Organometallics **1990**, *9*, 2149–2154

Organometallic Complexes of Alkylidenecycloproparenes: Reactions with Rhodium(I) and Platinum(0) Reagents

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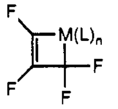
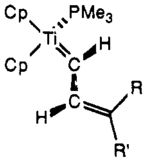
Received December 18, 1989

(Diarylmethylene)cycloproparenes **1** react with chlorotris(triphenylphosphine)rhodium(I) to give 2-alkylidene-1-rhodacyclobutarenes **11** as air-stable crystalline solids in high (60–73%) yields. In comparison, *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) oxidatively inserts the metal and CO ligand regiospecifically into a strained σ-bond of **1** to give 1-rhoda-3-alkylideneindan-2-ones **14** (70–90%). Insertion of carbon monoxide into the rhodacyclobutarene **11b** gives the isomeric 2-rhodaindan-1-one **15b** as the major product in a reaction whose regiochemistry is temperature-dependent. Tetrakis(triphenylphosphine)platinum(0) affords the analogous platinacyclobutarenes **12b**,**c** with **1b**,**c**. X-ray crystallographic analyses are reported for $(m\text{-}CF_3C_6H_4)_2C{=}\overline{CC_{10}H_6Rh}(PPh_3)_2Cl$ (**11d**) and $Ph_2C{=}\overline{CC_{10}H_6Rh(Ph_3P)_2C}OCl$ (**14b**).

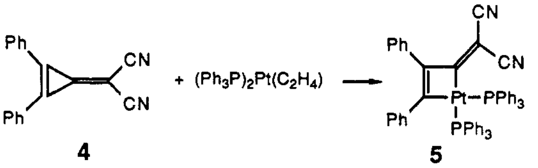
Since their discovery[1] in 1984 the readily accessible alkylidenecycloproparenes,[2] e.g. **1**, have provided a wealth of fascinating chemistry.[3] However, the attraction that these compounds hold has not yet been probed with regard to their behavior with organometallic reagents. The unique characteristics of these compounds provide a minimum of four sites for possible interaction with metal systems. Thus, aromatic π-complexation with the cycloproparenyl moiety, exocyclic olefin π- and/or σ-bonding, addition across the strained aromatic bridge bond, and interaction with a three-membered-ring σ-bond offer themselves as possibilities for complexation. Moreover, highly strained ring systems are well-known to undergo interesting reactions with metal complexes to form unique organometallic compounds. For example, reactions of cyclopropenes with stoichiometric quantities of transition-metal complexes have been extensively studied.[4] Opening of the three-membered ring to give a transitory metallacyclobutene, e.g. **2**, or vinylcarbene complex, e.g. **3**, is common, but only **2**[5] and **3**[6] have been isolated. With methylenecyclopropenes, of which **1** may be regarded as an unusual ring-fused analogue, the only reaction reported[7] is with (ethene)bis(triphenylphosphine)platinum(0), which cleaves the strained σ-bond of **4** to give **5**. By comparison, the diyne **6** is cyclized by diiron nonacarbonyl to give the only known[8] methylenecyclopropene complex **7**. To our knowledge there are no recorded examples of the transition-metal chemistry of the strained radialenes, but the use of nickel(0) as a catalyst for their formation has been documented.[9]



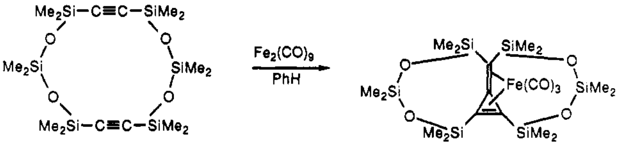
2 M(L)$_n$ = Pt(PPh$_3$)$_2$,
Ir(PPh$_3$)$_2$(CO)Cl,
Ir(PPh$_3$)$_2$(CO)Me or
Ir(PMe$_3$)$_2$(CO)Cl



3a: R = R' = Ph
3b: R = Me; R' = Ph

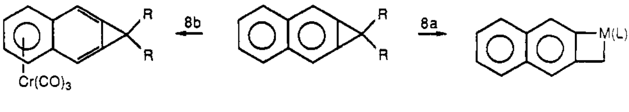


4 **5**



6 **7**

The cycloproparenes have only recently begun to be assessed in their reactions with organometallic reagents.[10] The disilyl species **8b** complexes[11] chromium as the carbonyl **9**, but the same process does not occur for hydrocarbon **8a** or with the cyclopropabenzene homologues. With rhodium(I) and platinum(0) **8a** gives isolable metalacyclobutarenes **10**,[12] which has its parallel in the behavior



9 **8a**: R = H **10**
8b: R = SiMe$_3$

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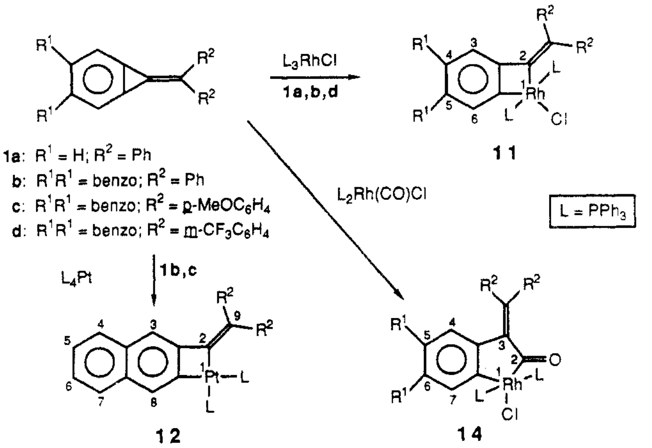
Scheme I



of cyclopropabenzene with several,[13] but not all,[14] nickel(0) complexes.

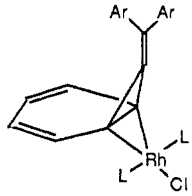
As part of our ongoing program on alkylidenecyclopropaene chemistry,[1-3] we now wish to report upon the reactions of $(Ph_3P)_3RhCl$, *trans*-$(Ph_3P)_2Rh(CO)Cl$, and $(Ph_3P)_4Pt$ with selected 1-(diarylmethylene)-1*H*-cyclopropaenes (1).

