ORGANOMETALLICS

Interaction of rhodium(I) with cyclopropenones: decarbonylation and formation of 1-rhodacyclopentene-2,5-diones and cationic oxygen .sigma.-bound cyclopropenone complexes. X-ray crystal structure of trans-carbonylbis(triphenylphosphine)(di-tert-butylcyclopropenone)rhodium trifluoromethanesulfonate

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$J(Rh,H) = 2.1$, $J_{gem} = 2$, H of $H_2C{=}C(7)$ cis to C(6)), 0.55 (dd, $J(Rh,H) = 2.1$ $J_{gem} = 2$, H of $H_2C{=}C(6)$ cis to C(7)), 0.08 (d, $J_{gem} = 3$, H of $H_2C{=}C(3)$ cis to C(4)), −0.08 (d, $J_{gem} = 2.5$, H of $H_2C{=}C(4)$ cis to C(3)). ^{13}C NMR (90.55 MHz, $CDCl_3$ [relative $Yb(thd)_3$-induced δ_C]): δ 225.8 (t, $J(Rh,C) = 50$ Hz, μ-CO(*Rh–Rh*) [8.2]), 208.7 (br s, $Fe(CO)_3$ [5.8]), 201.7 (s, C(8) [21.6]), 126.6, 126.3, 125.2, 124.9, 121.4, 120.8, 119.7 and 118.6 (8 dd, $^1J(C,H) = 170$, $^3J(C,H) = 8$), 116.0, 115.7, 113.7, 113.5 (4 s), 107.9 (s, C(4) [26.6]), 99.8 (s, C(3) [52.8]), 96.9, 95.8, 82.7, 82.5, 78.3 and 76.5 (6 dd, $^1J(C,H) = 176$, $J(Rh,C) = 5$), 76.2 (d, $J(Rh,C) = 8$, C(6) [23.2]), 75.1 (d, $^1J(C,H) = 150$, C(2) [100]), 70.8 (d, $J(Rh,C) = 8$, C(7) [38.7]), 60.1 (d, $^1J(C,H) = 150$, C(1) [46.9]), 56.9 (d, $^1J(C,H) = 150$, C(5) [20.8]), 37.8 (t, $^1J(C,H) = 158$, $CH_2{=}C(3)$ [34.3]), 36.7 (t, $^1J(C,H) = 158$, $CH_2{=}C(4)$ [14.5]), 27.0 (td, $^1J(C,H) = 159$, $J(Rh,C) = 15$, $CH_2{=}C(7)$ [34.6]), 21.9 (td, $^1J(C,H) = 159$, $J(Rh,C) = 15$, $CH_2{=}C(6)$ [15.1]). MS (70 eV; *m/e* (relative intensity)): 792 ($M^{\bullet+}$, 19), 791 (10), 493 (7), 492 (26), 437 (8), 436 (55), 334 (7), 333 (67), 274 (11), 246 (7), 218 (57), 116 (60), 115 (84), 106 (43), 105 (23), 103 (13), 92 (16), 91 (100), 89 (12), 86 (20), 84 (25), 77 (11), 74 (11), 65 (11), 63 (16), 58 (52), 57 (22), 52 (10), 51 (39), 49 (44), 45 (12). Anal. Calcd for $C_{34}H_{26}O_6FeRh_2$ (M_r 792.24): C, 51.55; H, 3.31. Found: C, 51.41; H, 3.41.

[*cis*-μ-[(1*RS*,2*SR*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Fe*):*C*,6,7,*C*-η(*Rh*–*Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh*–*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh*–*Rh*)](tricarbonyliron) (28). A mixture of 26 (8 mg, 0.01 mmol), Ac_2O (1 mL), and anhydrous pyridine (1 mL) was stirred at 20 °C for 3 h. After addition of toluene (5 mL) the solvent was evaporated to dryness and the residue purified by FC (Lobar, column A, Et_2O/CH_2Cl_2/petroleum ether 2:9:10): yield 7.5 mg (90%); red crystals; mp 140 °C dec. ^1H NMR (360 MHz, $CDCl_3$): δ 7.63 and 7.54 (2 m, 2 H), 7.39 and 7.17 (2 m, 4 H), 7.11 and 6.92 (2 m, 2 H), 6.56, 6.26, 5.97, 5.84, 5.80 and 5.73 (6 m, 6 H, two indenyl groups), 5.52 (d, J(HC(1),HC(2)) = 6 Hz, HC(2) syn to C(8)), 2.75 (dd, J(HC(1),HC(2)), = 6, $^4J(HC(1),HC(5)) = 1$, HC(1)), 2.74 (dd, $J_{gem} = 2.5$, $J(Rh,H) = 2.4$, H of $H_2C{=}C(7)$ trans to C(6)), 2.37 (dd, $J_{gem} = 2.5$, $J(Rh,H) = 2.4$, H of $H_2C{=}C(6)$ trans to C(7)), 2.12 (s, Ac), 1.65 (d, $J_{gem} = 3.5$, H of $H_2C{=}C(3)$ trans to C(4)), 1.26 (d, $J_{gem} = 2.5$, H of $H_2C{=}C(4)$ trans to C(3)), 1.19 (br s, HC(5)), 0.74 (dd, $J(Rh,H) = 2.1$, $J_{gem} = 2.5$, H of $H_2C{=}C(7)$ cis to C(6)), 0.61 (dd, $J(Rh,H) = 2.1$, $J_{gem} = 2.5$, H of $H_2C{=}C(6)$ cis to C(7)), 0.04 (d, $J_{gem} = 3.5$, H of $H_2C{=}C(3)$ cis to C(4)), −0.01 (d, $J_{gem} = 2.5$, H of $H_2C{=}C(4)$ cis to C(3)).

Interaction of Rhodium(I) with Cyclopropenones: Decarbonylation and Formation of 1-Rhodacyclopentene-2,5-diones and Cationic Oxygen σ-Bound Cyclopropenone Complexes. X-ray Crystal Structure of *trans*-Carbonylbis(triphenylphosphine)(di-*tert*-butylcyclopropenone)rhodium Trifluoromethanesulfonate

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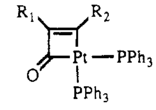
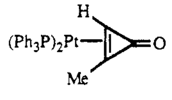
Cyclopropenones **5a**,**b** react with chlorotris(triphenylphosphine)rhodium to form *trans*-chlorocarbonylbis(triphenylphosphine)rhodium and acetylenes **7a**,**b**. Reactions of **5a**,**b** with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium result in the formation of rhodacyclopentenediones **8a**,**b** through the insertion of both the rhodium and the carbonyl into the three-membered ring. Di-*tert*-butylcyclopropenone, **5c**, in contrast, does not react with chlorotris(triphenylphosphine)rhodium or *trans*-chlorocarbonylbis(triphenylphosphine)rhodium under similar reaction conditions. All three cyclopropenones **5a–c** react with *trans*-carbonylbis(triphenylphosphine)rhodium trifluoromethanesulfonate (triflate) to give the cationic rhodium complexes **10a–c** without ring opening. However, **5a**,**b** yield the insertion products **12a**,**b** when the reactions are done in benzene at ca. 60 °C. The X-ray crystal structure of *trans*-carbonylbis(triphenylphosphine)(di-*tert*-butylcyclopropenone)rhodium triflate, **10c**, is reported.

