720 *Organometallics* 1983, 2, 720–725

Cumulenes as Ligands. Synthesis and Properties of π Complexes of Substituted Butatrienes with Rhodium. X-ray Crystal Structure of Bis(triphenylphosphine)chloro[1,1,2,2-tetramethyl-3-(3-methyl-1,2-butadienylidene)cyclopropane]rhodium

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Received November 23, 1982

The interaction of four butatrienes with chlorotris(triphenylphosphine)rhodium produced several new π complexes. All of the complexes are air-stable, crystalline solids, although they are slightly oxygen sensitive in solution. The IR spectra of these complexes show a band between 2205 and 2235 cm^{-1}, attributable to the cumulenic absorption, and all other spectra are consistent. An X-ray crystal structure determination of bis(triphenylphosphine)chloro[1,1,2,2-tetramethyl-3-(3-methyl-1,2-butadienylidene)cyclopropane]rhodium was undertaken to confirm the structural assignments. This complex crystallizes in the monoclinic space group $P2_1/c$, with a = 14.234 (2) Å, b = 11.105 (1) Å, c = 27.287 (12) Å, β = 92.86 (2)°, and Z = 4. The X-ray study clearly shows the η^2-butatriene ligand occupying the position trans to the chloride, oriented perpendicular to the rhodium coordination plane and π bound to the metal using the central olefin bond. The cyclopropane ring of the ligand is intact. The complexes were subjected to hydrogenation conditions, but the unsaturated linkage was not hydrogenated. Carbon monoxide readily displaced the butatrienes from the complexes. These results are discussed in detail.

Compounds with cumulated double bonds have been of interest to organic chemists since the first reports of allenes nearly a century ago.[1] Since then, the chemistry of allenes has grown to a large body of information,[2] with higher homologues comprising a much smaller portion of the data.[3] The transition-metal organometallic chemistry of the cumulenic linkage is limited to a handful of examples, despite the fact that there is a variety of ways to attach a cumulene ligand to a metal. Three simple modes are carbene 1, η^1-allenyl (cumulenyl), 2, and η^2-olefin, 3. To our knowledge, only four examples of allenylidene carbene complexes exist,[4] while higher homologues have not been reported. There are a few examples of η^1-allenyl complexes[5] but only two reports of η^1-butatrienyl complexes.[6]

The π-complex chemistry of allenes, the simplest cumulenes, is fairly extensive and has been reviewed.[7] There are several reports of butatrienes π bound to metals, but many involve binuclear complexes, usually with bonding modes other than η^2.[8] The examples of mononuclear π complexes of butatrienes include a (η^2-butatriene)(η^5-cyclopentadienyl)dicarbonyliron cation (4),[9] tetracarbonyl(η^2-tetraphenylbutatriene)iron (5),[10] and some diquinoethylene complexes of rhodium (6, 7).[11] Two of these complexes have had their structures determined by X-ray diffraction.[11,12] Tetracarbonyl(tetra-*tert*-butylhexapentaene)iron (8) has also been reported.[13] We wish to report a high-yield synthesis of some new η^2-butatriene complexes of rhodium, three of which have a cyclopropane ring as an integral part of the ligand, as well as an X-ray diffraction determination of the structure of one of these complexes.

Results and Discussion

The interaction of butatrienes 9–12 with an equivalent of Wilkinson's catalyst, chlorotris(triphenylphosphine)-

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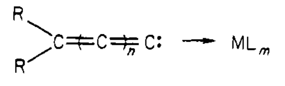
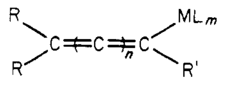
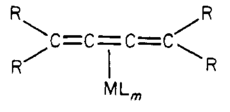

$R_2C{=}(C{=})_nC{:} \rightarrow ML_m$

1, n = 0, 1, ..., ∞



2, n = 0, 1, ..., ∞



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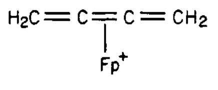
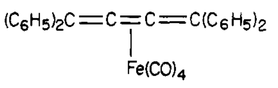
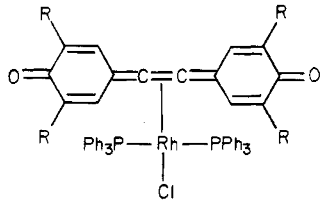

$H_2C{=}C{=}C{=}CH_2$ (Fp^+)

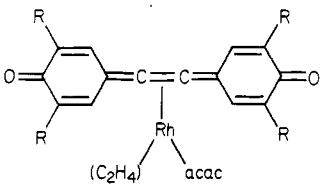
4, Fp = $C_5H_5Fe(CO)_2$


$(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2$ ($Fe(CO)_4$)

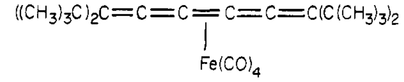
5



6a, R = isopropyl
b, R = *tert*-butyl



7a, R = isopropyl
b, R = *tert*-butyl


$((CH_3)_3C)_2C{=}C{=}C{=}C{=}C{=}C(C(CH_3)_3)_2$ ($Fe(CO)_4$)

8

rhodium (**13**), in benzene led to the isolation of four new complexes, initially assigned the structures **14**–**17** by analogy to **4**–**7** (Scheme I).

