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# REACTIONS OF TRANSITION METAL COMPOUNDS WITH MACROCYCLIC ALKADIYNES

## IV*. INTRAMOLECULAR TRANSANNULAR CYCLIZATIONS WITH CYCLOPENTADIENYLDICARBONYLRHODIUM

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## Summary

The macrocyclic alkadiynes, 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne react with $C_5H_5Rh(CO)_2$ in boiling cyclooctane to give pale yellow to white volatile compounds of the composition $C_5H_5Rh$(alkadiyne) in which the macrocyclic alkadiyne has undergone an intramolecular transannular cyclization to form a tricyclic cyclobutadiene derivative. The reaction of 1,7-cyclododecadiyne with $C_5H_5Rh(CO)_2$ also gives a dimer of 1,7-cyclododecadiyne containing a benzene ring. Corresponding reactions of the simple alkynes $RC{\equiv}CR$ ($R = C_2H_5$ and $C_6H_5$) with $C_5H_5Rh(CO)_2$ in boiling cyclooctane failed to give any rhodium—cyclobutadiene derivatives. Instead the reaction of 3-hexyne with $C_5H_5Rh(CO)_2$ under these conditions gave orange-red $(C_5H_5)_2Rh_2(CO)C_4(C_2H_5)_4$ and purple-black $(C_5H_5)_3Rh_3(CO)(C_2H_5C{\equiv}CC_2H_5)$ and the reaction of diphenylacetylene with $C_5H_5Rh(CO)_2$ gave a low yield of the orange complex $(C_5H_5)_3Rh_3(C_6H_5C{\equiv}CC_6H_5)$. The infrared, $^1H$ NMR, and mass spectra of these new cyclopentadienylrhodium complexes are described.

## Introduction

The first paper of this series [2] reported the reactions of the macrocyclic alkadiynes (I) ($m = 4$, $n = 4,5$, and 6; $m = 5$, $n = 5$ and 6) with $C_5H_5Co(CO)_2$ to give the cyclopentadienylcobalt derivatives of tricyclic cyclobutadienes of the type (II) ($M = Co$, $m = 4$, $n = 4,5$, and 6; $m = 5$, $n = 5$ and 6). In addition,

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[*] For Part III of this series see ref. 1.

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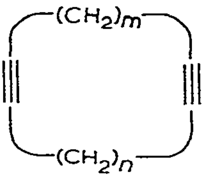
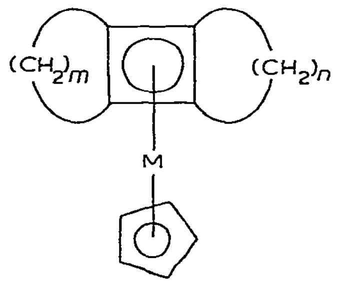
the reaction of 1,8-cyclotetradecadiyne [(I): $m = 5, n = 5$] with $C_5H_5Co(CO)_2$ also gave the black trimetallic cluster compound $(C_5H_5)_3Co_3(C_{14}H_{20})(CO)$.

The reactions of the macrocyclic alkadiynes (I) with $C_5H_5Co(CO)_2$ to give good yields of the cyclobutadiene derivatives (II) (M = Co) made of interest the corresponding reactions of the macrocyclic alkadiynes (I) with the analogous $C_5H_5Rh(CO)_2$ since all previous attempts to prepare simple rhodium cyclobutadiene derivatives of type (III) (M = Rh) from reactions of simple alkynes RC≡CR with $C_5H_5Rh(CO)_2$ have failed [3]. Known cyclobutadiene rhodium derivatives are limited to $C_5H_5RhC_4H_4$ [(III): M = Rh, R = H] obtained [4] from $C_5H_5Rh(CO)_2$ and α-pyrone and $C_5H_5RhC_4(C_6H_5)_4$ [(III): M = Rh, R = $C_6H_5$] obtained [5] in very low yield (≈ 3% or less) from $C_5H_5$-Rh(1,5-$C_8H_{12}$) and molten diphenylacetylene at 180°.

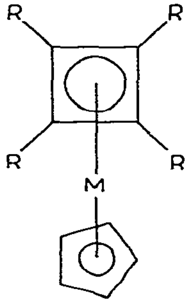
This paper describes the reactions of the macrocyclic alkadiynes (I) ($m = 4$, $n = 4$,5 and 6; $m = 5$, $n = 5$ and 6) with $C_5H_5Rh(CO)_2$ in boiling cyclooctane to give the tricyclic cyclobutadienerhodium derivatives of type (II) (M = Rh; $m = 4$, $n = 4$, 5, and 6; $m = 5$, $n = 5$ and 6) in yields of 15 to 68%. Reactions of $C_5H_5Rh(CO)_2$ with the simple alkynes RC≡CR (R = $C_2H_5$ and $C_6H_5$) under the same conditions (boiling cyclooctane) are also discussed; these reactions failed to give the corresponding cyclobutadiene derivatives $C_5$-$H_5RhC_4R_4$ [(III): R = $C_2H_5$ and $C_6H_5$].