Introduction

There is considerable interest in the organometallic chemistry of organic molecules containing small rings;[1] however, cyclopropenones are less studied. To our knowledge, only a few cyclopropenone complexes have been reported and fully characterized. Thus, $(PPh_3)_4Pt$ or $(PPh_3)_2PtC_2H_4$ reacts with selected cyclopropenones to form metallacyclobutenones **1a**,**b** through the insertion of platinum into the strained three-membered ring.[2,3] It has been proposed that these reactions go through an intermediate **2** in which platinum is bound to the cyclopropenone in an η^2 fashion. This intermediate has been detected by NMR spectroscopy at low temperature in the case of methylcyclopropenone. When allowed to react with $Pt_3(t\text{-}BuNC)_6$, diphenylcyclopropenone gave an interesting



1a $R_1{=}R_2{=}Ph$
1b $R_1{=}Me$, $R_2{=}H$



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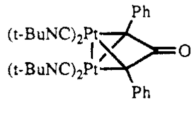

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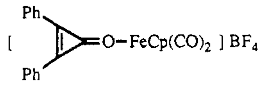

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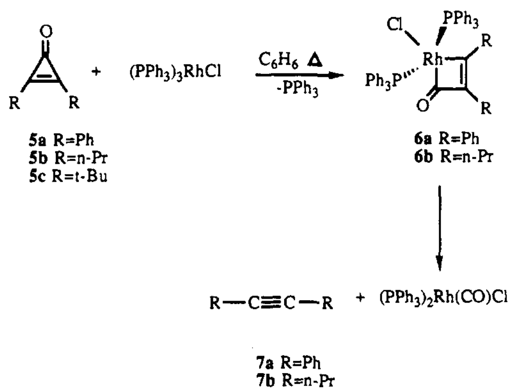
dinuclear complex **3** through the cleavage of the C═C bond.[4] All these insertion reactions are related to the strained property of cyclopropenones. In contrast, their polarity makes cyclopropenones act as oxygen-donor ligands in some cases. For example, when allowed to react with $[CpFe(CO)_2]BF_4$, diphenylcyclopropenone gives complex **4** in which the cyclopropenone is bound to the iron through the oxygen atom and the three-membered ring is retained.[5,6] In this paper, we wish to report the decarbonylation of cyclopropenones with rhodium(I) and the formation of 1-rhodacyclopentene-2,5-diones **8a,b** and cationic oxygen σ-bound cyclopropenone complexes **10a–c**.

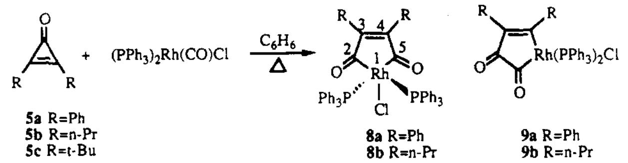
Results and Discussion

Reactions with Chlorotris(triphenylphosphine)rhodium. Cyclopropenones **5a,b** were reacted with chlorotris(triphenylphosphine)rhodium in benzene at ca. 50 °C in anticipation of forming the rhodacyclobutenones **6a,b**. However upon addition of methanol or hexanes to the reaction mixture, a yellow solid, identified as *trans*-chlorocarbonylbis(triphenylphosphine)rhodium, was isolated from both reactions in 90% and 61% yields, respectively. The IR (chloroform) spectrum shows a strong absorption at ca. 1974 cm^{-1}, which is typical of the terminal rhodium–carbonyl moiety. The ^{31}P NMR spectrum displays a ^{103}Rh-coupled ^{31}P doublet centered at 29.6 ppm ($^1J_{Rh-P}$ = 127.0 Hz). These data are identical with those of an authentic sample of *trans*-$(PPh_3)_2Rh(CO)Cl$.[7] The only possible carbonyl source in the reaction is the starting cyclopropenone, and if this is true, acetylenes **7a,b** should also be formed. In fact, diphenylacetylene **7a** was indeed isolated via silica gel chromatography in 57% yield from the reaction of **5a** with chlorotris(triphenylphosphine)rhodium. In the reaction of **5b**, 4-octyne **7b** was detected by GC. In contrast, cyclopropenone **5c** does not react with $(PPh_3)_3RhCl$ under the reaction conditions used for **5a,b**. We believe that a rhodacyclobutenone intermediate **6** is formed first, which then decomposes via decarbonylation to acetylenes **7a,b** and *trans*-chlorocarbonylbis(triphenylphosphine)rhodium through the cleavage of a C–C bond and a C–Rh bond (Scheme I). In the case of **5c**, the steric interactions between the *tert*-butyl groups and the triphenylphosphine ligands prevent the formation of the intermediate **6**; therefore, no reaction between **5c** and $(PPh_3)_3RhCl$ is observed under the same reaction conditions used for **5a,b**.

