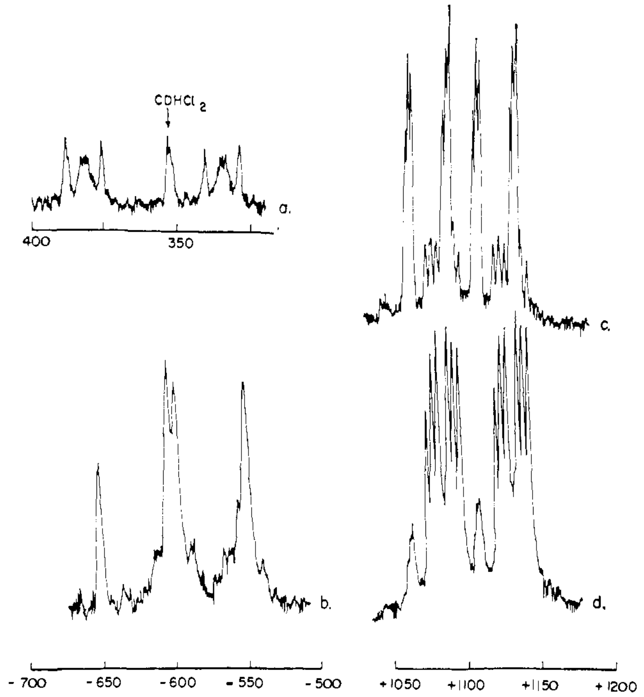

Figure 1. (a) ^{1}H spectrum of adduct of I with IIb or IIc; recorded at 60 MHz in CD_2Cl_2; shift relative to external TMS. (b) ^{19}F spectrum of same adduct. (c) ^{19}F spectrum of IIc. (d) ^{19}F spectrum of IIb. All ^{19}F spectra recorded at 94.1 MHz in CH_2Cl_2; shift relative to external C_6F_6.

and $^3J_{F-D} < 10$ Hz (unresolved)).[10] These data are only consistent with the formation of approximately equimolar quantities of the two diastereomers IIIb and IIIc from either IIb or IIc.

(iv) The addition of *trans*- or *cis*-1-bromo-2-fluorocyclohexane to I is efficiently initiated by oxygen to give the Ir(III) adducts which were isolated in high yield and fully characterized.[11] The products from both trans and cis show identical ^{19}F spectra also indicating loss of configuration at carbon during this process. Although an unambiguous structural assignment cannot be made from the observed spectra,[12] our original claim that these reactions occurred with stereospecific inversion of configuration is incorrect.[2]

(v) Competitive experiments with or without initiator indicate the following relative reactivity sequence: II > 1-bromo-2-phenylethane $\sim$ *trans*-1-bromo-2-fluorocyclohexane $\sim$ *cis*-1-bromo-2-fluorocyclohexane > bromocyclohexane. The accelerating effect of an electron-withdrawing substituent in these reactions has precedent in related radical processes involving alkyl halides.[13]

In analogy with related reactions of alkyl halides with complexes of Co(II) and Cr(II) which occur *via* radical pathways,[14] an attractive mechanism presents itself for oxidative addition to Ir(I).

$$\begin{aligned} &\mathrm{Ir^I} + \mathrm{Q}\cdot \longrightarrow \mathrm{Ir^{II}\text{-}Q} \\ &\mathrm{Ir^{II}\text{-}Q} + \mathrm{R\text{-}Br} \longrightarrow \mathrm{Br\text{-}Ir^{III}\text{-}Q} + \mathrm{R}\cdot \qquad (\mathrm{Q}\cdot = \text{initiator}) \\ &\mathrm{Ir^I} + \mathrm{R}\cdot \longrightarrow \mathrm{Ir^{II}\text{-}R} \\ &\mathrm{Ir^{II}\text{-}R} + \mathrm{RBr} \longrightarrow \mathrm{Br\text{-}Ir^{III}\text{-}R} + \mathrm{R}\cdot \end{aligned}$$

However, it is noteworthy that CH_3I reacts extremely rapidly with I (unlike systems known to follow a radical path[14b]) even in the presence of radical inhibitors, indicating that an alternate pathway(s) can be operative for certain substrates.