(I)



(II)



(III)

## Experimental

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany; Atlantic Microlab Inc., Atlanta, Georgia; and Mr. W. Swanson and coworkers of the microanalytical laboratory at the University of Georgia. Melting points (Table 1) were taken in capillaries and are uncorrected. Infrared spectra were taken in the indicated media (generally KBr pellets) and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Laser Raman spectra were obtained on a Spex Ramalog instrument using an argon 5145 Å laser. Proton NMR spectra (Table 1) were taken in $CDCl_3$ solutions and recorded at 100 MHz on a Varian HA-100 spectrometer. Mass spectra were taken at 70 eV on a Perkin-Elmer-Hitachi Model RMU-6 mass spectrometer with a 210° chamber temperature.

Commercial rhodium trichloride trihydrate (42.5% rhodium) from Englehard Industries (Newark, New Jersey) was converted to $C_5H_5Rh(CO)_2$ by carbonylation [6] followed by reaction of the intermediate $[Rh(CO)_2Cl]_2$ with thallium cyclopentadienide [7]. The macrocyclic alkadiynes were purchased from Farchan Research Laboratories, Willoughby, Ohio.

*General procedure for isolation of the $C_5H_5Rh$(alkadiyne) derivatives [(II): M = Rh] from reactions of $C_5H_5Rh(CO)_2$ with macrocyclic alkadiynes (Table 1)*

A mixture of 0.3 ml (0.52 g, 2.33 mmoles) of $C_5H_5Rh(CO)_2$, 4.7 to 5.2 mmoles of the macrocyclic alkadiyne (I) and 25 ml of cyclooctane was boiled under reflux for 2 to 3 days. The resulting reaction mixture was chromatographed on a 2 × 50 cm alumina column. The chromatogram was developed with hexane and the cyclooctane eluted with additional hexane. After removal of the cyclooctane, further elution with hexane gave a pale yellow eluate of the $C_5H_5Rh$(alkadiyne) derivative (II) (M = Rh). Evaporation of this eluate at 25°/35 mm. followed by low temperature crystallization of the residue from hexane and a final sublimation at ≈ 55° to 75°/0.1 mm gave the indicated yields (Table 1) of the $C_5H_5Rh$(alkadiyne) derivatives (III) as white to pale yellow air-stable solids. Since the isolation and purification of the $C_5H_5Rh$-(alkadiyne) derivatives (II) (M = Rh) appeared to be somewhat wasteful, the actual amounts of products formed in the reactions of $C_5H_5Rh(CO)_2$ with the macrocylic alkadiynes (I) can be assumed to be somewhat higher than the yield figures given in Table 1. The colors of the $C_5H_5Rh$(alkadiyne) derivatives (II) are so pale that they are not readily observed as bands on the chromatography column.

The analytical data and proton NMR spectra of the $C_5H_5Rh$(alkadiyne) derivatives [(II): M = Rh] are given in Table 1. The following infrared spectra were obtained in KBr pellets:

*A. $C_5H_5RhC_{12}H_{16}$ [(II): M = Rh, m = 4, n = 4].* 2940 (m), 2855 (m), 1434 (m), 1416 (w), 1402 (w), 1337 (w), 1322 (m), 1284 (w), 1228 (m), 1128 (vw), 1104 (m), 1051 (w), 1002 (m), 932 (w), 786 (s), and 765 (w) $cm^{-1}$.

*B. $C_5H_5RhC_{13}H_{18}$ [(II): M = Rh, m = 4, n = 5].* 3110 (vw), 2935 (s), 2870 (m), 2855 (m), 2830 (m), 1438 (s), 1322 (m), 1289 (w), 1227 (m), 1104 (m), 998 (m), 783 (s), and 755 (w) $cm^{-1}$.

*C. $C_5H_5RhC_{14}H_{20}$ [(II): M = Rh, m = 5, n = 5].* 2925 (m), 2870 (vw), 2850 (vw), 2825 (w), 1438 (m), 1426 (vw), 1400 (w), 1350 (w), 1324 (m), 1300 (vw), 1263 (vw), 1227 (m), 1218 (vw), 1104 (m), 1000 (m), 800 (m), and 791 (s) $cm^{-1}$.

*D. $C_5H_5RhC_{14}H_{20}$ [(II): M = Rh, m = 4, n = 6].* 3105 (vw), 2935 (s), 2865 (w), 2850 (w), 2830 (w), 1463 (w), 1446 (w), 1437 (m), 1432 (m), 1417 (m), 1402 (w), 1329 (m), 1321 (m), 1286 (w), 1259 (w), 1249 (vw), 1227 (w), 1200 (vw), 1153 (vw), 1105 (m), 1001 (s), 971 (w), 884 (w), 787 (s), and 733 (w) $cm^{-1}$.

*E. $C_5H_5RhC_{15}H_{22}$ [(II): M = Rh, m = 5, n = 6].* 3110 (vw), 2920 (s), 2870 (m), 2825 (m), 1462 (w), 1442 (m), 1401 (vw), 1349 (w), 1326 (m), 1297 (w), 1252 (w), 1222 (m), 1106 (m), 1000 (m), and 787 (s) $cm^{-1}$.