Scheme I



Reactions with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium. When allowed to react with *trans*-$(PPh_3)_2Rh(CO)Cl$ in refluxing benzene, **5a,b** gave air-stable 1:1 adducts in high isolated yields (96% and 93%, respectively). The new products are assigned as the 1-rhodacyclopentene-2,5-diones **8a,b** based on the IR and NMR data. In the infrared spectra, the typical terminal rhodium–carbonyl band at ca. 1975 cm^{-1} has been replaced by new bands at 1649 cm^{-1} for **8a** and 1634 cm^{-1} for **8b**, indicating the insertion of both the rhodium and the carbonyl into the three-membered ring. The proton-decoupled ^{31}P NMR spectra of **8a,b** display only one ^{103}Rh-coupled ^{31}P doublet (**8a** 28.0 ppm, $^1J_{Rh-P}$ = 128.1 Hz; **8b** 28.1 ppm, $^1J_{Rh-P}$ = 130.7 Hz), indicating the two triphenylphosphine ligands in each compound are magnetically equivalent. The ^1H NMR spectrum of **8a** shows a distinct doublet of doublet at 6.27 ppm (J = 8.4, 1.5 Hz) corresponding to four protons by integration. This resonance is assigned to the H2 (H6) protons of the phenyl substituents at C3 and C4. In the proton-decoupled ^{13}C NMR spectra of **8a,b**, only one carbonyl resonance is observed as a doublet of triplet due to the coupling to the ^{103}Rh and the two equivalent ^{31}P atoms (**8a** 228.92 ppm, $^1J_{Rh-C}$ = 34.7, $^2J_{P-C}$ = 6 Hz; **8b** 231.60 ppm, $^1J_{Rh-C}$ = 33.3, $^2J_{P-C}$ = 6 Hz). Only three single resonances are observed for the *n*-propyl substituents in the proton-decoupled ^{13}C NMR spectrum of **8b**, indicating that the two *n*-propyl groups in **8b** are, as expected, magnetically equivalent. All these data support the symmetrical structure **8** rather than the unsymmetrical isomer **9** in which neither the two carbonyl groups nor the two *n*-propyl groups are equivalent as the structure for these adducts. The C3 (C4) of **8a** resonates at 163.11 ppm as a broad singlet, whereas the C3 (C4) of **8b** resonates at 166.97 ppm as a broad doublet with a coupling constant of $^2J_{Rh-C}$ = 2.7 Hz. Di-*tert*-butylcyclopropenone, **5c**, on the other hand, does not react with *trans*-$(PPh_3)_2Rh(CO)Cl$ when heated in refluxing benzene for 37 h or even in refluxing toluene for 45 h as monitored by FT-IR spectroscopy.



Reactions with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (OTf = OSO_2CF_3). In contrast to the reactions with $(PPh_3)_3RhCl$ and *trans*-$(PPh_3)_2Rh(CO)Cl$ discussed above, all three cyclopropenones **5a–c** react with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ at room temperature to form the cationic complexes **10a–c**. In these compounds, the cyclopropenone is bound to rhodium through the oxygen atom without the opening of the three-membered ring. The structural assignments are made based on the IR and NMR data and in the case of **10c** an X-ray crystal structure.

The IR spectra of **10a–c** display the typical terminal rhodium–carbonyl absorptions (e.g., 1994 cm^{-1} for **10a**) and the two typical bands characteristic of intact cyclopropenones although slightly shifted (e.g., 1859 and 1556 cm^{-1} for **10a**). These data indicate that the rhodium and carbonyl are not inserted into the three-membered ring as they are in **8**. The ^{31}P NMR spectra of **10a–c** display only one ^{103}Rh-coupled ^{31}P doublet (31.9 ppm, $^1J_{Rh-P}$ = 127.0 Hz for **10a**), indicating the magnetic equivalence of the two triphenylphosphine ligands. In the ^{13}C NMR spectra, the terminal rhodium–carbonyl is observed as a doublet of triplet due to the coupling to the ^{103}Rh and the two equivalent ^{31}P atoms (e.g., **10a** 188.84 ppm, $^1J_{Rh-C}$ = 76.1, $^2J_{P-C}$ = 16 Hz). The cyclopropenone carbonyls of

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[4] Carroll, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, *1*, 1472.

[5] Boudjouk, P.; Woell, J. B.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 582.

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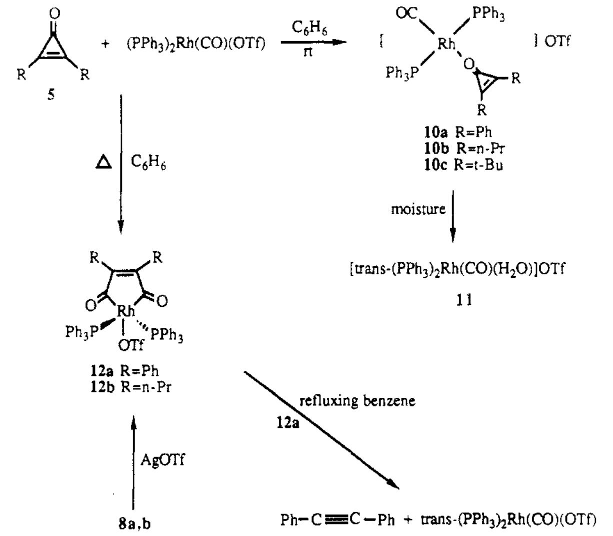
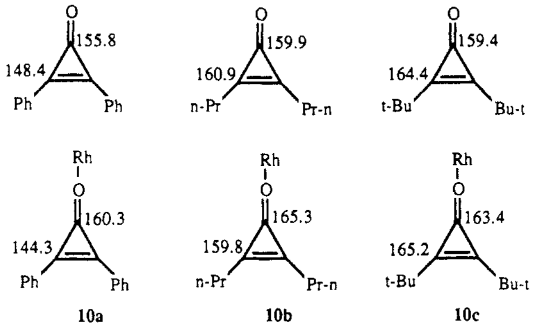


10a–c resonate as singlets at 160.25, 165.33, and 163.43 ppm, respectively, and are all shifted downfield compared to the free cyclopropenones. In comparison, the other two equivalent carbons in the three-membered ring are only slightly shifted (Chart I). Three ^{13}C signals for the two *n*-propyl substituents in **10b** (27.59, 19.61, and 13.88 ppm) and two for the two *tert*-butyl groups in **10c** (33.76 and 28.29 ppm) are observed in the ^{13}C NMR spectra, consistent with the magnetic equivalence of the two *n*-propyl groups in **10b** and the two *tert*-butyl groups in **10c**. The ^1H NMR spectrum of **10c** displays only a single resonance for the two *tert*-butyl groups at 1.14 ppm, also consistent with the magnetic equivalence of the two *tert*-butyl substituents.