Investigations are proceeding toward determining the scope of free-radical processes in oxidative addition and the potential utility of such processes in synthesis and catalytic behavior in transition metal chemistry.

Acknowledgments. This work was supported by grants from the National Science Foundation (GP-16761; D. D.) and from E. I. du Pont de Nemours (J. A. O.). A Fellowship from the Henry and Camille Dreyfus Foundation is gratefully acknowledged (J. A. O.).

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[10] A deuterium isotope effect on the ^{19}F chemical shift of IIIb and c (*ca.* 26 Hz) and IIb and c (10.5 Hz) is evident (Figure 1b–d). Spectra measured at 56.45 MHz confirm the presence of two species.

[11] Despite extreme precautions we find that adduct formation still occurs (albeit slowly) in the absence of initiator. This is contrary to other observations.[5] This uninitiated reaction is, however, inhibited by duroquinone. These differing observations therefore may result from the presence of a trace of inhibitor or initiator under differing experimental conditions.

[12] Unlike the solution ^{19}F data previously reported,[2] the spectra of the isolated adducts are most consistent with the presence of two species with almost coincident chemical shifts.

[13] L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

[14] (a) J. Kochi, *Rec. Chem. Progr.*, 27, 207 (1966); (b) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970), and references cited therein.

[15] National Science Foundation Predoctoral Fellow.

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Received March 22, 1972

Some Ring Size Effects in the Intramolecular Transannular Cyclizations of Macrocyclic Alkadiynes with Iron Carbonyls

Sir:

Recent work[1,2] has shown that macrocyclic alkadiynes of the type I (m = 4, n = 4, 5, or 6; m = 5, n = 5 or 6) undergo an intramolecular transannular cyclization reaction with $C_5H_5Co(CO)_2$ to give the tricyclic cyclobutadiene derivatives II of stoichiometry C_5H_5Co(alkadiyne). Previous work[3] has also shown that the macrocyclic alkadiyne 1,8-cyclotetradecadiyne (I, $m = n = 5$) reacts with $Fe(CO)_5$ to undergo a different type of intramolecular transannular cyclization reaction resulting in the formation of the tricyclic cyclopentadienyl derivative $[C_{14}H_{19}Fe(CO)_2]_2$ of structure III (m = 4; n = 5). This communication reports other intramolecular transannular cyclization reactions of macrocyclic alkadiynes of the type I with iron carbonyls. Of particular interest is the observation of a strong dependence of the nature of the intramolecular transannular cyclization product on the number of methylene groups (m and n in I) bridging each side of the pair of carbon–carbon triple bonds, an effect not observed in the previously reported[1,2] intramolecular transannular cyclizations of the same macrocyclic alkadiynes (I) with $C_5H_5Co(CO)_2$.

The macrocyclic alkadiyne 1,7-cyclotetradecadiyne (I, m = 4; n = 6) unlike the isomeric but more sym-

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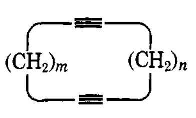
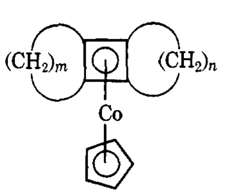
[1] R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **92**, 6071 (1970).

[2] R. B. King and A. Efraty, *ibid.*, **94**, 3021 (1972).

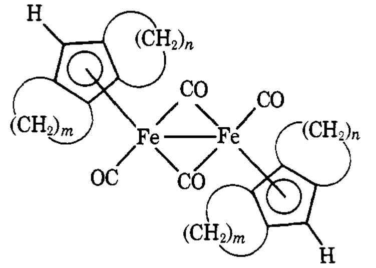
[3] R. B. King and C. W. Eavenson, *J. Organometal. Chem.*, **16**, P75 (1969).