The following ions were the most abundant in the mass spectra of the

TABLE 1

TRICYCLIC CYCLOBUTADIENE–RHODIUM DERIVATIVES FROM $C_5H_5Rh(CO)_2$ AND MACROCYCLIC ALKADIYNES

| Macrocyclic alkadiyne | Product | Structure[a] | | Yield | M.p. | Analyses | | | Proton NMR ($\tau$)[b] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *m* | *n* | (%) | (°C) | *C* | H | Rh | $C_5H_5$ | $CH_2$ |
| 1, 7-Cyclododecadiyne | $C_5H_5RhC_{12}H_{16}$ | 4 | 4 | 21 | 96 - 98 | 62.3<br>(62.2) | 6.5<br>(6.4) | 31.3<br>(31.4) | 4.93(5) | 7.77(8)<br>≈8.3(8) |
| 1,7-Cyclotridecadiyne | $C_5H_5RhC_{13}H_{18}$ | 4 | 5 | 68 | 82 - 83 | 63.2<br>(63.2) | 6.7<br>(6.8) | 30.1<br>(30.1) | 4.87(5) | ≈7.7(4),<br>≈8.1(10)<br>≈8.4(4) |
| 1,8-Cyclotetradecadiyne | $C_5H_5RhC_{14}H_{20}$ | 5 | 5 | 15 | 128 - 130 | 64.2<br>(64.0) | 7.1<br>(7.1) | 29.0<br>(28.9) | 4.80(5) | ≈8.1(14)<br>≈8.5(6) |
| 1,7-Cyclotetradecadiyne | $C_5H_5RhC_{14}H_{20}$ | 4 | 6 | 55 | 58 - 60 | 64.1<br>(64.0) | 7.1<br>(7.1) | 28.8<br>(28.9) | 4.90(5) | ≈7.9(8)<br>≈8.4(12) |
| 1,8-Cyclopentadecadiyne | $C_5H_5RhC_{15}H_{22}$ | 5 | 6 | 39 | 92 - 94 | 65.0<br>(64.9) | 7.4<br>(7.4) | 28.3<br>(27.8) | 4.83(5) | ≈8.0(8)<br>≈8.5(14) |

[a] See structure (II); M = Rh. [b] The $C_5H_5$ resonances were sharp singlets whereas the $CH_2$ resonances were broad and/or complex multiplets. Relative intensities are given in parentheses.

$C_5H_5Rh$(alkadiyne) derivatives [(II): M = Rh] (relative intensities given in parentheses):

*A. $C_5H_5RhC_{12}H_{16}$ [(II): M = Rh, m = 4, n = 4]*. $C_{17}H_{21}Rh^+$ (100), $C_{17}H_{15}Rh^+$ (95), $C_{12}H_9Rh^+$ (47), $C_{12}H_8Rh^+$ (26), $C_{12}H_7Rh^+$ (18), $C_5H_5Rh^+$ (84), and $Rh^+$ (21).

*B. $C_5H_5RhC_{13}H_{18}$ [(II): M = Rh, m = 4, n = 5].* $C_{18}H_{23}Rh^+$ (100), $C_{16}H_{19}Rh^+$ (14), $C_{16}H_{18}Rh^+$ (26), $C_{13}H_{15}Rh^+$ (14), $C_{13}H_{13}Rh^+$ (19), $C_{13}H_{11}Rh^+$ (30), $C_{13}H_9Rh^+$ (27), $C_{12}H_{14}Rh^+$ (13): $C_5H_5Rh^+$ (37), and $Rh^+$ (15).

*C. $C_5H_5RhC_{14}H_{20}$ [(II): M = Rh, m = 5, n = 5]*. $C_{19}H_{25}Rh^+$ (100), $C_{19}H_{24}Rh^+$ (34), $C_{17}H_{20}Rh^+$ (20), $C_{16}H_{18}Rh^+$ (21), $C_{15}H_{17}Rh^+$ (8), $C_{15}H_{16}Rh^+$ (9), $C_{14}H_{17}Rh^+$ (11), $C_{14}H_{15}Rh^+$ (16), $C_{14}H_{13}Rh^+$ (12), $C_{14}H_{11}Rh^+$ (10), $C_{14}H_{10}Rh^+$ (8), $C_{14}H_9Rh^+$ (9), $C_{14}H_8Rh^+$ (8), $C_{12}H_{14}Rh^+$ (30), $C_{12}H_{12}Rh^+$ (12), $C_5H_5Rh^+$ (17), and $Rh^+$ (11).

*D. $C_5H_5RhC_{14}H_{20}$ [(II): M = Rh, m = 4, n = 6]*. $C_{19}H_{25}Rh^+$ (100), $C_{19}H_{24}Rh^+$ (20), $C_{16}H_{18}Rh^+$ (15), $C_{14}H_{17}Rh^+$ (12), $C_{14}H_{15}Rh^+$ (21), $C_{14}H_{13}Rh^+$ (22), $C_{14}H_{11}Rh^+$ (23), $C_{14}H_9Rh^+$ (14), $C_{11}H_{12}Rh^+$ (17), $C_5H_5Rh^+$ (35), $Rh^+$ (18).

