Reactions of Transition Metal Compounds with Macrocyclic Alkadiynes. III. Intramolecular Transannular Cyclizations and Related Processes with Iron Carbonyls[1-3]

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Abstract: The following types of intramolecular transannular cyclization products were obtained by various reactions of the indicated macrocyclic alkadiynes with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ and characterized in detail by chemical and spectroscopic methods: (1) the yellow-orange liquid tricyclic cyclobutadiene–iron tricarbonyl derivative of stoichiometry (alkadiyne)$Fe(CO)_3$ from 1,7-cyclotetradecadiyne; (2) the orange crystalline tricarbonylferrole–iron tricarbonyl of stoichiometry (alkadiyne)$Fe_2(CO)_6$ from 1,7-cyclododecadiyne; (3) dark red crystalline tricyclic cyclopentadienyl–iron carbonyl derivatives of stoichiometries [(alkadiyne-H)$Fe(CO)_2$]$_2$ from 1,7-cyclotridecadiyne, 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne. Other tricyclic cyclobutadiene–iron tricarbonyl derivatives of stoichiometries (alkadiyne)$Fe(CO)_3$ can be obtained in trace quantities from reactions of the other macrocyclic alkadiynes with the iron carbonyls. The formation of tricyclic cyclopentadienyliron carbonyl derivatives from reactions of the corresponding macrocyclic alkadiynes with iron carbonyls appears to require the presence of at least one bridge of exactly five methylene groups between the pair of carbon–carbon triple bonds in the macrocyclic alkadiyne. The tricyclic cyclopentadienyliron carbonyl derivatives of stoichiometries [(alkadiyne-H)-$Fe(CO)_2$]$_2$ can be converted to the corresponding yellow pentafluorophenyl derivatives $C_6F_5Fe(CO)_2$(alkadiyne-H) and the corresponding yellow triphenyltin derivatives $(C_6H_5)_3SnFe(CO)_2$(alkadiyne-H) by reaction with sodium amalgam in tetrahydrofuran followed by addition of excess hexafluorobenzene and of triphenyltin chloride, respectively. Furthermore, reaction of the tricyclic cyclopentadienyliron carbonyl derivative $[C_{14}H_{19}Fe(CO)_2]_2$ with iodine in chloroform solution gives the black iodide $C_{14}H_{19}Fe(CO)_2I$. The reaction between 1,7-cyclotridecadiyne and $Fe(CO)_5$ also gives the yellow crystalline tricarbonylferrole–iron tricarbonyl derivative $(C_{13}H_{18})_2Fe_2(CO)_6$ which appears to be an intermolecular cyclization product.

The first paper of this series[1b] describes the intramolecular transannular cyclizations of the macrocyclic alkadiynes I ($m = 4$, $n = 4$, 5, or 6; $m = 5$, $n = 5$ or 6) with the cyclopentadienylcobalt derivatives $C_5H_5Co(CO)_2$ and $C_5H_5Co(1,5\text{-}C_8H_{12})$ to give the tricyclic cyclobutadiene derivatives II ($m = 4$, $n = 4$, 5, or 6; $m = 5$, $n = 5$ or 6). This paper describes the reactions of the same macrocyclic alkadiynes I with the iron carbonyls $Fe(CO)_5$ and $Fe_3(CO)_{12}$. These reactions were found to be much more complex than the corresponding reactions of the macrocyclic alkadiynes I with the cyclopentadienylcobalt derivatives. Thus intramolecular transannular cyclization reactions were observed to give either tricyclic cyclobutadiene–iron tricarbonyl derivatives of stoichiometry (alkadiyne)$Fe(CO)_3$ and structure III ($m = 4$, $n = 4$, 5, or 6; $m = 5$, $n = 5$ or 6), a tricarbonylferrole–iron tricarbonyl derivative of stoichiometry (alkadiyne)-$Fe_2(CO)_6$ and structure IV ($m = 4$, $n = 4$),[5a] or tricyclic cyclopentadienyliron carbonyl derivatives of stoichiometry [(alkadiyne-H)$Fe(CO)_2$]$_2$ and structure V ($m = 4$, $n = 4$, 5, and probably 6) depending upon the macrocyclic alkadiyne used and the reaction conditions. In addition we isolated the tricarbonylferrole–iron tricarbonyl derivative of stoichiometry $(C_{13}H_{18})_2$-$Fe_2(CO)_6$ (*i.e.*, (alkadiyne)$_2Fe_2(CO)_6$) and possible structure VI which clearly must arise from an intermolecular rather than an intramolecular interaction of the

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(1) (a) For part II of this series see R. B. King, I. Haiduc, and A. Efraty, *J. Organometal. Chem.*, **47**, 145 (1973); (b) for part I see R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **94**, 3021 (1972).

(2) For preliminary communications of some of this work see the following papers: (a) R. B. King and C. W. Eavenson, *J. Organometal. Chem.*, **16**, P75 (1969); (b) R. B. King and I. Haiduc, *J. Amer. Chem. Soc.*, **94**, 4044 (1972).

(3) Portions of this work were presented at the Symposium on the Chemistry of Hydroformylation and Related Reactions in Veszprem, Hungary, June 1972.

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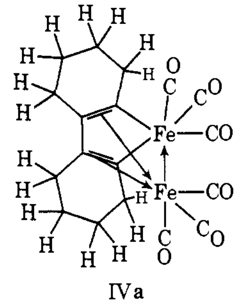
(5a) NOTE ADDED IN PROOF. After this paper was accepted for publication, results from an X-ray crystallographic study (R. Bau, private communication, late 1972) on the complex $C_{12}H_{16}Fe_2(CO)_6$ from 1,7-cyclododecadiyne and iron carbonyls became available. This study confirmed the tricarbonylferrole–iron tricarbonyl nature of this complex proposed in this paper and a preliminary communication[2b] but indicated structure IVa rather than the structure IV ($m = 4$, $n = 4$) proposed in this paper. Structure IVa is as consistent as structure IV ($m = 4$, $n = 4$) with the spectroscopic and other properties of $C_{12}H_{16}Fe_2(CO)_6$ but was not given serious consideration when the work described in this paper was carried out, since formation of IVa from 1,7-cyclododecadiyne and iron carbonyls requires cleavage of carbon–carbon bonds in the macrocyclic ring. The demonstration of structure IVa rather than structure IV ($m = 4$, $n = 4$) for the product $C_{12}H_{16}Fe_2(CO)_6$ from 1,7-cyclodecadiyne and iron carbonyls does not appear to alter any of the basic conclusions in this paper. Implications of this unexpected crystallographic result will be discussed in a future publication giving the details of this crystallographic work.



IVa

Table I. New Compounds Obtained from Reactions of Macrocyclic Alkadiynes with Iron Carbonyls

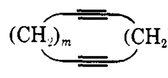
Compound	Structure[a]	m	n	Color	Mp, °C		Analyses, %				Mol wt[b]
							C	H	Fe	O	
$C_{12}H_{16}Fe_2(CO)_6$	IV[c]	4	4	Orange	97–98	Calcd	49.2	3.7	25.4	21.8	
						Found	49.7	3.5	25.1	21.7	
$[C_{13}H_{17}Fe(CO)_2]_2$	V	4	4	Red-brown	123–125	Calcd	63.2	6.0	19.5	11.2	570
						Found	64.0	6.2	18.8	10.8	608
$(C_{13}H_{18})_2Fe_2(CO)_6$	VI	4	5	Yellow	133	Calcd	61.1	5.7	17.8	15.3	628
		(or 5	4)			Found	61.4	5.7	17.8	15.0	614
$[C_{14}H_{19}Fe(CO)_2]_2$	V	4	5	Red-brown	163–165	Calcd	64.0	6.7	18.6	10.7	598
						Found	63.3	6.5	18.8	11.7	591
$C_{14}H_{20}Fe(CO)_3$	III	4	6	Yellow-orange	Liquid	Calcd	62.2	6.1	14.6	17.0	
						Found	62.0	6.0	14.9	17.1	
$[C_{15}H_{21}Fe(CO)_2]_2$	V	4	6	Red-brown	125–127	Calcd	65.2	6.7	17.8	10.2	626
						Found	64.9	6.8	18.0	10.6	653

[a] See the text for these structures. [b] These molecular weights were determined osmometrically in benzene solution. [c] See ref 5a.

Table II. Some Derivatives of the Tricyclic Cyclopentadienyliron Carbonyls

Compound	Structure[a]	m	n	Color	Mp, °C		Analyses, %		
							C	H	Fe
				(A) Triphenyltin Derivatives					
$Ph_3SnFe(CO)_2C_{13}H_{17}$	XI	4	4	Pale yellow	124–125	Calcd	62.4	5.0	8.7
						Found	61.8	5.2	8.4
$Ph_3SnFe(CO)_2C_{14}H_{19}$	XI	4	5	Pale yellow	108–110	Calcd	62.9	5.3	8.6
						Found	62.7	5.4	8.6
$Ph_3SnFe(CO)_2C_{15}H_{21}$	XI	4	6	Pale yellow	119–120	Calcd	63.4	5.4	8.4
		(or 5	5)			Found	63.1	5.5	8.3
				(B) Pentafluorophenyl Derivatives					
$C_6F_5Fe(CO)_2C_{14}H_{19}$	X	4	5	Yellow	128–129	Calcd[b]	56.5	4.3	12.0
						Found[b]	56.8	4.1	11.8
$C_6F_5Fe(CO)_2C_{15}H_{21}$	X	4	6	Yellow	93–95	Calcd	57.5	4.4	
		(or 5	5)			Found	57.5	4.5	
				(C) Iodide					
$C_{14}H_{19}Fe(CO)_2I$	IX	5	5	Gray	88–90	Calcd	45.1	4.5	
						Found	46.0	4.8	

[a] See the text for these structures. [b] Calcd: F, 20.3. Found: F, 19.0.