Results and Discussion

The previously reported alkylidenecyclopropaenes **1a–c** were prepared according to the literature method,[2] which, when applied to cyclopropa[*b*]naphthalene and 3,3′-bis(trifluoromethyl)benzophenone, afforded the previously unknown bis(trifluoromethyl) derivative **1d** in 73% yield. The spectroscopic data recorded for **1d** are fully consistent with the assigned structure, and the C2/C7 methine carbons appear characteristically[10] shielded at 108.45 ppm. When allowed to react with tris(triphenylphosphine)rhodium(I) chloride in refluxing benzene, compounds **1a**,**b**,**d** provide yellow, air-stable, microcrystalline solids identified as the 2-alkylidenerhodacyclobutarenes **11a**,**b**,**d**, respectively (Scheme I). Each of the compounds shows a symmetrical arrangement for the triphenylphosphine ligands from the appearance of only one rhodium-coupled phosphorus doublet ($^1J_{Rh-P} \approx 124$ Hz). Furthermore, the compounds are characterized by the appearance of a high-field aromatic proton (**11a**, δ 4.71 (d, $J = 7.2$ Hz); **11b**, δ 5.10 (s); **11d**, δ 5.18 (s)), due to marked shielding of one of the methine protons adjacent to the sites of four-membered ring fusion, and also by shielding of H3′/H5′ (δ ~6.1) of one of the arylethene groups of **11a**,**b**. In **11d** only one such proton (H5′) is shielded, as C3′ is trifluoromethyl-substituted. Confirmation of the assigned structure has come from an X-ray crystallographic analysis of **11d** (vide infra), and to the best of our knowledge this provides the first such analysis of a metallacyclobutarene.[12,13,15]

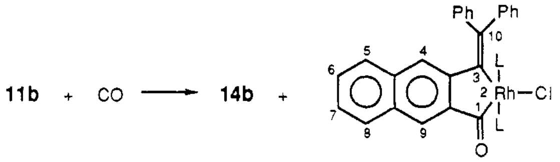
When the strained olefins **1b**,**c** are allowed to react with tetrakis(triphenylphosphine)platinum(0), analogous yellow solids result. These are also assigned as cyclobutarenes **12b**,**c** (72 and 85%, respectively). The compounds display magnetically nonequivalent phosphorus atoms, and the aromatic proton at C8 (closest to the metal center) is distinguishable by its appearance at 6.48 ppm as a doublet ($^4J_{P-H} = 6$ Hz) and with the ^{195}Pt satellites clearly discernable in **12c**. Apart from this shielding the sole uncoupled aromatic proton (H3) is markedly influenced by an aromatic ring(s) and resonates as a singlet at ca. 5.9 ppm. Other less readily discernable shielding effects of the phenyl substituents are also noted (Experimental Section) but do not justify discussion here.

The formation of the alkylidenemetallacyclobutarenes **11** and **12** results from oxidative insertion of the metal into a highly strained three-membered-ring σ-bond. Their appearance parallels the behavior of the parent (cyclopropaene) hydrocarbons with the same reagents[12] and also with several,[13] but not all,[14] nickel(0) species. Whether the ring expansion reaction proceeds by direct interaction with the strained σ-bond or by way of initial addition to the bridge bond to give metallabicyclobutanes, e.g. **13** (by analogy with the isolable analogues from 1,1-difluorocyclopropabenzene[16]), which then rearranges to **11** (**12**), is not known.



13: L = PPh$_3$

When the alkylidenecyclopropaenes **1** are reacted with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I), single 1:1 complexes are formed in 70–90% yield. The characteristically shielded C2 of the cyclopropaenyl moiety is no longer observed, and the typical metal–carbonyl frequency (2080 cm^{-1}) is replaced by a conjugated carbonyl stretching frequency at ca. 1670 cm^{-1}. These data suggest ring cleavage of the cyclopropaene with ligand and metal insertion, and regioisomers **14** and **15** offer themselves as likely candidates. Each of **1a–d** provides a product with equivalent phosphorus ligands ($^1J_{Rh-P} \approx 127$ Hz), with one of the protons originally adjacent to a site of three-membered-ring fusion highly shielded (from **1a**, dd, 5.63 ppm; from **1b–d**, s, 5.98–6.18 ppm) and with the two diarylmethylene aromatic rings nonequivalent (from **1c**, MeO 3.80 and 3.85 ppm), in which shielding of the coupled ortho and meta protons of one of these rings occurs (Experimental Section). These data do not distinguish between structures **14** and **15**. The product from **1b** is established as the 1-rhodaindan-2-one **14b** by X-ray crystallographic analysis (vide infra), and the analogues from **1a**,**c**,**d** are assigned as **14a**,**c**,**d** accordingly.



15b: L = PPh$_3$

The formation of **14** from **1** in excellent yields and with obvious high regioselectivity may well involve π-complexation with the exocyclic olefin prior to the insertion of the metal and carbonyl ligand into the reactive σ-bond. The observed regioselectivity is consistent with interaction of the metal with the center of highest electron density, and this has direct analogy[10] to the ring-opening reactions

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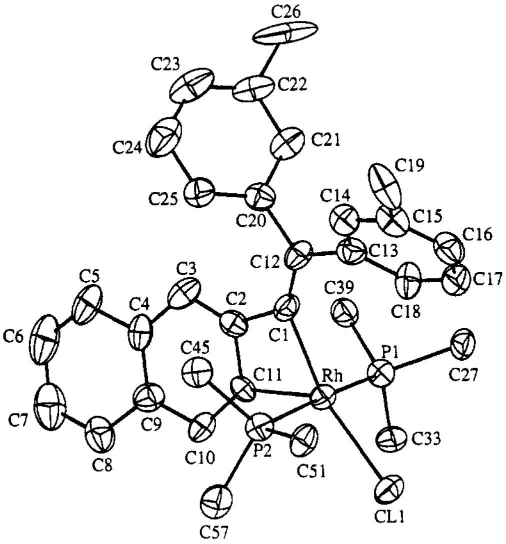
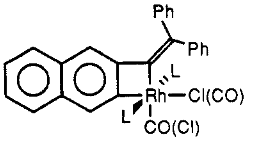


Figure 1. ORTEP diagram of complex **11d**.

of cyclopropaarenes with Ag(I). However, the cyclopropaarene hydrocarbons themselves are *unaffected*[12] by *trans*-$(Ph_3P)_2Rh(CO)Cl$, and therefore, the presence of the exocyclic olefin is critical.

The available rhodacyclobutarenes **11b,c** have potential as an alternative source of the rhodaindanones **14b,c**. Indeed, when carbon monoxide is reacted with **11b** at temperatures below 40 °C, a complex is formed that is identified not as **14b** but its regioisomer **15b**, which displays spectral characteristics distinctly different from those of **14b** (Experimental Section); e.g., the uncoupled aromatic proton is slightly more shielded (**14b**, 5.98 ppm; **15b**, 5.78 ppm). When the reaction is performed at an elevated temperature (70 °C), not only is CO consumed but also **15b** dominates in a mixture of isomers (**14b**:**15b** ≈ 1:5). By comparison, the reaction between **1b** and *trans*-$(Ph_3P)_2Rh(CO)Cl$ at the same temperature provides **14b** (86%) with apparent regiospecificity; no evidence was obtained (NMR) for the presence of **15b**. This dichotomy in behavior of **1** and **11** likely stems from an arene–rhodium interaction in the σ-bond cleavage of **1**, while carbon monoxide insertion into **11** will preferentially cleave the weakest Rh–C bond.