A definitive structural assignment for **10c** was established by X-ray crystallography. Suitable crystals were grown from $CHCl_3/Et_2O$. Both the main molecule and the OTf sit on a mirror plane, and one ether molecule is trapped during the process of crystallization, which lies on a C2 axis and is disordered. A summary of the crystallographic data and selected bond distances and bond angles are listed in Tables I–III. The ORTEP diagram of the cation of **10c** (Figure 1) clearly shows that the di-*tert*-butylcyclopropenone is σ-bound to the rhodium through the oxygen atom and the three-membered ring is retained. The coordination around rhodium can be described as square planar. There is a perfect plane going through O1, C1, Rh, O2, C2, C3, C4, C5, C7, C8, and C9 atoms that is perpendicular to the least-squares plane defined by Rh, C1, O2, and the two phosphorus atoms. The two triphenylphosphine ligands are mirror images to each other, and therefore, only one of them is labeled. The bond distance of Rh–O2 is 2.086 Å, shorter than the Rh–O distance of 2.316 Å in complex **11**.[8] The three-membered ring of the cyclopropenone becomes unsymmetrical with the bond distances of C2–C3 and C2–C4 being 1.42 and 1.39 Å, respectively. Although binding to the rhodium with a Rh–O2–C2 angle of 128.3°, the angles of O2–C2–C3 and O2–C2–C4 are essentially equivalent, being 150 and 152°, respectively. Without the structural data of the free di-*tert*-butylcyclopropenone, it is impossible to accurately describe its structural changes upon coordination. However, compared with the known diphenylcyclopropenone in which the bond distances of C1–O, C1–C2, and C2–C3 are 1.226, 1.409, and 1.354 Å, respectively,[9] coordination to rhodium does not cause significant change in the bond distances of the cyclopropenone. This is consistent with the fact that the coordinated cyclopropenones in **10** still display the two typical bands of the free ligands, although

Chart I. ^{13}C NMR Data for both the Starting[a] and the Coordinated Cyclopropenones



[a] Dehmlow, E. V.; Zeisberg, R.; Dehmlow, S. S. *Org. Magn. Reson.* **1975**, *7*, 418.

Table I. Summary of the Crystallographic Data for 10c

formula	$C_{49}H_{48}F_3O_5SP_2Rh{\cdot}(C_2H_5)_2O$
fw	1044.962
space group	*C*2/*m*
space group no.	12
cryst syst	monoclinic
cell dimens	
a, Å	25.084 (7)
b, Å	16.515 (6)
c, Å	12.613 (4)
α, deg	90.0000
β, deg	107.63 (2)
γ, deg	90.0000
cell vol, $Å^3$	4979.69
Z	4.0
d(calcd), g/cm^3	1.394
crystal size, mm	0.27 × 0.24 × 0.19
abs coeff, cm^{-1}	43.225
radiation, Å	Cu, 1.540 56
no. of rflns measd	4512
no. of unique rflns	4402
2θ range, deg	4.00–130.00
scan technique	θ/2θ
scan width, deg	0.9000 + 0.1400 tan θ
data collecn position	bisecting, with ω = 0
abs correction	empirical
min % transmissn	73.8245
max % transmissn	99.9514
av % transmissn	89.4638
highest peak in final diff Fourier, $e/Å^3$	0.527
max ρ value in final diff Fourier, $e/Å^3$	1564.530
ignorance factor (*P*)	0.07
no. of observns	3294
no. of variables	356
data to param ratio	9.253
shift to error ratio	0.000
R	0.0744
R_w	0.0772

Table II. Selected Bond Distances for 10c[a]

atom 1	atom 2	distance, Å	atom 1	atom 2	distance, Å
Rh	P1	2.343 (2)	O2	C2	1.24 (1)
Rh	O2	2.086 (7)	C2	C3	1.42 (1)
Rh	C1	1.84 (1)	C2	C4	1.39 (1)
P1	C11	1.830 (7)	C3	C4	1.37 (2)
P1	C17	1.830 (8)	C3	C5	1.49 (2)
P1	C23	1.827 (7)	C4	C8	1.52 (2)
O1	C1	1.10 (1)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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(8) Stang, P. J.; Song, L.; Huang, Y. H.; Arif, A. M. *J. Organomet. Chem.*, in press.

(9) Ammon, H. L. *J. Am. Chem. Soc.* **1973**, *95*, 7093.

Table III. Selected Bond Angles for 10c

atom 1	atom 2	atom 3	angle, deg	atom 1	atom 2	atom 3	angle, deg
P1	Rh	O2	89.85 (5)	Rh	C1	O1	179 (1)
P1	Rh	C1	90.20 (5)	O2	C2	C3	150 (1)
O2	Rh	C1	176.5 (3)	O2	C2	C4	152 (1)
Rh	P1	C11	113.2 (2)	C3	C2	C4	58.3 (9)
Rh	P1	C17	115.3 (3)	C2	C3	C4	59.8 (8)
Rh	P1	C23	116.2 (3)	C2	C3	C5	150 (1)
C11	P1	C17	105.9 (3)	C4	C3	C5	150.6 (9)
C11	P1	C23	100.9 (3)	C2	C4	C3	61.9 (8)
C17	P1	C23	103.7 (4)	C2	C4	C8	151 (1)
Rh	O2	C2	128.3 (8)	C3	C4	C8	147 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

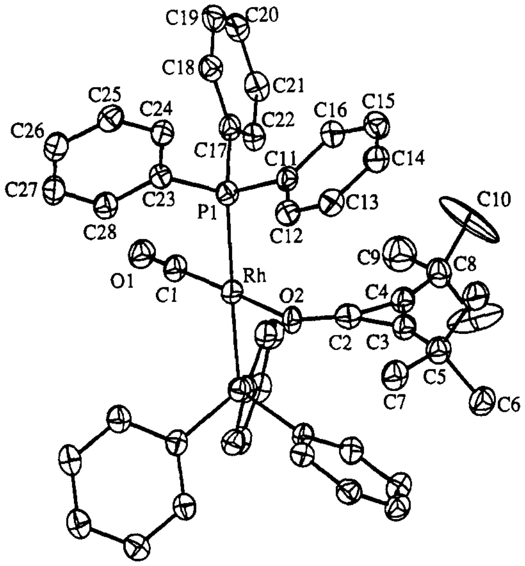


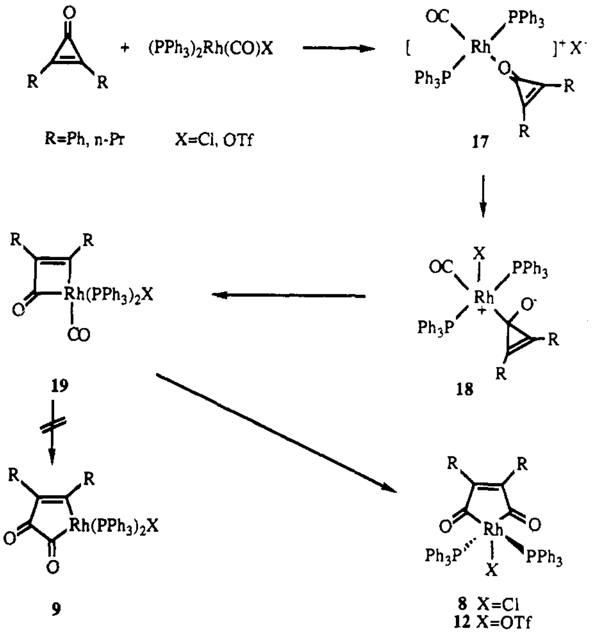
Figure 1. ORTEP diagram of complex **10c**. $CF_3SO_3^-$ counterion and $(C_2H_5)_2O$ of crystallization are omitted for clarity.

shifted, in their IR spectra (e.g., **5a** 1839 and 1618 cm^{-1}; **10a** 1859 and 1556 cm^{-1}). Also consistent with the minor structural change are the slightly shifted ^{13}C resonances as shown in Chart I.