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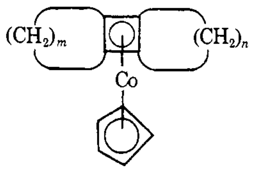

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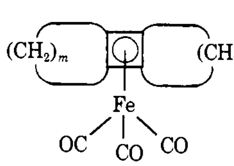

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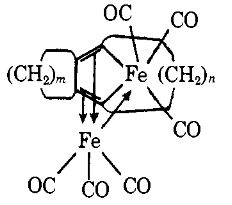

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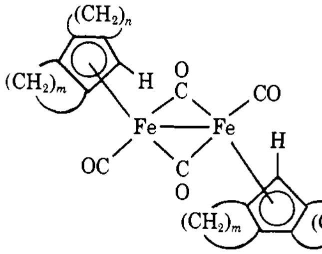
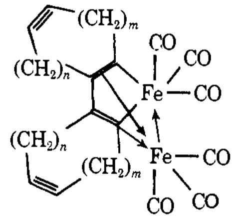


V



VI

two carbon–carbon triple bonds in the macrocyclic alkadiyne 1,7-cyclotridecadiyne (I, $m = 4$, $n = 5$).

Experimental Section

Microanalyses (Tables I and II) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Meade Microanalytical Laboratory, Amherst, Mass.; Atlantic Microlab Inc., Atlanta, Ga; Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; and Mr. W. Swanson and coworkers of the microanalytical laboratory at the University of Georgia. Melting points (Tables I and II) were taken in capillaries and are uncorrected. Infrared spectra in the 2000-cm^{-1} ν(CO) region (Table III) were taken in saturated hydrocarbon solvents (pentane, hexane, etc.) and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated with the 1601- or 1944-cm^{-1} band of a polystyrene film. Proton nmr spectra (Table III) were taken in $CDCl_3$, CS_2, or $(CD_3)_2CO$ solutions and recorded either at 60 MHz on a Perkin-Elmer Hitachi R-20 spectrometer or at 100 MHz on a Varian HA-100 spectrometer.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) admitting to evacuated vessels; and (c) handling filtered solutions of organometallic compounds. In addition, the analytical samples were recrystallized in an atmosphere of nitrogen with complete exclusion of air by using Schlenk tubes and related apparatus.

The $Fe(CO)_5$ was purchased from GAF Corp., New York, N. Y., and converted to $Fe_3(CO)_{12}$ by the "triethylamine method" as described in the literature.[6] The macrocyclic alkadiynes were purchased from Farchan Research Laboratories, Willoughby, Ohio.

Numerous reactions between the five macrocyclic alkadiynes (I, $m = 4$, $n = 4$, 5, and 6; $m = 5$, $n = 5$ and 6) and the iron carbonyls in various hydrocarbon solvents were carried out. Only those reactions which were significant in providing identifiable products in useful quantities and purities are described in detail in this paper.

Reaction of 1,7-Cyclododecadiyne (I, $m = n = 4$) with $Fe(CO)_5$. A mixture of 3.20 g (20 mmol) of 1,7-cyclododecadiyne, 8.0 ml (11.7 g, 60 mmol) of $Fe(CO)_5$, and 500 ml of toluene was boiled under reflux for 20 hr. Solvent was removed from the reaction

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(6) W. McFarlane and G. Wilkinson, *Inorg. Syn.*, **8**, 181 (1966).

Table III. Infrared and Proton Nmr Spectra of New Compounds Prepared in This Work

					Proton nmr spectrum, τ			
Compound	Structure[a]	*m*	*n*	Infrared spectrum[b] ν(CO) frequencies, cm⁻¹	Solvent	CH_2	C_5 ring	Other
				(A) Tricyclic Cyclobutadiene Derivative				
$C_{14}H_{20}Fe(CO)_3$	III	4	6	2029 (s), 1958 (vs)	Neat	7.8 (8), 8.42 (12)		
				(B) Ferrole–Iron Tricarbonyl Derivatives				
$C_{12}H_{16}Fe_2(CO)_6$	IV[d]	4	4	2063 (m), 2023 (vs), 1985 (s), 1979 (s), 1917 (w)	CS_2	~7.2 (4), ~7.5 (4), ~8.3 (8)		
$(C_{13}H_{18})_2Fe_2(CO)_6$	VI	4 (or 5	5 4)	2063 (m), 2027 (s), 1982 (vs), 1935 (m)	CS_2	~7.8 (20), ~8.4 (16)		
				(C) Tricyclic Cyclopentadienyl Derivatives				
$[C_{13}H_{17}Fe(CO)_2]_2$	V	4	4	1988 (m), 1940 (s), 1768 (s)	CS_2	7.68 (8), ~8.2 (8)	*c*	
$[C_{14}H_{19}Fe(CO)_2]_2$	V	4	5	1988 (m), 1940 (s), 1763 (s)	CS_2	~7.7 (8), ~8.2 (10)	*c*	
$[C_{15}H_{21}Fe(CO)_2]_2$	V	4	6[b]	1986 (m), 1938 (s), 1768 (s)	CS_2	7.74, 8.24, 8.68	*c*	
$Ph_3SnFe(CO)_2C_{13}H_{17}$	XI	4	4	1981 (s), 1936 (s)	$CDCl_3$	~7.5 (4), ~8.0 (6), ~8.2 (4), ~8.6 (2)	5.52 (1)	C_6H_5, ~2.4, ~2.7
$Ph_3SnFe(CO)_2C_{14}H_{19}$	XI	4	5	1985 (s), 1935 (s)	$CDCl_3$	~7.6 (4), ~8.1 (6), ~8.4 (8)	5.50 (1)	C_6H_5, ~2.4, ~2.7
$Ph_3SnFe(CO)_2C_{15}H_{21}$	XI	4	6[b]	1985 (s), 1939 (s)	$CDCl_3$	~7.4 (4), ~7.8 (2), ~8.2 (6), ~8.6 (6)	5.50 (1)	C_6H_5, ~2.4, ~2.7
$C_6F_5Fe(CO)_2C_{14}H_{19}$	X	4	5	2031 (s), 1980 (s)	CS_2	~7.8 (8), ~8.3 (10)	5.66 (1)	
$C_6F_5Fe(CO)_2C_{15}H_{21}$	X	4	6[b]	2033 (s), 1980 (s)				
$C_{14}H_{19}Fe(CO)_2I$	IX	4	5	2027 (vs), 1971 (vs)	C_6F_6	~7.4 (8), 8.1 (10)	5.94 (1)	

[a] See the text for these structures. [b] These $C_{15}H_{21}$ derivatives could also have structures where $m = n = 5$ but this is much less probable (see text). [c] These spectra were rather broad apparently because of the presence of paramagnetic impurities. Therefore the single proton on the cyclopentadienyl ring (*cf.* structure V in the text) could not be detected in the background noise. [d] See ref 5a.

mixture at 50° (35 mm). The residue was extracted with pentane. The pentane extract was concentrated to 25 ml and chromatographed on a 2 × 60 cm alumina column. The yellow-orange band was eluted with pentane. Evaporation of the pentane extracts followed by low-temperature recrystallization from pentane gave a total of 3.1 g (31% yield) of orange $C_{12}H_{16}Fe_2(CO)_6$ (IV, $m = 4, n = 4$).[5a]

Slow removal of solvent from the mother liquors from the crystallization of the $C_{12}H_{16}Fe_2(CO)_6$ gave a mixture of yellow crystals and orange crytals which were separated mechanically. The orange crystals were some more $C_{12}H_{16}Fe_2(CO)_6$ (IV, $m = 4, n = 4$).[5a] The yellow crystals were the tricyclic cyclobutadiene derivative $C_{12}H_{16}Fe(CO)_3$ (III, $m = 4$, $n = 4$), mp 79–80°. Insufficient pure $C_{12}H_{16}Fe(CO)_3$ was obtained for a satisfactory elemental analysis. However, this compound was identified by its mass spectrum (see below).

Reaction of 1,7-Cyclotridecadiyne (I, $m = 4$, $n = 5$) with $Fe_3(CO)_{12}$. A mixture of 1.74 g (10 mmol) of 1,7-cyclotridecadiyne, 5.05 g (10 mmol) of $Fe_3(CO)_{12}$, and 600 ml of heptane was boiled under reflux for 7 hr. After cooling to room temperature, the reaction mixture was filtered. Much brown insoluble pyrophoric residue was obtained. The filtrate was concentrated to 50 ml at 50° (35 mm) and then chromatographed on a 2 × 60 cm Florsil column. The column was first developed with hexane. An initial band containing very small amounts of $Fe_3(CO)_{12}$ and an orange oil was eluted with hexane. The major brown-purple band was then eluted with hexane containing ~20% benzene. Evaporation of the eluate gave 0.25 g (9% yield) of brown-purple $[C_{13}H_{17}Fe(CO)_2]_2$ (V, $m = 4$, $n = 4$), mp 123–125°.