The complexes **14**–**17** are all yellow, air-stable crystalline solids, and the yields are uniformly good. Reaction times for their formation are fairly short and conditions mild, with the exception of **14**, which required several hours at benzene reflux. These compounds exhibit some sensitivity on long exposure to air in solution but can be isolated by chromatography on unactivated silica gel using $CHCl_3$/CCl_4 mixtures where no particular care has been taken to exclude air or water. Again, the exception is complex **14**, which could not be chromatographed, and had to be crystallized from $CHCl_3$. Table I summarizes the spectral data for complexes **14**–**17**.

The IR spectra of complexes **15**–**17** reveal the existence of a medium-strength, broad band in the region of 2205–2235 cm^{-1}, which we attribute to the cumulene stretch in the complexed ligand. This amounts to a shift of 140–180 cm^{-1} to higher energy compared to the uncomplexed butatriene; for example, **11** has a cumulene absorption at 2055 cm^{-1}, while complex **16** has a band at 2230 cm^{-1}. This band has not been reported in previous examples, perhaps due to the high symmetry of the cumulenes used in earlier studies.

The ^{1}H NMR spectra of complexes **15**–**17** show that the rhodium is attached in such a manner that it causes otherwise equivalent methyls to become nonequivalent. Complex **15** shows this most clearly—the four methyls on the cyclopropane ring of the ligand are split into two pairs ($CDCl_3$, δ 0.57, 0.90) and the isopropylidene methyls are also differentiated ($CDCl_3$, δ 1.27, 1.67). The nearness of the methyls to rhodium also causes a significant upfield shift of these groups compared to the starting cumulene. Thus, in **10** the cyclopropane methyls are at δ 1.26, and the isopropylidene methyls are at δ 1.93 in $CDCl_3$. It is therefore clear that in **15**, the methyls on the same side as the rhodium ("*Z*-like") are at the higher field positions, while the others ("*E*-like") are closer to the shifts in the starting butatriene. A further confirmation of the structure comes from the fast atom bombardment (FAB) mass spectra of complexes **15** and **16** that show peaks at *m/z* 789 and 914, respectively, which are assigned to the molecular ions of these complexes, minus chloride. The details of the FAB mass spectra of complexes **15** and **16** have been recently discussed.[14]

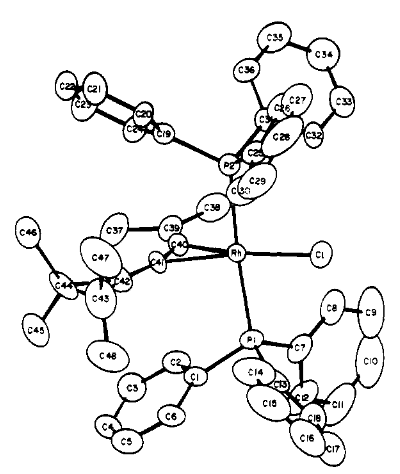
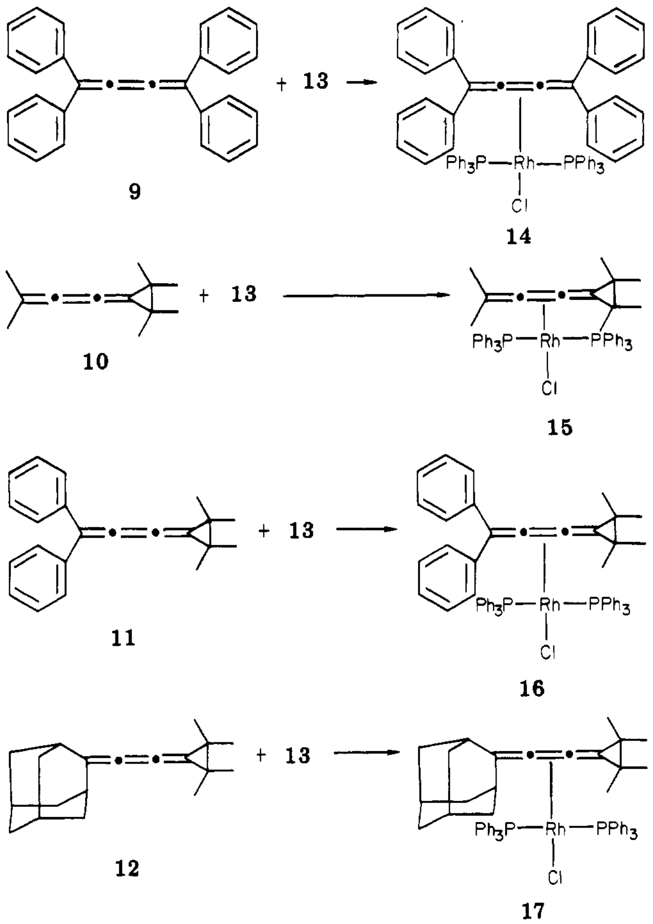