*E. $C_5H_5RhC_{15}H_{22}$ [(II): M = Rh, m = 5, n = 6].* $C_{20}H_{27}Rh^+$ (100), $C_{20}H_{26}Rh^+$ (29), $C_{17}H_{20}Rh^+$ (33), $C_{15}H_{17}Rh^+$ (21), $C_{15}H_{15}Rh^+$ (17), $C_{12}H_{14}Rh^+$ (25), $C_5H_5Rh^+$ (32), and $Rh^+$ (18).

*Other products from reactions of $C_5H_5Rh(CO)_2$ with the macrocyclic alkadiynes*

*A. Dimer of 1,7-Cyclododecadiyne.* The reaction of $C_5H_5Rh(CO)_2$ with 1,7-cyclododecadiyne [(I): *m* = 4, *n* = 4] gave the cyclobutadiene complex $C_5H_5RhC_{12}H_{16}$ [(II): M = Rh, *m* = 4, *n* = 4] which was eluted from the chromatogram with hexane as described above. After removal of the $C_5H_5RhC_{12}H_{16}$ further elution of the chromatogram with 1/4 dichloromethane/hexane followed by evaporation of this eluate gave a pale yellow solid. Low temperature crystallization of this product from hexane gave 0.155 g (≈ 19% yield based on the 0.827 g of 1,7-cyclododecadiyne used for the reaction) of white crystalline $C_{24}H_{32}$, m.p. 147 - 149°. (Found: C, 89.3; H, 10.1. $C_{24}H_{32}$ calcd.: C, 89.9; H, 10.1%.)

Infrared spectrum (KBr pellet): 2934 (s), 2867 (m), 2841 (w), 1466 (m), 1448 (m), 1434 (w), 1426 (m), 1400 (w), 1338 (w), 1312 (vw), 1284 (vw), 1278 (vw), 1256 (w), 1241 (vw), 1193 (w), 1138 (vw), 1097 (vw), 1062 (vw), 1052 (vw), 981 (vw), 966 (vw), 957 (vw), 857 (vw), 835 (vw), 828 (vw), 755 (vw), 738 (vw), and 677 (vw) $cm^{-1}$.

Raman spectrum: Apparent $\nu(C{\equiv}C)$ at 2323 (w) and 2245 (m) $cm^{-1}$.

Ultraviolet spectrum: Maxima at 209 nm ($\epsilon$ 43,000) and 273 nm ($\epsilon$ 510) in cyclohexane solution.

Proton NMR spectrum: Broad ill-defined resonances at $\tau \approx 7.2$, $\approx 7.4$, $\approx 7.7$, and $\approx 8.1$ of approximate relative intensities 2/1/1/4.

Mass spectrum: The following ions were the most abundant in the mass spectrum of $C_{24}H_{32}$: $C_{24}H_{32}^+$, $C_{17}H_{25}^+$, $C_{14}H_{19}^+$, $C_{14}H_{18}^+$, $C_{13}H_{17}^+$, $C_{12}H_{16}^+$, $C_{12}H_{15}^+$, $C_{11}H_{17}^+$, $C_{11}H_{13}^+$, $C_{10}H_{12}^+$, $C_{10}H_{11}^+$, $C_9H_9^+$, $C_9H_7^+$, $C_8H_9^+$, $C_8H_8^+$, $C_7H_7^+$, $C_6H_{14}^+$ and/or $C_7H_2^+$, $C_6H_7^+$, $C_6H_6^+$, $C_6H_5^+$, $C_5H_{11}^+$, $C_5H_9^+$, $C_4H_9^+$, $C_4H_8^+$, $C_4H_7^+$, $C_3H_5^+$, $C_3H_3^+$.

*B. Orange* $(C_5H_5)_2Rh_2(C_{14}H_{20})_3(CO)_n$ *from 1,8-cyclotetradecadiyne.* After removal of $C_5H_5RhC_{14}H_{20}$ [(II): M = Rh, $m = 5$, $n = 5$] and unreacted 1,8-cyclotetradecadiyne from the alumina chromatogram obtained from the reaction between $C_5H_5Rh(CO)_2$ and 1,8-cyclotetradecadiyne, further development and elution with 2/1 dichloromethane/hexane gave a low yield ($\approx$ 3% maximum) of an orange product of stoichiometry $(C_5H_5)_2Rh_2(C_{14}H_{20})_3(CO)_n$ which was purified by rechromatography and low temperature crystallization from hexane. The limited quantity available prevented its detailed characterization. (Found: C, 67.5; H, 7.5; O, 3.0; Rh, 24.4. Mol. wt., 960 (acetone). $C_{54}H_{70}O_2Rh_2$ ($n = 2$) calcd.: C, 67.8; H, 7.3; O, 3.3; Rh, 21.6. Mol wt., 956. $C_{53}H_{70}ORh_2$ ($n = 1$) calcd.: C, 68.5; H, 7.5; O,1.7; Rh, 22.2%. Mol. wt., 928.)

Infrared spectrum: $\nu$(CO) at 1662 (s) $cm^{-1}$ (KBr).