The orange oil was distilled at 140° (0.1 mm) in a small evaporative distillation apparatus. The infrared spectrum of the distillate in hexane solution in the ν(CO) region exhibited bands at 2025 (s) and 1958 (s) cm⁻¹ corresponding to the tricyclic cyclobutadiene–iron tricarbonyl derivative $C_{13}H_{18}Fe(CO)_3$ (III, $m = 4$, $n = 5$) and bands at 2063 (m), 1990 (s), 1981 (s), and 1935 (w) corresponding to a tricarbonylferrole–iron tricarbonyl derivative probably $C_{13}H_{18}Fe_2(CO)_6$ (IV, $m = 4$, $n = 5$) or the $(C_{13}H_{18})_2Fe_2(CO)_6$ (VI) reported below. The mass spectrum of the distillate (see below) corresponded to that expected for the tricyclic cyclobutadiene–iron tricarbonyl derivative $C_{13}H_{18}Fe(CO)_3$ (III, $m = 4$, $n = 5$) which apparently was introduced into the mass spectrometer preferentially over the less volatile tricarbonylferrole–iron tricarbonyl derivative.

Attempts to scale-up this reaction without a corresponding increase in the volume of the solvent gave drastically reduced yields of $[C_{13}H_{17}Fe(CO)_2]_2$ (V, $m = 4$, $n = 4$). Thus a similar reaction between 8.70 g (50 mmol) of 1,7-cyclotridecadiyne and 25.12 g (50 mmol) of $Fe_3(CO)_{12}$ in only 1200 ml (rather than 3000 ml) of heptane gave only 0.4 g (2.8% yield) of $[C_{13}H_{17}Fe(CO)_2]_2$ (V, $m = 4$, $n = 4$).

Reaction of 1,7-Cyclotridecadiyne with $Fe(CO)_5$. A mixture of 5.75 g (33 mmol) of 1,7-cyclotridecadiyne, 4.0 ml (5.8 g, 30 mmol) of $Fe(CO)_5$, and 100 ml of toluene was boiled under reflux for 16 hr. The reaction mixture was cooled to room temperature and then filtered. No insoluble residue was obtained. The filtrate was concentrated to 25 ml at 50° (35 mm) and then chromatographed on a 2 × 60 cm alumina column prepared in hexane. Separation on the chromatogram was incomplete. The first two zones (yellow-brown and brown) contained some of the desired $(C_{13}H_{18})_2Fe_2(CO)_6$. These were eluted with pentane and the eluates evaporated to dryness. The products were purified further by rechromatography on a Florisil column to give a total of 1.31 g (14% yield) of yellow crystalline $(C_{13}H_{18})_2Fe_2(CO)_6$.

The third and fourth zones (brown and orange-brown) of the original chromatogram gave less well-defined products upon elution with pentane. Rechromatography of the product isolated from the third zone, however, gave 0.40 g (4.5% yield) of a brown solid, mp 90–93°, of stoichiometry $(C_{13}H_{18})_3Fe_2(CO)_6$ (Calcd: C, 67.3; H, 6.7. Found: C, 66.9; H, 6.8). The infrared spectrum of this product (pentane solution) in the ν(CO) region exhibited typical tricarbonylferrole–iron tricarbonyl frequencies at 2065 (w), 2030 (m), 1984 (s), and 1934 (m) cm⁻¹. The product from the fourth zone was a foamy solid which could not be crystallized.

Reaction of 1,8-Cyclotetradecadiyne with $Fe_3(CO)_{12}$ in Heptane. A mixture of 9.4 g (50 mmol) of 1,8-cyclotetradecadiyne, 25.15 g (50 mmol) of $Fe_3(CO)_{12}$, and 1200 ml of heptane was boiled under reflux for 10 hr with stirring. The reaction mixture was cooled to room temperature and then filtered. The brown residue was pyrophoric. Evaporation of the filtrate at 35° (35 mm) gave 7.75 g (52% yield) of brown-purple crystals of $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4$, $n = 5$). In this case chromatography was unnecessary to obtain a pure product.

Reaction of 1,8-Cyclotetradecadiyne with $Fe_3(CO)_{12}$ in Benzene. A mixture of 9.4 g (50 mmol) of 1,8-cyclotetradecadiyne, 25.15 g (50 mmol) of $Fe_3(CO)_{12}$, and 1200 ml of benzene was boiled under reflux for 5 hr. The reaction mixture was then filtered. Solvent was removed from the filtrate at 35° (35 mm). The residue was dissolved in a minimum of 1:1 hexane-benzene. This solution was chromatographed on a 2 × 60 cm alumina column. The first yellow band containing a trace of the tricyclic cyclobutadiene derivative $C_{14}H_{20}Fe(CO)_3$ (III, $m = n = 5$) was eluted with hexane. The major brown-purple band was eluted with benzene. Evaporation of this eluate gave 5.8 g (39% yield) of brown-purple $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4$, $n = 5$), mp 165–167°.

Evaporation of the eluate from the first yellow band gave a very small amount (~0.1 g) of an orange oil. This was distilled in an evaporative distillation apparatus at 155–160° (0.05 mm). The mass spectrum of the distillate (see below) indicated it to be the tricyclic cyclobutadiene derivative $C_{14}H_{20}Fe(CO)_3$ (III, $m = 5$, $n = 5$).

Reaction of 1,8-Cyclotetradecadiyne with $Fe(CO)_5$. A mixture of 9.55 g (50 mmol) of 1,8-cyclotetradecadiyne, 20.0 ml (29.2 g, 150 mmol) of $Fe(CO)_5$, and 400 ml of toluene was boiled under reflux with stirring for 24 hr. The reaction mixture was filtered to give a deep red filtrate and a large amount of black pyrophoric residue. Solvent was removed from the filtrate. A concentrated benzene solution of the residue was chromatographed on a 3 × 60 cm alumina column. The chromatogram was developed with benzene. After eluting a small yellow band with benzene, the main dark red band was eluted with benzene. Evaporation of this eluate at 25° (35 mm) gave dark red crystals which were recrystallized from mixtures of dichloromethane and hexane to give 3.5 g (23% yield) of dark red crystalline $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4$, $n = 5$). A yellow band followed the dark red band; the product from this yellow band has not yet been identified.

Reaction of 1,7-Cyclotetradecadiyne with $Fe(CO)_5$. A mixture of 1.88 g (10 mmol) of 1,7-cyclotetradecadiyne, 6.0 ml (8.8 g, 45 mmol) of $Fe(CO)_5$, and 500 ml of toluene was boiled under reflux for 20 hr with magnetic stirring. Solvent was removed from the filtered reaction mixture at 35° (35 mm). A solution of the resulting viscous brown liquid in 25 ml of pentane was chromatographed on a 2 × 60 cm alumina column. The clearly separated yellow band was eluted with pentane. Evaporation of the eluate gave 0.95 g (26% yield) of yellow liquid $C_{14}H_{20}Fe(CO)_3$ (III, $m = 4$, $n = 6$). Further purification was accomplished by distillation at 150° (0.01 mm) in an evaporative distillation apparatus.

Reaction of 1,8-Cyclopentadecadiyne with $Fe_3(CO)_{12}$. A mixture of 2.0 g (10 mmol) of 1,8-cyclopentadecadiyne, 5.0 g (10 mmol) of $Fe_3(CO)_{12}$, and 600 ml of heptane was refluxed vigorously for 3 hr. The filtered reaction mixture was concentrated to 50 ml at 35° (35 mm) and then chromatographed on a 2 × 60 cm Florisil column prepared in hexane. A yellow band followed by a large red-brown band appeared. Elution of the yellow band with hexane followed by evaporation of the eluate at 25° (35 mm) gave 0.07 g of a yellow liquid purified by evaporative distillation at 140° (0.2 mm). The mass spectrum of this distillate (see below) corresponded to that expected for the tricyclic cyclobutadiene derivative $C_{15}H_{22}Fe(CO)_3$ (III, $m = 5$, $n = 6$).

The red-brown band was eluted with hexane containing a small amount of benzene. Evaporation of this eluate at 25° (35 mm) gave 0.55 g (17% yield) of red-brown $[C_{15}H_{21}Fe(CO)_2]_2$ (V, $m = 4$, $n = 6$), mp 125–127°. The analytical sample was purified further by low-temperature crystallization from pentane in a nitrogen atmosphere.

Similarly performed reactions of 1,8-cyclopentadecadiyne with excess (~4.5 equiv) of $Fe(CO)_5$ in toluene solution (17 hr boiling) gave up to a 22% yield of $[C_{15}H_{21}Fe(CO)_2]_2$ (V, $m = 4$, $n = 6$).

