

at 77°K for 1 hr with 3-MeV bremsstrahlung of up to 100 Mrads/hr intensity. Second, boron trifluoride was irradiated in a similar manner, then xenon added to the excited BF_3 at 77°K. In neither case was a reaction between xenon and boron trifluoride observed. Interestingly, however, a reaction did occur by irradiating a mixture of xenon and boron trifluoride containing 1–2% fluorine at 77°K to produce largely compound A and some XeF_2 . In this case, the catalytic effect of fluorine can be explained by assuming that $\cdot\text{XeF}$ was produced which then reacted with BF_3 .

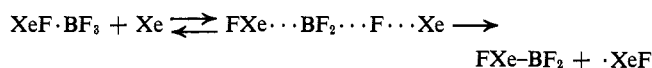
Meinert, *et al.*,^{14,15} have shown that a $\text{XeF}_2 \cdot \text{BF}_3$ adduct is formed by combining XeF_2 and BF_3 . The possibility that this was an intermediate in our work was discounted when we found that the complex $\text{XeF}_2 \cdot \text{BF}_3$ would not yield compound A. We suggest that in our studies¹⁶ an adduct $\text{FXe} \cdot \text{BF}_3$ is present in an excited state capable of reacting further with

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(16) Results of irradiation studies on Xe, BF_3 , F_2 and Kr, BF_3 , F_2 mixtures are being submitted for publication.

xenon to yield compound A and $\cdot\text{XeF}$. A possible reaction path for this reaction could be as follows



The proposed structure, $\text{FXe} \cdot \text{BF}_2$, certainly has not been proven beyond the shadow of a doubt; however, we believe our experimental evidence favors this structure over the structure $\text{Xe} \cdot \text{BF}_3$. Further experiments on this system, such as F^{19} magnetic resonance and X-ray diffraction studies, would be desirable to establish the structural parameters of this intriguing molecule more firmly.

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Reactions of Transition Metal Compounds with Macrocyclic Alkadiynes. I. Intramolecular Transannular Cyclizations with Cyclopentadienyldicarbonylcobalt¹

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Abstract: The macrocyclic alkadiynes 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne react with $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ or, in some cases, $\text{C}_5\text{H}_5\text{Co}(1,5\text{-C}_8\text{H}_{12})$ in boiling octane or cyclooctane to give yellow to orange volatile compounds of the composition $\text{C}_5\text{H}_5\text{Co}(\text{alkadiyne})$ in which the macrocyclic alkadiyne has undergone an intramolecular transannular cyclization to form a tricyclic cyclobutadiene derivative. The reaction of 1,8-cyclotetradecadiyne with $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ also gives the black trimetallic derivative $(\text{C}_5\text{H}_5)_3\text{Co}_3(\text{CO})(\text{C}_{14}\text{H}_{20})$. The infrared, proton nmr, and mass spectra of these new cyclopentadienyldicarbonylcobalt derivatives are discussed.

Since 1958 extensive studies have been carried out on reactions of numerous types of transition metal derivatives with diverse alkynes.³ This work has resulted in the preparation of many unusual transition metal organometallic compounds including metal complexes of monodentate monometallic, bidentate bimetallic, and bidentate monometallic alkynes,⁴ as well as cyclobutadienes, cyclopentadienones, benzenes, tropones, metallacyclopentadienes, metallacyclohexadienones, etc. This rich variety of interesting transition metal organometallic compounds that can be obtained from reactions of transition metal carbonyls, halides, etc., with alkynes containing one carbon–carbon triple bond suggested that analogous reactions of similar transition metal derivatives with acetylenic derivatives

containing two or more carbon–carbon triple bonds might provide useful synthetic routes to novel transition metal organometallic derivatives.

The reported studies on reactions of transition metal derivatives with alkadiynes have been mainly confined to acyclic 1,3-alkadiynes.^{5–7} In most cases, the carbon–carbon triple bonds of such acyclic 1,3-alkadiynes interact individually with transition metal atoms. Thus, acyclic 1,3-alkadiynes react with $\text{Co}_2(\text{CO})_8$ to give complexes of the type $(\text{alkadiyne})[\text{Co}_2(\text{CO})_6]_2$ which correspond to two $(\text{alkyne})\text{Co}_2(\text{CO})_6$ units linked by carbon–carbon bonds.^{5,7} The limited amount of work on reactions of iron carbonyls with acyclic 1,3-alkadiynes suggests that only one of the two carbon–carbon triple bonds interacts with iron atoms to give ultimately com-

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pounds similar to those formed by simple alkynes but containing a substituent with an uncomplexed carbon-carbon triple bond.