Proton NMR spectrum: Singlet $C_5H_5$ resonance at $\tau$ 4.81; complex aliphatic $CH_2$ region with peaks at $\tau$ 7.3, 7.4, 7.8, and 8.4 with the last resonance corresponding to about 70% of the total $CH_2$ area.

*C. Purple apparently trimetallic products.* The chromatograms from all of the reactions between $C_5H_5Rh(CO)_2$ and the five macrocyclic alkadiynes used in this work contained variable but small amounts of a relatively strongly adsorbed purple material which, after removing all of the less strongly adsorbed materials from the chromatogram, was eluted with dichloromethane sometimes containing tetrahydrofuran. These products exhibited a strong $\nu$(CO) frequency around 1685 $cm^{-1}$. Analytical data were consistent with the stoichiometry $(C_5H_5)_3Rh_3(C_8H_{12})_3(CO)_2$ suggesting that these products originate from the cyclooctane solvent. $C_{41}H_{51}O_2Rh_3$ [i.e. $(C_5H_5)_3Rh_3(C_8H_{12})_3(CO)_2$] calcd.: C, 55.7; H, 5.8; O, 3.6; Rh, 35.0%.

Found on product from 1,7-$C_{12}H_{16}$: C, 56.9; H, 6.1%. Found on product from 1,8-$C_{14}H_{20}$: C, 56.1; H, 6.0; O, 4.0%. Found on product from 1,8-$C_{15}H_{22}$: C, 55.7; H, 6.1; O, 3.9; Rh, 35.9%.

### *Reaction of* $C_5H_5Rh(CO)_2$ *with 3-hexyne in boiling cyclooctane*

A mixture of 0.30 ml (0.52 g, 2.33 mmoles) of $C_5H_5Rh(CO)_2$, 0.60 ml (0.43 g, 5.3 mmoles) of 3-hexyne, and 25 ml of cyclooctane was boiled under reflux for 69 h. The reaction mixture was chromatographed on a 2 X 50 cm alumina column. After elution of the cyclooctane the following identifiable products were isolated from the chromatogram in the order indicated:

*A. Yellow* $C_5H_5Rh(1,5\text{-}C_8H_{12})$ *(0.02 g, ≈ 3% yield).* Eluted with hexane and purified by sublimation at 25°/0.1 mm. Identified by melting point (found 105 - 106°; lit. [8] m.p. 107 - 108°), mass spectrum (molecular ion at *m/e* 276), and proton NMR spectrum.

*B. Red-orange* $(C_5H_5)_2Rh_2(CO)C_4(C_2H_5)_4$ *(0.101 g, 16% yield), m.p. 258 - 260°.* Eluted with 1/2 hexane/dichloromethane and purified by rechromatography and recrystallization from a mixture of dichloromethane and hexane. (Found: C, 52.0; H, 5.8; O, 3.4; Rh, 39.5. Mol. wt., 557 (acetone). $C_{23}H_{30}ORh_2$ calcd.: C, 52.3; H, 5.7; O, 3.0; Rh, 39.0%. Mol. wt., 528.)

Infrared spectrum: $\nu$(CO) at 1645 (s) $cm^{-1}$ (KBr).

Proton NMR spectrum: Resonances at $\tau$ 4.76 (singlet), $\tau$ 7.19 (multiplet), $\tau \approx$ 8.0 (broad), $\tau$ 8.84 (triplet, $J$ 7 Hz), and $\tau$ 9.04 (triplet, $J$ 7 Hz) of approximate relative intensities 10/4/4/6/6, respectively.

*C. Purple-black* $(C_5H_5)_3Rh_3(CO)(C_2H_5C{\equiv}CC_2H_5)$ *(0.118 g, 25% yield), m.p. 201 - 203°.* Eluted with 50/100/3 hexane/dichloromethane/tetrahydrofuran and purified by rechromatography and washing with hexane. (Found: C, 43.1; H, 4.1; O, 3.1; Rh, 51.7. Mol. wt., 594 ($CHCl_3$). $C_{22}H_{25}ORh_3$ calcd.: C, 43.0; H, 4.1; O, 2.6; Rh, 50.3%. Mol. wt., 614.)

Infrared spectrum: $\nu$(CO) at 1685 (s) $cm^{-1}$ (KBr).

Proton NMR spectrum: Resonances at $\tau$ 4.74 (singlet), $\tau$ 7.28 (quartet, $J$ 7 Hz), and $\tau$ 8.84 (triplet, $J$ 7 Hz) of approximate relative intensities 15/4/6, respectively.

*Reaction of* $C_5H_5Rh(CO)_2$ *with diphenylacetylene in boiling cyclooctane*

A mixture of 0.30 ml (0.52 g, 2.33 mmoles) of $C_5H_5Rh(CO)_2$, 0.89 g (5.0 mmoles) of diphenylacetylene, and 25 ml of cyclooctane was boiled under reflux for 48 h. Chromatography of the reaction mixture gave after removal of the cyclooctane some $C_5H_5RhC_8H_{12}$ (0.152 g, 24% yield) followed by *trans*-stilbene (0.02 g, 2% yield) and then 0.017 g (3% yield) of orange crystalline $(C_5H_5)_3Rh_3(C_6H_5C{\equiv}CC_6H_5)$, m.p. 232 - 233°. (Found: C, 50.8; H, 3.6; Rh, 45.0; O, 0.7. Mol. wt., 667 (acetone). $C_{29}H_{25}Rh_3$ calcd.: C, 51.1; H, 3.7; Rh, 45.4; O, 0.0%. Mol. wt., 682).