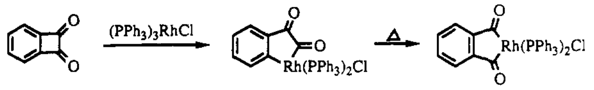
The σ-coordinated cyclopropenones in **10** are weakly bound to the rhodium. As a result, displacement of the diphenylcyclopropenone in **10a** by H_2O to give the rhodium–water complex **11** has been observed. In fact the water complex **11** can be formed by the direct reaction of *trans*-$(PPh_3)_2Rh(CO)(OTf)$ with H_2O.[8] The weak coordination of the cyclopropenones in **10** is also obvious in the mass spectra in which $(PPh_3)_2Rh(CO)$ (m/z 655) and $(PPh_3)_2Rh$ (m/z 627) are observed as the major fragments.

Interestingly, the reaction of **5a** with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ in benzene at 60–65 °C leads to the formation of the insertion product **12a**, an analogue of **8a**, which can also be obtained by treating **8a** with AgOTf in dichloromethane. In one experiment, pure **10a** was isolated first and then heated in benzene at 60–65 °C. The same insertion to form **12a** was observed as indicated by IR spectroscopy (**12a** ν_{CO} = 1664 cm^{-1}). When heated in refluxing benzene for ca. 74 h, **12a** completely decomposes to diphenylacetylene and *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (experimental). In contrast, reaction of **5b** with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ in benzene at 60–65 °C always yields a mixture of the unreacted *trans*-$(PPh_3)_2Rh(CO)(OTf)$ and **12b** even when an excess of **5b** is used. Pure **12b**, however, can be prepared by treating **8b** with AgOTf. Di-*tert*-butylcyclopropenone, **5c**, on the other hand, results in the formation of only **10c**. No insertion product is observed when heated in benzene at 60–65 °C for 35 h as monitored by FT-IR spectroscopy.

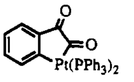
Scheme II



Mechanistic Considerations. It has been reported that benzocyclobutenedione **13** reacts with $(PPh_3)_3RhCl$ to form complex **14** through the insertion of the rhodium into the bond between the benzene ring and the carbonyl group. However, **14** undergoes isomerization when heated at 110 °C for 5 h to give isomer **15** in which the rhodium is inserted into the bond between the two carbonyl groups.[10] The reaction of **13** with tetrakis(triphenylphosphine)platinum, on the other hand, led to the formation of **16** as a stable compound, and no further isomerization was reported.[11,12]



13 14 15



16

In order to investigate the possibility of forming **9**, which then isomerized to **8**, **5a** was reacted with *trans*-$(PPh_3)_2Rh(CO)Cl$ for 40 min in $CDCl_3$ in an NMR tube heated at ca 63 °C. After cooling to room temperature, it was checked by ^{31}P NMR spectroscopy and showed the presence of only **8a** (28.0 ppm, $^1J_{Rh-P}$ = 128.1 Hz) and unreacted *trans*-$(PPh_3)_2Rh(CO)Cl$ (29.6 ppm, $^1J_{Rh-P}$ = 127 Hz) in a ratio of 10:90 by integration. There was no indication for the formation of **9a**. Also the reaction of **5b** with *trans*-$(PPh_3)_2Rh(CO)Cl$ showed only one increasing band at ca. 1637 cm^{-1} as monitored by FT-IR spectroscopy; the multiple absorption expected from **9b** were not observed. We propose that the reaction proceeds via a mechanism outlined in Scheme II. The first step is the formation of an oxygen-coordinated complex **17**, which has been isolated in the case of X = OTf (**10a–c**). The rho-

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dium then inserts into the three-membered ring via an intermediate **18** to form the rhodacyclobutenone **19**. A similar process has been proposed for the reaction of diphenylcyclopropenone with ketenes catalyzed by nickel tetracarbonyl.[13] The insertion of the carbonyl in **19** into the rhodium–alkenyl bond results in the formation of **8** and **12**. The alternative insertion of the carbonyl into the rhodium–acyl bond to form the unsymmetrical complex **9** is not observed because this is an unfavorable process.[14] Examples involving the insertion of carbon monoxide into transition-metal–acyl bonds are rare, and it occurs only in the presence of NO gas and in the absence of available metal–alkyl bonds.[15] When R is a *tert*-butyl group, the insertion to form the corresponding rhodacyclobutenone **19** is prevented by the steric effect of the bulky *tert*-butyl groups; therefore, no insertion reaction between **5c** and *trans*-$(PPh_3)_2Rh(CO)X$ (X = Cl, OTf) was observed. We also observed that the insertion reaction was much faster when X = OTf than when X = Cl. This is because the formation of **17** will be more facile when X = OTf due to the stronger electron-withdrawing ability of OTf.