The independent behavior of the two carbon-carbon triple bonds in 1,3-alkadiynes is undoubtedly a consequence of the linear sp hybrids which place the carbon-carbon triple bonds in such alkadiynes as far as possible from each other thereby minimizing the chance of their interaction. One possible method of allowing two carbon-carbon triple bonds to get sufficiently close to each other for some interaction to occur uses alkadiynes where the carbon-carbon triple bonds are part of a ring system in which the geometry of the ring system forces the carbon-carbon triple bonds sufficiently close together for some interaction to take place. One example of a compound of this type is *o*-bis(phenylethynyl)benzene (I) where some interaction between carbon-carbon triple bonds has been demonstrated.⁸ The reaction of I with $Fe(CO)_5$ has been shown to give an unusual complex, $[C_6H_4C_2(C_6H_5)_2]_2[Fe(CO)_3][FeCO]$ (II).^{8,9} The formation of II clearly represents an indication of interaction between the carbon-carbon triple bonds in *o*-bis(phenylethynyl)benzene.

In I the carbon-carbon triple bonds are not actually part of a ring system but instead are side chains with their geometry fixed by the benzenoid ring system. Another type of alkadiyne with possible interactions between the carbon-carbon triple bonds has the carbon-carbon triple bonds as actual parts of a ring system. Because of the constraints introduced by the linear sp hybridization of the carbon atoms forming the triple bonds, a rather large macrocyclic ring is necessary for the presence of two carbon-carbon triple bonds. Appropriate compounds of this type have the general structure III. At least four CH_2 groups between each

pair of ends of the carbon-carbon triple bonds (*i.e.*, $n = 4$ in III) are necessary for such macrocyclic alkadiynes to be stable and preparable in reasonable yields.^{10,11}

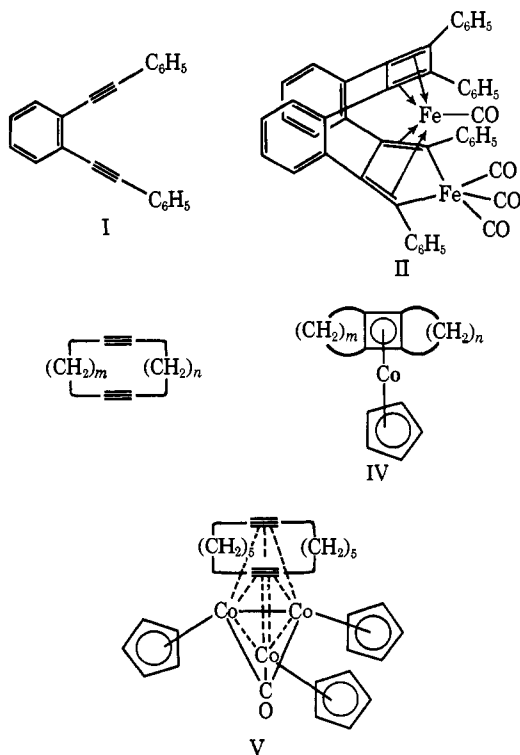
We have investigated reactions of macrocyclic alkadiynes of the type III ($m = n = 4$ or 5 ; $n = 5$ or 6 ; $m = 5$, $n = 6$) with various metal carbonyls such as $Fe(CO)_5$,¹² $C_5H_5Co(CO)_2$,¹ and $[C_5H_5NiCO]_2$. This paper describes the reactions of macrocyclic alkadiynes of the type III with $C_5H_5Co(CO)_2$. Such reactions are of interest in yielding the novel tricyclic cyclobutadiene derivatives IV by unusual intramolecular transannular cyclization reactions clearly involving some type of interaction between the two carbon-carbon triple bonds. Previously reported work¹³ had shown that this type of cyclization of macrocyclic alkadiynes to tricyclic cyclobutadienes does not take place in the absence of transition metals, at least in the case of 1,7-cyclododecadiyne, which should be the most favorable case because the two end rings are six-membered rings rather than seven- or eight-membered rings. The reaction between 1,8-cyclotetradecadiyne (III, $m = n = 5$) and $C_5H_5Co(CO)_2$, besides yielding the tricyclic butadiene derivative IV ($m = n = 5$), also yields the unusual trinuclear derivative $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$, apparently of structure V. This trinuclear derivative V represents an apparent example of novel bonding of both carbon-carbon triple bonds of an alkadiyne to a metal triangle.¹⁴