In an attempt to gain further insight into the **11** → **14**/**15** conversion, **11b** was treated with CO at 3 °C in the NMR probe. Spectral evidence collected (^1H, ^{31}P NMR) shows that **11b** is converted to a new complex, proposed as **16b**,



16b: L = PPh_3

which subsequently rearranges to **15b**. Compound **16b** has a Rh–P coupling (^1J = 112 Hz) distinctly different from those of **11b**, **14b**, and **15b**, shows the shielded arene proton at higher field (5.37 ppm), and when deposited upon an infrared plate, gives a metal–carbonyl frequency at 2080 cm^{-1}. When it is warmed, **16b** is transformed predominantly into **15b**; the proportion of **14b** depends upon the temperature chosen.

Single-Crystal Molecular Structure Determinations of 11d and 14b. Suitable single crystals of **11d** and **14b** were grown from benzene–hexane solutions. However, the isolation procedure employed for **11d** resulted in the occlusion of 1 mol equiv of dichloromethane, and this was retained through the crystallization procedure. In a similar vein **14b** occludes 1 mol equiv of benzene. The parameters for these solvent molecules are included in the supplementary material only. ORTEP diagrams[17] of **11d** and **14b** are provided in Figures 1 and 2, respectively, while crystal

Table I. Summary of Crystallographic Data for 11d

mol formula	$C_{62}H_{44}ClF_6P_2Rh{\cdot}CH_2Cl_2$
mol wt	1181.271
cryst syst	monoclinic
space group	$P2_1/c$
space group no.	14
cell dimens	
a, Å	14.359 (4)
b, Å	13.612 (4)
c, Å	28.471 (8)
α, deg	90.00 (0)
β, deg	94.06 (2)
γ, deg	90.00 (0)
V, Å^3	5550.58
Z	4.0
d_{calcd}, g/cm^3	1.422
cryst dimens, mm	0.38 × 0.23 × 0.10
abs coeff, cm^{-1}	5.624
radiation, Å (monochromatized)	Mo, 0.71073
no. of rflns measd	6233
no. of unique rflns	3794
scan technique	θ–2θ
2θ range, deg	3.00–41.00
scan speed, deg/min	3.0–8.0
scan range	k – 1.0 to k + 1.0
total bkgd time/scan time	0.5
no. of rflns between stds	98
ignorance factor, P	0.07
no. of observns, $I > 3.00\sigma(I)$	3529
no. of variables	657
data to param ratio	5.371
shift error ratio	0.011
R factor	0.0673
weighted R factor	0.0687

Table II. Selected Bond Distances (Å) for 11d[a]

Rh–Cl	2.4229 (9)	C2–C3	1.389 (5)
Rh–P1	2.3836 (9)	C2–C11	1.395 (5)
Rh–P2	2.344 (1)	C3–C4	1.430 (6)
Rh–C1	2.030 (3)	C4–C5	1.426 (5)
Rh–C11	1.984 (3)	C4–C9	1.378 (6)
P1–C27	1.867 (4)	C5–C6	1.311 (8)
P1–C33	1.812 (3)	C6–C7	1.412 (9)
P1–C39	1.824 (4)	C7–C8	1.354 (8)
P2–C45	1.843 (4)	C8–C9	1.444 (6)
P2–C51	1.832 (4)	C9–C10	1.434 (6)
P2–C57	1.842 (5)	C10–C11	1.352 (5)
C1–C2	1.480 (5)	C12–C13	1.465 (6)
C1–C12	1.353 (5)	C12–C20	1.488 (5)

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

Table III. Selected Interbond Angles (deg) for 11d[a]

Cl1–Rh–P1	89.47 (3)	C1–C2–C11	99.3 (3)
Cl1–Rh–P2	90.00 (3)	C3–C2–C11	121.6 (3)
Cl1–Rh–C1	164.2 (1)	C2–C3–C4	117.6 (3)
Cl1–Rh–C11	129.6 (1)	C3–C4–C5	120.4 (4)
P1–Rh–P2	174.50 (3)	C3–C4–C9	119.1 (3)
P1–Rh–C1	90.0 (1)	C4–C9–C10	122.3 (4)
P1–Rh–C11	89.9 (1)	C9–C10–C11	117.1 (3)
P2–Rh–C1	92.0 (1)	C2–C11–C10	122.0 (3)
P2–Rh–C11	86.2 (1)	Rh–C11–C2	99.5 (2)
C1–Rh–C11	66.2 (1)	Rh–C11–C10	138.5 (3)
Rh–C1–C2	94.6 (2)	C1–C12–C13	122.6 (3)
Rh–C1–C12	132.8 (3)	C1–C12–C20	120.9 (3)
C2–C1–C12	131.5 (3)	C13–C12–C20	116.3 (3)
C1–C2–C3	139.0 (3)		

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

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[17] The atom-numbering system employed for **11d** and **14b** in Figures 1 and 2, respectively, is used for convenience purposes only.

Table IV. Summary of Crystallographic Data for 14b

mol formula	$C_{61}H_{46}ClOP_2Rh{\cdot}C_6H_6$
mol wt	1073.467
cryst syst	triclinic
space group	$P\bar{1}$
space group no.	2
cell dimens	
a, Å	15.551 (8)
b, Å	14.085 (6)
c, Å	13.633 (6)
α, deg	103.71 (3)
β, deg	87.65 (4)
γ, deg	105.49 (4)
V, Å^3	2794.96
Z	2.0
d_{calcd}, g/cm^3	1.275
cryst dimens, mm	0.25 × 0.20 × 0.18
abs coeff, cm^{-1}	4.444
radiation, Å (monochromatized)	Mo, 0.71073
no. of rflns measd	6324
no. of unique rflns	6038
scan technique	θ–2θ
2θ range, deg	3.00–46.00
scan speed, deg/min	3.0–8.0
scan range	k - 1.0 to k + 1.0
total bkgd time/scan time	0.5
no. of rflns between stds	98
ignorance factor, P	0.07
no. of observns, $I > 3.00\sigma(I)$	4727
no. of variables	590
data to param ratio	8.012
shift error ratio	0.010
R factor	0.0537
weighted R factor	0.0674

Table V. Selected Bond Distances (Å) for 14b[a]

Rh–Cl	2.443 (1)	C2–C13	1.355 (6)
Rh–P1	2.345 (1)	C3–C4	1.384 (6)
Rh–P2	2.348 (1)	C3–C12	1.444 (6)
Rh–C1	1.962 (5)	C4–C5	1.404 (7)
Rh–C12	1.989 (5)	C5–C6	1.431 (7)
P1–C26	1.829 (6)	C5–C10	1.424 (7)
P1–C32	1.831 (5)	C6–C7	1.407 (7)
P1–C38	1.829 (5)	C7–C8	1.436 (8)
P2–C44	1.841 (5)	C8–C9	1.372 (8)
P2–C50	1.834 (5)	C9–C10	1.420 (7)
P2–C56	1.806 (5)	C10–C11	1.418 (7)
O1–C1	1.218 (5)	C11–C12	1.389 (6)
C1–C2	1.502 (6)	C13–C14	1.487 (7)
C2–C3	1.465 (6)	C13–C20	1.484 (6)

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

data and selected bond lengths and interbond angles are collated in Tables I–III for **11d** and Tables IV–VI for **14b**.