Figure 1. Perspective view of complex **15** with atom numbering given. Only non-hydrogen atoms are shown.

Scheme I



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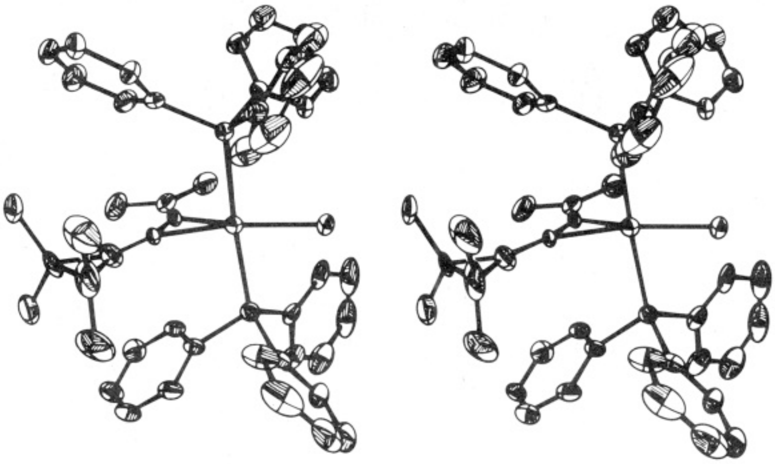


Figure 2. A stereoscopic view of complex **15**. The hydrogen atoms have been omitted for clarity.

Table I. Properties of (Cumulene)rhodium Complexes 14–17

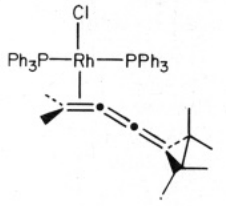
compd	yield,[a] %	mp,[b] °C	IR[c] ν_{max}, cm^{-1}	^{1}H NMR[d] δ (H's, mult)	MS, m/z
14	69.7	243–246	3055, 2985, 1480, 1435, 1090, 770, 755, 700	7.0–7.8 (complex m)	
15	73.8	167–169	3050, 2900, 2860, 2205, 1480, 1430, 1095, 745, 695	0.57 (6, s), 0.90 (6, s), 1.27 (3, s), 1.67 (3, s), 7.2–7.8 (30, m)	789
16	72.7	178–179.5	3055, 2910, 2860, 2230, 1480, 1435, 1095, 745, 700	0.57 (6, s), 0.90 (6, s), 6.7–7.9 (40, m)	913
17	90.0	153–155	3050, 2990, 2900, 2850, 2235, 1840, 1480, 1430, 1095, 915, 745, 695	0.61 (6, s), 0.74 (6, s), 1.00–1.66 (12, complex m), 2.58 (1, s), 3.47 (1, s), 7.13–7.87 (30, m)	

[a] Isolated yield. [b] All decomposing. [c] KBr pellet. [d] $CDCl_3$, Me_4Si internal standard.

Table II. Crystal Data of 15

formula	$C_{48}H_{48}ClP_2Rh$
fw	825.22
a, Å	14.234 (2)
b, Å	11.105 (1)
c, Å	27.287 (12)
β, deg	92.86 (2)
space group	$P2_1/c$
Z	4
D_{calcd}, g cm^{-3}	1.272
μ(Mo Kα), cm^{-1}	5.546

While the existence of sets of methyls with different shifts in the ^{1}H NMR spectrum suggests that the rhodium is bound analogously to that in complexes **3** and **4**, it does not conclusively prove the position of the metal. Structures such as **18** or **19** are ruled out by the two methyl singlets at δ 1.27 and 1.67 in complex **15**, but the possibility of an oxidative addition of the rhodium into one cyclopropane bond (**20**) could explain the spectral data. Indeed, many group 8 metal complexes oxidatively insert into the ring bonds of cyclopropane[15] and substituted cyclopropanes,[16] as well as methylenecyclopropanes[17] and vinylcyclopropanes.[18] In order to unambiguously assign the structure as well as the exact geometry of these complexes, we determined the X-ray crystal structure of compound **15** as a representative member of the series.