I



II



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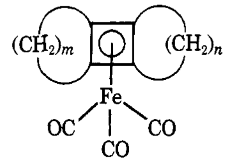

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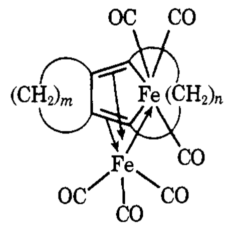
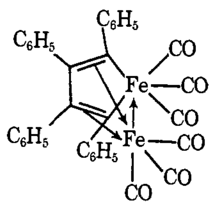
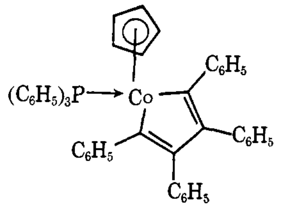


V



VI



VII

metrical 1,8-cyclotetradecadiyne (I, $m = n = 5$) does not form a tricyclic cyclopentadienyliron carbonyl derivative of type III upon reaction with iron carbonyls in saturated or aromatic hydrocarbon solvents. Instead the reaction of 1,7-cyclotetradecadiyne (I, $m = 4$; $n = 6$) with excess $Fe(CO)_5$ in boiling toluene for 20 hr gives a 26% yield of yellow-orange liquid $C_{14}H_{20}Fe(CO)_3$ after isolation by chromatography on alumina in pentane solution and purification by vacuum distillation [bp 150 ± 5° (0.01 mm)]. *Anal.* Calcd for $C_{17}H_{20}FeO_3$: C, 62.2; H, 6.1; mol wt, 328. Found: C, 62.1; H, 6.1; mol wt (mass spectrum), 328. Formulation of this $C_{14}H_{20}Fe(CO)_3$ as the tricyclic cyclobutadiene derivative IV ($m = 4$; $n = 6$) analogous to the cobalt derivatives II 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 7.90 and 8.42 in 2:3 integrated area ratio; (2) the presence of ν (CO) frequencies (pentane solution) at 2029 (s) and 1958 (vs) cm^{-1} close to the reported[4] ν (CO) frequencies at 2055 and 1985 cm^{-1} for the unsubstituted cyclobutadiene–iron tricarbonyl, $C_4H_4Fe(CO)_3$. The formation of $C_{14}H_{20}Fe(CO)_3$ (IV, $m = 4$; $n = 6$) from the reaction of 1,7-cyclotetradecadiyne with excess $Fe(CO)_5$ coupled with the formation of $[C_{14}H_{19}Fe(CO)_2]_2$ (III, $m = 4$; $n = 5$) from the reaction of 1,8-cyclotetradecadiyne (I, $m = n = 5$) with excess $Fe(CO)_5$ indicates that iron carbonyls can form either tricyclic cyclobutadiene derivatives IV or tricyclic cyclopentadienyl derivatives III upon reactions with macrocyclic alkadiynes of type I.

The macrocyclic alkadiyne 1,7-cyclododecadiyne (I, $m = n = 4$) gives still another type of intramolecular transannular cyclization product upon reaction with iron carbonyls. Thus the reaction of 1,7-cyclododecadiyne (I, $m = n = 4$) with excess $Fe(CO)_5$ in boiling toluene for 32 hr gives a 31% yield of orange crystalline $C_{12}H_{16}Fe_2(CO)_6$, mp 97–98°, isolated by chromatography and purified by low-temperature crystallization from pentane. *Anal.* Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.2; H, 3.7; Fe, 25.4; O, 21.8; mol wt, 440. Found: C, 49.3; H, 3.4; Fe, 25.1; O, 21.7; mol wt (mass spectrum), 440. This compound $C_{12}H_{16}Fe_2(CO)_6$ is formulated as the tricarbonylferrole–iron tricarbonyl derivative V ($m = n = 4$) on the basis of the following spectroscopic evidence: (1) the presence of only saturated CH_2 resonances in its proton nmr spectrum; (2) the absence in its infrared spectrum of bridging ν (CO) frequencies 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[5] 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 VI. The reaction of 1,7-cyclododecadiyne (I, $m = n = 4$) with excess $Fe(CO)_5$ also gave trace quantities (<1% yield) of a tricyclic cyclobutadiene derivative $C_{12}H_{16}Fe(CO)_3$ (IV, $m = n = 4$), mp 79.5–80°, but no tricyclic cyclopentadienyl derivative of type III.