In conclusion, cyclopropenones **5a**,**b** undergo decarbonylation reactions with chlorotris(triphenylphosphine)rhodium via a rhodacyclobutenone intermediate **6** to form *trans*-chlorocarbonylbis(triphenylphosphine)rhodium and acetylenes **7a**,**b**. Di-*tert*-butylcyclopropenone, **5c**, does not react because of steric effect. Both **5a** and **5b** undergo insertion reactions with *trans*-$(PPh_3)_2Rh(CO)Cl$ regiospecifically to yield the rhodacyclopentene-2,5-dione products **8a**,**b**. Reaction with *trans*-$(PPh_3)_2Rh(OTf)(CO)$ gives different products depending on the reaction conditions. At room temperature, **5a**–**c** all yield the cationic rhodium complexes **10a**–**c** in which the cyclopropenone is σ-bound to the rhodium through the oxygen atom and the three-membered ring is retained. In contrast, when heated in benzene at ca. 60 °C, **5a**,**b** undergo insertion reactions with *trans*-$(PPh_3)_2Rh(OTf)(CO)$ to give **12a**,**b**. Di-*tert*-butylcyclopropenone **5c**, on the other hand, only gives the cationic product **10c** and no insertion product is observed.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of nitrogen but worked up in air. All solvents were either reagent grade or purified by using standard methods. Chlorotris(triphenylphosphine)rhodium,[16] *trans*-chlorocarbonylbis(triphenylphosphine)rhodium,[7] and *trans*-chlorocarbonylbis(triphenylphosphine)rhodium trifluoromethanesulfonate[17] were prepared by using literature procedures. Diphenylcyclopropenone, **5a**, was purchased from Aldrich and was used without further purification. Di-*n*-propylcyclopropenone, **5b**, was prepared according to published procedure.[18] Di-*tert*-butylcyclopropenone, **5c**, was kindly supplied by Dr. Gerhard Maas. Melting points were recorded on a Mel-Temp capillary apparatus and were not corrected. The infrared spectra were recorded on a Mattson-Polaris FT-IR spectrometer for chloroform-evaporated thin film on a sodium chloride plate. The ^1H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Tetramethylsilane was used as internal reference for the ^1H NMR spectra and 85% H_3PO_4 was used as external reference for the ^{31}P NMR spectra. The ^{13}C NMR spectrum was referenced to the solvent (77.00 ppm for $CDCl_3$ and 53.80 ppm for CD_2Cl_2) and $CFCl_3$ was used as external reference for the ^{19}F NMR spectrum. The fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical 750-E instrument using 3-nitrobenzyl alcohol as the matrix. GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph.

Reaction of 5a with Chlorotris(triphenylphosphine)rhodium. Diphenylcyclopropenone (**5a**, 23.5 mg, 0.114 mmol) and chlorotris(triphenylphosphine)rhodium (100.2 mg, 0.108 mmol) were stirred in refluxing benzene (5 mL) for 7 h. Benzene was removed, and the residue obtained was dissolved in a minimum amount of dichloromethane. $(PPh_3)_2Rh(CO)Cl$ was precipitated upon the addition of methanol. It was filtered off, washed with hexanes (3 × 2 mL) and dried in air (64.4 mg, 90%): IR (cm^{-1}) 1975, 1478, 1433, 1095, 750, 693; ^{31}P NMR ($CDCl_3$) δ 29.6 (d, $^1J_{Rh-P}$ = 127 Hz).

The mother liquor obtained above was chromatographed on silica gel. The most labile band was eluted with hexanes, and diphenylacetylene (11 mg, 57%) was obtained after removing hexanes under vacuum: ^{13}C NMR ($CDCl_3$) δ 130.4, 127.1, 127.0, 122.0, 88.2. The same result was obtained when the reaction was done at 50 °C.

Reaction of 5b with Chlorotris(triphenylphosphine)rhodium. Chlorotris(triphenylphosphine)rhodium (47.5 mg, 0.0514 mmol) and **5b** (16.0 mg, 0.116 mmol) were heated in benzene (5 mL) at 50 °C for 4 h. The solution was concentrated to ca. 2 mL, and *trans*-$(PPh_3)_2Rh(CO)Cl$ was precipitated (21.7 mg, 61%) upon the addition of hexane (ca. 8 mL). The filtrate from which *trans*-$(PPh_3)_2Rh(CO)Cl$ was isolated was concentrated to dryness, and the residue was washed with hexane (ca. 2 mL). The hexane solution was analyzed by GC and 4-octyne **7b** was detected (by comparing the retention time to that of an authentic sample).

1-Chloro-1,1-bis(triphenylphosphine)-1-rhoda-3,4-diphenylcyclopentene-2,5-dione, 8a. Diphenylcyclopropenone (**5a**, 52.0 mg, 0.252 mmol) and *trans*-$(PPh_3)_2Rh(CO)Cl$ (145.4 mg, 0.211 mmol) were heated in benzene (8 mL) at reflux for 65 h. The solution was then concentrated to ca. 1 mL, and addition of hexanes gave a yellow precipitate. It was filtered off and wahed with 1:1 benzene–hexanes (4 × 2 mL). After dyring, 181 mg of **8a** was obtained (96%): mp 229–231 °C (dec); IR (cm^{-1}) 3056, 1649, 1635, 1573, 1482, 1435, 1296, 1189, 1096, 1035, 1021, 999, 747, 693; ^1H NMR ($CDCl_3$) δ 7.75–7.62 (m, 12 H), 7.44–7.30 (m, 18 H), 7.14–7.06 (m, 2 H), 7.06–6.95 (m, 4 H), 6.27 (dd, J = 8.4, 1.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 228.92 (dt, $^1J_{Rh-C}$ = 34.7, $^2J_{P-C}$ = 6.1 Hz, CO), 163.11, 134.73 (t, J = 5.7 Hz), 131.11, 130.22, 129.99 (t, J = 24.1 Hz), 129.45, 128.26 (t, J = 4.9 Hz), 128.20, 127.07; ^{31}P NMR ($CDCl_3$) δ 28.0 (d, $^1J_{Rh-P}$ = 128.1 Hz); MS, *m/z* (%) 861 (5), 662 (39), 627 (69), 543 (30), 393 (33), 287 (100), 286 (89). Anal. Calcd for $C_{52}H_{40}ClP_2O_2Rh$: C, 69.61; H, 4.49. Found: C, 69.45; H, 4.54.

1-Chloro-1,1-bis(triphenylphosphine)-1-rhoda-3,4-di-*n*-propylcyclopentene-2,5-dione, 8b. Di-*n*-propylcyclopropenone (**5b**, 30.0 mg, 0.217 mmol) and *trans*-$(PPh_3)_2Rh(CO)Cl$ (106.3 mg, 0.154 mmol) were heated in benzene (10 mL) under reflux for 89 h. The solution was concentrated, and the product **8b** was precipitated upon the addition of hexane. It was filtered off, washed with hexane (2 × 3 mL), and air dried (118.3 mg, 93%): mp 213–215 °C (dec); IR (cm^{-1}) 3053, 2962, 2933, 2872, 1634, 1482, 1435, 1096, 1064, 1029, 917, 745, 693; ^1H NMR ($CDCl_3$) δ 7.66–7.55 (m, 12 H), 7.42–7.29 (m, 18 H), 1.62–1.49 (m, 4 H), 0.75–0.65 (m, 4 H), 0.65–0.52 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 231.60 (dt, $^1J_{Rh-C}$ = 33.3, $^2J_{P-C}$ = 6 Hz, CO), 166.97 (d, $^2J_{Rh-C}$ = 2.7 Hz, =*C*—CO), 134.83 (t, J = 6 Hz), 130.34 (t, J = 23.7 Hz), 130.17, 128.11 (t, J = 5.0 Hz), 29.32, 21.33, 14.72; ^{31}P NMR ($CDCl_3$) δ 28.1 (d, $^1J_{Rh-P}$ = 130.7 Hz); MS, *m/z* (%) 793 (10), 627 (25), 287 (100), 262 (61). Anal. Cacld for $C_{46}H_{44}ClP_2O_2Rh$: C, 66.63; H, 5.35. Found: C, 66.46; H, 5.40.