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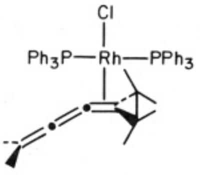

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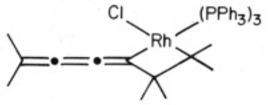

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The results of the X-ray diffraction study on complex **15** are summarized in Tables II–VIII. An ORTEP drawing and stereoview of complex **15** is given in Figures 1 and 2, respectively. Table II gives crystal data, Table III gives the final coordinates of the non-hydrogen atoms, and Table IV gives bond lengths and angles. The remaining tables are available as supplementary material: Table V lists the hydrogen positions, Table VI gives the thermal parameters for the heavy atoms, Table VII shows some selected torsion angles, and Table VIII is a listing of observed and calculated structure factors.

Several features of the structure of **15** deserve mention. The coordination about rhodium can be described as

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Table III. Final Coordinates ($\times 10^4$) of Non-Hydrogen Atoms in 15[a]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Rh	2914.7 (4)	1985.4 (6)	1569.5 (2)	C23	1931 (6)	−99 (12)	−180 (4)
Cl	4370 (2)	2536 (3)	1969 (1)	C24	2402 (5)	114 (10)	281 (3)
P1	2185 (1)	2738 (2)	2248 (1)	C25	4729 (5)	2122 (7)	767 (3)
P2	3740 (1)	1181 (2)	927 (1)	C26	5578 (5)	1673 (7)	643 (3)
C1	907 (5)	2894 (6)	2195 (3)	C27	6276 (7)	2446 (10)	501 (4)
C2	342 (5)	1865 (6)	2179 (3)	C28	6114 (9)	3652 (10)	464 (4)
C3	−626 (5)	1966 (8)	2115 (3)	C29	5306 (9)	4115 (9)	595 (4)
C4	−1044 (6)	3064 (8)	2071 (3)	C30	4578 (8)	3366 (9)	754 (4)
C5	−495 (6)	4085 (7)	2082 (4)	C31	4244 (4)	−299 (6)	1081 (3)
C6	475 (5)	3993 (7)	2151 (3)	C32	4599 (5)	−503 (7)	1553 (3)
C7	2327 (6)	1826 (7)	2810 (3)	C33	4971 (5)	−1630 (8)	1686 (3)
C8	2999 (7)	955 (8)	2842 (3)	C34	4968 (7)	−2528 (8)	1355 (4)
C9	3115 (8)	208 (9)	3285 (5)	C35	4625 (8)	−2323 (8)	880 (4)
C10	2522 (8)	515 (10)	3624 (5)	C36	4277 (6)	−1196 (7)	740 (4)
C11	1837 (8)	1385 (12)	3624 (4)	C37	418 (7)	−273 (11)	1137 (4)
C12	1741 (7)	2078 (9)	3193 (3)	C38	1834 (7)	−1013 (9)	1688 (4)
C13	2614 (5)	4220 (6)	2419 (3)	C39	1370 (6)	−23 (8)	1390 (3)
C14	2803 (7)	4989 (8)	2046 (4)	C40	1758 (5)	1066 (7)	1344 (2)
C15	3118 (7)	6157 (9)	2147 (5)	C41	1710 (5)	2159 (7)	1136 (2)
C16	3303 (6)	6471 (9)	2608 (5)	C42	1302 (6)	3008 (9)	868 (3)
C17	3127 (6)	5751 (9)	2999 (4)	C43	1360 (8)	4311 (12)	641 (4)
C18	2790 (5)	4589 (7)	2889 (3)	C44	580 (7)	3365 (11)	511 (3)
C19	3120 (5)	916 (8)	325 (3)	C45	−441 (8)	3475 (15)	707 (4)
C20	3409 (6)	1499 (8)	−97 (3)	C46	465 (8)	2555 (14)	15 (4)
C21	2952 (7)	1267 (11)	−547 (3)	C47	2049 (9)	4451 (13)	252 (5)
C22	2219 (6)	529 (12)	−584 (3)	C48	1104 (10)	5374 (11)	947 (5)

[a] Esd's are in parentheses.