The intramolecular transannular cyclization reactions of iron carbonyls with the various macrocyclic alkadiynes I are thus strongly dependent upon the ring size of the alkadiyne and the relative locations of the carbon–carbon triple bonds as summarized by the products listed below which have been obtained from the indicated macrocyclic alkadiyne and excess $Fe(CO)_5$ or $Fe_3(CO)_{12}$: (a) 1,7-cyclododecadiyne, $C_{12}H_{16}$ (I, $m = n = 4$): $C_{12}H_{16}Fe_2(CO)_6$ (V, $m = n = 4$) and a trace of $C_{12}H_{16}Fe(CO)_3$ (IV, $m = n = 4$); (b) 1,7-cyclotridecadiyne, $C_{13}H_{18}$ (I, $m = 4$; $n = 5$): $[C_{13}H_{17}Fe(CO)_2]_2$, mp 154° (III, $m = n = 4$), in rather poor yield (~6%); (c) 1,8-cyclotetradecadiyne, $C_{14}H_{20}$ (I, $m = n = 5$): $[C_{14}H_{19}Fe(CO)_2]_2$ (III, $m = 4$; $n = 5$) in yields up to 50%; (d) 1,7-cyclotetradecadiyne, $C_{14}H_{20}$ (I, $m = 4$; $n = 6$): $C_{14}H_{20}Fe(CO)_3$ (IV, $m = 4$; $n = 6$); (e) 1,8-cyclopentadecadiyne, $C_{15}H_{22}$ (I, $m = 5$; $n = 6$): $[C_{15}H_{21}Fe(CO)_2]_2$ (III, $m = n = 5$ or $m = 4$, $n = 6$) in about 22% yield.

These observations can be explained by the scheme shown in Scheme I for the intramolecular transannular cyclizations of the macrocyclic alkadiynes with metal carbonyls. In this scheme the first detectable intermediate is the bimetallic metallacyclopentadiene (metallole) derivative 1A. The compound $C_{12}H_{16}Fe_2(CO)_6$ (V, $m = n = 4$) isolated in this work is an example of this intermediate. Furthermore, Yamazaki and Hagihara[6] have demonstrated the related monometallic cobaltacyclopentadiene (cobaltole) derivative C_5H_5Co-

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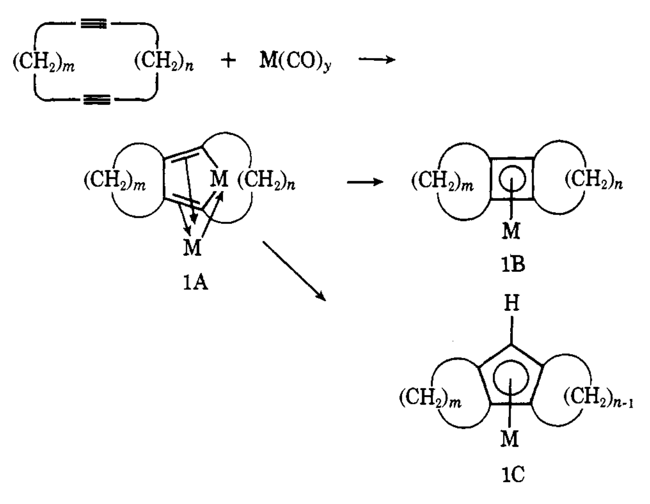
(4) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965).

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

(6) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, 7, P22 (1967).