Experimental Section

Materials. The $C_5H_5Co(CO)_2$ was prepared by the reaction of commercial $Co_2(CO)_8$ (Strem Chemical Company, Danvers, Mass.) with monomeric cyclopentadiene in dichloromethane solution at room temperature.¹⁶ The $C_5H_5Co(1,5-C_8H_{12})_2$ was prepared by reaction of $C_5H_5Co(CO)_2$ with 1,5-cyclooctadiene according to the published procedure.¹⁷ The macrocyclic alkadiynes were purchased from Farchan Research Laboratories, Willoughby, Ohio.

Reactions of $C_5H_5Co(CO)_2$ with the Macrocyclic Alkadiynes (See Table I). Equimolar quantities of $C_5H_5Co(CO)_2$ and the macrocyclic alkadiyne indicated in Table I were boiled under reflux in *n*-octane (bp 126°) for 17–27 hr. About 10–20 mmol of each reactant was used with about 50 ml of the *n*-octane for each 10 mmol of both reactants. After the reaction period was over, the solvent was removed at 40–60° (30 mm). The residue was extracted with pentane or hexane (about three 50-ml portions). The extracts were concentrated to about 50 ml at 25° (30 mm) and then chromatographed on a 3 × 75 cm alumina column. The yellow to yellow-orange band of the product (IV) was eluted with pentane or hexane. The eluate was evaporated to dryness at 25° (40 mm). The reactions of $C_5H_5Co(CO)_2$ with 1,7- $C_{12}H_{16}$ (III, $m = n = 4$), 1,7- $C_{13}H_{18}$ (III, $m = 4$, $n = 5$), and 1,8- $C_{14}H_{20}$ (III, $m = n = 5$) gave crystalline products at this point. These were purified further by low-temperature crystallization from pentane or hexane followed by sublimation at 65–75° (0.3–0.05 mm) to give yellow crystals of the final product.

The reactions of $C_5H_5Co(CO)_2$ with 1,7- $C_{14}H_{20}$ (III, $m = 4$, $n = 6$) and 1,8- $C_{15}H_{22}$ (III, $m = 5$, $n = 6$) gave orange liquid products



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Table I. Compounds Obtained from $C_5H_5Co(CO)_2$ and Macrocyclic Alkadiynes

Macrocyclic alkadiyne	Product	Structure ^a		Yield, % ^b	Mp, ^c °C	Analyses, %				
		<i>m</i>	<i>n</i>			Calcd	H ^d	Co ^d	Mol wt ^e	
1,7-Cyclododecadiyne	$C_5H_5CoC_{12}H_{16}$	4	4	86	85.5	Calcd	71.8	7.4	20.8	
						Found	71.8	7.5	20.4	
1,7-Cyclotridecadiyne	$C_5H_5CoC_{13}H_{18}$	4	5	65	75	Calcd	72.5	7.8	19.7	298
						Found	72.9	7.7	19.6	281
1,8-Cyclotetradecadiyne	$C_5H_5CoC_{14}H_{20}$	5	5	2	103–105	Calcd	73.2	8.1	18.7	
						Found	72.5	8.0	18.6	
	$(C_5H_5)_3Co_3(CO)C_{14}H_{20}$	8	242–245	Calcd	61.3	5.9	30.1	588		
				Found ^f	61.2	6.0	29.3	577		
1,7-Cyclotetradecadiyne	$C_5H_5CoC_{14}H_{20}$	4	6	40	Liquid	Calcd	73.2	8.1	18.7	
						Found	72.7	8.0	18.4	
1,8-Cyclopentadecadiyne	$C_5H_5CoC_{15}H_{22}$	5	6	52	47–48	Calcd	73.6	8.3	18.1	
						Found	73.7	8.4	17.0	

^a The values of *m* and *n* indicate the numbers of CH_2 groups as depicted in structure IV. ^b All yields reported were obtained from reactions of the macrocyclic alkadiyne with $C_5H_5Co(CO)_2$ in boiling *n*-octane as described in the Experimental Section. ^c These melting points were determined in capillaries and are uncorrected. ^d These analyses were determined by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. ^e These molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using a vapor pressure osmometer in dichloromethane solution. ^f Calcd, O, 2.7; found, O, 3.0.

after evaporation of the eluate from the chromatography column. These were purified by chromatography two additional times, followed by vacuum distillation two times at 0.05 mm in a molecular still using heating by an oil bath at temperatures up to 130°. The distilled sample of $C_5H_5CoC_{15}H_{22}$ (IV, *m* = 5, *n* = 6) solidified upon prolonged standing.

