Reaction of Cyclobutenones with Low-Valent Metal Reagents To Form η^4- and η^2-Vinylketene Complexes. Reaction of η^4-Vinylketene Complexes with Alkynes To Form Phenols

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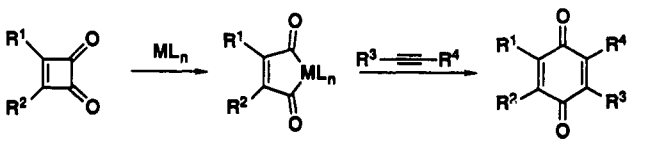
The reactivity of cyclobutenones toward some low-valent transition-metal reagents has been investigated. Treatment of 3-substituted and 2,3-disubstituted cyclobutenones with $ClRh(PPh_3)_3$ led to η^2-vinylketene complexes $Cl(PPh_3)_2RhC(O)C(R^1)=C(R^2)CH_2$ (**4**). Complex **4e** (R^1 = H, R^2 = $C(O)C_6H_5$) has been characterized by X-ray crystallography: triclinic, $P\bar{1}$ (No. 2), a = 12.868 (4) Å, b = 13.158 (3) Å, c = 15.241 (4) Å, α = 81.49 (2)°, β = 79.45 (2)°, γ = 60.72 (2)°, V = 2209 (1) Å^3, Z = 2. Treatment of $ClRh(PPh_3)_3$ with benzocyclobutenones gave mixtures of 2-rhodaindanones and 1-rhodaisoindanones. Reaction of 3-substituted and 3,4-disubstituted cyclobutenones with $(\eta^5\text{-}C_9H_7)Co(PPh_3)_2$ (**9**) gave η^4-vinylketene complexes $(\eta^5\text{-}C_9H_7)Co(\eta^4\text{-}C(O)=C(H)C(R^1)=CHR^2)$ (**10**). Anti isomers of **10** were formed as the major kinetic products; isomerization to the syn isomer was observed in two cases. Reversible conversion of an η^4-vinylketene complex to the η^2-mode was induced by addition of PPh_3 or CO to **10a** (R^1 = Ph, R^2 = H). Structurally different metallacycles $(\eta^5\text{-}C_9H_7)(PPh_3)CoC(O)CH_2C(R^1)=CH$ (**13**) were obtained from **9** and cyclobutenones in the presence of $ZnCl_2$. Upon treatment with alkynes, **10a** gave a series of substituted phenols. Complex **10b** (R^1 = Ph, R^2 = CH_3) reacted only with dimethyl acetylenedicarboxylate to give both a phenol and an η^4-cyclohexadienone complex. Mechanisms are discussed for the insertion reactions of **9** and for the phenol-producing alkyne reactions.

Introduction

Low-valent transition-metal reagents insert into various strained small ring organic compounds. Reaction of the resulting complexes with unsaturated substrates provides a general strategy for the synthesis of ring-expanded products.[3-14] A general, convergent synthesis of 1,4-quinones has been developed by applying the strategy to the combination of cyclobutenediones and alkynes (eq 1).[15-18] Described here are efforts to develop an analogous synthesis of substituted phenols via insertion into cyclobutenones and reaction with alkynes (eq 2).

The key intermediates envisioned in this phenol synthesis are η^2- or η^4-vinylketene complexes (**1** or **2**). η^4-Vinylketene complexes of type **2** have been synthesized



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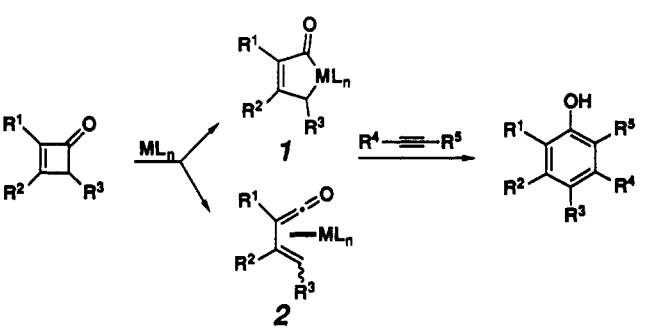

(2)

previously by several methods, most of which involve CO insertion into an intermediate vinylcarbene ligand (eq 3).