Infrared spectrum (KBr pellet): No $\nu$(CO) frequencies; other bands at 1580 (w), 1472 (w), 1432 (w), 1407 (w), 1340 (w), 1256 (vw), 1167 (vw), 1103 (w), 1053 (vw), 1027 (vw), 1007 (w), 996 (w), 922 (vw), 903 (vw), 830 (m), 790 (s), 769 (vw), 725 (m), 692 (s), and 670 (w) $cm^{-1}$.

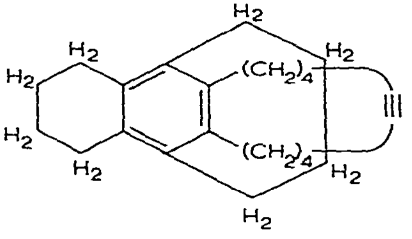
Proton NMR spectrum: Resonances at $\tau$ 2.35 (multiplet: 4 discernible lines), $\tau$ 2.85 (multiplet: 4 discernible lines), and $\tau$ 4.95 (singlet) of relative intensities 4/6/15, respectively.

## Discussion

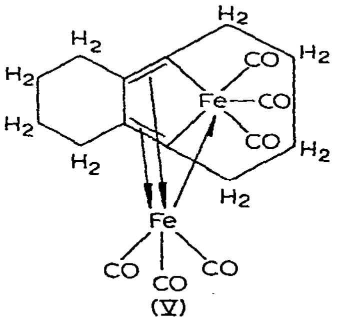
Each of the macrocyclic alkadiynes studied in this work reacted with $C_5H_5Rh(CO)_2$ in boiling cyclooctane to give a volatile air-stable white to pale yellow solid of the stoichiometry $C_5H_5Rh$(alkadiyne) with complete loss of both carbonyl groups. These compounds are formulated as the tricyclic cyclobutadiene—rhodium derivatives (II) (M = Rh, $m = 4$, $n = 4$, 5, and 6; $m = 5$, $n = 5$ and 6) on the basis of the similarity of their physical and spectroscopic properties (e.g. infrared, proton NMR, and mass spectra) to those of the corresponding cobalt derivatives [2] (II) (M = Co; $m = 4$, $n = 4$, 5 and 6; $m = 5$, $n = 5$ and 6). In all cases the rhodium derivatives (II) had higher melting points than the corresponding cobalt derivatives. In the cases of both the cobalt and rhodium derivatives (II) the compounds from 1,8-cyclotetradecadiyne [(I): $m = 5$, $n = 5$] had the highest melting points and the compounds from 1,7-cyclotetradecadiyne [(I): $m = 4$, $n = 6$] had the lowest melting points with intermediate melting points for the remaining three types of compounds. The cyclopentadienyl NMR chemical shifts of both the cobalt and rhodium series of tricyclic cyclobutadiene derivatives (II) decreased consistently in the sequence $C_5H_5MC_{12}H_{16}$ [(II): $m = 4$, $n = 4$] > $C_5H_5MC_{14}H_{20}$ [(II): $m = 4$, $n = 6$] > $C_5H_5MC_{13}H_{18}$ [(II): $m = 4$, $n = 5$] > $C_5H_5MC_{15}H_{22}$ [(II): $m = 5$, $n = 6$] > $C_5H_5MC_{14}H_{20}$ [(II): $m = 5$, $n = 5$] indicating that the effectiveness of a

$(CH_2)_n$ bridge between adjacent carbons on the cyclobutadiene ring in compounds of the type (II) in shielding the opposite cyclopentadienyl ring decreases in the sequence $n = 4$ (most effective) $> n = 6 > n = 5$ (least effective).

The reaction of 1,7-cyclododecadiyne [(I): $m = 4$, $n = 4$] with $C_5H_5Rh(CO)_2$ besides giving the tricyclic cyclobutadiene derivative $C_5H_5RhC_{12}H_{16}$ [(II):$m = 4$, $n = 4$] also gave a colorless crystalline hydrocarbon indicated by its elemental analyses and mass spectrum to be a dimer of 1,7-cyclododecadiyne of stoichiometry $C_{24}H_{32}$. The proton NMR spectrum of this $C_{24}H_{32}$ hydrocarbon exhibited only resonances in the range $\tau$ 7.2 to 8.2 which can be assigned to various kinds of saturated $CH_2$ groups. The ultraviolet spectrum of this $C_{24}H_{32}$ hydrocarbon exhibited maxima at 210 and 273 nm suggesting the presence of a benzenoid ring. The laser Raman spectrum of this $C_{24}H_{32}$ hydrocarbon exhibited bands at 2323 and 2245 $cm^{-1}$ which can be assigned to $\nu(C{\equiv}C)$ frequencies; this assignment is supported by the presence of similar bands in the Raman spectra of 3-hexyne and 1,7-cyclotetradecadiyne but their absence in the Raman spectrum of cyclohexane. These data are consistent with the formulation of the hydrocarbon $C_{24}H_{36}$ as a dimer of 1,7-cyclodecadiyne in which three of the four available triple bonds have cyclized to form a benzene ring without involving the fourth triple bond. Such a dimerization of 1,7-cyclododecadiyne [(I): $m = 4$, $n = 4$] can take place without carbon—carbon bond cleavage to form a dimer of structure (IV); however, in view of the recent demonstration by X-ray crystallography [10] that the $C_{12}H_{16}Fe_2(CO)_6$ product from $Fe_3(CO)_{12}$ and 1,7-cyclododecadiyne [1] does not have structure (V), which can be formed from 1,7-cyclododecadiyne without carbon—carbon bond cleavage, but instead structure (VI), which requires carbon—carbon bond cleavage for formation from 1,7-cyclododecadiyne, structure (VII) must be regarded as at least equally probable to structure (IV) for the dimer of 1,7-cyclododecadiyne obtained in this work.