Reaction of $C_5H_5Co(CO)_2$ with 1,8-Cyclotetradecadiyne in Boiling Cyclooctane. A mixture of 3.9 g (21.7 mmol) of $C_5H_5Co(CO)_2$, 4.2 g (22.3 mmol) of 1,8-cyclotetradecadiyne, and 75 ml of cyclooctane was boiled under reflux for 11 hr. After cooling to room temperature, the reaction mixture was filtered. The trimetallic compound $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ could be isolated from the residue as described below. The cyclooctane filtrate was chromatographed on a 3 × 75 cm alumina column. The yellow band of $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5) was eluted with pentane. Solvent was removed from the eluate at 25° (35 mm). The residue was dried at 25° (0.05 mm). Sublimation of this residue at 80–90° (0.05 mm) gave 0.25 g (3.6% yield) of yellow $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5).

The residue from the original cyclooctane solution was extracted with four 50-ml portions of dichloromethane. The filtered dichloromethane extracts were concentrated to ~30 ml and then chromatographed on the same alumina column used for the isolation of $C_5H_5CoC_{14}H_{20}$ (III, *m* = *n* = 5) described above. In order to remove any impurities, the chromatogram was eluted with various mixtures of dichloromethane and hexane. The chromatogram was finally developed with dichloromethane. A black band of $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ slowly formed and descended the column. This band was eluted with dichloromethane. The filtered dichloromethane eluate was treated with 60–90° petroleum ether. Solvent was removed at 25° (35 mm) until the black crystals of $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ separated. These were removed by filtration. After further purification by Soxhlet extraction with heptane and recrystallization from a mixture of dichloromethane and hexane 0.21 g (5% yield) of black crystalline $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ was obtained.

Reactions of $C_5H_5CoC_8H_{12}$ with the Macrocyclic Alkadiynes. A mixture of 0.4 g (1.72 mmol) of $C_5H_5CoC_8H_{12}$, 0.4 g of 1,7-cyclotridecadiyne (2.3 mmol) or 1,8-cyclotetradecadiyne (2.13 mmol), and 15 ml of cyclooctane was boiled under reflux for 21 hr. The reaction mixture was then cooled to room temperature and solvent removed at 60° (25 mm). The residue was extracted with 100 ml of pentane. The pentane solution was concentrated to ~30 ml and then chromatographed on a 2 × 40 cm alumina column. The yellow band of product was eluted with pentane. Evaporation of the eluate at 25° (35 mm) gave a solid residue. Sublimation of this residue at 25–40° (0.3 mm) removed a small amount of unreacted $C_5H_5CoC_8H_{12}$. After removal of all of the $C_5H_5CoC_8H_{12}$, further sublimation at 70–75° (0.3 mm) gave the C_5H_5Co (alkadiyne) derivative. The yield of $C_5H_5CoC_{13}H_{18}$ (IV, *m* = 4, *n* = 5) from $C_5H_5CoC_8H_{12}$ and 1,7-cyclotridecadiyne by this method was 0.20 g (39%). The yield of $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5) by this method was 0.055 g (10%).

Infrared Spectra. The infrared spectra were taken in potassium bromide pellets (unless otherwise indicated) and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Spectra were calibrated against the 1601-cm⁻¹ band of polystyrene film.

(A) $C_5H_5CoC_{12}H_{16}$ (IV, *m* = *n* = 4). $\nu(CH)$ frequencies at 2943 (sh), 2926 (s), 2909 (m), 2848 (w), 2835 (w, sh), and 2820 (vw, sh) cm⁻¹; other bands at 1439 (s), 1420 (m), 1402 (m), 1340 (w), 1324 (w), 1286 (m), 1227 (m), 1108 (m), 1097 (w), 1055 (vw), 1049 (vw), 999 (m), 932 (w), 857 (vw), 839 (m), 802 (s), and 762 (m) cm⁻¹.