(3)

The vinylcarbene intermediates have been generated via metal insertion into cyclopropenes,[19-27] deoxygenation of

(1) National Institutes of Health Postdoctoral Fellow, 1989–1991.
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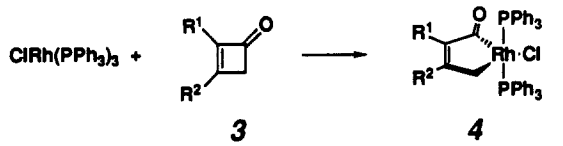
Table I. Reaction of $ClRh(PPh_3)_3$ with Cyclobutenones



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entry	product	R^1	R^2	conditions	yield, %[a]
1	**4a**	Et	Et	90 °C, 18 h	75
2	**4b**	H	Bu	90 °C, 5 h	71
3	**4c**	H	Ph	60 °C, 18 h	87
4	**4d**	H	OEt	60 °C, 5 h	92
5	**4e**	H	C(O)Ph	60 °C, 5 h	89

[a] Yields represent precipitated products either pure or containing traces of solvent and PPh_3.

complexed vinylketones,[28] alkylation of acryloyl metalates,[29] coupling of Fischer carbenes with alkynes,[30-32] and other methods.[33-35] η^2-Vinylketene complexes of type 1 are less common.[29,36,37] For the purpose of a phenol synthesis, insertion into cyclobutenones was a more attractive route to vinylketene complexes than those previously reported because it offers the potential for greater generality in the pattern of vinylketene substitution.

Transient η^4-vinylketene complexes have been widely implicated as intermediates en route to phenols and naphthols, from reaction of Fischer carbenes with alkynes[38,39] and from metal insertion into vinylcyclopropenes.[4,5] While isolated η^4-vinylketene complexes have previously been induced to give furan, 2-furanone, and α-pyrone products,[30,31] only very recently has an example been reported which yields phenols.[32]

Reported herein are full details of the synthesis of η^2- and η^4-vinylketene complexes by insertion of Rh(I) and Co(I) reagents into cyclobutenones. Also reported are reactions of some of the cobalt complexes with alkynes to give phenols. In addition, experiments are presented which bear on the mechanisms of both the insertion and alkyne cycloaddition reactions. Preliminary reports of this work have appeared.[40,41]

Results and Discussion

I. Reaction of $ClRh(PPh_3)_3$ with Cyclobutenones. (a) Insertion into Simple Cyclobutenones. Heating slurries of $ClRh(PPh_3)_3$ with a slight excess of cyclobutenones **3** led to good yields of rhodacyclopentenones **4** as air-stable yellow solids (Table I). The metallacycles **4** are characterized in the infrared region by carbonyl absorptions around 1645 cm^{-1}. The ^1H NMR spectra are consistent with the symmetric metallacycle structure, revealing equivalent ring methylene protons (2.2–3.3 ppm) and equivalent PPh_3 ligands. In the ^{13}C NMR spectrum, the metallacycle ring carbons gave the following characteristic signals: C1 (CO), 210–224 ppm (dt, J_{Rh-C} = 23–28 Hz, J_{P-C} = 6–7 Hz); C2, 104–143 ppm (m); C3, 169–190

Table II. Crystal Data and Data Collection Parameters for 4e·THF

empirical formula	$C_{47}H_{38}ClO_2P_2Rh \cdot C_4H_8O$
color; habit	yellow; parallelepiped
space group	triclinic, $P\bar{1}$ (No. 2)
a, Å	12.868 (4)
b, Å	13.158 (3)
c, Å	15.241 (4)
α, deg	81.49 (2)
β, deg	79.45 (2)
γ, deg	60.72 (2)
V, Å^3	2209 (1)
fw	907.23
d(calcd), g/cm^3	1.36
Z	2
cryst dimen, mm	0.30 × 0.55 × 0.55
2θ range, deg	$3.5 < 2\theta < 45$
no. of reflns	6114
no. of unique reflns	5811
cryst decomp, %	14
abs coef, cm^{-1}	5.50
transm factors	0.68–0.85
R	0.0594
R_w	0.0898

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for the Core Atoms of 4e

	x	y	z	U(eq)
Rh1	320 (1)	2773 (1)	2148 (1)	29 (1)
Cl1	−187 (2)	1189 (2)	2331 (1)	54 (1)
P1	2076 (1)	1656 (1)	1212 (1)	33 (1)
P2	−1343 (1)	3737 (1)	3215 (1)	35 (1)
O1	−727 (4)	4307 (4)	744 (3)	46 (2)
O2	1562 (9)	5208 (7)	3229 (4)	115 (6)
C1	−126 (5)	4171 (5)	1308 (4)	34 (3)
C2	309 (6)	4985 (5)	1445 (4)	38 (3)
C3	982 (6)	4651 (5)	2113 (4)	39 (3)
C4	1200 (6)	3510 (5)	2602 (4)	37 (3)
C5	1403 (7)	5381 (7)	2450 (5)	55 (4)
C6	1663 (6)	6262 (6)	1871 (5)	43 (3)
C7	1953 (7)	6226 (6)	957 (5)	55 (4)
C8	2250 (8)	7056 (8)	454 (6)	72 (5)
C9	2265 (8)	7905 (7)	894 (6)	70 (5)
C10	1972 (8)	7932 (7)	1802 (6)	66 (4)
C11	1653 (7)	7142 (6)	2286 (5)	4 (4)