Compound **11d** is trigonal bipyramidal about rhodium, but the trigonal plane angles deviate significantly from 120° (Cl–Rh–C11 = 66.2°, Cl–Rh–C1 = 164.2°, Cl–Rh–C11 = 129.6°) because of the distorted but planar four-membered ring and the bulky nature of the substituents. While the Rh–C1 (2.03 Å) and Rh–C11 (1.98 Å) bond lengths are unexceptional,[18] they elongate the rhodacyclobutene ring (C1–C2 = 1.48 Å, C2–C11 = 1.395 Å) and the remaining angles are widened (Rh–C1–C2 = 94.6°, C1–C2–C11 = 99.3°, Rh–C11–C2 = 99.5°). The length of the exocyclic double bond (C1–C12 = 1.35 Å) is within the usual range, and C12 is essentially coplanar with the metallacyclobutene ring, which, in turn, has an out-of-plane angle to the fused benzenoid ring of ca. 6°. The P1–Rh–P2 angle is 174°, and the plane containing P1, Rh, P2, and Cl is essentially orthogonal to the rhodacyclobutenyl moiety. Bond length alternation in the fused naphthalene is expected on the basis of the structures of both naphthalene[19] and cyclobuta[*b*]naphthalene.[20] The bond lenghs and interbond angles reported herein match those for these latter compounds with the exception of the bridging bonds (C4–C9 = 1.38 Å, C2–C11 = 1.395 Å), which are somewhat shorter than in naphthalene (1.42 Å)[9] and cyclobuta[*b*]naphthalene (C3a–C7a = 1.43 Å, C2a–C8a = 1.41 Å).[20]

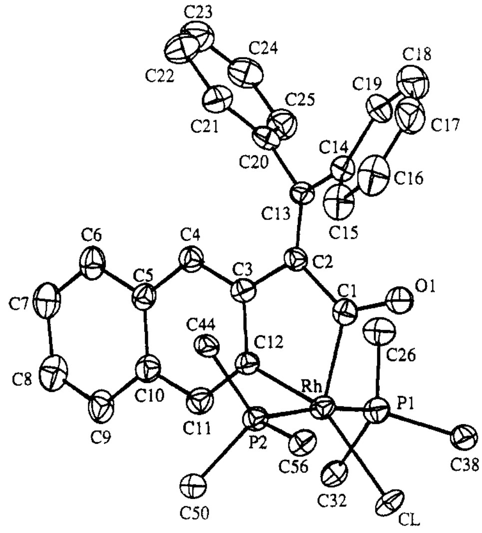

Figure 2. ORTEP diagram of complex **14b**.

Table VI. Selected Interbond Angles for 14b[a]

Cl–Rh–P1	90.92 (5)	C4–C3–C12	119.0 (4)
Cl–Rh–P2	88.51 (4)	C3–C4–C5	121.1 (4)
Cl–Rh–C1	124.0 (2)	C4–C5–C6	120.1 (5)
Cl–Rh–C12	156.0 (1)	C4—C5–C10	120.5 (4)
P1–Rh–P2	170.22 (5)	C6–C5–C10	119.3 (5)
P1–Rh–C1	93.4 (1)	C5–C6–C7	120.0 (5)
P1–Rh–C12	85.9 (1)	C6–C7–C8	118.8 (5)
P2–Rh–C1	95.0 (1)	C7–C8–C9	121.9 (5)
P2–Rh–C12	90.7 (1)	C8–C9–C10	119.6 (5)
C1–Rh–C12	80.0 (2)	C5–C10–C9	120.3 (5)
Rh–C1–O1	116.5 (4)	C5–C10–C11	118.1 (4)
Rh–C1–C2	118.3 (3)	C10–C11–C12	121.3 (4)
O1–C1–C2	125.1 (4)	Rh–C12–C3	118.3 (3)
C1–C2–C3	109.7 (4)	Rh–C12–C11	121.8 (3)
C1–C2–C13	121.7 (4)	C3–C12–C11	119.8 (4)
C3–C2–C13	128.5 (4)	C2–C13–C14	124.8 (4)
C2–C3–C4	128.0 (4)	C2–C13–C20	121.6 (4)
C2–C3–C12	112.8 (4)		

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

Compound **14b** is trigonal bipyramidal about rhodium, with the distortion of the angles in the trigonal plane (Cl–Rh–C1 = 124.0°, Cl–Rh–C12 = 156°, C1–Rh–C12 = 80.0°) reduced by comparison with **11d** above, as expected. The plane containing P1, Rh, P2, and Cl is orthogonal (91.7°) to that of the five-membered ring, and the P1–Rh–P2 angle is 170.2°. The carbonyl (1.22 Å), exocyclic olefin (1.355 Å), and Rh–C bonds (Rh–C1 = 1.96 Å, Rh–C12 = 1.99 Å) are all within expectation and compare favorably with those for **11d** above. The naphthalene ring system is also consistent with expectation.

Conclusion

The above data clearly indicate that the novel alkylidenecycloproparenes 1 react with Wilkinson's catalyst and with tetrakis(triphenylphosphine)platinum(0) to give 11

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(19) Cruickshank, D. W. J.; Sparks, R. A. *Proc. R. Soc. London, Ser. A* **1960**, *258*, 270. Almenningen, A.; Bastiansen, O.; Dyvik, F. *Acta Crystallgr.* **1961**, *14*, 1056.

(20) Crawford, J. L.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1973**, *29*, 1238.

and **12**, respectively, by cleavage of a strained σ-bond in an analogous manner to both parent cyclopropa[*b*]naphthalene[12] and the methylenecyclopropene **4**. However, the present results provide, to the best of our knowledge, the first structural study of a metallacyclobutarene, namely **11d**. The reaction of **1** with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) to give the rhodaindanones **14** regiospecifically is in marked contrast to the lack of reactivity of the parent hydrocarbon. The fact that **11** inserts carbon monoxide predominantly to give indanone **15** under kinetic control provides an excellent route to the 2-rhodaindanone **15**. The use of other organometallic reagents to effect arene and olefin complexation remains to be realized.