(B) $C_5H_5CoC_{13}H_{18}$ (IV, *m* = 4, *n* = 5). $\nu(CH)$ frequencies at 2910 (m), 2840 (w, br), and 2810 (w, br) cm⁻¹; other bands at 1436 (m), 1399 (m), 1313 (w), 1280 (w), 1098 (w), 998 (m), 801 (m), 796 (s), and 751 (w) cm⁻¹.

(C) $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5). $\nu(CH)$ frequencies at 2925 (m), 2912 (m), 2845 (w), and 2815 (w) cm⁻¹; other bands at 1441 (s), 1401 (m), 1346 (w), 1327 (w), 1300 (w), 1258 (vw), 1227 (w), 1216 (w), 1107 (w), 1024 (vw), 996 (w), 801 (s), and 730 (w) cm⁻¹.

(D) $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ (V). $\nu(CH)$ frequencies at 2920 (w) and 2850 (vw) cm⁻¹; three-way bridging $\nu(CO)$ frequency at 1655 (s) cm⁻¹; other bands at 1400 (m), 1111 (vw), 1003 (w), and 808 (m) cm⁻¹.

(E) $C_5H_5CoC_{14}H_{20}$ (IV, *m* = 4, *n* = 6) (run as neat liquid film). $\nu(CH)$ frequencies at 3097 (w), 2930 (s), 2853 (s), and 2835 (m, sh) cm⁻¹; other bands at 1463 (m, sh), 1441 (m), 1421 (w, sh), 1349 (vw, sh), 1337 (w), 1324 (w), 1290 (vw), 1228 (w), 1110 (m), 1050 (vw), 1003 (m), 883 (vw), 854 (vvw), 803 (s), and 733 (w) cm⁻¹.

(F) $C_5H_5CoC_{15}H_{22}$ (IV, *m* = 5, *n* = 6). $\nu(CH)$ frequencies at 2921 (m), 2904 (w, sh), 2866 (w), 2852 (w, sh), and 2817 (w) cm⁻¹; other bands at 1640 (vw), 1520 (vw), 1460 (w), 1448 (w, sh), 1440 (w), 1430 (w), 1403 (w), 1350 (vw), 1329 (w), 1319 (vw), 1298 (vw), 1255 (vw), 1223 (w), 1109 (w), 1000 (w), and 800 (m) cm⁻¹.

Mass Spectra. The mass spectra listed below were run at 70 eV on a Perkin-Elmer Hitachi Model RMU-6 mass spectrometer with a 220° chamber temperature and sample temperatures in the range 120–150°. Relative abundances are given in parentheses with the molecular ion being assigned an arbitrary value of 100. Only ions with a relative abundance at least 14% of that of the molecular ion are listed. In all cases, about 50–75 additional weaker, less significant ions were also observed.

(A) $C_5H_5CoC_{12}H_{16}$ (IV, *m* = *n* = 4). $C_5H_5CoC_{12}H_{16}^+$ (100), $C_5H_5CoC_{12}H_{10}^+$ (31), $C_{12}H_{11}Co^+$ (25), $C_{12}H_{10}Co^+$ (50), $C_{12}H_9Co^+$ (93), $C_5H_5Co^+$ (27), $C_5H_5Co^+$ (35), and Co^+ (30).

(B) $C_5H_5CoC_{13}H_{18}$ (IV, *m* = 4, *n* = 5). $C_5H_5CoC_{13}H_{18}^+$ (100), $C_5H_5CoC_{13}H_{14}^+$ (15), $C_5H_5CoC_{13}H_{13}^+$ (15), $C_{13}H_{15}Co^+$ (14), $C_{13}H_{14}Co^+$ (29), $C_{13}H_{11}Co^+$ (23), $C_{13}H_9Co$ (16), $C_5H_5Co^+$ (21), $C_7H_7^+$ (15), and Co^+ (26).

(C) $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5). $C_5H_5CoC_{14}H_{20}^+$ (100), $C_5H_5CoC_{14}H_{16}^+$ (14), $C_{14}H_{15}Co^+$ (15), $C_{14}H_{13}Co^+$ (14), $C_{12}H_{14}Co^+$ (15), $C_5H_5Co^+$ (18), and Co^+ (18).