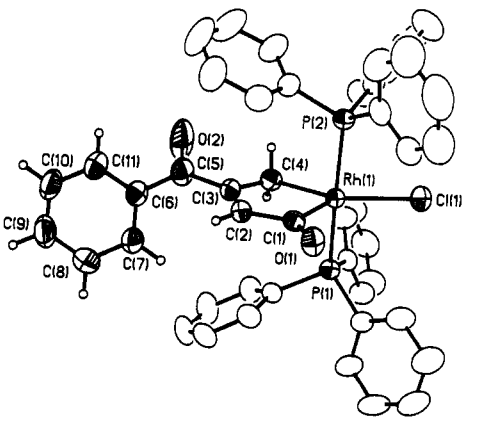

Figure 1. Molecular structure of η^2-vinylketene complex **4e**.

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Table IV. Selected Distances (Å) and Angles (deg) for 4e

Rh1–Cl1	2.436 (3)	O2–C5	1.211 (10)
Rh1–P1	2.344 (2)	C1–C2	1.483 (12)
Rh1–P2	2.349 (2)	C2–C3	1.341 (10)
Rh1–C1	1.973 (6)	C3–C4	1.491 (9)
Rh1–C4	2.064 (9)	C3–C5	1.495 (14)
O1–C1	1.197 (9)	C5–C6	1.458 (12)
Cl1–Rh1–P1	89.8 (1)	Rh1–C1–C2	116.1 (4)
Cl1–Rh1–P2	87.7 (1)	Rh1–C4–C3	112.5 (5)
P1–Rh1–P2	173.7 (1)	O1–C1–C2	125.3 (6)
Cl1–Rh1–C1	132.1 (2)	C1–C2–C3	115.1 (6)
Cl1–Rh1–C4	147.2 (2)	C2–C3–C4	115.6 (8)
P1–Rh1–C1	92.8 (2)	C2–C3–C5	125.1 (6)
P1–Rh1–C4	89.5 (2)	C4–C3–C5	119.0 (6)
P2–Rh1–C1	93.2 (2)	C3–C5–C6	123.1 (6)
P2–Rh1–C4	89.4 (2)	O2–C5–C3	117.2 (9)
C1–Rh1–C4	80.6 (3)	O2–C5–C6	119.7 (10)
Rh1–C1–O1	118.6 (6)		

ppm; C4, 22–34 ppm (dt, J_{Rh-C} = 30–34 Hz, J_{P-C} = 6 Hz).

The insertion proceeded well with 2,3-disubstituted and 3-substituted cyclobutenones and a variety of substituent types. Only cyclobutenones substituted in the 4-position failed to give clean products. This is presumably a steric result, with the C4 substituent hindering access to the C1–C4 bond and/or destabilizing the metallacycle product. The rate of reaction varies as a function of substituent. As shown by the reaction conditions given in Table I, electronegative groups allow for shorter reaction times and lower temperatures.

(b) Structure of 4-Benzoylrhodacyclopent-3-en-2-one (4e). Diffusion of hexane vapors into a tetrahydrofuran (THF) solution of **4e** gave single crystals containing one molecule of **4e** and one THF molecule in the asymmetric unit. A view of the structure of **4e** is shown in Figure 1, with selected bond distances and angles listed in Table IV.

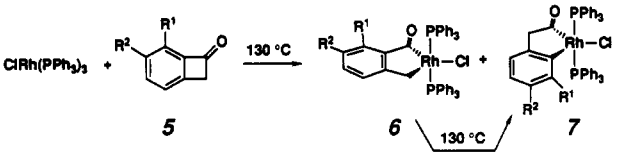
The geometry about the rhodium atom is approximately trigonal bipyramidal, with phosphine ligands occupying the axial positions. The main distortion is due to the small bite angle of the η^2-vinylketene ligand. The Rh–Cl bond does not bisect the C4–Rh–C1 angle, rather it is bent toward C1 by 7.6°. The phosphine ligands are bent slightly away from C1, giving a P1–Rh–P2 angle of less than 180°.

The metallacyclopentenone unit is nearly planar, the maximum deviation being 0.029 Å. The benzoyl carbonyl carbon C5 is displaced out of this plane by 0.186 Å, and the C5–O2 bond is rotated substantially away from planarity with the metallacycle π system (torsion angle C2–C3–C5–O2 = 151.0°). The phenyl group is rotated away from planarity with the carbonyl in the same direction (torsion angle O2–C5–C6–C11 = −23.1°), giving an angle between the phenyl and metallacycle planes of 46.6°.