General Procedure for 10. *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (OTf = OSO_2CF_3) and the appropriate cyclopropenone **5** were stirred in benzene at room temperature. The product **10** was precipitated upon addition of hexane and collected by filtration followed by hexane washing (pale yellow powder).

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Product **10a** (140.3 mg, 98%) was obtained by stirring *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (113.9 mg, 0.142 mmol) and **5a** (30.9 mg, 0.150 mmol) in benzene (7 mL) for 3.5 h. It can be recrystallized by diffusing dry diethyl ether into its dry chloroform solution: mp 136–138 °C (dec); IR (cm^{-1}) 3059, 3008, 1994, 1859, 1597, 1556, 1480, 1447, 1436, 1386, 1272, 1224, 1151, 1096, 1031, 754, 693, 637; ^1H NMR ($CDCl_3$) δ 7.83–7.77 (m, 4 H), 7.72–7.65 (m, 2 H), 7.65–7.55 (m, 16 H), 7.44–7.28 (m, 18 H); ^{13}C NMR (CD_2Cl_2) δ 188.84 (dt, $^1J_{Rh-C} = 76.1$, $^2J_{P-C} = 16.3$ Hz, Rh—*C*O), 160.25 (*C*═O—Rh), 144.31 (═*C*—C═O), 135.03, 134.39 (t, J = 7 Hz), 132.15, 131.50, 130.02 (t, J = 23.4 Hz), 129.84, 129.17 (t, J = 5 Hz), 121.24, 121.22 (q, $^1J_{F-C}$ = 321 Hz, CF_3); ^{31}P NMR ($CDCl_3$) δ 31.9 (d, $^1J_{Rh-P}$ = 127.0 Hz); ^{19}F NMR ($CDCl_3$) δ −77.5; MS, m/z (%) 861 (3, M − OTf), 776 (3, $(PPh_3)_2RhOTf$), 655 (45, $(PPh_3)_2RhCO$), 627 (100, $(PPh_3)_2Rh$), 287 (70), 286 (64). Anal. Calcd for $C_{53}H_{40}F_3O_5P_2SRh$: C, 62.98; H, 3.99. Found: C, 63.12; H, 4.03.

Product **10b** (110.0 mg, 91%) was obtained from the reaction of *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (103.5 mg, 0.129 mmol) and **5b** (30.0 mg, 0.217 mmol) in benzene (6 mL) for 6.5 h. It can be recrystallized by slowly adding hexane to its dry dichloromethane solution while stirring: mp 116–117 °C (dec); IR (cm^{-1}) 3057, 3008, 2967, 2937, 2878, 1992, 1854, 1556, 1481, 1436, 1272, 1224, 1150, 1096, 1032, 998, 752, 695, 637; ^1H NMR ($CDCl_3$) δ 7.67–7.55 (m, 12 H), 7.54–7.41 (m, 18 H), 2.15 (t, J = 7 Hz, 4 H), 1.40 (q, J = 7 Hz, 4 H), 0.84 (t, J = 7 Hz, 6 H); ^{13}C NMR (CD_2Cl_2) δ 165.33 (*C*═O—Rh), 159.83 (═C—C═O), 134.40 (t, J = 7 Hz), 131.53, 130.43 (t, J = 23 Hz), 129.18 (t, J = 5 Hz), 120.82 (q, $^1J_{F-C}$ = 320 Hz, CF_3), 27.59, 19.61, 13.88; ^{31}P NMR ($CDCl_3$) δ 31.2 (d, $^1J_{Rh-P}$ = 127.3 Hz); ^{19}F NMR ($CDCl_3$) δ −77.6; MS, m/z (%) 793 (4, M − OTf), 776 (4, $(PPh_3)_2RhOTf$), 655 (58, $(PPh_3)_2RhCO$), 627 (100, $(PPh_3)_2Rh$), 287 (86), 286 (78). Anal. Calcd for $C_{47}H_{44}F_3O_5P_2SRh$: C, 59.88; H, 4.70. Found: C, 59.60; H, 4.73.

Product **10c** (125.9 mg, 97%) was obtained from the reaction of *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (107.9 mg, 0.134 mmol) and **5c** (24.6 mg, 0.148 mmol) in benzene (8 mL) for 4 h. It can be recrystallized by diffusing dry diethyl ether into its dry chloroform solution: mp 171–174 °C (dec); IR (cm^{-1}) 3014, 2976, 2971, 1975, 1831, 1568, 1544, 1480, 1436, 1266, 1225, 1151, 1095, 1032, 764, 748, 698, 637; ^1H NMR ($CDCl_3$) δ 7.67–7.56 (m, 12 H), 7.55–7.41 (m, 18 H), 1.14 (s, *t*-Bu, 18 H); ^{13}C NMR (CD_2Cl_2) δ 187.99 (dt, $^1J_{Rh-C}$ = 75.4, $^2J_{P-C}$ = 17 Hz, Rh—*C*O), 165.21 (═*C*—*t*-Bu), 163.43 (*C*═O—Rh), 134.44 (t, J = 7 Hz), 131.61, 130.54 (t, J = 23 Hz), 129.27 (t, J = 5 Hz), 121.14 (q, $^1J_{F-C}$ = 321 Hz), 33.76 (*C*Me_3), 28.29 (Me); ^{31}P NMR ($CDCl_3$) δ 30.2 (d, $^1J_{Rh-P}$ = 126.9 Hz); ^{19}F NMR ($CDCl_3$) δ −77.5; MS, m/z (%) 655 (45, $(PPh_3)_2RhCO$), 627 (100, $(PPh_3)_2Rh$), 287 (78), 286 (70).