Conversion of the $[(alkadiyne\text{-}H)Fe(CO)_2]_2$ Derivatives to the Pentafluorophenyl Derivatives $C_6F_5Fe(CO)_2(alkadiyne\text{-}H)$. A solution of 0.1–0.5 g of the $[(alkadiyne\text{-}H)Fe(CO)_2]_2$ derivative (V, $m = 4$, $n = 5$ or 6) in 150 ml of redistilled tetrahydrofuran was stirred with excess ~1% sodium amalgam for 4 hr to form a yellow-brown solution. This solution was stirred overnight with an excess (4 ml) of hexafluorobenzene at room temperature. Solvent was then removed from the reaction mixture at 35° (35 mm). The residue was extracted with 25 ml of hexane. This extract was chromatographed on a 2 × 30 cm Florisil column. The yellow band of the $C_6F_5Fe(CO)_2(alkadiyne\text{-}H)$ derivative was eluted with hexane. Evaporation of the eluate followed by low-temperature crystallization of the residue from pentane or hexane gave yellow crystals of the $C_6F_5Fe(CO)_2(alkadiyne\text{-}H)$ derivative (Table II) in about 20% yield.

Conversion of the $[(alkadiyne\text{-}H)Fe(CO)_2]_2$ Deriviatives to the Triphenyltin Derivatives $(C_6H_5)_3SnFe(CO)_2(alkadiyne\text{-}H)$. A solution of 0.5–1.0 mmol (0.3–0.6 g) of the $[(alkadiyne\text{-}H)Fe(CO_2]_2$ derivative (V, $m = 4$, $n = 4$, 5, and 6) in 150 ml of redistilled tetrahydrofuran was stirred for at least 3 hr with excess ~1% sodium amalgam to form a yellow-brown solution. This solution was treated with an equivalent quantity of triphenyltin chloride dissolved in 50 ml of tetrahydrofuran. After stirring overnight, the solvent was removed at ~25° (35 mm). The residue was extracted with 120 ml of pentane or hexane in three portions. Evaporation of this extract gave crystals which were purified further by low-temperature crystallization from pentane or hexane to give the yellow crystalline $(C_6H_5)_3SnFe(CO)_2(alkadiyne\text{-}H)$ derivative in ~25–50% yield.

Preparation of $C_{14}H_{19}Fe(CO)_2I$. A solution of 1.14 g (2 mmol) of $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4$, $n = 5$) in 100 ml of chloroform was treated with a solution of 0.75 g (3 mmol as I_2) of iodine in 100 ml of chloroform. The reaction mixture was then boiled under reflux until no bridging $\nu(CO)$ frequency around 1760 cm^{-1} was observed in the infrared spectrum (~1 hr). The resulting reaction mixture was shaken with excess aqueous sodium thiosulfate solution to remove the excess iodine. The chloroform layer was then separated, dried over anhydrous sodium sulfate, and evaporated at 25° (35 mm) to give 1.23 g (72% yield) of dark gray $C_{14}H_{19}Fe(CO)_2I$, mp 85–90°. The analytical sample, mp 88–90°, was purified further by crystallization from a mixture of hexane and benzene.

Mass Spectra. The mass spectra listed below were obtained at 70 eV on a Perkin-Elmer Hitachi Model RMU-6 mass spectrometer with a 200–210° chamber temperature (unless otherwise indicated). Relative abundances are given in parentheses. For brevity and clarity only metal-containing ions of the highest intensities (generally 5–20% that of the most abundant metal-containing ion) are given here. In all cases about 25–50 additional weaker, less significant ions were also observed.

The samples of $C_{13}H_{18}Fe(CO)_3$ (III, $m = 4$, $n = 5$), $C_{14}H_{20}Fe(CO)_3$ (III, $m = 5$, $n = 5$), and $C_{15}H_{22}Fe(CO)_3$ (III, $m = 5$, $n = 6$) for which the mass spectra are reported below were the vacuum-distilled oils obtained in trace quantities and impure condition from the experiments described above. For these compounds only the ions with m/e values above those of the free alkadiyne are given because of the possibility of the lower ions arising from metal-free impurities.

(A) $C_{12}H_{16}Fe(CO)_3$ (III, $m = 4$, $n = 4$) (sample temperature 98°). $C_{12}H_{16}Fe(CO)_3^+$ (34), $C_{12}H_{16}Fe(CO)_2^+$ (38), $C_{12}H_{16}FeCO^+$ (35), $C_{12}H_{14}FeCO^+$ (47), $C_{12}H_{16}Fe^+$ (74), $C_{12}H_{14}Fe^+$ (73), $C_{12}H_{12}Fe^+$ (41), $C_{12}H_{10}Fe^+$ (100), $C_{12}H_8Fe^+$ (24), $C_6H_5Fe^+$ (63), and Fe^+ (80).

(B) $C_{13}H_{18}Fe(CO)_3$ (III, $m = 4$, $n = 5$) (sample temperature 100°). $C_{13}H_{18}Fe(CO)_3^+$ (33), $C_{13}H_{18}Fe(CO)_2^+$ (33), $C_{13}H_{18}FeCO^+$ (60), $C_{13}H_{16}FeCO^+$ (53), $C_{13}H_{18}Fe^+$ (42), $C_{13}H_{16}Fe^+$ (100), $C_{13}H_{14}Fe^+$ (55), $C_{13}H_{12}Fe^+$ (22), and $C_{13}H_{10}Fe^+$ (15)

(C) $C_{14}H_{20}Fe(CO)_3$ (III, $m = 5$, $n = 5$) (sample temperature 140°). $C_{14}H_{20}Fe(CO)_3^+$ (32), $C_{14}H_{20}Fe(CO)_2^+$ (27), $C_{14}H_{20}FeCO^+$ (73), $C_{14}H_{18}FeCO^+$ (53), $C_{14}H_{20}Fe^+$ (49), $C_{14}H_{18}Fe^+$ (100), $C_{14}H_{16}Fe^+$ (65), and $C_{14}H_{14}Fe^+$ (19).

(D) $C_{14}H_{20}Fe(CO)_3$ (III, $m = 4$, $n = 6$) (sample temperature 150°). $C_{14}H_{20}Fe(CO)_3^+$ (32), $C_{14}H_{20}Fe(CO)_2^+$ (34), $C_{14}H_{20}FeCO^+$ (63), $C_{14}H_{20}Fe^+$ (100), $C_{14}H_{18}Fe^+$ (85), $C_{14}H_{16}Fe^+$ (54), $C_{10}H_{12}Fe^+$ (32), $C_{10}H_{10}Fe^+$ (29), $C_{10}H_8Fe^+$ (28), $C_6H_7Fe^+$ (41), $C_6H_6Fe^+$ (37), and Fe^+ (62).

(E) $C_{15}H_{22}Fe(CO)_3$ (III, $m = 5$, $n = 6$) (sample temperature 145°). $C_{15}H_{22}Fe(CO)_3^+$ (29), $C_{15}H_{22}Fe(CO)_2^+$ (26), $C_{15}H_{22}FeCO^+$ (79), $C_{15}H_{22}Fe^+$ (85), $C_{15}H_{20}Fe^+$ (100), and $C_{15}H_{18}Fe^+$ (59).

(F) $C_{12}H_{16}Fe_2(CO)_6$ (IV, $m = 4$, $n = 4$) (chamber temperature 100°, sample temperature 110°). $C_{12}H_{16}Fe_2(CO)_6^+$ (7), $C_{12}H_{16}Fe_2(CO)_5^+$ (5), $C_{12}H_{16}Fe_2(CO)_4^+$ (9), $C_{12}H_{16}Fe_2(CO)_3^+$ (8), $C_{12}H_{16}Fe_2(CO)_2^+$ (12), $C_{12}H_{16}Fe_2CO^+$ (56), $C_{12}H_{16}Fe_2^+$ (27), $C_{12}H_{16}FeCO^+$ (56), $C_{12}H_{14}FeCO^+$ (52), $C_{12}H_{16}Fe^+$ (65), $C_{12}H_{14}Fe^+$ (77), $C_{12}H_{12}Fe^+$ (44), $C_{12}H_{10}Fe^+$ (100), $C_{10}H_{12}Fe^+$ (10), $C_{10}H_8Fe^+$ (19), $C_9H_6Fe^+$ (4), $C_8H_8Fe^+$ (11), $C_6H_6Fe^+$ (50), $C_{12}H_{16}FeCO^{2+}$ (7), $C_{12}H_{16}Fe^{2+}$ (6), $FeCO^+$ (6), and Fe^+ (62).

(G) $(C_{13}H_{18})_2Fe_2(CO)_6$ (VI, $m = 4$, $n = 5$ or $m = 5$ $n = 4$) (sample temperature ~200°). $(C_{13}H_{18})_2Fe_2(CO)_6^+$ (10), $(C_{13}H_{18})_2Fe_2(CO)_5^+$ (1), $(C_{13}H_{18})_2Fe_2(CO)_4^+$ (6), $(C_{13}H_{18})_2Fe_2(CO)_3^+$ (90), $(C_{13}H_{18})_2Fe_2(CO)_2^+$ (29), $(C_{13}H_{18})_2Fe_2CO^+$ (15), $C_{26}H_{36}Fe_2^+$ (91), $C_{26}H_{34}Fe_2^+$ (67), $C_{26}H_{32}Fe_2^+$ (54), $C_{26}H_{30}Fe_2^+$ (41), $C_{26}H_{28}Fe_2^+$ (21), $C_{26}H_{36}Fe^+$ (100), $C_{26}H_{34}Fe^+$ (55), $C_{25}H_{32}Fe^+$ (36), $C_{26}H_{30}Fe^+$ (16), and $C_{26}H_{36}^+$ (107).