(c) Insertion into Benzocyclobutenones. The reaction of $ClRh(PPh_3)_3$ with benzocyclobutenones was more sluggish than with simple cyclobutenones and required heating the reactants to 130 °C. Yellow powders were obtained which consisted of mixtures of isomeric rhodaindanones **6** and **7** (Table V). The isomers were distinguished spectroscopically by the ^1H NMR signals for the metallacycle CH_2 protons which are multiplets (~3.5 ppm) in **6** due to coupling to Rh and P and are singlets (~2.0 ppm) in **7**. The infrared carbonyl absorptions are also distinctive: ~1695 cm^{-1} for **7**, shifting down to ~1660 cm^{-1} for **6** from conjugation with the aromatic system.

The two isomers could arise from insertion into the benzocyclobutenone at either of two positions. Isomer **6** is analogous to the simple cyclobutenone insertion products **4**, while **7** could arise from insertion into the carbonyl–aryl bond. However the ratio of **6** to **7** was found to decrease

Table V. Reaction of $ClRh(PPh_3)_3$ with Benzocyclobutenones



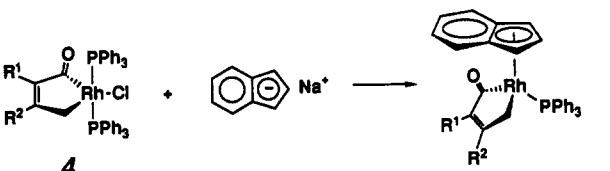
5 **6** **7**

entry	product	R^1, R^2	reaction time, h	ratio 6:7	yield, %
1	**6a, 7a**	H, H	24	1:3	71
2	**6b, 7b**	OCH_2O	5	1:2	50

with reaction time, suggesting that **7** might form from **6** under the reaction conditions. To test this possibility, isolated mixtures of **6a,7a** and **6b,7b** were heated to 130 °C in PhCl-d_5. Monitoring by ^1H NMR integration against an internal ferrocene standard showed that **6** did isomerize to **7** in both cases, the rearrangement occurring faster in the case of **6b,7b**. Decomposition occurred competitive with rearrangement, so equilibrium ratios could not be determined.

A similar rearrangement has been proposed to occur in the formation of ferracyclopent-4-en-2-one complexes analogous to **7** from η^4-vinylketene complexes, but the intermediates corresponding to **6** were not observed.[29] A related isomerization in the opposite direction has also been suggested to occur in rhodacyclopentenediones derived from insertion of $ClRh(PPh_3)_3$ into benzocyclobutenedione.[42] In that case the symmetrical metallacycle corresponding to **6** was the isolated thermodynamic product.

(d) Reactions of Rhodacyclopentenones 4. Attempted reactions of the metallacycles **4** with alkynes were carried out thermally and in the presence of $AgBF_4$ as a chloride abstracting reagent. In no case were any phenol products detected. Some ligand-exchange reactions were carried out in an attempt to produce more reactive complexes. Thus reaction between sodium indenylide and **4a** or **4c** occurred with loss of the chloride and one phosphine ligand to give the new metallacycles **8a** and **8b** (eq 4). Reaction of **4a** with sodium cyclopentadienide also gave the cyclopentadienyl analogue **8c**, the X-ray crystallographic analysis of which has been reported previously.[40]



(4)

4

$R^1 = R^2 = Et$; **8a**; 82 %

$R^1 = H$, $R^2 = Ph$; **8b**; 70 %

The metallacyclopentenone cores in **8** are spectroscopically similar to those of **4**. The carbonyl bands in the infrared spectrum appear between 1605 and 1625 cm^{-1}. The now inequivalent methylene protons give rise to ^1H NMR resonances in the ranges 3.5–4.0 and 1.75–2.15 ppm with geminal coupling constants of 15–16 Hz. The ^{13}C NMR resonances of the metallacycle carbons are as follows: C1 (CO), 230–239 ppm (dd, J_{Rh-C} = 30–32 Hz, J_{P-C} = 11–13 Hz); C2, 135–150 ppm; C3, 175–176 ppm; C4, 18–21 ppm (dd, J_{Rh-C} = 31–33 Hz, J_{P-C} = 11 Hz).

Like their precursors **4**, the metallacycles **8** were found to be unreactive toward alkynes. Believing that the inertness of these complexes was a result of strong metal–

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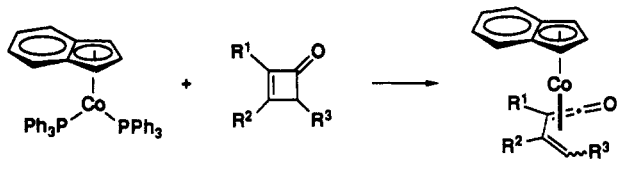
Table VI. Synthesis of η^4-Vinylketene Cobalt Complexes



9 3 10

entry	product	R^1	R^2	R^3	anti/syn	yield, %
1	10a	H	Ph	H		32
2		Et	Et	H		
3		H	OEt	H		a
4	10b	H	Ph	Me	95:5	80
5	10c	H	$SiMe_3$	Me	78:22	81
6	10d	H	t-Bu	Me	>98:2	42
7		Et	Et	Me		
8	10e	H	t-Bu	Ph	>98:2	17

[a] A different product was obtained (vide infra).

ligand bonds involving the second-row transition-metal rhodium, we proceeded to explore the chemistry of some first-row cobalt analogues.