(D) $C_5H_5CoC_{14}H_{20}$ (IV, *m* = 4, *n* = 6). $C_5H_5CoC_{14}H_{20}^+$ (100), $C_5H_5CoC_{14}H_{16}^+$ (21), $C_{14}H_{15}Co^+$ (18), $C_{14}H_{13}Co^+$ (18), $C_{14}H_{11}Co^+$ (30), $C_5H_5Co^+$ (24), and Co^+ (28).

(E) $C_5H_5CoC_{15}H_{22}$ (IV, *m* = 5, *n* = 6). $C_5H_5CoC_{15}H_{22}^+$ (100), $C_5H_5CoC_{15}H_{20}^+$ (16), $C_5H_5CoC_{15}H_{18}^+$ (26), $C_{15}H_{17}Co^+$ (20), $C_{15}H_{15}Co^+$ (18), $C_5H_5Co^+$ (22), and Co^+ (15).

Discussion

Each of the macrocyclic alkadiynes studied in this work reacted with $C_5H_5Co(CO)_2$ to give a volatile air-

Table II. Proton Nmr Spectra of the Macrocyclic Alkadiynes and the Complexes Formed by Reaction with $C_5H_5Co(CO)_2^a$

Compound	Structure ^b		Proton nmr spectrum, τ^c	
	<i>m</i>	<i>n</i>	CH_2	$\pi-C_5H_5$
1,7- $C_{12}H_{16}$	4	4	7.97 (8), 8.35 (8)	
1,7- $C_{13}H_{18}$	4	5	~7.95 (8), ~8.38 (6), ~8.6 (4)	
1,8- $C_{14}H_{20}$	5	5	~7.9 (8), ~8.35 (4), ~8.70 (8)	
1,7- $C_{14}H_{20}$	6	4	7.90 d, (8), 8.40 t (4), 8.50 (8)	
1,8- $C_{15}H_{22}$	6	5	7.87 (8), 8.53 (14)	
$C_5H_5CoC_{12}H_{16}$	4	4	~7.8 (4), ~8.2 (8), ~8.5 (4)	5.46 (5)
$C_5H_5CoC_{13}H_{18}$	4	5	~8.0 (10), ~8.4 (8)	5.37 (5)
$C_5H_5CoC_{14}H_{20}$	5	5	~8.1 (12), ~8.4 (8)	5.28 (5)
$C_5H_5CoC_{14}H_{20}$	4	6	~7.9 (4), ~8.1 (4), 8.3-8.6 (12)	5.45 (5)
$C_5H_5CoC_{15}H_{22}$	5	6	~8.0 (8), 8.3-8.6 (14)	5.35 (5)
$(C_5H_5)_3Co_3(CO)C_{14}H_{20}^d$			7.00 (4), 7.64 (8), 8.25 (8)	5.42 (15)

^a These proton nmr spectra were taken at 100 MHz on a Varian HA-100 spectrometer. The free macrocyclic alkadiynes were run in CS_2 solution. The cobalt complexes were run in $CDCl_3$ solution. ^b The values of *m* and *n* indicate the numbers of CH_2 groups as depicted in structure IV for the cobalt complexes or structure III for the free macrocyclic alkadiynes. ^c The number of protons corresponding to each resonance is indicated in parentheses. ^d The CH_2 resonances in this compound were all unusually broad.

stable yellow solid of the general composition C_5H_5Co (alkadiyne), with complete loss of both carbonyl groups. These compounds are formulated as the tricyclic cyclobutadiene derivatives IV on the basis of the following observations.

(1) The infrared spectra show no bands in the region 2200–1500 cm^{-1} associated with the $\nu(CO)$ of various types of carbon-carbon double or triple bonds. In addition the infrared spectra of all of the C_5H_5Co (alkadiyne) derivatives exhibit bands in the 1500–800- cm^{-1} region reasonably close to the bands at 1408, 1308, 1210, 1101, 997, and 815 cm^{-1} reported¹⁸ for the unsubstituted cyclopentadienylcyclobutadienecobalt, $C_5H_5CoC_4H_4$.