Table IV. Bond Lengths (Å) and Angles (deg) in 15

Bond Lengths

Rh-Cl	2.372 (2)	C39-C37	1.516 (12)
Rh-P1	2.322 (2)	C39-C38	1.500 (13)
Rh-P2	2.336 (2)	C39-C40	1.339 (12)
Rh-C40	2.008 (8)	C40-C41	1.340 (11)
Rh-C41	2.043 (6)	C41-C42	1.312 (11)
P1-C1	1.826 (7)	C42-C43	1.577 (15)
P1-C7	1.841 (8)	C42-C44	1.435 (11)
P1-C13	1.809 (8)	C43-C44	1.556 (19)
P2-C19	1.850 (7)	C43-C47	1.489 (16)
P2-C25	1.824 (8)	C43-C48	1.500 (18)
P2-C31	1.834 (7)	C44-C45	1.579 (15)
		C44-C46	1.626 (16)

Bond Angles

Cl-Rh-P1	87.5 (1)	C37-C39-C40	119.1 (8)
Cl-Rh-P2	89.0 (1)	C38-C39-C40	122.7 (8)
P1-Rh-P2	175.7 (1)	C39-C40-Rh	140.0 (6)
Cl-Rh-C40	162.9 (2)	C39-C40-C41	147.8 (7)
Cl-Rh-C41	158.5 (2)	C41-C40-Rh	72.1 (5)
C40-Rh-C41	38.6 (3)	C40-C41-C42	154.0 (8)
P1-Rh-C40	92.0 (2)	C42-C41-Rh	136.7 (7)
P1-Rh-C41	91.8 (2)	C40-C41-Rh	69.3 (4)
P2-Rh-C40	90.6 (2)	C41-C42-C43	148.0 (9)
P2-Rh-C41	92.3 (2)	C41-C42-C44	149.3 (11)
Rh-P1-C1	117.1 (2)	C43-C42-C44	62.0 (8)
Rh-P1-C7	115.6 (3)	C42-C43-C44	54.5 (6)
Rh-P1-C13	112.0 (2)	C42-C43-C47	115.1 (10)
C1-P1-C7	100.6 (3)	C42-C43-C48	119.1 (9)
C1-P1-C13	104.8 (3)	C47-C43-C48	120.0 (12)
C7-P1-C13	105.3 (3)	C44-C43-C47	113.2 (11)
Rh-P2-C19	119.5 (2)	C44-C43-C48	117.9 (10)
Rh-P2-C25	112.6 (2)	C43-C44-C42	63.5 (7)
Rh-P2-C31	112.1 (2)	C43-C44-C45	121.9 (10)
C19-P2-C25	102.6 (4)	C43-C44-C46	127.3 (9)
C19-P2-C31	103.0 (3)	C42-C44-C45	115.5 (8)
C25-P2-C31	105.7 (3)	C42-C44-C46	116.8 (8)
C37-C39-C38	118.2 (8)	C45-C44-C46	105.6 (10)

square planar, with the least-squares plane of the butatriene being nearly perpendicular to the P_2RhCl plane. Although triphenylphosphine ligands occupy trans positions,[19] they are not exactly linearly opposed, the angle P1-Rh-P2 being 175.7°. The coordination of rhodium to the central bond of the butatriene is somewhat asymmetric (2.008 and 2.043 Å). The average Rh–C bond length (2.025 Å) is only slightly longer than the distance reported by West and co-workers in the (diquinoethylene)rhodium complex (2.000 Å). The length of the complexed olefin bond is essentially the same as in the diquinoethylene complex (1.340 Å vs. 1.339 Å) and also in the (tetraphenylbutatriene)iron complex (1.35 Å).[12] Although these bond lengths are comparable to simple olefins (1.34 Å), they are significantly longer than the central double bond in simple butatrienes (1.26 Å).[21] The ORTEP drawings show that there is considerable cis bending of the uncomplexes diene portion of the ligand in **15**, the C39–C40–C41 and C40–C41–C42 angles being 147.8 and 154.0°, respectively, rather than the 180° in the uncomplexes cumulene. This bending of metal-complexed butatrienes seems general and is essentially identical with those of the rhodium complex (149.7 and 153.8°) and the iron complex (151° each) already mentioned above.[11,12]

The bond lengths in the cyclopropane ring of complex **15** do not fit expectations. In both methylenecyclopropane[22] and a rhodium-complexed methylenecyclopropane,[23] the two bonds adjacent to the double bond are shorter than the distal bond, and the values of C42–C44 and C43–C44 agree with these findings. However, the C42–C43 bond appears to be too long by approximately 0.12 Å. Whether this is due to steric interactions between the C47 and C48 methyl groups and the phenyl rings of

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(19) We suspected that the triphenylphosphines were trans to each other, on the basis of numerous literature precedents[11] and also from inspection of the aromatic region of the ^{13}C NMR spectrum of **12**, which shows the phenomenon known as virtual coupling, leading to triplets for each carbon of the phenyl rings.[20]

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the phosphines or is just an artifact of the data set cannot be determined.[24]

In the first report of chlorotris(triphenylphosphine)rhodium, Wilkinson and co-workers showed this compound to be an efficient homogeneous catalyst for hydrogenation.[25] Since then, considerable attention has been focused on the nature of the various species in the catalytic cycle.[26] Both Osborn[27] and Halpern[28] and their co-workers have shown that hydrogenation does not occur directly on the isolable olefin complexes derived from Wilkinson's catalyst. However, Oro and Heras[29] have reported the production of a catalytically active species from a rhodium–diene complex and hydrogen. This fact combined with the highly unsaturated nature of our butatriene ligands prompted us to try to hydrogenate complexes **14**–**17**.