II. Reaction of $(\eta^5\text{-}C_9H_7)Co(PPh_3)_2$ with Cyclobutenones. (a) Synthesis of η^4-Vinylketene Complexes. $ClCo(PPh_3)_3$, which is known to insert into cyclobutenediones,[16,18] was found not to react with cyclobutenones. Poor results were also obtained with $(\eta^5\text{-}C_5H_5)Co(CO)_2$. However, reaction of the more electron-rich $(\eta^5\text{-}C_9H_7)Co(PPh_3)_2$ (**9**) with 3-phenylcyclobutenone gave the η^4-vinylketene complex **10a** in moderate yield (Table VI). A small amount (<2%) of another product was obtained, later identified as the monophosphine cobaltacyclopentenone **11b**. Other 3-substituted and 2,3-disubstituted cyclobutenones gave very low yields of mixtures of products tentatively identified as the η^4-vinylketenes and metallacyclopentenones (e.g. entry 2). The exception is 3-ethoxycyclobutenone which gave a moderate yield of metallacyclic product (vide infra).

3,4-Disubstituted cyclobutenones were found to react more cleanly and in higher yield, giving η^4-vinylketenes (entries 4–6), but 2,3,4-trisubstitution shut the reaction down (entry 7). These substituent effects are quite different from those observed in the rhodium insertion chemistry, and their mechanistic implications are discussed in a later section.

These η^4-complexes are spectroscopically quite distinct from the rhodium η^2-vinylketenes. In particular, the infrared carbonyl bands appear at substantially higher energy in the range 1756–1787 cm^{-1}. This is similar to what has been reported for other η^4-vinylketene complexes.[19–35] The vinylketene core ^{13}C NMR signals appear in the following ranges: C1 (CO), 224–229 ppm; C2, 21–28 ppm; C3, 104–144 ppm; C4, 35–59 ppm.

(b) Stereochemistry of 4-Substituted η^4-Vinylketene Complexes. In all cases of 4-substituted η^4-vinylketenes, the anti isomers were formed as the major kinetic products (Table VI, entries 4–6 and 8). In those cases where R^2 was not *tert*-butyl, minor syn isomers were also observed. Stereoisomer assignments were made on the basis of ^1H NMR chemical shifts. The syn H (anti isomer) has been shown to have a lower field resonance than the anti H (syn isomer) in related compounds.[27] In the case of **10b**, the stereochemical assignments were confirmed by NOE measurements (Figure 2). Complex *anti*-**10b** showed a small enhancement only of the C4–H upon presaturation of the methyl group resonance. In contrast, presaturation of the methyl resonance of *syn*-**10b** produced enhancements of 15% to one of the indenyl–Cp signals, 12% to

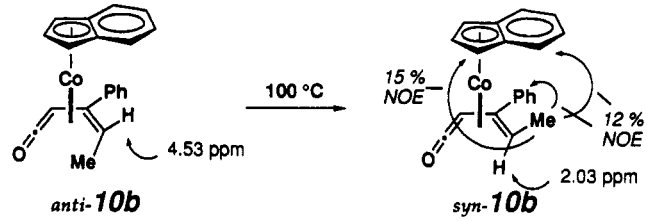
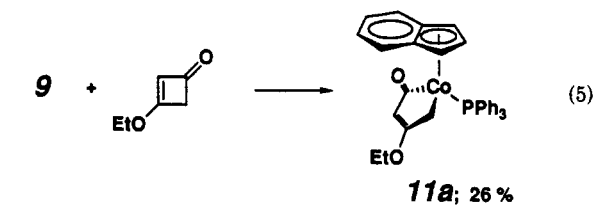


Figure 2. Assignment of stereochemistry to **10b** by NOE.

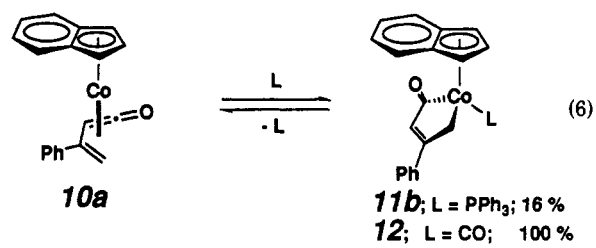
one of the indenyl–aryl protons, and 12% to the multiplet for the ortho phenyl hydrogens. This is fully consistent with the assigned syn stereochemistry since crystal structures of related compounds indicate that the syn substituent should reside closer to the indenyl ligand than does the anti substituent, as depicted in Figure 2.[26] Heating solutions of **10b** or **10c** to 100 °C for several hours led to mixtures enriched in the syn isomers, indicating that the kinetic anti products are thermodynamically less stable in these cases.