(H) $C_{14}H_{19}Fe(CO)_2C_6F_5$ (X, $m = 4$, $n = 5$). $C_{14}H_{19}Fe(CO)_2C_6F_5^+$ (7), $C_{14}H_{19}FeCOC_6F_5^+$ (8), $C_{14}H_{19}FeC_6F_5^+$ (33), $C_{14}H_{18}Fe^+$ (36), $C_{14}H_{16}Fe^+$ (100), $C_{14}H_{14}Fe^+$ (52), $C_{14}H_{12}Fe^+$ (48), $C_{14}H_{10}Fe^+$ (29), $C_{14}H_{19}FeCOC_6F_5^{2+}$ (2), and $C_{14}H_{19}FeC_6F_5^{2+}$ (4).

Discussion

A. General Comments. The reactions of the macrocyclic alkadiynes I ($m = 4$, $n = 4$, 5, and 6; $m = 5$, $n = 5$ and 6) with the iron carbonyls gave a much more complex mixture of products than the reactions of the macrocyclic alkadiynes I with $C_5H_5Co(CO)_2$ discussed in the first paper of this series.[1b] In most cases chromatography was necessary to separate pure products from the mixtures obtained from the reactions of the macrocyclic alkadiynes I with the iron carbonyls. Furthermore, in addition to the compounds described in this paper other products were obtained which could not be identified mainly because they could not be obtained in sufficient quantities and purities for complete characterization. However, the colors and spectroscopic properties of the intramolecular transannular cyclization products of the types III, IV, and V are sufficiently characteristic that it is unlikely that additional quantities of compounds of these types are present in the uncharacterized materials.

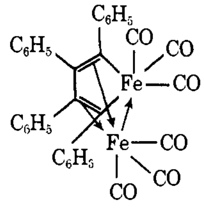
B. Tricyclic Cyclobutadiene–Iron Tricarbonyl Derivatives of the Stoichiometry (alkadiyne)Fe(CO)$_3$ (III). The major product from the reaction between 1,7-cyclotetradecadiyne (I; $m = 4$, $n = 6$) and Fe(CO)$_5$ was a yellow-orange liquid of stoichiometry $C_{14}H_{20}$-Fe(CO)$_3$ which could be purified by distillation at 150° (0.1 mm). Formulation of this $C_{14}H_{20}Fe(CO)_3$ as the tricyclic cyclobutadiene–iron tricarbonyl derivative III ($m = 4$, $n = 6$) analogous to compounds of the type II obtained from the macrocyclic alkadiynes and $C_5H_5Co(CO)_2$ or $C_5H_5Co(1,5\text{-}C_8H_{12})$ is supported by the following spectroscopic evidence: (1) the presence of only saturated CH_2 resonances in the proton nmr spectrum of neat $C_{14}H_{20}Fe(CO)_3$ at τ 7.8 and 8.4 in a 2:3 integrated area ratio, and (2) the presence of ν(CO) frequencies (pentane solution) at 2029 (s) and 1958 (vs) cm^{-1} close to the reported[7] ν(CO) frequencies at 2055 and 1985 cm^{-1} for the unsubstituted cyclobutadiene–iron tricarbonyl C_4H_4Fe-(CO)$_3$.

The other macrocyclic alkadiynes of type I gave only trace quantities of the tricyclic cyclobutadiene–iron tricarbonyl derivatives of stoichiometry (alkadiyne)-Fe(CO)$_3$ and structure III upon reactions with iron carbonyls. In the case of 1,7-cyclododecadiyne a very low yield of yellow crystals was obtained which exhibited the expected mass spectrum for a $C_{12}H_{16}Fe$-(CO)$_3$ derivative and thus is formulated as the tricyclic cyclobutadiene–iron tricarbonyl III ($m = 4$, $n = 4$). In the cases of 1,7-cyclotridecadiyne (I; $m = 4$, $n = 5$), 1,8-cyclotetradecadiyne (I; $m = 5$, $n = 5$), and 1,8-cyclopentadecadiyne (I; $m = 5$, $n = 6$) trace quantities of yellow liquids were obtained during the original chromatographic separation. Mass spectra of these liquids indicated a major component to be the corresponding (alkadiyne)Fe(CO)$_3$ derivatives presumably the tricyclic cyclobutadiene–iron tricarbonyls III. The infrared spectra of these liquids exhibited the characteristic ν(CO) frequencies of a cyclobutadiene–iron tricarbonyl derivative around 2030 and 1960 cm^{-1}, but these spectra also indicated significant contamination of these liquids with the corresponding tricarbonylferrole–iron tricarbonyl derivative (IV). Unfortunately the yields of the (alkadiyne)Fe(CO)$_3$ derivatives from the reactions of the macrocyclic alkadiynes 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne were too low for complete purification and characterization of these compounds.

These observations demonstrate that the macrocyclic alkadiynes I can undergo transannular cyclization to form tricyclic cyclobutadiene derivatives with iron carbonyls as well as with cyclopentadienylcobalt derivatives. However, the intramolecular transannular cyclizations of the macrocyclic alkadiynes I to form tricyclic cyclobutadiene derivatives proceed efficiently with the cyclopentadienylcobalt derivatives, but, in all cases except 1,7-cyclotetradecadiyne (I; $m = 4$, $n = 6$), very inefficiently with the iron carbonyls.

The mass spectra of the tricyclic cyclobutadiene–iron tricarbonyl derivatives of structure III were investigated. A rather large number (40–80) of ions were observed owing to the occurrence of numerous dehydrogenation processes arising from the relative lability of hydrogens attached to sp^3 carbon atoms particularly when the sp^3 carbon atom is attached to another carbon atom bonded to a transition metal.[8] In all cases the complete series of ions (alkadiyne)-Fe(CO)$_n^+$ ($n = 3$, 2, 1, and 0) was observed followed by dehydrogenation of the hydrocarbon ligand. In some cases dehydrogenation was even competitive with loss of the last carbonyl group. Fragmentation of the hydrocarbon ligand while still bonded to the iron atom occurred to a large extent with ions containing ten and six carbon atoms (*e.g.*, $C_{10}H_8Fe^+$ and $C_6H_6Fe^+$) being particularly favored.

C. Substituted Tricarbonylferrole–Iron Tricarbonyl Derivatives of the Stoichiometry (alkadiyne)Fe$_2$(CO)$_6$ (IV). The major product from the reaction between 1,7-cyclododecadiyne (I; $m = 4$, $n = 4$) and Fe(CO)$_5$ was an orange crystalline solid of stoichiometry $C_{12}H_{16}$-$Fe_2(CO)_6$. Formulation of this compound as the tricarbonylferrole–iron tricarbonyl derivative IV ($m = 4$, $n = 4$) is supported by the following spectroscopic evidence:[5a] (1) the presence of only saturated CH_2 resonances in its proton nmr spectrum and (2) the absence of bridging ν(CO) frequencies in its infrared spectrum but the presence of terminal ν(CO) frequencies at 2063 (m), 2023 (vs), 1985 (s), 1979 (s), and 1917 (w) cm^{-1} close to the reported[9] ν(CO) frequencies at 2074, 2026, 1991, 1977, and 1929 cm^{-1} for the compound $(C_6H_5C_2C_6H_5)_2Fe_2(CO)_6$ from diphenylacetylene and $Fe_3(CO)_{12}$ known to be the tricarbonylferrole–iron tricarbonyl derivative VII.



VII

The mass spectrum of the tricarbonylferrole–iron tricarbonyl $C_{12}H_{16}Fe_2(CO)_6$ (IV; $m = 4$, $n = 4$)[5a] was obtained. This spectrum exhibited the bimetallic ions $C_{12}H_{16}Fe_2(CO)_n^+$ ($n = 6$, 5, 4, 3, 2, 1, 0) and the monometallic ions $C_{12}H_{16}Fe(CO)_n^+$ ($n = 1$ and 0) as well as the ions $C_{12}H_xFe^+$ ($x = 14$, 12, and 10) formed by dehydrogenation processes.

No similar tricarbonylferrole–iron tricarbonyl derivatives of the stoichiometry (alkadiyne)Fe$_2$(CO)$_6$ were isolated in the pure state from the reactions of the other macrocyclic alkadiynes of type I with the iron

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(7) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

(8) R. B. King, *Appl. Spectrosc.*, **23**, 536 (1969).