(IV)



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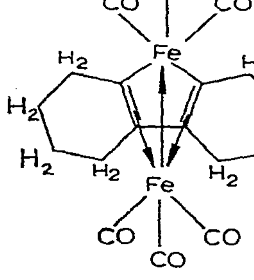

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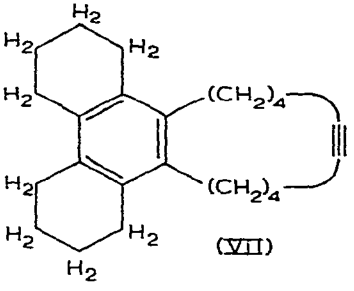
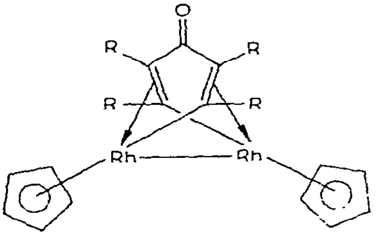


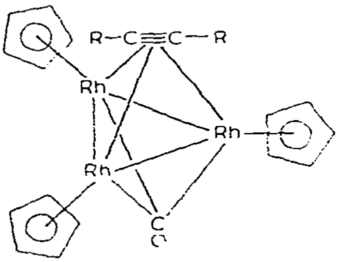
(VII)

The reaction of 1,8-cyclotetradecadiyne [(I): $m = 5, n = 5$] with $C_5H_5Rh(CO)_2$ besides giving the tricyclic cyclobutadiene derivative $C_5H_5RhC_{14}H_{20}$ [(II): $m = 5, n = 5$] also gave a low yield of an orange to red-orange product of approximate stoichiometry $(C_5H_5)_2Rh_2(C_{14}H_{20})_3(CO)_n$ ($n = 1$ or 2). The small quantities of this orange compound coupled with possible complexities in the organic portion of the molecule prevented the complete elucidation of its structure. This orange product exhibited a single strong $\nu(CO)$ frequency at 1662 $cm^{-1}$ which is reasonably close to the 1643 $cm^{-1}$ $\nu(CO)$ frequency reported [11] for the likewise orange-red complex $(C_5H_5)_2Rh_2(CO)C_4(CF_3)_4$ [(VIII): $R = CF_3$] obtained from hexafluoro-2-butyne and $C_5H_5Rh(CO)_2$. We therefore feel that $n$ in $(C_5H_5)_2Rh_2(C_{14}H_{20})_3(CO)_n$ is probably one and that the bonding of the rhodium atoms to the organic ligands in this molecule is probably similar to that in the complexes (VIII); however, spectroscopic techniques provide insufficient information for elucidation of the structure of the organic portion of $(C_5H_5)_2Rh_2(C_{14}H_{20})_3(CO)_n$.

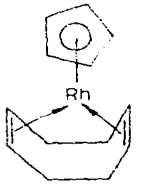
All of the reactions of the macrocyclic alkadiynes (I) with $C_5H_5Rh(CO)_2$ in boiling cyclooctane also gave low and erratic yields of purple complexes exhibiting a single strong $\nu(CO)$ frequency around 1685 $cm^{-1}$. This suggests formulation of these purple complexes as trimetallic $(C_5H_5)_3Rh_3(CO)$(alkyne) derivatives (IX) particularly since the reported [11] hexafluorobutyne complex $(C_5H_5)_3Rh_3(CO)(CF_3C{\equiv}CCF_3)$ is purple and exhibits a single strong $\nu(CO)$ frequency at 1710 $cm^{-1}$. All of the purple complexes from the macrocyclic alkadiynes (I) and $C_5H_5Rh(CO)_2$ are indistinguishable by spectroscopic techniques and analyses, the latter suggesting a stoichiometry $(C_5H_5)_3Rh_3(C_8H_{12})_3(CO)_2$. These observations as well as the observation of an apparently similar purple product from reactions of $C_5H_5Rh(CO)_2$ and 1,3-cyclooctadiene or cyclooctane in the absence of macrocyclic alkadiynes suggest that these purple products arise from interaction of $C_5H_5Rh(CO)_2$ with the cyclooctane solvent without involving the macrocyclic alkadiyne.