(c) Synthesis of Cobaltacyclopentenones. As mentioned above, reaction of **9** with 3-ethoxycyclobutenone did not produce the expected η^4-vinylketene complex. Instead, cobaltacyclopentenone **11a** was obtained (eq 5). A spec-



(5)

troscopically similar minor product was detected in the reaction of **9** with 3-phenylcyclobutenone. This latter product, **11b**, could be isolated in somewhat higher yield by heating the η^4-vinylketene **10a** to 100 °C with a large excess of triphenylphosphine (eq 6). The equilibrium



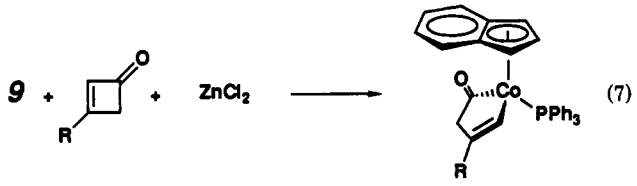
(6)

favors **10a**, which can be regenerated at 100 °C from isolated **11b**. A similar transformation was achieved in much higher yield by exposing **10a** to CO (80 psi, 25 °C). The resulting metallacycle **12** underwent rapid CO loss in THF at reflux, regenerating **10a**. An analogous metallacycle could *not* be formed from the 4-methylvinylketene complex **10b**, even at 1500 psi of CO, presumably because of steric strain in the desired α-methyl metallacycle.

Spectroscopically, these cobaltacyclopentenones are similar to their rhodium analogues **8**. Thus metallacycle carbonyl absorptions appear in the infrared spectrum at 1605–1609 cm^{-1} for **11** and 1639 cm^{-1} for **12**. The ^1H NMR spectra show metallacycle methylene protons at 2.9–3.6 and 1.3–2.1 ppm with geminal couplings of about 15 Hz. The ^{13}C NMR signals for the η^2-vinylketene core appear close to the ranges described for **8**.

Since electronegative cyclobutenone substituents increased the ease of insertion by $ClRh(PPh_3)_3$, it seemed possible that withdrawal of electron density might also facilitate reaction with cobalt. Therefore 3-phenylcyclobutenone was reacted with **9** in the presence of Lewis acids. With $ZnCl_2$, the yield of the reaction was improved, but

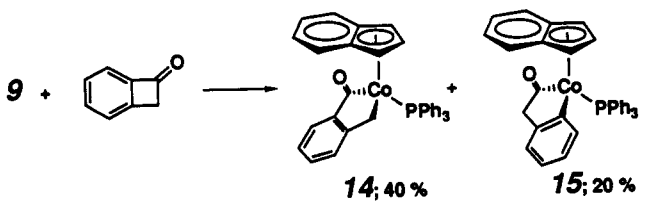
the product isolated was not the expected η^4-vinylketene complex. Instead it was a phosphine-containing metallacycle, but not identical to the η^2-vinylketene complex **11b**. Closer inspection of the spectroscopic data indicated the isomeric metallacycle structure **13a**. The analogous product **13b** was obtained from 3-butylcyclobutenone (eq 7). Compounds **13** are distinguished from the isomeric



(7)

form **11** by the former's higher energy infrared CO stretching absorptions (1640–1660 cm^{-1} vs ~1607 cm^{-1}) and larger ^1H NMR CH_2 geminal coupling constants (~20 Hz vs 15 Hz). Also distinctive are the NMR signals for the metallacycle carbons: C1 (CO), 265–269 ppm (d, J_{P-C} = 23 Hz); C2, 65–67 ppm (d, J_{P-C} = 9 Hz); C3, 142–144 ppm; C4, 136–151 ppm (d, J_{P-C} = 30–32 Hz).

Metallacycles were also obtained from the reaction of **9** with benzocyclobutenone (eq 8). A 2:1 mixture was isolated of isomeric cobaltaindanones **14** and **15**, which are spectroscopically similar to **11** and **13** respectively. Unlike the rhodaindanone isomers **6** and **7**, no isomerization was observed when pure samples of **14** or **15** were heated in solution (100 °C, 16 h).