Reaction of 8 with Silver Triflate. General Procedure for 12. Silver triflate and 8 were stirred in dry dichloromethane (6 mL) under nitrogen at room temperature for 1.5 h, and then the mixture was filtered through a coarse frit to remove the precipitate. Slow addition of hexane to the concentrated filtrate gave the desired product as yellow powder.

From AgOTf (19.8 mg, 0.0770 mmol) and **8a** (65.6 mg, 0.0732 mmol) was obtained **12a** (72.1 mg, 98%): mp 162–164 °C (dec); IR (cm^{-1}) 3058, 3023, 1664, 1482, 1436, 1318, 1231, 1211, 1175, 1096, 1020, 999, 748, 693, 631; ^1H NMR ($CDCl_3$) δ 7.71–7.56 (m, 12 H), 7.51–7.34 (m, 18 H), 7.13 (tt, J = 7.2, 1.5 Hz, 2 H), 7.01 (t of m, J = 7.2 Hz, 4 H), 6.25 (d of m, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 223.45 (dt, $^1J_{Rh-C}$ = 39.2, $^2J_{P-C}$ = 6.0 Hz, CO), 161.94 (d, $^2J_{Rh-C}$ = 5.4 Hz, C3/C4), 134.55 (t, J = 6.0 Hz), 131.05, 130.36, 129.38, 128.74 (t, J = 4.9 Hz), 127.91 (t, J = 24.0 Hz), 127.22, 118.87 (q, $^1J_{F-C}$ = 319 Hz, CF_3); ^{31}P NMR ($CDCl_3$) δ 24.5 (d, $^1J_{Rh-P}$ = 129.4 Hz); ^{19}F NMR ($CDCl_3$) δ −78.1 (s); MS, m/e (%) 861 (29, M − OTf), 655 (17, $(PPh_3)_2RhCO$), 627 (96, $(PPh_3)_2Rh$), 543 (28, M − OTf − PPh_3 − 2CO), 393 (20, $(PPh_3)RhCO$), 287 (100), 286 (50).

From AgOTf (29.4 mg, 0.114 mmol) and **8b** (89.6 mg, 0.108 mmol) was obtained **12b** (75.3 mg, 74%): mp 170–173 °C (dec); IR (cm^{-1}) 3056, 3022, 2962, 2932, 2872, 1645, 1483, 1435, 1315, 1260, 1231, 1212, 1174, 1096, 1066, 1024, 918, 746, 693, 632; ^1H NMR ($CDCl_3$) δ 7.62–7.49 (m, 12 H), 7.49–7.33 (m, 18 H), 1.55 (t, J = 8.1 Hz, 4 H), 0.69 (t, J = 7.0 Hz, 6 H), 0.63–0.52 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 225.37 (dt, $^1J_{Rh-C}$ = 37.9, $^2J_{P-C}$ = 5.8 Hz, CO), 165.9 (unresolved m, ═*C*—CO), 134.53 (t, J = 6.0 Hz), 130.89, 128.47 (t, J = 5.2 Hz), 128.07 (t, J = 24.1 Hz), 118.87 (q, $^1J_{F-C}$ = 320 Hz, CF_3), 29.50, 21.34, 14.74; ^{31}P NMR ($CDCl_3$) δ 24.8 (d, $^1J_{Rh-P}$ = 132.2 Hz); ^{19}F NMR ($CDCl_3$) δ −78.1 (s); MS, m/e (%) 793 (40, M − OTf), 627 (57, $(PPh_3)_2Rh$), 393 (39, $(PPh_3)RhCO$), 287 (100), 286 (44).

Reactions of 5 with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ in Heated Benzene. Diphenylcyclopropenone (**5a**, 23.5 mg, 0.114 mmol) and the rhodium triflate (86.3 mg, 0.107 mmol) were heated in dry, degassed benzene (7 mL) at 60–65 °C for 45 h. The solution was filtered through a coarse frit, and benzene was then removed from the filtrate under vacuum. The residue thus obtained was crystallized from dichloromethane/hexane. The product was collected by filtration and identified as **12a** by IR and NMR data (78.0 mg, 72%).

Di-*n*-propylcyclopropenone (**5b**, 6.1 mg, 0.044 mmol) and the rhodium triflate (32.6 mg, 0.0405 mmol) were heated in dry, degassed benzene (4 mL) at ca. 60 °C for 30 h and monitored by FT-IR spectroscopy. The complete consumption of the cyclopropenone was indicated by the disappearance of the band at ca. 1854 cm^{-1} in the IR spectrum. The solution showed the following bands in the carbonyl region: 1990 from the starting rhodium triflate, 1748 (unknown), and 1653 cm^{-1} from **12b**. Benzene was then removed under vacuum, and the ^{31}P NMR spectrum of the residue showed two doublets centered at 29.2 ppm ($^1J_{Rh-P}$ = 124.8 Hz, starting rhodium triflate) and 24.8 ppm ($^1J_{Rh-P}$ = 133.0 Hz, **12b**) with a ratio of ca. 27:12 by integration.

Di-*tert*-butylcyclopropenone (**5c**, 5.6 mg, 0.034 mmol) and the rhodium triflate (25.3 mg, 0.0315 mmol) were heated in dry, degassed benzene (4 mL) at 60–65 °C for 35 h. The solution was filtered, and benzene was removed from the filtrate. The residue thus obtained was crytallized from dichloromethane/hexane to give 20.4 mg of yellow powder, which was identified as **10c** by its IR spectrum (67%).

Reaction of 5a with *trans*-$(PPh_3)_2Rh(CO)(OTf)$ in Refluxing Benzene. Diphenylcyclopropenone (**5a**, 28.0 mg, 0.136 mmol) and the rhodium triflate (104.5 mg, 0.130 mmol) were heated in dry, degassed benzene (8 mL) under reflux for 74 h. As monitored by FT-IR spectroscopy, the insertion product **12a** ($\nu_{CO} \sim 1663$ cm^{-1}) was first formed but decomposed as the reaction proceeded. Benzene was removed and the residue crystallized from dichloromethane/hexane to give *trans*-$(PPh_3)_2Rh(CO)(OTf)$ (70.6 mg). The filtrate from which the rhodium triflate was isolated was chromatographed on a silica gel column. The most mobile band was eluted with hexanes. After concentrating under vacuum and cooling with dry ice, 15.0 mg of colorless solid was obtained and identified as diphenylacetylene (65%) by comparing its IR spectrum and gas chromatogram to those of an authentic sample of diphenylacetylene.

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Supplementary Material Available: Experimental details of the X-ray structure determination of complex **10c**, including tables of atomic positional and thermal parameters and intramolecular distances and angles (12 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.