(2) The proton nmr spectra show only the expected single sharp π -cyclopentadienyl resonance and the expected broad saturated CH_2 resonances in the region τ 7.8–8.7, indicating that all of the hydrogen atoms derived from the macrocyclic alkadiyne are saturated CH_2 groups. This means that all of the carbon atoms in the C_5H_5Co (alkadiyne) product which are derived from the macrocyclic diacetylene, except for the four carbon atoms forming the cyclobutadiene ring, are saturated CH_2 groups. Therefore, the complexing cyclobutadiene derivative formed from the macrocyclic alkadiyne cannot have any carbon-carbon double bond other than the two carbon-carbon double bonds of the cyclobutadiene ring; otherwise, the nmr spectrum of the C_5H_5Co (alkadiyne) derivatives would exhibit distinctive resonances for olefinic hydrogen atoms. Furthermore, the cyclobutadiene ring cannot contain any hydrogen substituents since a hydrogen attached to a cyclobutadiene ring such as in $C_5H_5CoC_4H_4$ ¹⁷ would have a distinctive nmr resonance outside the aliphatic CH_2 region. The combination of the nmr indication of only saturated CH_2 (or possibly saturated CH) groups in the cyclobutadiene ligand obtained from the macrocyclic alkadiyne and the determination of the exact composition from the mass spectrum, including particularly the number of hydrogen atoms, demonstrate that the cyclobutadiene ligand in the C_5H_5Co (alkadiyne) derivatives must be a tricyclic system (Table II).

(3) Reactions of $C_5H_5Co(CO)_2$ with the isomeric macrocyclic alkadiynes 1,7-cyclotetradecadiyne (III, *m* = 4, *n* = 6) and 1,8-cyclotetradecadiyne (III, *m* =

n = 5) give distinctly different but yet isomeric products. The more symmetrical $C_5H_5CoC_{14}H_{20}$ (IV, *m* = *n* = 5) derived from the higher melting 1,8-cyclotetradecadiyne (III, *m* = *n* = 5) is a crystalline solid at room temperature, whereas the less symmetrical $C_5H_5CoC_{14}H_{20}$ (IV, *m* = 4, *n* = 6) derived from the lower melting 1,7-cyclotetradecadiyne (III, *m* = 4, *n* = 6) is a liquid at room temperature.

(4) The mass spectra of the C_5H_5Co (alkadiyne) derivatives exhibited a relatively large number (70–100) of ions because of 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.¹⁹ In all of the mass spectra of the C_5H_5Co (alkadiyne) derivatives, the molecular ion was the strongest ion. Only relatively few of the large number of ions had relative intensities of at least ~15% of that of the molecular ion. Besides the molecular ion the relatively intense ions included dehydrogenation products of the ions (alkadiyne) Co^+ as well as the expected simpler fragments $C_5H_5Co^+$ and Co^+ .

The intramolecular reaction of the macrocyclic alkadiynes III with $C_5H_5Co(CO)_2$ to form the C_5H_5Co (alkadiyne) derivatives IV is the first example of the intramolecular cyclization of an alkadiyne with a transition metal to form a cyclobutadiene derivative. This new reaction is very closely related to the reported²⁰ intermolecular dimerization of alkynes $RC\equiv CR'$ with $C_5H_5Co(CO)_2$ to give cyclopentadienylcobalt derivatives of the type $C_5H_5CoC_4R_2R_2'$. The reaction of $C_5H_5Co(CO)_2$ with alkynes of the type $RC\equiv CR'$ is also reported²¹ to give cyclopentadienone derivatives of the type $C_5H_5CoC_4R_2R_2'CO$. However, no derivatives containing the cyclopentadienone system were observed in any of the reactions of the macrocyclic alkadiynes with $C_5H_5Co(CO)_2$.

The 1,5-cyclooctadiene complex $C_5H_5CoC_8H_{12}$ is reported also to react with alkynes (e.g., $C_6H_5C\equiv CC_6H_5$) to form the substituted derivatives of the type $C_5H_5CoC_4R_4$.^{22–24} The macrocyclic alkadiynes 1,7-cyclotri-

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decadiyne (III, $m = 4$, $n = 5$) and 1,8-cyclotetradecadiyne (III, $m = n = 5$) reacted similarly with $C_5H_5CoC_8H_{12}$ to give the corresponding tricyclic cyclobutadiene derivatives IV.