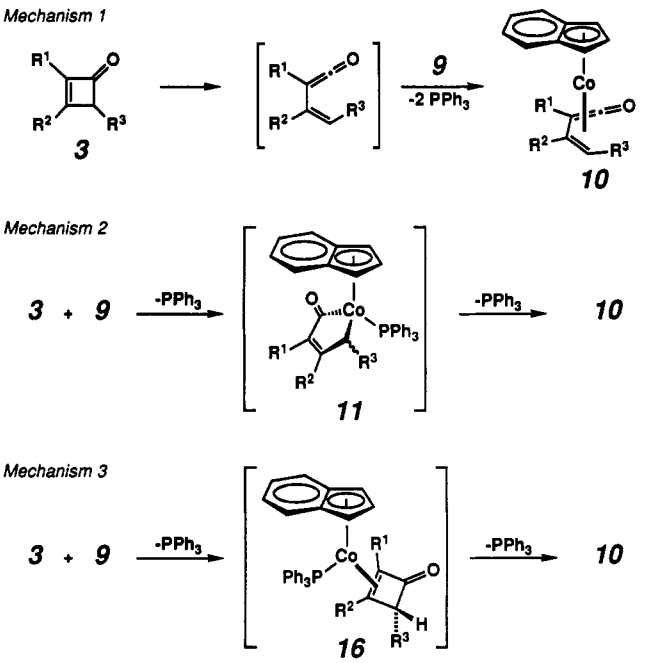
(8)

(d) Mechanism of η^4-Vinylketene Complex Formation. Three plausible mechanisms for the formation of η^4-vinylketene complexes **10** from **9** and cyclobutenones are shown in Scheme I. Mechanism 1 involves thermal electrocyclic ring opening of the cyclobutenone to a free vinylketene which is then trapped by cobalt. Two experimental facts provide evidence against this mechanism. First, although the best yields are obtained at 100–110 °C, the insertion into 3-phenylcyclobutenone proceeds rapidly at 25 °C where electrocyclic ring opening is slow. Second, the reaction with 3-phenylcyclobutenone can be carried out using 2-propanol as solvent (60 °C, 5.5 h, 11% yield of **10a**) where any free vinylketene should be rapidly trapped by alcohol addition to the ketene.

Mechanism 2 proceeds by direct oxidative addition of 16-electron η^5-$C_9H_7CoPPh_3$ to the C1–C4 bond of the cyclobutenone, resulting in initial formation of the monophosphine metallacycle **11**, which is followed by loss of phosphine to give **10**. This mechanism appears to be inconsistent with the observed effects of 2,3- and 3,4-substitution of the cyclobutenone. A methyl group in the 4-position would be expected to hinder metallacyclopentenone formation, as was observed for insertion with $ClRh(PPh_3)_3$. Yet the highest yields of **10** were obtained when R^3 = Me. In contrast 2,3-disubstitution did not hinder metallacycle formation with rhodium, but did prevent the isolation of significant amounts of **10** or **11**.

The experiment which provides the best evidence against the intermediacy of **11** was made possible by the

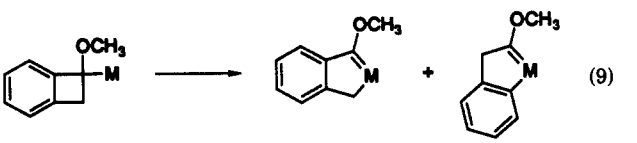
Scheme I



isolation of **11b** from the route shown in eq 6. When the reaction of 3-phenylcyclobutenone with **9** is carried out in the presence of **11b** (60 °C, 60 min), the yield of **10a** is unchanged and 73% of the added **11b** is recovered. Hence the rate of conversion of **11b** to **10a** under reaction conditions is too slow to account for the formation of **10a**. The small amount of **11b** normally observed in the reaction must arise from a pathway different than the one leading to **10a**. In the case of 3-ethoxycyclobutenone, which was one of the most reactive cyclobutenones toward insertion by $ClRh(PPh_3)_3$, the former pathway predominates and **11a** is the major product.

The mechanism most consistent with the experiments is the third, involving prior coordination of the cyclobutenone carbon–carbon double bond to the (η^5-C_9H_7)-$Co(PPh_3)$ fragment followed by phosphine loss and ring opening. This mechanism has precedent in the ring opening of cyclobutenes coordinated to iron[43] and it accounts for the observed kinetic anti stereochemistry. Electrocyclic ring opening in **16** is predicted to occur in a disrotatory fashion with the breaking σ-bond being bent toward the metal atom.[44] If the intermediate complex is the sterically favored one, with cobalt coordinating the face opposite the methyl substituent, then this mode of cleavage will result in the methyl rotating inward, giving the observed kinetic product. The unreactivity of 2,3-disubstituted cyclobutenones is also consistent with this mechanism, since the intermediate would be a sterically disfavored π-complex of a tetrasubstituted olefin.

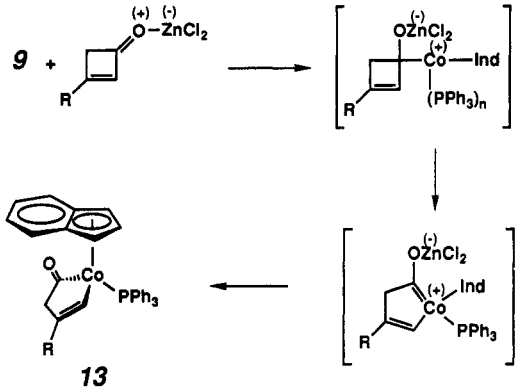
(e) Mechanism of Cobaltacycle Formation. Jones and co-workers have reported that α-methoxybenzocyclobutenyl complexes undergo α-carbon elimination, yielding isomeric pairs of metallacycles (eq 9).[45,46] A



(9)

(43) Slegeir, W.; Case, R.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 287.
(44) Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15.

