, 1258, 1191,....

10. 3030, 2919, 2084 (CO), 2044 (CO), 1993 (CO), 1648, 1460, 1406, 1359, 1317, 1310,....

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The Reaction of L-Carnosine with Cobalt(II)[1]

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Abstract: The temperature-jump method has been used to determine the complexation rate constants for the reaction of L-carnosine with cobalt(II) at 25° and ionic strength 0.1 *M*. The association rate constant is consistent with a mechanism in which release of a water molecule from the metal ion's inner coordination sphere is rate determining. The rate constants for the reaction, $Co^{2+} + HL \rightleftharpoons CoHL^{2+}$ (where HL represents the neutral form of the ligand), are $k_1 = 4.2 \times 10^5$ ($\pm 20\%$) M^{-1} sec^{-1} and $k_{-1} = 87$ ($\pm 20\%$) sec^{-1}. Since the cobalt complex is a seven-membered ring system, the results are taken as evidence that the ligand entropy contribution to steric effects in fast metal-complex substitution reactions is considerably less significant than the ring-strain contribution.

Many transition metal complexation reactions have been studied by fast-reaction techniques. The conclusion, which has been reached on the basis of the experimental data, is that these reactions require at least two steps.[3] First, there is a diffusion-limited ion-pair formation between the aquated metal ion and the reactant ligand—a process which may, itself, involve more than one discrete step. Second, and rate determining, is the substitution of the reactant ligand into the inner coordination shell. For most systems, the slowest or rate-determining part of this second step is the release of an inner-coordination-sphere water molecule from the fully aquated metal ion. This reaction is characteristic of the metal and is not affected by the ligand.

Recent studies of the reactions of cobalt(II) with β-alanine and β-aminobutyric acid have shown that, for these systems, the association rate constants are ligand dependent.[4,5] These observations were accounted for by demonstrating that the rate of complex formation becomes a characteristic of the ligand when control of the rate passes from the release of a water molecule coordinated in the metal ion's inner hydration sphere to a sterically hindered formation of a metal chelate ring system. The bidentate ligands β-alanine and β-aminobutyric acid form six-membered rings with metal ions rather than the five-membered rings formed by most other chelating ligands. The anomalously slow complexation rates were postulated to be the result of a ring-strain effect and an entropy-loss effect when forming a six-membered chelate ring as compared to a five-membered ring. A thermodynamic study of metal binding with amino acids and diamine bases has demonstrated that, when chelate ring size increases beyond five members, the stability of the complex formed decreases.[6] Although part of this effect could be accounted for on the basis of a chelate entropy effect,[7] the magnitude of the destabilization

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