In a typical hydrogenation attempt, complex **15** was dissolved in degassed benzene, and hydrogen was added at 1 atm with vigorous stirring. No new organics could be detected, even at long reaction times or with heating.[30] The addition of excess triphenylphosphine (10 equiv) likewise had no noticeable effect, and in each case starting complex could be recovered by chromatography.

Since Wilkinson's catalyst reacts irreversibly with carbon monoxide to give *trans*-bis(triphenylphosphine)carbonylchlororhodium,[25] we felt the interaction of complexes **14**–**17** with carbon monoxide should free the butatriene linkage. Such a displacement is precedented in the release of allene from the complex (allene)bis(triphenylphosphine)chlororhodium on exposure to carbon monoxide.[27] Indeed, the butatriene ligands are readily freed from complexes **14**–**17** and can be recovered by chromatography.

In conclusion, we have shown that the interaction of Wilkinson's catalyst with hydrocarbon butatrienes is a simple, high-yield, and general route to (η^2-butatriene)rhodium complexes. The existence of a methylenecyclopropane-like end on the cumulene does not alter the course of the reaction. The X-ray structure determination of complex **15** confirms the structural assignment of complexes **14**–**17** initially made from the spectral data. While hydrogen did not react with the complexes, carbon monoxide did, freeing the cumulene. Although this last result is not unexpected, it has a unique consequence; since the complexes are air-stable solids, they represent a stable means for storing a moderately unstable organic compound. Further chemistry as well as extension of this preparative method to even higher cumulenes and other transition metals will be the subject of future reports.

Experimental Section

General Data. Melting points were recorded on a Mel-Temp capillary apparatus. Infrared spectra were recorded on a Perkin-Elmer 298 or a Nicolet 6000 FT spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian EM-360 or EM-390 spectrometer, and ^{13}C NMR spectra were recorded on a Varian FT-80 or SC-300 spectrometer. Routine mass spectra were recorded on a Micromass 7070 mass spectrometer with a DS2050 data system. Fast atom bombardment mass spectra were recorded on a VG Micromass ZAB reverse-geometry mass spectrometer with DS2035 data system or a Kratos MS-950 spectrometer with DS55 data system. All FAB spectra were confirmed by oscillographic chart output. Analytical GC work was done on a Hewlett-packard 5711A flame ionization chromatograph coupled to a Hewlett-Packard 3380A integrator.

Materials. All commercial reagents were ACS reagent grade. Solvents were purified and rigorously dried immediately prior to use. An initial portion of chlorotris(triphenylphosphine)rhodium was purchased from Strem Chemicals; larger amounts were prepared according to Wilkinson and co-workers.[25]

3-(2-Adamantylidene)propyn-3-yl Triflate (21). This triflate was made in seven steps from 2-adamantanone in the following manner. Farcasiu's three-step procedure for making 2-adamantanecarboxylic acid[31] gave the acid in 74% overall yield. The acid chloride was prepared[32] and used to produce the title compound in three further steps:[33] overall yield 67.7%; mp 31–33 °C; IR (neat film) 3315, 2920, 2860, 2160, 1630, 1455, 1105, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.38 (s, 1 H), 3.04 (s, 2 H), 2.92 (s, 12 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 154.50, 120.0, 118.8 (q, J_{C-F} = 320.9 Hz), 84.69, 74.18, 38.82, 38.43, 36.48, 34.86, 32.34, 27.65; MS, *m/z* (%) 320 (M$^+$, 45.4), 187 (100), 159 (22.3), 131 (26.4), 117 (43.2), 91 (89.3), 79 (63.4).

1,1,2,2-Tetramethyl-3-(3-methyl-1,2-butadienylidene)cyclopropane (10) and 1,1,2,2-Tetramethyl-3-(3,3-diphenyl-1,2-propadienylidene)cyclopropane (11). These two butatrienes were prepared as reported by Stang and Fisk[34] and purified by chromatography on silica immediately prior to use.