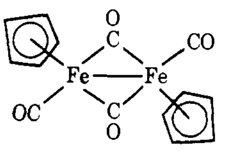
(9) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

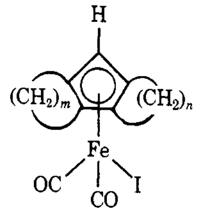
carbonyls. However, the infrared spectra of some of the crude samples of the tricyclic cyclobutadiene–iron tricarbonyl derivatives (alkadiyne)$Fe(CO)_3$ (III) suggested the presence of the corresponding tricarbonylferrole–iron tricarbonyl derivative IV[5a] as an impurity. For the identification of tricarbonylferrole–iron tricarbonyl derivatives (IV) as impurities in the crude tricyclic cyclobutadiene–iron tricarbonyl derivatives (III), the single ν(CO) frequency around 2070 cm^{-1} and the closely spaced pair of ν(CO) frequencies around 1980 cm^{-1} are particularly useful since the ν(CO) frequency of the tricarbonylferrole–iron tricarbonyl derivative around 2030 cm^{-1} can be obscured by the higher ν(CO) frequency of the tricyclic cyclobutadiene–iron tricarbonyl derivative and the ν(CO) frequency of the tricarbonylferrole–iron tricarbonyl derivative around 1920 cm^{-1} is very weak.

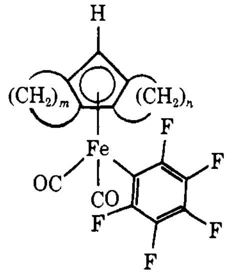
D. Tricyclic π-Cyclopentadienyliron Carbonyl Derivatives of the Stoichiometry [(alkadiyne-H)$Fe(CO)_2$]$_2$ (V). The reaction between the macrocyclic alkadiynes with at least one pentamethylene bridge between the carbon–carbon triple bonds (I; $m = 4, n = 5$; $m = 5, n = 5$ or 6) and the iron carbonyls gave dark red products of the stoichiometries [(alkadiyne-H)$Fe(CO)_2$]$_2$. The infrared spectra of these compounds exhibited strong terminal ν(CO) frequencies at 1987 ± 1 and 1939 ± 1 cm^{-1} and a strong bridging ν(CO) frequency at 1765 ± 3 cm^{-1}. These infrared ν(CO) frequencies are close to those found for the π-cyclopentadienyliron carbonyl derivative $[C_5H_5Fe(CO)_2]_2$ (VIII) (reported[10] ν(CO) for VIII: 2007, 1962, and 1764 cm^{-1}) but with the decrease expected upon multiple substitution of hydrogen atoms with saturated alkyl groups.[10] Accordingly the compounds [(alkadiyne-H)$Fe(CO)_2$]$_2$ are formulated as the substituted cyclopentadienyliron dicarbonyl dimers V containing a tricyclic cyclopentadienyl ligand.

In an attempt to provide further evidence for structures of the type V for the [(alkadiyne-H)$Fe(CO)_2$]$_2$ derivatives, their nmr spectra were investigated. In each compound several resonances in the τ 7.5–9.0 region associated with saturated CH_2 groups were observed. However, the presence of paramagnetic impurities in the solutions investigated (mainly CS_2) broadened the spectrum to the extent that the signal-to-noise ratio was insufficient for detection of the single proton bonded to each π-cyclopentadienyl ring. Attempts were also made to obtain mass spectra of the [(alkadiyne-H)$Fe(CO)_2$]$_2$ derivatives, but satisfactory mass spectra could not be obtained apparently because of insufficient volatility at temperatures where these compounds are stable.

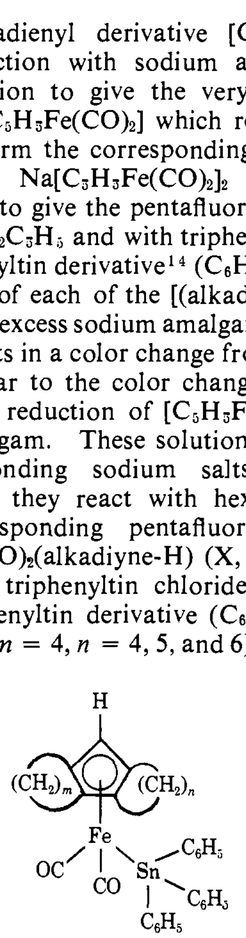
In order to obtain additional evidence for structures of the type V for the [(alkadiyne-H)$Fe(CO)_2$]$_2$ derivatives, some reactions characteristic of the iron–iron bond were investigated. Thus, the reaction of $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4$, $n = 5$) with iodine in boiling chloroform gave the corresponding iodide $C_{14}H_{19}Fe(CO)_2I$ (IX, $m = 4$, $n = 5$) completely analogous to the reported[11] formation of $C_5H_5Fe(CO)_2I$ from $[C_5H_5Fe(CO)_2]_2$ (VIII) and iodine.

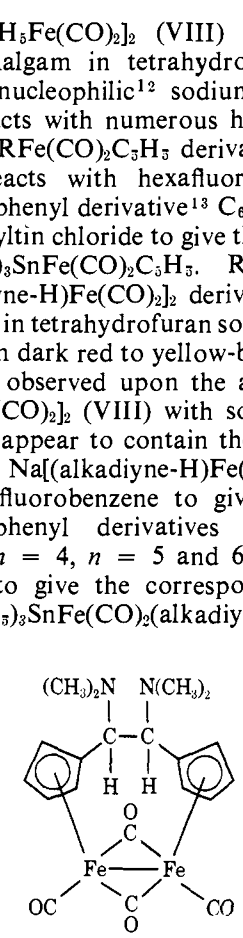

VIII


IX


X

A characteristic reaction of the unsubstituted cyclopentadienyl derivative $[C_5H_5Fe(CO)_2]_2$ (VIII) is its reduction with sodium amalgam in tetrahydrofuran solution to give the very nucleophilic[12] sodium salt $Na[C_5H_5Fe(CO)_2]$ which reacts with numerous halides to form the corresponding $RFe(CO)_2C_5H_5$ derivatives. Thus $Na[C_5H_5Fe(CO)_2]_2$ reacts with hexafluorobenzene to give the pentafluorophenyl derivative[13] $C_6F_5Fe(CO)_2C_5H_5$ and with triphenyltin chloride to give the triphenyltin derivative[14] $(C_6H_5)_3SnFe(CO)_2C_5H_5$. Reduction of each of the [(alkadiyne-H)$Fe(CO)_2$]$_2$ derivatives with excess sodium amalgam in tetrahydrofuran solution results in a color change from dark red to yellow-brown similar to the color change observed upon the analogous reduction of $[C_5H_5Fe(CO)_2]_2$ (VIII) with sodium amalgam. These solutions appear to contain the corresponding sodium salts Na[(alkadiyne-H)$Fe(CO)_2$] since they react with hexafluorobenzene to give the corresponding pentafluorophenyl derivatives $C_6F_5Fe(CO)_2$(alkadiyne-H) (X, $m = 4$, $n = 5$ and 6) and with triphenyltin chloride to give the corresponding triphenyltin derivative $(C_6H_5)_3SnFe(CO)_2$(alkadiyne-H) (XI, $m = 4$, $n = 4$, 5, and 6).


XI


XII

The following properties of the pentafluorophenyl derivatives $C_6F_5Fe(CO)_2$(alkadiyne-H) (X) provide additional evidence for the formulation of the [(alkadiyne-H)$Fe(CO)_2$]$_2$ derivatives from which they are derived as the tricyclic cyclopentadienyl derivatives of type V. (1) The proton nmr spectrum of $C_6F_5Fe(CO)_2C_{14}H_{19}$ (X, $m = 4$, $n = 5$) exhibits not only the usual saturated methylene resonances (in this case at τ 7.8 and 8.3) but also a sharp singlet resonance at

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[10] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

[11] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

[12] R. B. King, *Accounts Chem. Res.*, **3**, 417 (1970).

[13] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964).

[14] R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962).

τ 5.66 of the expected relative intensity to correspond to the single proton remaining on the cyclopentadienyl ring. The ability to observe this resonance in the proton nmr spectrum of $C_6F_5Fe(CO)_2C_{14}H_{19}$ (X, $m = 4, n = 5$) but not in the spectrum of $[C_{14}H_{19}Fe(CO)_2]_2$ (V, $m = 4, n = 5$) appears to arise from the inability to get solutions of the latter compound free of paramagnetic impurities which cause significant broadening of the spectrum. (2) The mass spectrum of $C_6F_5Fe(CO)_2C_{14}H_{19}$ (X, $m = 4, n = 5$) indicates it to be monomeric. This demonstrates that the two tricyclic cyclopentadienyl rings bonded to the different iron atoms in the [(alkadiyne-H)Fe(CO)$_2$]$_2$ dimers (V) are not also joined by carbon–carbon bonds as is the case with the cyclopentadienyliron dicarbonyl dimer derivatives $[C_5H_4CHN(CH_3)_2Fe(CO)_2]_2$ (XII) obtained[15] from dimethylaminofulvene and $Fe(CO)_5$.

The proton nmr spectrum of each of the three triphenyltin derivatives $(C_6H_5)_3SnFe(CO)_2$(alkadiyne-H) (XI, $m = 4$; $n = 4$, 5, and 6) exhibits a sharp singlet resonance at τ 5.51 ± 1 corresponding to the single proton remaining on the cyclopentadienyl ring. However, these triphenyltin derivatives are insufficiently volatile below their decomposition temperatures to obtain satisfactory mass spectra.