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



$M = Fe(CO)_x$ or C_5H_5Co

$(C_6H_5C_2C_6H_5)_2P(C_6H_5)_3$ (VII) to be an intermediate in the formation of the tetraphenylcyclobutadiene complex $C_5H_5CoC_4(C_6H_5)_4$ from the alkyls $C_5H_5CoR_2P(C_6H_5)_3$ (R = isopropyl, etc.) and diphenylacetylene. The metallacyclopentadiene derivative 1A in Scheme I can undergo loss of one of the two metal atoms with carbon–carbon bond formation to form a four-membered central ring giving the tricyclic cyclobutadiene derivative 1B in Scheme I. Alternatively the metallacyclopentadiene derivative 1A in Scheme I can undergo hydrogen migration and hydrogen loss along with loss of one of the two metal atoms with carbon–carbon bond formation to form a five-membered central ring giving the tricyclic cyclopentadienyl derivative 1C in Scheme I. 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 the sizes of the two outer rings in the final tricyclic system.

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 ring in a tricyclic 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 of type I are relatively simple[1,2] and in all cases proceed relatively efficiently to give 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 cyclobutadiene 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. The following principles account for the observations summarized in this and the previous[3] communication on the reactions of macrocyclic alkadiynes with iron carbonyls.

(1) The presence of a bridge of exactly five CH_2 groups (*i.e.*, either *m* or *n* or both = 5) is necessary for the transannular cyclization forming a tricyclic cyclopentadienyl derivative of type III (*i.e.*, 1C in Scheme I). Such a five CH_2 group bridge would give a six-membered outer ring upon cyclization to a cyclopentadienyl derivative but a seven-membered outer ring upon cyclization to a cyclobutadiene derivative (*i.e.*, 1B in Scheme I). In 1,8-cyclotetradecadiyne (I, *m* = *n* = 5) with two bridges of five CH_2 groups the tendency for formation of a tricyclic cyclopentadienyl derivative (1C in Scheme I) is particularly high.

(2) A bridge of four CH_2 groups is sufficient for formation of a tricyclic cyclobutadiene derivative (1B in Scheme I) but a bridge of more than four CH_2 groups is necessary for the conversion of the intermediate metallacyclopentadiene derivative (1A in Scheme I) to the tricyclic cyclobutadiene derivative (1B in Scheme I) to take place at a significant rate.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347X.

(7) Permanent staff member of the Department of Chemistry, Babeş Bolyai University, Cluj, Romania, on leave during 1971–1972 in the Department of Chemistry, University of Georgia.

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Received February 28, 1972

Photochromic Aziridines. I. The Mechanism of Photochromism in 1,3-Diazabicyclo[3.1.0]hex-3-enes and Related Aziridines

Sir:

The synthesis of a series of photochromic bicyclic aziridines has been described by Heine and coworkers.[1] We present evidence that the colored species produced in these photoinduced reversible reactions are 1,3 dipoles (azomethine ylides). In addition, structural requirements for the photochromism are outlined, and the suggestion is made that the formation of the colored intermediate may involve vibrationally excited ground-state species.

Typical of the compounds investigated (Table I)

Table I. Photochromic Bicyclic Aziridines

Colored intermediate	$\lambda_{max}^{77°K}$, nm	Glass	$\lambda_{max}^{KBr; 25°}$, nm	Color
1a[a]	605	MTHF	625,580 (sh)	Blue
1b[b]	512,485 (sh)	EtOH	526,495 (sh)	Pink
1c[c]	610,570 (sh)	MTHF	645,600 (sh)	Green

[a] Heine, *et al.*[1a] [b] A. Padwa, S. Clough, and E. Glazer (*J. Amer. Chem. Soc.*, **92**, 1778 (1970)) isolated **1b** when preparing the exo-trans isomer according to the Heine procedure. [c] Mp 166–167°; we prepared **1c** and its exo-trans isomer (mp 175–176°) using Heine–Padwa methods.

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(1) (a) H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, 32, 2708 (1967); (b) H. W. Heine, A. B. Smith, III, and J. D. Bower, *ibid.*, 33, 1097 (1968); (c) H. W. Heine and R. P. Hanzel, *ibid.*, 34, 171 (1969).