1,1,2,2-Tetramethyl-3[(2-adamantylidene)ethenylidene]cyclopropane (12). This new butatriene was prepared in similar fashion to **10** and **11**,[34] using **21** as carbene precursor, in 70.9% yield: mp 125.5–126.5 °C; IR (KBr pellet) 2980, 2910, 2850, 2570, 1725, 1445, 1090 cm^{-1}; ^{1}H NMR, ($CDCl_3$, Me_4Si) δ 2.68 (s, 2 H), 1.97 (br s, 12 H), 1.26 (s, 12 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 170.3, 159.0, 128.7, 111.4, 39.18, 39.09, 38.97, 37.26, 28.20, 21.17; MS, *m/z* (%) 254 (M$^+$, 26.9), 239 (43.1), 215 (76.6), 186 (17.9), 164 (100), 135 (16.1), 119 (22.7), 105 (24.6), 93 (21.8), 91 (40.6).

Tetraphenylbutatriene (9). This compound was prepared according to the three-step procedure of Sisenwine and Day,[35] in 37.7% overall yield, mp 234–235 °C (lit.[35] mp 235–236 °C).

General Procedure for the Formation of Rhodium(I) Complexes of Butatrienes. Bis(triphenylphosphine)chloro[η^2-1,1,2,2-tetramethyl-3-(3-methyl-1,2-butadienylidene)cyclopropane]rhodium (15). A 50-mL, three-neck round-bottom flask was fitted with an argon inlet, bubbler, and magnetic stirring, and then 185 mg of chlorotris(triphenylphosphine)rhodium (**13**) (200 μmol) was introduced and the system flushed with argon. After the addition of 25 mL of degassed benzene, 34.1 mg of butatriene **10** (210 μmol, 5% excess) in 5 mL of benzene was added by syringe. This mixture was stirred for 2 h at room temperature, and then the benzene was removed. The red-brown residue 73.01; chromatographed 6.18; P, 6.23. (20 × 1.8 cm column) by using first 1:4 $CHCl_3/CCl_4$ to remove triphenylphosphine and excess butatriene, and then 1:2 $CHCl_3/CCl_4$, and finally 1:1 $CHCl_3/CCl_4$ to elute the yellow complex.[11] The yellow-orange solid that remained after removal of solvent was dissolved in minimal dichloromethane and was crystallized at −15 °C by the diffusion addition of pentane to give 121.8 mg (73.8%) of air-stable, yellow-orange square plates: mp 167–169 °C dec; ^{13}C NMR ($CDCl_3$ Me_4Si) δ 135.15 (t, *J* = 6.1 Hz), 132.46 (t, *J* = 21.1 Hz), 132.32, 132.01, 129.93, 127.82 (t, *J* = 4.8 Hz), 121.20, 116.37, 28.96, 24.92, 24.61, 23.08, 21.24, 21.09. Anal. Calcd for $C_{48}H_{48}ClP_2Rh$: C, 69.86; H, 5.86; P, 7.51. Found: C, 70.00; H, 5.69; P, 7.50.

Bis(triphenylphosphine)chloro[η^2-1,1,2,2-tetramethyl-3-(3,3-diphenyl-1,2-propadienylidene)cyclopropane]rhodium

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[24] Some large deviations from the average aromatic C–C bond lengths in the phenyl rings point to the latter explanation. However, the large thermal motions of C47 and C48 indicate some steric interactions, and a refinement on a data set from a different crystal produced similar results.

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(16). This complex was prepared from 185 mg of **13** (200 μmol) and 60 mg of **11** (210 μmol) according to the general procedure, but with a 5-h reaction time. The yield was 138 mg (72.2%) of air-stable, deep yellow needles: mp 178–179.5 °C dec; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 141.98, 141.44, 135.06 (t, J = 5.9 Hz), 131.79 (t, J = 21.7 Hz), 130.31, 129.57, 128.25, 127.62 (t, J = 5.0 Hz), 127.00, 126.13, 125.03, 116.03, 29.76, 24.82, 21.31, 20.96. Anal. Calcd for $C_{58}H_{52}ClP_2Rh$: C, 73.38; H, 5.52; P, 6.53. Found: C, 73.01; H, 6.18; P, 6.23.

Bis(triphenylphosphine)chloro{η^2-1,1,2,2-tetramethyl-3-[(2-adamantylidene)ethenylidene]cyclopropane}rhodium (17). This complex was prepared from 92.5 mg of **13** (100 μmol) and 26.3 mg of **12** (105 μmol) according to the general procedure, buth with a 1-h reaction time. The yield was 82.6 mg (90.0%) of air-stable, yellow needles, mp 153–155 °C dec. Anal. Calcd for $C_{55}H_{56}ClP_2Rh$: C, 72.04; H, 6.16; P, 6.72. Found: C, 71.79; H, 6.23; P, 6.46.