(VIII)



(IX)

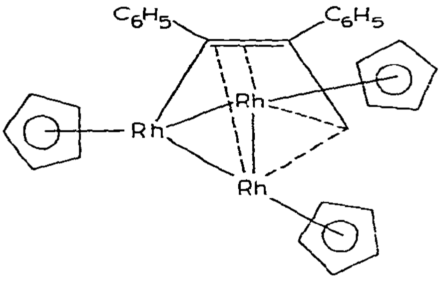


(X)

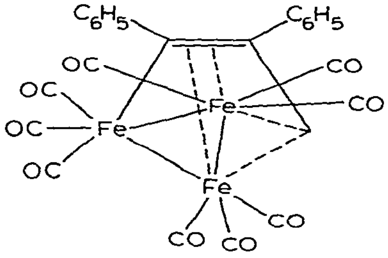
The success in obtaining the tricyclic cyclobutadiene rhodium derivatives (II) ($M = Rh$) from reactions of the macrocyclic alkadiynes (I) with $C_5H_5Rh(CO)_2$ contrasts with the failure [3] to obtain simple cyclopentadienylrhodium cyclobutadiene derivatives of type (III) ($M = Rh$) from reactions of simple alkynes $RC{\equiv}CR$ with $C_5H_5Rh(CO)_2$. Indeed, the only recorded example of the cyclodimerization of an alkyne in the presence of a rhodium compound to give a cyclobutadiene—rhodium derivative is the formation of $C_5H_5RhC_4(C_6H_5)_4$ [(III): $M = Rh$, $R = C_6H_5$] in yields of 3% and less from reaction of the

1,5-cyclooctadiene complex $C_5H_5RhC_8H_{12}$ (X) with diphenylacetylene [5]. In order to see whether the use of boiling cyclooctane as a solvent would promote formation of cyclobutadiene—rhodium derivatives from simple alkynes as well as the macrocyclic alkadiynes, (I), we investigated reactions of 3-hexyne (diethylacetylene) and diphenylacetylene with $C_5H_5Rh(CO)_2$ in boiling cyclooctane. However, identifiable quantities of the corresponding cyclobutadiene derivative $C_5H_5RhC_4R_4$ were not isolated from either of these reactions.

The reaction of 3-hexyne with $C_5H_5Rh(CO)_2$ in boiling cyclooctane gave red-orange $(C_5H_5)_2Rh_2(CO)C_4(C_2H_5)_4$ [(VIII): $R = C_2H_5$] and purple-black $(C_5H_5)_3Rh_3(CO)(C_2H_5CC{\equiv}CC_2H_5)$ [(IX): $R = C_2H_5$] as the only products containing 3-hexyne units. These compounds appear to be completely analogous to previously reported [11] compounds (VIII) ($R = CF_3$) and (IX) ($R = CF_3$) obtained from hexafluoro-2-butyne and $C_5H_5Rh(CO)_2$. The reaction of diphenylacetylene with $C_5H_5Rh(CO)_2$ in boiling cyclooctane did not appear to give products of types (VIII) and (IX). Instead a low yield of an orange crystalline carbonyl-free complex of stoichiometry $(C_5H_5)_3Rh_3(C_6H_5\text{-}C{\equiv}CC_6H_5)$ was obtained. The analogy between $C_5H_5Rh$ and $Fe(CO)_3$ units, both of which lack four electrons of the favored rare gas electronic configuration [12] suggests structure (XI) for the rhodium complex $(C_5H_5)_3Rh_3(C_6H_5\text{-}C{\equiv}CC_6H_5)$ analogous to the structure (XII) demonstrated by X-ray crystallography [13] for the iron complex $(C_6H_5C{\equiv}CC_6H_5)Fe_3(CO)_9$. This compound $(C_5H_5)_3Rh_3(C_6H_5C{\equiv}CC_6H_5)$ was independently obtained in likewise low yield from $C_5H_5Rh(CO)_2$ and diphenylacetylene in boiling xylene [14].



(XI)



(XII)

The reactions of $C_5H_5Rh(CO)_2$ with the simple alkynes $RC{\equiv}CR$ ($R = C_2H_5$ and $C_6H_5$) in boiling cyclooctane also gave some of the yellow 1,5-cyclooctadiene complex $C_5H_5RhC_8H_{12}$ (X) apparently arising from the cyclooctane solvent. This further demonstrates the great ease of formation of 1,5-cyclooctadiene—rhodium complexes in accord with the previously observed [15] reaction of 1,3-cyclooctadiene with hydrated rhodium trichloride to give the 1,5-cyclooctadiene complex $(C_8H_{12}RhCl)_2$.

The most striking feature of the present work is the demonstrated ability for the macrocyclic alkadiynes (I) to undergo intramolecular transannular cyclization in the presence of rhodium compounds to form cyclobutadiene—rhodium derivatives under conditions where simple alkynes do not undergo the corresponding intermolecular dimerization to give cyclobutadiene—rhodium derivatives. This represents one of the most dramatic influences of the geometry of the macrocyclic rings in (I) on the chemistry of their interactions with transition metal derivatives which has been observed up to the present time.

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