Experimental Section

General Considerations. All melting points are uncorrected and were recorded on a Mel-Temp capillary apparatus. Infrared spectra (in cm^{-1}) were obtained for KBr pellets on a Perkin-Elmer 298 IR spectrometer. All NMR spectra were recorded on a Varian XL-300 spectrometer. ^{1}H chemical shifts were recorded at 299.69 MHz for chloroform-*d* solutions and are relative to internal tetramethylsilane (Me_4Si) (unless otherwise stated), while ^{13}C spectra were measured at 75.43 MHz for either chloroform-*d* or dichloromethane-d_2 solutions and resonances are reported in ppm with use of the carbon resonance of the solvent (77.0 and 53.8 ppm, respectively) as standard. ^{19}F NMR data were obtained for chloroform-*d* solutions at 281.96 MHz and are referenced to external trifluoroacetic acid. ^{31}P data were obtained at 121.32 MHz for chloroform-*d* solutions with external 85% H_3PO_4 as standard at 0.0 ppm. Fast atom bombardment (FAB) mass spectra were measured with a VG Analytical 750-E instrument employing chloform–3-nitrobenzyl alcohol as the matrix.

Materials. Solvents either were reagent grade or were purified according to known procedures. Deuterated NMR solvents were purified by drying over calcium hydride and then vacuum-transferred.

1-(Diphenylmethylene)-1*H*-cyclopropabenzene, 1-(diphenylmethylene)cyclopropa[*b*]naphthalene, and 1-(bis(*p*-methoxyphenyl)methylene)-1*H*-cyclopropa[*b*]naphthalene were prepared according to the literature method.[2] Wilkinson's catalyst (tris(triphenylphosphine)rhodium(I) chloride) was prepared by using the established procedure,[21] as were *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I)[22] and tetrakis(triphenylphosphine)platinum(0).[23]

1-(Bis(*m*-(trifluoromethyl)phenyl)methylene)-1*H*-cyclopropa[*b*]naphthalene (1d). The reaction of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (102 mg, 0.359 mmol) with 3,3′-bis(trifluoromethyl)benzophenone (168 mg, 0.527 mmol) employing the published general procedure[2] afforded the title compound **1d** (116 mg, 73%) as bright yellow crystals: mp 109–110 °C; IR 1775, 1760, 1610, 1585, 1540, 1485, 1440, 1330, 1270, 1175, 1165, 1120, 1090, 1070, 995, 940, 900, 850, 800, 790, 765, 740, 700, 690, 650 cm^{-1}; ^{1}H NMR δ 8.06 (br s, 2 H), 7.94 (m, 2 H), 7.87 (br d, $J = 7.2$ Hz, 2 H), 7.67 (s, 2 H), 7.66–7.52 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 108.45 (C2/7), 114.37/116.15 (both s, C1 and C8), 124.05 (q, $^3J_{C-F} = 3.7$ Hz, $CH{=}CCF_3$), 124.20 (q, $^1J_{C-F} = 273$ Hz, CF_3), 124.46 (q, $^3J_{C-F} = 3.8$ Hz, $F_3CC{=}CH$), 126.09 (C1a/7a), 127.32 (C4/5), 129.02/129.12 (C3/6 + 1 CH), 130.92 (CH), 130.99 (q, $^2J_{C-F} = 32$ Hz, CCF_3), 139.12/139.68 (C2a/C6a + C1′/C1″); ^{19}F NMR δ 15.1, s; MS *m*/*e* 440 (100, M), 370 (28%, M − CF_3H). Anal. Calcd for $C_{26}H_{14}F_6$: C, 70.91; H, 3.21. Found: C, 70.74, H, 3.00.

2-(Diarylmethylene)-1-chloro-1,1-bis(triphenylphosphine)-1-rhoda-2*H*-cyclobutarenes (11). A mixture of the relevant (diarylmethylene)cycloproparene **1** and Wilkinson's catalyst, with or without added triphenylphosphine (see below), in dry degassed benzene (6 mL) was heated under reflux and under an inert atmosphere for ca. 20 h. The cooled solution was filtered, the filtrate concentrated under vacuum, and the residue thus obtained crystallized from dichloromethane–hexane.

(i) Rhodacyclobutabenzene 11a. From 1-(diphenylmethylene)cyclopropabenzene (**1a**; 20.0 mg, 0.079 mmol), Wilkinson's catalyst (68.0 mg, 0.074 mmol), and triphenylphosphine (21 mg, 0.080 mmol) was obtained **11a** (41 mg, 61%) as yellow microcrystals: mp 186–188 °C dec; IR 3050, 1590, 1575, 1485, 1435, 1090, 740, 690 cm^{-1}; ^{1}H NMR δ 7.46–6.95 (complex m, 38 H), 6.78 (br d, $J \approx 7$ Hz, 1 H), 6.27 (t, $J = 7.5$ Hz, 1 H), 6.09 (br t, $J = 9.0$ Hz, 1 H), 5.96 (br d, $J = 7.2$ Hz, H3′/5′), 4.71 (d, $J = 7.2$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 117.17 (d of t, $^1J_{Rh-C} = 28.2$, $^2J_{P-C} = 9.4$ Hz, C2 or C6a), 119.94, 121.31, 124.08 (d of t, $^1J_{Rh-C} = 21.0$, $^2J_{P-C} = 6.6$ Hz, C6a or C2), 125.0–132.3 (complex), 127.68 (t, $J = 4.8$ Hz, 12 × CH), 129.64 (s, 6 × CH), 131.13 (t, $J = 22.7$ Hz), 134.81 (t, $J = 5.5$ Hz, 12 × CH), 141.53, 144.41, 156.70 (q, $^2J_{Rh-C} \approx {}^3J_{P-C} = 3.9$ Hz, C2a); ^{31}P NMR δ 30.8 (d, $^1J_{Rh-P} = 124.6$ Hz); MS *m*/*e* 916 (1, M), 881 (14, M − Cl), 654 (10), 619 (100), 286 (62%).

(ii) Rhodacyclobuta[*b*]naphthalene 11b. From 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**1b**; 20 mg, 0.066 mmol) Wilkinson's catalyst (59 mg, 0.064 mmol), and triphenylphosphine (17 mg, 0.066 mmol) was obtained **11b** (37 mg, 60%) as a yellow microcrystalline solid: mp 195–197 °C; IR 3050, 1585, 1570, 1480, 1430, 1090, 865, 740, 690 cm^{-1}; ^{1}H NMR δ 7.52–6.90 (complex m, 43 H), 6.08 (d, $J = 7.8$ Hz, 2 H), 5.10 (s, 1 H); ^{13}C NMR (CD_2Cl_2) δ 116.83 (br s, C9), 117.00 (d of t, $^1J_{Rh-C} = 28.7$, $^2J_{P-C} = 9.8$ Hz, C2), 123.52, 124.21, 125.29, 126.56, 126.79, 127.56, 127.75 (12 CH), 128.47, 128.67, 128.83, 129.61, 130.14 (6 × CH), 130.94, 131.02, 131.25, 131.55, 132.09, 132.22, 132.80, 134.83, 135.10 (12 × CH), 142.09/144.84 (C3a/7a), 154.83 (q, $^2J_{Rh-C} \approx {}^3J_{P-C} = 3.8$ Hz, C2a); ^{31}P NMR δ 29.7 (d, $^1J_{Rh-P} = 123.9$ Hz); MS *m*/*e* 931 (2), 669 (9), 307 (100), 289 (88), 279 (31), 154 (100%).