An apparent requirement for a macrocyclic alkadiyne of type I to form a derivative of the type [(alkadiyne-H)Fe(CO)$_2$]$_2$ (V) upon reaction with iron carbonyls is the presence of exactly five methylene groups in at least one of the polymethylene chains bridging the two carbon–carbon triple bonds (*i.e.*, in structure I either m or n or both must be exactly five). Thus no evidence was observed for the formation of the corresponding [(alkadiyne-H)Fe(CO)$_2$]$_2$ derivatives (V) from the reactions of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with the macrocyclic alkadiynes 1,7-cyclododecadiyne (I, $m = 4, n = 4$) and 1,7-cyclotetradecadiyne (I, $m = 4$, $n = 6$), neither of which contain a bridge of exactly five methylene groups between the two carbon–carbon triple bonds. Furthermore, the yield of the [(alkadiyne-H)Fe(CO)$_2$]$_2$ derivative (V) obtained from the reaction of the iron carbonyls with 1,8-cyclotetradecadiyne (I, $m = 5, n = 5$) which has two bridges of five methylene groups is much higher than the yields of the [(alkadiyne-H)Fe(CO)$_2$]$_2$ derivatives (V) obtained from the reactions of the iron carbonyls with 1,7-cyclotridecadiyne or 1,8-cyclopentadecadiyne which have only one bridge with exactly five methylene groups.

The formation of an [(alkadiyne-H)Fe(CO)$_2$]$_2$ derivative V from the corresponding macrocyclic alkadiyne I and iron carbonyls necessarily involves loss of one hydrogen atom from a methylene group adjacent to a carbon–carbon triple bond followed by a 1,2 shift of the remaining hydrogen atom. The apparent requirement of a bridge of exactly five methylene groups for this process to take place suggests that this pentamethylene bridge is always involved in this hydrogen loss and 1,2 shift. Such involvement of a pentamethylene bridge in a process of this type leads to the formation of a new six-membered ring. The requirement of a pentamethylene bridge for the formation of an [(alkadiyne-H)Fe(CO)$_2$]$_2$ (V) derivative from a macrocyclic alkadiyne (I) and iron carbonyls thus relates to the ease of formation and minimum strain in a six-membered ring fused to the cyclopentadienyl system relative to either a five-membered ring (where the angular strain would be too high) or to seven-membered and larger rings which would form with more difficulty. The involvement of the pentamethylene bridge of the macrocyclic alkadiyne I in the hydrogen loss and 1,2-shift sequence necessary for formation of the corresponding [(alkadiyne-H)Fe(CO)$_2$]$_2$ derivative means that the $[C_{13}H_{17}Fe(CO)_2]_2$ formed from 1,7-cyclotridecadiyne (I; $m = 4, n = 5$) and iron carbonyls must have the "6,5,6" tricyclic structure (V, $m = 4, n = 4$) rather than the "5,5,7" tricyclic structure (V, $m = 3, n = 5$) and that the $[C_{15}H_{21}Fe(CO)_2]_2$ formed from 1,8-cyclopentadecadiyne (I, $m = 5, n = 6$) and iron carbonyls must have the "6,5,8" tricyclic structure (V, $m = 4, n = 6$) rather than the "7,5,7" tricyclic structure (V, $m = 5, n = 5$). However, none of the available chemical and spectroscopic data enables the differentiation between possible structures V ($m = 4, n = 4$) and V ($m = 3, n = 5$) for $[C_{13}H_{17}Fe(CO)_2]_2$ and between possible structures V ($m = 4, n = 6$) and V ($m = 5, n = 5$) for $[C_{15}H_{21}Fe(CO)_2]_2$. X-Ray diffraction crystal structure data will probably be necessary before this point can be unambiguously settled.

E. Intermolecular Cyclization Products from the Macrocyclic Alkadiynes I and Iron Carbonyls. The formation of the tricyclic cyclobutadiene derivatives of stoichiometry (alkadiyne)Fe(CO)$_3$ and structure III, the tricarbonylferrole–iron tricarbonyl derivatives of stoichiometry (alkadiyne)Fe$_2$(CO)$_6$ and structure IV,[5a] and the tricyclic cyclopentadienyl–iron carbonyl derivatives of stoichiometry [(alkadiyne-H)Fe(CO)$_2$]$_2$ and structure V from the macrocyclic alkadiynes I and various iron carbonyls as well as the formation of the tricyclic cyclobutadiene derivatives of stoichiometry C_5H_5Co(alkadiyne) and structure II from the macrocyclic alkadiynes I and $C_5H_5Co(CO)_2$ occurs by an intramolecular transannular cyclization process involving interaction between the two carbon–carbon triple bonds of a single macrocyclic ring. The reaction between 1,7-cyclotridecadiyne (I, $m = 4, n = 5$) and $Fe(CO)_5$ provided the first evidence for *intermolecular* rather than intramolecular cyclization of a macrocyclic alkadiyne of type I with a metal carbonyl derivative. Such an intermolecular cyclization of a macrocyclic alkadiyne I involves interaction between the two carbon–carbon triple bonds of two different macrocyclic rings.

The best characterized example of such an intermolecular cyclization product formed from a macrocyclic alkadiyne I and iron carbonyls is the yellow solid of stoichiometry $(C_{13}H_{18})_2Fe_2(CO)_6$ isolated from the reaction between 1,7-cyclotridecadiyne (I, $m = 4$, $n = 5$) and $Fe(CO)_5$. The infrared spectrum of this compound in the ν(CO) region exhibits bands of similar frequencies and approximate relative intensities to the ν(CO) bands of other tricarbonylferrole–iron tricarbonyl derivatives including the compound $C_{12}H_{16}Fe_2(CO)_6$ (IV, $m = 4, n = 4$)[5a] characterized in this paper. The main difference between the ν(CO) frequencies of $(C_{13}H_{18})_2Fe_2(CO)_6$ and those of $C_{12}H_{16}Fe_2(CO)_6$ (IV, $m = 4, n = 4$) is the splitting by ~6 cm^{-1} of the band around 1980 cm^{-1} in $C_{12}H_{16}Fe_2(CO)_6$ but not in $(C_{13}H_{18})_2Fe_2(CO)_6$. These infrared spectroscopic data thus indicate formulation of $(C_{13}H_{18})_2Fe_2(CO)_6$ as some type of tricar-

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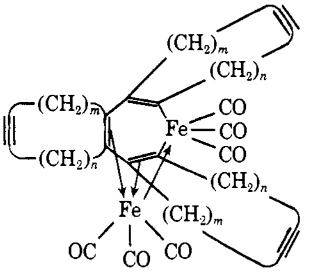
[15] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 801 (1964).

bonylferrole–iron tricarbonyl derivative. The proton nmr spectrum of $(C_{13}H_{18})_2Fe_2(CO)_6$ exhibits only saturated methylene resonances. This indicates that the saturated methylene groups of the macrocyclic alkadiyne I (m = 4, n = 5) are retained in the structure of $(C_{13}H_{18})_2Fe_2(CO)_6$. The combined requirements of a tricarbonylferrole–iron tricarbonyl unit and retention of the saturated methylene groups in $(C_{13}H_{18})_2Fe_2(CO)_6$ indicate a structure of type VI for this complex. In a structure of this type (VI) the ferrole ring is formed by interaction of an iron atom with two carbon–carbon triple bonds from two different macrocyclic rings and the 13-membered macrocyclic ring of the 1,7-cyclotridecadiyne (I, m = 4, n = 5) is retained. The yield of $(C_{13}H_{18})_2Fe_2(CO)_6$ is best if the 1,7-cyclotridecadiyne is used in slight excess relative to the $Fe(CO)_5$ in accord with the need to maintain sufficient concentrations of the macrocyclic alkadiyne to facilitate the intermolecular cyclization process.

Attempts to obtain direct evidence for the retention of uncomplexed carbon–carbon triple bonds in $(C_{13}H_{18})_2Fe_2(CO)_6$ (VI) from its laser Raman spectrum were unsuccessful because of decomposition of the compound in the laser beam.

Other less well characterized products from reactions of the macrocyclic alkadiynes I, particularly 1,7-cyclotridecadiyne (I, m = 4, n = 5), may also involve intermolecular cyclizations with carbon–carbon triple bonds of different macrocyclic rings. Thus a product of stoichiometry $(C_{13}H_{18})_3Fe_2(CO)_6$ was obtained from a reaction of 1,7-cyclotridecadiyne with $Fe(CO)_5$. This compound exhibited infrared ν(CO) frequencies of roughly similar positions and relative intensities to those observed in tricarbonylferrole–iron tricarbonyl derivatives such as $C_{12}H_{16}Fe_2(CO)_6$ (IV, m = 4, n = 4)[5a] and $(C_{13}H_{18})_2Fe_2(CO)_6$ formulated as VI (m = 4, n = 5 or *vice versa*). One possible structure of $(C_{13}H_{18})_3Fe_2(CO)_6$ is XIII (m and n = 4 and 5) in which one iron atom and three carbon–carbon triple bonds in different macrocyclic rings combine to form a ferrepin (ferracycloheptatriene) derivative.