The reaction between 1,8-cyclotetradecadiyne and $C_5H_5Co(CO)_2$ was somewhat anomalous in accord with the likewise anomalously high chemical stability and low heat of combustion of 1,8-cyclotetradecadiyne relative to other macrocyclic alkadiynes.^{10,11} The yield of the tricyclic cyclobutadiene derivative $C_5H_5CoC_{14}H_{20}$ (IV, $m = n = 5$) from 1,8-cyclotetradecadiyne (III, $m = n = 5$) and $C_5H_5Co(CO)_2$ (2 to 4%) was much lower than any other observed yield of a tricyclic cyclobutadiene derivative $C_5H_5Co(alkadiyne)$ (IV) from the corresponding alkadiyne and $C_5H_5Co(CO)_2$ (40–86%). Furthermore, the reaction of 1,8-cyclotetradecadiyne with $C_5H_5Co(CO)_2$ gave, in addition to the monometallic derivative $C_5H_5CoC_{14}H_{20}$ (IV, $m = n = 5$), the trimetallic derivative $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$. Similar trimetallic derivatives were not obtained from reactions of $C_5H_5Co(CO)_2$ with any other of the macrocyclic alkadiynes.

The trimetallic derivative $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ was a relatively air-stable black solid. Its molecular formula was established by complete elemental analyses on two independent preparations. Molecular weight determinations by osmometry in dichloromethane established the trimetallic formula rather than a multiple thereof. An attempt to obtain a mass spectrum of $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ resulted in apparent decomposition; only the mass spectrum of free $C_{14}H_{20}$ (molecular ion m/e 188) was observed. The presence of the complexed $C_{14}H_{20}$ ligand is also established by the presence of the expected three broad aliphatic CH_2 resonances in a 1:2:2 relative intensity ratio in addition to the expected single sharp C_5H_5 resonance. No high-field transition metal hydride resonances were observed.

The most distinctive spectroscopic property of $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ is the strong $\nu(CO)$ frequency at 1655 cm^{-1} in the expected region for a carbonyl group bridging all three cobalt atoms in the triangle. A compound somewhat related to $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ is the reported²⁵ oxygen complex $(C_5H_5)_3Co_3(CO)(O)$ shown by X-ray crystallography to have structure VI with a three-way bridging carbonyl group. The infrared spectrum of the oxygen complex VI exhibits a single infrared $\nu(CO)$ frequency at 1720 cm^{-1} .

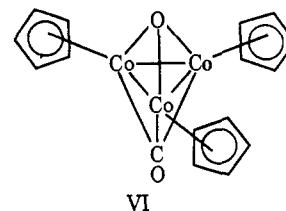
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All of these data on $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ suggest structure V similar to structure VI for the oxo complex $(C_5H_5)_3Co_3(CO)(O)$. In structure V an intact 1,8-cyclotetradecadiyne unit (III, $m = n = 5$) is bonded to the cobalt triangle. The involvement of both carbon-carbon triple bonds in the bonding of 1,8-cyclotetradecadiyne to the cobalt triangle in V is proposed in order to account for the apparent failure to obtain similar complexes from simple alkynes or from the other macrocyclic alkadiynes used in this work, where the different numbers of CH_2 groups bridging the carbon-carbon triple bonds modify the relative positions of the carbon-carbon triple bonds as discussed by Dale, Hubert, and King.¹¹ The formation of the complex $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ (V) from 1,8-cyclotetradecadiyne and $C_5H_5Co(CO)_2$ appears to be the first example of an interaction of an alkadiyne with transition metals which is clearly different from known interactions of simple alkynes with transition metals.³ Furthermore, the complex $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ (V) can be regarded as a derivative of $[C_5H_5CoCO]_3$,²⁶ where each carbon-carbon triple bond in 1,8-cyclotetradecadiyne acts as a monodentate monometallic ligand⁴ by replacing a carbonyl group. The lower frequency (1655 cm^{-1}) of the three-way bridging carbonyl group in the alkadiyne complex $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$ (V) relative to that of the three-way bridging carbonyl group (1720 cm^{-1}) in the oxo complex $(C_5H_5)_3Co_3(CO)(O)$ (VI) may be ration-



alized by the high electronegativity of the oxo oxygen atom in VI relative to the alkadiyne carbon atoms in V. The oxo oxygen atom in VI thus will withdraw electrons from the cobalt atoms in the triangle in complex VI to a much greater extent than the carbon-carbon triple bonds of the coordinated alkadiyne in complex V. This will make the electron density on the cobalt atoms available for retrodonative bonding to the three-way bridging carbon group much less in the oxo complex VI than in the alkadiyne complex V; this difference in retrodonative bonding can account for the difference in the $\nu(CO)$ frequencies.

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