(iii) Rhodacyclobuta[*b*]naphthalene 11d. From 1-(bis(*m*-(trifluoromethyl)phenyl)methylene)-1*H*-cyclopropa[*b*]naphthalene (**1d**; 117 mg, 0.266 mmol), and Wilkinson's catalyst (234 mg, 0.253 mmol) was obtained **11d** (204 mg, 73%) as a yellow microcrystalline solid: mp 201–203 °C; IR 3055, 2985, 1585, 1480, 1430, 1325, 1245, 1215, 1160, 1120, 1090, 1065, 995, 905, 860, 800, 785, 740, 705, 690 cm^{-1}; ^{1}H NMR δ 8.43 (d, $J = 7.5$ Hz, 1 H), 7.54 (d, $J = 7.8$ Hz, 1 H), 7.48 (d, $J = 7.8$ Hz, 1 H), 7.42–6.90 (complex m, 37 H), 6.84 (s, 1 H), 6.60 (s, 1 H), 6.28 (d, $J = 7.8$ Hz, 1 H), 5.18 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.49 (br s, C9), 116.67 (d of t, $^1J_{Rh-C} \approx 28.6$, $^2J_{P-C} = 9.8$ Hz, C2), 122–132 (complex), 127.84 (t, $J = 4.5$ Hz, 12 × CH), 130.11 (s, 6 × CH), 132.85, 132.95, 134.72 (t, $J = 5.6$ Hz, 12 × CH), 141.72, 145.10, 153.49 (q, $^2J_{Rh-C} \approx {}^3J_{P-C} = 3.3$ Hz, C2a); ^{19}F NMR δ 15.5 and 14.8 (both s); ^{31}P NMR δ 29.4 (d, $^1J_{Rh-P} = 121.7$ Hz); MS *m*/*e* 1102 (1, M), 1067 (12, M − Cl), 840 (24), 805 (63), 727 (26), 286 (100), 210 (63), 183 (44%). Anal. Calcd for $C_{62}H_{44}ClF_6P_2Rh$: C, 67.49; H, 4.02; P, 5.61. Found: C, 67.09; H, 3.93, P, 5.66.

2-(Diarylmethylene)-1,1-bis(triphenylphosphine)-1-platina-2*H*-cyclobutarenes (12). A mixture of tetrakis(triphenylphosphine)platinum(0) (129.7 mg, 0.104 mmol) and the relevant alkylidenecycloproparene **1** (0.109 mmol) in dry degassed benzene was heated at reflux under an inert atmosphere for 16 h. The resultant clear yellow solution was concentrated under vacuum, and the residue thus obtained was crystallized (dichloromethane–methanol) to yield the product as a yellow powder.

(i) Platinacyclobuta[*b*]naphthalene 12b. From tetrakis(triphenylphosphine)platinum(0) and **1b** was obtained complex **12b** (76 mg, 72%): mp 157–160 °C; IR 3050, 1593, 1572, 1480, 1435, 1265, 1093, 873, 740, 695 cm^{-1}; ^{1}H NMR δ 7.55–6.90 (complex m, 41 H), 6.62 (t, $J = 7$ Hz, 1 H), 6.48 (d, $^4J_{P-H} = 6.3$ Hz, H8), 6.41 (t, $J = 7.6$ Hz, 2 H), 5.78 (s, H3); ^{13}C NMR ($CDCl_3$) δ 113.84 (t (with ^{195}Pt satellites), $^1J_{Pt-C} = 81$, $^2J_{P-C} = 3.6$ Hz, C2), 123.02, 123.11, 124.62, 126.07, 126.7–128.9 (complex), 129.6, 130.75, 131.7–133.6 (complex), 133.95 (d, $^2J_{P-C} = 11.8$ Hz, 6 × CH), 135.00 (d, $^2J_{P-C} = 11.5$ Hz, 6 × CH), 137.00, 137.14, 137.7 (br m), 145.32 (d (with ^{195}Pt satellites), $^2J_{Pt-C} \approx 45$, $^3J_{P-C} = 4.5$ Hz, C9), 147.26 (d (with ^{195}Pt satellites), $^1J_{Pt-C} \approx 86$, $^2J_{P-C} = 10.6$ Hz, C8a), 165.64 (d (with ^{195}Pt satellites), $^2J_{Pt-C} \approx 65$, $^3J_{P-C} = 2.3$ Hz, C2a); ^{31}P NMR δ 18.7 (d (with ^{195}Pt satellites), $^1J_{Pt-P} = 2156$, $^2J_{P-P} = 10$ Hz), 18.2 (d (with ^{195}Pt satellites), $^1J_{Pt-P} = 1853$, $^2J_{P-P} = 10$ Hz); MS *m*/*e* 1024 (28, M), 762 (93), 719 (44), 456 (100), 378 (98), 303 (52), 183 (83%). Anal. Calcd for $C_{60}H_{46}P_2Pt$: C, 70.37; H, 4.53. Found: C, 70.15; H, 4.55.

(ii) Platinacyclobuta[*b*]naphthalene 12c. From tetrakis-

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(triphenylphosphine)platinum(0) and **1c** was obtained complex **12c** (96 mg, 85%): mp 166–169 °C; IR 3050, 2835, 1601, 1572, 1504, 1435, 1242, 1170, 1094, 1035, 740, 695 cm^{-1}; ^{1}H NMR δ 7.55–6.82 (complex m, 40 H), 6.48 (d (with ^{195}Pt satellites), $^{3}J_{Pt-H} \approx 65$, $^{4}J_{P-H} = 6$ Hz, H8), 5.97 (d, $J \approx 9$ Hz, 2 H), 5.95 (s, H3), 3.86 (s, OMe), 3.41 (s, OMe); ^{13}C NMR (CDCl$_3$) δ 54.91/55.33 (2 × OCH$_3$), 112.39/113.61 (4 × HC=COMe), 113.30 (br t, $^{2}J_{P-C} \approx 3.5$ Hz, C2), 113.81, 122.99, 126.8–129.8 (complex), 127.17 (d, $^{3}J_{P-C} = 9.8$ Hz, 6 × CH), 127.60 (d, $^{3}J_{P-C} = 9.7$ Hz), 131.5–131.7 (complex), 133.93 (d, $^{2}J_{P-C} = 11.8$ Hz, 6 × CH), 134.99 (d, $^{2}J_{P-C} = 11.5$ Hz, 6 × CH), 136.5–137.5 (m), 139.07 (d (with ^{195}Pt satellites), $^{2}J_{Pt-C} \approx 45$, $^{3}J_{P-C} = 4.3$ Hz, C9), 139.68 (d, $^{2}J_{P-C} = 10.5$ Hz, C8a), 154.49, 157.26/158.21 (2 × COMe), 166.06 (d, $^{3}J_{P-C} = 2.3$ Hz, C2a); ^{31}P NMR δ 18.7 (d (with ^{195}Pt satellites), $^{1}J_{Pt-P} = 2155$, $^{2}J_{P-P} = 10$ Hz), 18.4 (d (with ^{195}Pt satellites), $^{1}J_{Pt-P} = 1829$, $^{2}J_{P-P} = 10$ Hz); MS *m/e* 1084 (7, M), 822 (9), 455 (42), 378 (54), 183 (100%).