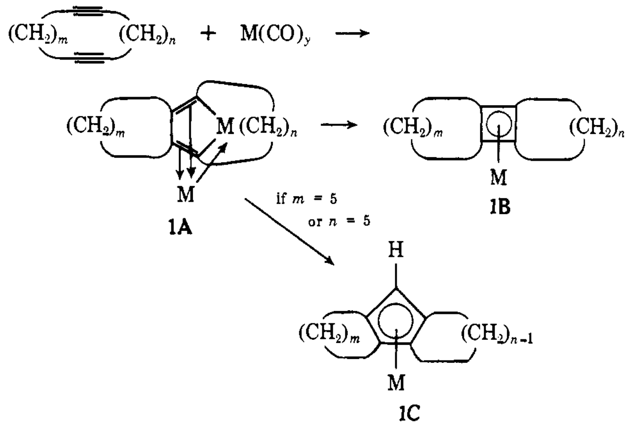


XIII

Intermolecular cyclization of a macrocyclic alkadiyne of type I means that each of the two carbon–carbon triple bonds can bond to a different metal atom. If each metal atom can combine with two carbon–carbon triple bonds as would be the case if cyclization to a cyclobutadiene, metallacyclopentadiene (*e.g.*, ferrole), or cyclopentadienyl derivative takes place, then the combination of two difunctional moieties (*i.e.*, the macrocyclic alkadiynes and the metal atoms) leads to the possibility of polymer formation. The poorly defined foamy noncrystalline products from later fractions obtained from the chromatography of mixtures obtained from macrocyclic alkadiynes I and iron carbonyls may be examples of relatively low molecular weight (and hence still soluble) polymers arising from the combination of a difunctional metal atom with a difunctional macrocyclic alkadiyne. The brown-black insoluble residues obtained from many of the reactions of the macrocyclic alkadiynes I with iron carbonyls may contain higher molecular weight polymers of the same type.

F. Conclusions. The intramolecular transannular cyclizations of the macrocyclic alkadiynes I with iron carbonyls and cyclopentadienylcobalt derivatives discussed in this paper and a preceding paper[1b] follow the scheme depicted in Scheme I. In this scheme the first detectable intermediate is the bimetallic metallacyclopentadiene (metallole) derivative **1A**. An example of a characterized compound of this type is the tricarbonylferrole–iron tricarbonyl derivative $C_{12}H_{16}Fe_2(CO)_6$ (IV, m = 4, n = 4) discussed in this paper.[5a] The metallacyclopentadiene derivative **1A** (Scheme I) can undergo loss of one of the two metal atoms with concurrent formation of a new carbon–carbon bond to form a four-membered central ring giving the tricyclic cyclobutadiene derivative **1B** (Scheme I). Examples of characterized tricyclic cyclobutadiene derivatives of this type include the cyclopentadienylcobalt derivatives C_5H_5Co(alkadiyne) (II, m = 4, n = 4, 5, and 6; m = 5, n = 5 and 6)[1b] and the iron tricarbonyl derivative $C_{14}H_{20}Fe(CO)_3$ (III, m = 4, n = 6). Alternatively the metallacyclopentadiene derivative **1A** (Scheme I) can undergo hydrogen loss followed by a 1,2 hydrogen shift along with the loss of one of the two metal atoms with concurrent formation of a new carbon–carbon bond to form a five-membered central ring giving the tricyclic cyclopentadienyl derivative **1C**. Examples of characterized tricyclic cyclopentadienyl derivatives of the type **1C** (Scheme I) include the iron compounds $[C_{13}H_{17}Fe(CO)_2]_2$ (V, m = 4, n = 4), $[C_{14}H_{19}Fe(CO)_2]_2$ (V, m = 4, n = 5), and $[C_{15}H_{21}Fe(CO)_2]_2$ (V, m = 4, n = 6) discussed in this paper. Whether the end product is the tricyclic cyclobutadiene derivative **1B** (Scheme I) or the tricyclic cyclopentadienyl derivative **1C** (Scheme I) will depend upon the available coordination sites on the transition metal atom and on any ring size effects in the two outer rings of the tricyclic systems.

Scheme I. Proposed Scheme for the Intramolecular Transannular Cyclization of Macrocyclic Alkadiynes with Metal Carbonyls



M = $Fe(CO)_x$ or C_5H_5Co

In the reactions of the macrocyclic alkadiynes I with $C_5H_5Co(CO)_2$ the complete loss of both carbonyl groups from the cobalt atom provides sufficient free coordination sites for the four-electron donor cyclobutadiene derivative (**1B** in Scheme I) but not for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (**1C** in Scheme I). Therefore the reactions of $C_5H_5Co(CO)_2$ with the macrocyclic alkadiynes I are relatively simple[1b] and always proceed relatively efficiently to form the tricyclic cyclobutadiene derivatives II.

The reactions of the macrocyclic alkadiynes I with iron carbonyls are considerably more complex since the $Fe(CO)_3$ groups in the intermediate metallacyclopentadiene derivative (**1A** in Scheme I) either have enough free coordination sites for the four-electron donor cyclopentadienyl ring in a tricyclic cyclobutadiene derivative (**1B** in Scheme I) or can generate enough free coordination sites for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (**1C** in Scheme I) by losses of a carbonyl ligand to form $Fe(CO)_2$ groups. In all cases studied some formation of a tricyclic cyclobutadiene–iron tricarbonyl derivative of type III corresponding to **1B** in Scheme I can be detected. However, in cases where the macrocyclic alkadiyne I contains a pentamethylene bridge (*i.e.*, $m = 5$ and/or $n = 5$) the alternative transannular cyclization to form a tricyclic cyclopentadienyl–iron carbonyl derivative of type V corresponding to **1C** in Scheme I predominates apparently because of the formation of a six-membered end ring in the tricyclic product of type **1C**. A further feature of the transannular cyclizations of macrocyclic alkadiynes I with iron carbonyls is the apparent need of at least one bridge of at least five methylene groups for collapse of the tricarbonylferrole–iron tricarbonyl derivatives IV (*i.e.*, **1A** in Scheme I)[5a] to form either the tricyclic cyclobutadiene derivatives III (*i.e.*, **1B** in Scheme I) or the tricyclic cyclopentadienyl derivative V (*i.e.*, **1C** in Scheme I). Apparently in the case of the iron carbonyl derivatives a bridge of four methylene groups is too inflexible for the molecular motions in the tricarbonylferrole–iron tricarbonyl derivatives (*i.e.*, **1A** in Scheme I) necessary for extrusion of the ferrole iron atom and formation of a new carbon–carbon bond.

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Vapor-Phase Charge-Transfer Complexes. VIII. Charge-Transfer and Blue-Shifted Bands of Complexed Iodine by the Constant Activity Method

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Abstract: The vapor-phase charge-transfer bands and blue-shifted bands of iodine complexed with diethyl sulfide, dimethyl sulfide, and diethyl ether have been determined by a recently proposed method of maintaining a constant activity of iodine between two tetramethylammonium polyiodide solids. Band positions and shapes of the charge-transfer bands and the blue-shifted iodine bands, the ratio of the extinction coefficients (ϵ) of the CT band and the blue-shifted iodine band, and the $K_c\epsilon$ products of these bands are obtained from absorbance measurements of only a single mixture of donor with polyiodide solids. For the conditions of these experiments, a slow reaction occurred with diethyl sulfide, but the systems with dimethyl sulfide and diethyl ether were stable. Results for dimethyl sulfide–iodine agree fairly well with a previous study based on the usual regression analysis of data at several donor–acceptor concentrations. The present study establishes the shape of the vapor-phase blue-shifted iodine band complexed with diethyl ether. This band undergoes a blue shift in *n*-heptane solvent which is greater than that for sulfide–iodine complexes.

Recently, it has been shown that a blue-shifted iodine band exists in the vapor phase when iodine is complexed with diethyl sulfide,[1] dimethyl sulfide,[2] and diethyl ether.[3] For the stronger sulfide complexes, a reliable determination of the equilibrium constant (K_c) and extinction coefficient (ϵ) is possible[4,5] based on the spectrophotometric equation

$$\frac{C_D{}^0 b C_A{}^0}{A'} = \frac{C_D{}^0 + C_A{}^0}{\epsilon'} + \frac{1}{K_c\epsilon'} - \frac{A'}{b\epsilon'^2} \qquad (1)$$

where $C_D{}^0$ and $C_A{}^0$ are the initial concentrations of donor and acceptor, respectively, b is the cell path, and A is the absorbance. The primes on A and ϵ signify corrected values taking into account the contributions of free donor and free acceptor.[3,5]

The separation of the total iodine absorbance in the visible region into free and complexed components is quite sensitively dependent on the value of K_c;[1,3] *i.e.*, the calculated band shape and position of the blue-shifted iodine band changes markedly when K_c is altered by a factor of 2 or 3. For the stronger diethyl sulfide–iodine[1] and dimethyl sulfide–iodine[2] complexes, where K_c seems reliable, it may be assumed that characterization of the blue-shifted iodine bands is reasonably good.

The diethyl ether–iodine complex is much weaker.

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