Bis(triphenylphosphine)chloro(η^2-tetraphenylbutatriene)rhodium (14). This complex was prepared from 185 mg of **13** (200 μmol) and 71.3 mg of tetraphenylbutatriene (200 μmol) according to the general procedure. However, this compound required 10 h at benzene reflux for complete reaction and could not be chromatographed. Instead, the product was crystallized from chloroform to give 142 mg (69.7%) of yellow-orange, powdery needles, mp 243–246 °C dec.

Solution and Refinement of the Structure of 15. A crystal with maximum dimensions 0.33 × 0.24 × 0.13 mm was used for data collection. Lattice constants were determined from 25 doubly measured reflections in the range $9.86 \le \theta \le 12.02°$. Some crystal data are given in Table II. On a Philips PW 1100 four-circle diffractometer, 5624 independent reflections with indices $\pm h$, $+k$, $+l$ and θ values between 1.5 and 22.5° were recorded (niobium-filtered Mo Kα radiation, scan speed 0.03° s^{-1}, scan width $(0.80 + 0.35 \tan \theta)°$, detector aperture 2°). After the usual Lp correction, a Patterson synthesis was calculated, from which the coordinates of the Rh and one P atom were taken. From the remaining non-hydrogen atoms, all but two were localized in successive Fourier maps. Methyl carbons C47 and C48 were finally located in a ΔF map. After three cycles each of isotropic and anisotropic refinement of all atoms, the C(sp^2)-bonded hydrogens were calculated. For the methyl hydrogens, at least one per methyl group was picked from a ΔF map, and the remaining ones were then calculated. No hydrogens were found, however, for the C46 and C48 methyls. Thus, 42 out of 48 hydrogen atoms were included with B = 7.5 Å^2 in the structure factor calculation but not in the refinement. In the final stages, 469 variables were refined by a block-diagonal least-squares method, using 3443 reflections with $F_o > 4\sigma(F_o)$. The two strongest reflections (110 and 012) as well as four other low-indexed relfections were discarded because of high $|F_o| - |F_c|$ values. The weighting scheme was $w = 1/(\sigma^2 + 0.0009F_o^2)$. The procedure converged at $R = 0.0542$ and $R_w = (\sum w\Delta^2F/\sum wF_o^2)^{0.5} = 0.0605$. Scattering factors were taken from ref 36. Anomalous dispersion corrections were aplied for Rh, P, and Cl by using the values given by Cromer and Liberman.[37] For programs used, see ref 38.

General Procedures for Attempted Hydrogenations. A 25-mL, three-neck flask was fitted with both argon and hydrogen inlets and connected to a vacuum system. The apparatus was flushed for 10 min with argon, and then 40–50 mg of a complex (**14–17**) in 10 mL of degassed benzene was added. Vigorous stirring was started, with the stirrer tilted so that the stir bar mixed the reaction atmosphere with the solution. Hydrogen was introduced at 1 atm, and four successive pumpings/fillings replaced the inert gas. The mixture was stirred at room temperature, with successive samplings for GC and IR analyses taken at intervals ranging from an initial 15 min to an eventual 2 h over reaction times of up to 16 h. No new organics, or free cumulene, were noted. Variations of this procedure included the addition of triphenylphosphine (1 and 10 equiv) and/or heating (50 °C and reflux), with similar results.

General Procedure for Reaction of Complexes with Carbon Monoxide. A 50-mL, three-neck flask was fitted with both argon and carbon monoxide inlets, oil bubler, magnetic stirring, and syringe septum. A portion of a complex (**15–17**) was added and the system flushed with argon. Next, 20 mL of degassed benzene was added and stirring commenced. Carbon monoxide was added at 1 atm, and a nearly immediate lightening of the yellow color was noted. After 15 min the system was flushed with argon, and the light yellow solution was diluted with hexanes. The precipitated yellow solid was removed by filtration and the solvent removed from the filtrate. The yellow solid was shown to be bis(triphenylphosphine)carbonylchlororhodium by comparison (mp, IR, ^{1}H NMR) with authentic material. The filtrate residue was chromatographed on unactivated silica (5 × 0.8 cm, hexanes) and compared (IR, ^{1}H NMR) with the appropriate butatriene. A 105-mg scale reaction using complex **15** yielded 73.2 mg (83.4%) of rhodium carbonyl complex and 14.7 mg of recovered **10** (71.1%).

Acknowledgment. This research was supported by the NSF (Grant CHE 81-03596).

Registry No. 14, 84836-40-8; 15, 84836-41-9; 16, 84836-42-0; 17, 84836-43-1; 21, 84836-44-2.

Supplementary Material Available: Tables of hydrogen positions, anistropic thermal parameters, selected torsion angles, and observed and calculated structure factors (65 pages). Ordering information is given on any current masthead page.

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