3-(Diarylmethylene)-1-chloro-1,1-bis(triphenylphosphine)-1-rhoda-3*H*-indan-2-ones (14). A mixture of the alkylidenecycloproparene 1 (0.160 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) (104 mg, 0.150 mmol) in dry degassed benzene (6 mL) was heated to reflux under an inert atmosphere for 60 h. The solution was cooled, the solvent removed under vacuum, and the residue dissolved in the minimum volume of dichloromethane. Slow addition of hexane gave a yellow precipitate, which was collected by filtration and washed with hexane (4 × 3 mL). Recrystallization from dichloromethane–hexane afforded the 3-alkylidene-1-rhodaindan-2-ones 14 as yellow air-stable microcrystals.

(i) 1-Rhodaindan-2-one 14a: yield 125 mg, 88%; mp 209–210 °C; IR 3050, 1680, 1570, 1480, 1435, 1410, 1270, 1185, 1150, 1130, 1090, 1070, 1045, 1025, 1000, 980, 930, 870, 740, 730, 690 cm^{-1}; ^{1}H NMR δ 7.45–7.22 (complex m, 31 H), 7.20–7.08 (m, 6 H), 6.5 (br d of d, $J = 8$ and 1.3 Hz, 2 H), 6.37 (m, 2 H), 6.26 (m, 2 H), 5.63 (d of d, $J = 7.3$ and 1.9 Hz, 1 H); ^{13}C NMR (CD$_2$Cl$_2$) δ 122.63, 124.30, 126.5–129.0 (complex), 128.22 (t, $J = 4.8$ Hz, 12 × CH), 130.39 (s, 6 × CH), 130.66 (t, $J = 22.6$ Hz, ipso-C$_6$H$_5$P), 134.95 (t, $J = 5.6$ Hz, 12 × CH), 141.31, 142.80, 143.38 (br), 144.91, 145.30, 168.89 (d of t, $^{1}J_{Rh-C} = 33.0$, $^{2}J_{P-C} = 9.1$ Hz, C7a), 222.84 (d of t, $^{1}J_{Rh-C} = 27.8$, $^{2}J_{P-C} = 6.5$ Hz, CO); ^{31}P NMR δ 27.4 (d, $^{1}J_{Rh-P} = 127.5$ Hz); MS *m/e* 944 (2, M), 909 (91, M – Cl), 654 (44), 619 (100), 286 (68%). Anal. Calcd for C$_{57}$H$_{44}$ClOP$_2$Rh: C, 72.43; H, 4.69. Found: C, 72.25; H, 4.67.

(ii) 1-Rhodabenz[*f*]indan-2-one 14b: yield 135 mg, 90%; mp 215–217 °C; IR 3050, 1680, 1480, 1435, 1090, 930, 870, 740, 730, 690 cm^{-1}; ^{1}H NMR δ 7.45–7.29 (m, 20 H), 7.28–7.10 (m, 18 H), 7.05 (t, $J \approx 7$ Hz, 1 H), 6.97 (t, $J = 7$ Hz, 2 H), 6.58 and 6.39 (br AB, $J = 8$ Hz, 4 H), 5.98 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 123.0, 125.04, 125.19, 125.26, 127.0–131.0 (complex), 127.81 (t, $J = 4.8$ Hz, 12 × CH), 129.85 (s, 6 × CH), 132.25, 134.65 (t, $J = 5.5$ Hz, 12 × CH), 141.22, 142.05, 142.13, 142.90, 143.82, 144.21, 162.55 (d of t, $^{1}J_{Rh-C} = 33.3$, $^{2}J_{P-C} = 9.4$ Hz, C9a), 221.24 (d of t, $^{1}J_{Rh-C} = 28.6$, $^{2}J_{P-C} = 6.5$ Hz, CO); ^{31}P NMR δ 26.8 (d, $^{1}J_{Rh-P} = 127.0$ Hz); MS *m/e* 959 (35, M – Cl), 704 (15), 669 (47), 307 (100), 286 (54), 279 (99). Anal. Calcd for C$_{61}$H$_{46}$ClOP$_2$Rh: C, 73.61; H, 4.66; P, 6.22. Found: C, 73.28; H, 4.67; P, 6.18.

(iii) 1-Rhodabenz[*f*]indan-2-one 14c: yield 133 mg, 84%; mp 204–205 °C; IR 3050, 2950, 2830, 1680, 1600, 1570, 1480, 1430, 1285, 1245, 1170, 1090, 1040, 1025, 980, 920, 870, 825, 795, 740, 700, 690 cm^{-1}; ^{1}H NMR δ 7.4–7.3 (m, 18 H), 7.28–7.15 (m, 12 H), 7.15–6.94 (m, 5 H), 6.73 (d, $J = 8.7$ Hz, 2 H), 6.62 (d, $J = 9.0$ Hz, 2 H), 6.48 (d, $J = 9.0$ Hz, 2 H), 6.23 (d, $J = 9.0$ Hz, 2 H), 6.18 (s, 1 H), 3.85 (s, OMe), 3.80 (s, OMe); ^{13}C NMR (CD$_2$Cl$_2$) δ 55.50/55.67 (2 × OMe), 112.92/114.14 (4 × CH=COMe), 123.41, 124.91, 125.20, 125.57, 128.15 (t, $J = 4.7$ Hz, 12 × CH), 128.56, 129.9–131.5 (complex), 130.35 (6 × CH), 132.30, 134.15, 134.92 (t, $J = 5.6$ Hz, 12 × CH), 136.98, 141.67, 141.76, 144.02, 145.03, 159.38/159.72 (2 × COMe), 162.64 (d of t, $^{1}J_{Rh-C} = 33.1$, $^{2}J_{P-C} = 9.2$ Hz, C9a), 222.39 (d of t, $^{1}J_{Rh-C} = 28.2$, $^{2}J_{P-C} = 6.3$ Hz, CO); ^{31}P NMR δ 26.8 (d, $^{1}J_{Rh-P} = 127.9$ Hz); MS *m/e* 1019 (26, M – Cl), 764 (21), 729 (100), 286 (100%). Anal. Calcd for C$_{63}$H$_{50}$ClO$_3$P$_2$Rh: C, 71.94; H, 4.78. Found: C, 71.17; H, 5.02.

(iv) 1-Rhodabenz[*f*]indan-2-one 14d: yield 119 mg, 70%; mp 223–225 °C; IR 3060, 1670, 1570, 1485, 1430, 1330, 1255, 1175, 1165, 1125, 1090, 1070, 990, 955, 910, 870, 810, 745, 730, 705, 695 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.80–7.30 (m, 37 H), 7.00 (t, $J = 8.4$ Hz, 2 H), 6.86 (d, $J = 11.7$ Hz, 2 H), 6.78 (d, $J = 7.5$ Hz, 1 H), 6.67 (d, $J = 7.8$ Hz, 1 H), 5.92 (s, 1 H); ^{13}C NMR (CD$_2$Cl$_2$) δ 123.8–125.8 (complex), 126.59, 128.08, 128.42 (t, $J = 4.8$ Hz, 12 × CH), 128.78, 129.04, 130.0–131.8 (complex), 130.73 (s, 6 × CH), 132.89, 135.02 (t, $J = 5.7$ Hz, 12 × CH), 139.26, 141.23, 142.30, 142.24, 142.33, 144.95, 162.75 (d of t, $^{1}J_{Rh-C} = 33.5$, $^{2}J_{P-C} = 9.3$ Hz, C9a), 224.16 (d of t, $^{1}J_{Rh-C} = 27.7$, $^{2}J_{P-C} = 5.8$ Hz, CO); ^{19}F NMR δ 15.3 and 15.2; ^{31}P NMR δ 26.4 (d, $^{1}J_{Rh-P} = 124.6$ Hz); MS *m/e* 1095 (28, M – Cl), 840 (17), 805 (53), 727 (27), 286 (100), 263 (46), 262 (53), 210 (58), 183 (49%).

2-Chloro-3-(diphenylmethylene)-2,2-bis(triphenylphosphine)-2-rhoda-3*H*-benz[*f*]indanone 15b from rhodacyclobutarene 11b. (i) Intermediate 16b. Carbon monoxide was bubbled through a suspension of **11b** (46 mg, 0.048 mmol) in chloroform-*d* contained in an NMR tube to effect saturation; the tube was sealed and then inserted into the spectrometer. The reaction was monitored by ^{31}P NMR spectroscopy until the doublet of **11b** at 29.7 ppm had been replaced by a new doublet centered at 23.8 ppm ($^{1}J_{Rh-P} = 112.2$ Hz). The probe was cooled to 3 °C, and ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded. The new compound present is tentatively assigned as the octahedral rhodium complex **16b**: IR (from **16b** and CO after ca. 3 min) 2080 cm^{-1}; ^{1}H NMR δ 7.62 (br s, 1 H), 7.55–7.40 (m, 12 H), 7.35–7.22 (m, 6 H), 7.22–6.90 (m, 24 H), 6.07 (d, $J = 7.8$ Hz, 2 H), 5.37 (s, 1 H); ^{13}C NMR (CDCl$_3$)[24] δ 115.87, 155.99 (q, $J = 5.7$ Hz, C2a), 188.67 (d of t, $^{1}J_{Rh-C} = 46.8$, $^{2}J_{P-C} = 8.5$ Hz, CO); ^{31}P NMR δ 23.8 (d, $^{1}J_{Rh-P} = 112.2$ Hz).

(ii) 2-Rhodaindan-1-one 15b. The sample from (i) above was heated to 40 °C and rearrangement monitored by completed disappearance of the ^{31}P NMR doublet at 23.8 ppm and its replacement by a new doublet at 22.7 ppm. The tube was opened, the volume reduced, and hexane added to provide complex **15b** (42 mg, 89%) as a yellow solid: mp 193–196 °C; IR 3050, 1690, 1620, 1585, 1570, 1485, 1435, 1090, 1070, 965, 870, 740, 690 cm^{-1}; ^{1}H NMR δ 7.58 (s, 1 H), 7.53–7.40 (m, 10 H), 7.36 (s, 2 H), 7.32–7.18 (m, 15 H), 7.18–7.02 (m, 15 H), 6.19 (d, $J = 6.9$ Hz, 2 H), 5.78 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 120.72, 125.50, 126.15, 127.1–131.5 (complex), 127.57 (t, $J = 4.7$ Hz, 12 × CH), 129.65 (s, 6 × CH), 134.39, 134.46, 134.80 (t, $J = 5.2$ Hz, 12 × CH), 141.75, 143.21, 145.93, 146.13, 147.67, 161.22 (d of t, $^{1}J_{Rh-C} = 36.2$, $^{2}J_{P-C} = 7.6$ Hz, C3), 216.11 (d of t, $^{1}J_{Rh-C} = 31.1$, $^{2}J_{P-C} = 7.3$ Hz, CO); ^{31}P NMR δ 22.7 (d, $^{1}J_{Rh-P} = 127.0$ Hz); MS *m/e* 959 (2, M – Cl), 697 (11), 669 (10), 307 (100), 289 (75), 279 (98%). Anal. Calcd for C$_{61}$H$_{46}$ClOP$_2$Rh: C, 73.61; H, 4.66. Found: C, 73.41; H, 4.96.

(iii) Formation of 14b/15b Mixtures. A solution of **11b** (15 mg, 0.016 mmol) in chloroform-*d* was saturated with carbon monoxide and sealed as described in (i) above. After the solution was heated at 70 °C for 20 h, the ^{31}P NMR spectrum showed the presence of **14b** and **15b** as doublets centered at 26.8 and 22.7 ppm, respectively; integration gave the ratio of ca. 16:84.

At the same temperature, but for 70 h, a mixture of **1b** (7 mg, 0.023 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) (15 mg, 0.022 mmol) showed ^{31}P NMR resonances for **14b** (86%) and unchanged rhodium substrate (14%) only.

Acknowledgment. Financial assistance from the NSF (Grant No. CHE 8802622), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Visiting Professorship (to B.H.) are gratefully acknowledged. In New Zealand financial assistance from Victoria University and the receipt of a Claude McCarthy Fellowship from the New Zealand University Grants Committee (to B.H.) have greatly facilitated these collaborative studies. We also thank Johnson Matthey for loans of Rh and Pt via the Johnson Matthey metals loan program.

Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, thermal parameters, and least-squares planes for **11d** and **14b** (41 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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[24] During the 11-h acquisition period partial rearrangement of the complex to product **15b** occurred. Only signals clearly assignable to **16b** are given.