Scheme II



Scheme III

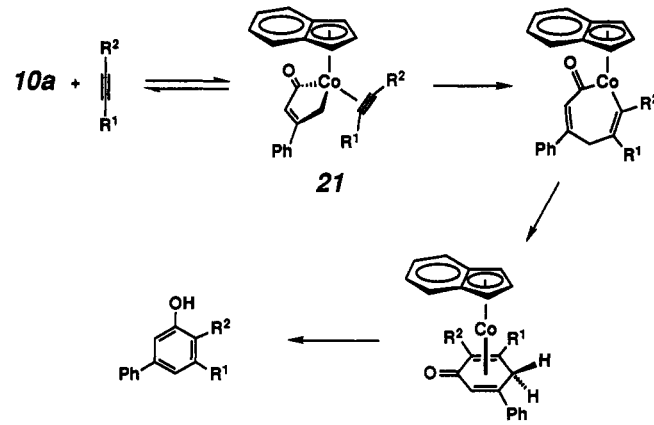
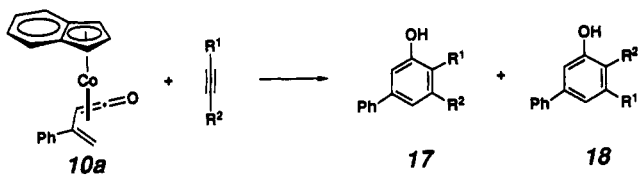


Table VII. Reaction of 10a with Alkynes



entry	products	R^1	R^2	ratio 17:18	yield, %
1	17a	Et	Et		65
2	17b, 18b	H	Bu	71:29	63
3	17c	CO_2Me	CO_2Me		45
4	17d, 18d	CO_2Et	Me	46:54	92

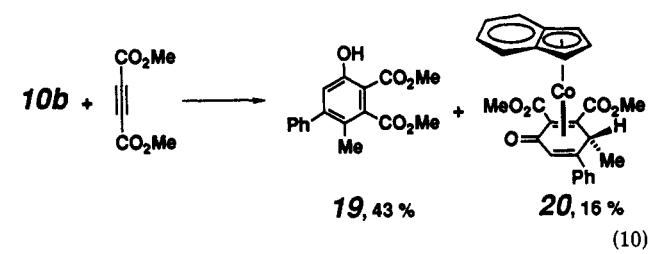
similar process can account for the formation of metallacycles **13** from the reactions of **9** with cyclobutenones in the presence of $ZnCl_2$ (Scheme II). Complexation of the cyclobutenone oxygen by zinc should render the ketone more susceptible to nucleophilic attack by an electron-rich cobalt center, a process which leads to an α-metalloxycyclobutenyl complex. α-Carbon elimination might occur from this intermediate in two directions, yielding **11** or **13** after loss of $ZnCl_2$. In fact only **13** is observed. Alternative mechanistic possibilities would be initial formation of **11** and subsequent $ZnCl_2$-induced isomerization to **13** by either CO deinsertion/insertion or a 1,3-hydrogen shift. However isolated **11a** was not converted to **13a** by $ZnCl_2$.

The reaction of **9** with benzocyclobutenone also may proceed via an α-elimination mechanism. η^4-Vinylketene formation is blocked since the cyclobutenone carbon–carbon double bond is tied up in the aromatic π-system. Alternative nucleophilic attack by cobalt on the acyl carbon would give a zwitterionic analogue of the α-methoxybenzocyclobutenyl σ-complexes. Then, in direct analogy to Jones's results, competitive migration of the benzyl and aryl α-carbons would lead to **14** and **15**, both of which were obtained.

III. Synthesis of Phenols from η^4-Vinylketene Complexes. As we had hoped, the cobalt η^4-vinylketene complexes turned out to be more reactive with alkynes than were the rhodium η^2-vinylketenes. When heated to 100 °C with alkynes, the complex of 3-phenylvinylketene, **10a**, gave substituted phenols (Table VII). Alkyne oligomerization was competitive with phenol formation, so excess alkyne was used along with 1,5-cyclooctadiene to complex the cobalt byproduct of the reaction.

Both internal and terminal alkyl substituted alkynes produced phenols. With 1-hexyne a mixture of regioisomers was obtained. A modest selectivity favored isomer **17b**, having the butyl substituent meta to the hydroxyl group (entry 2). Alkynes bearing carbonyl substituents also gave phenols (entries 3, 4) but more rapid alkyne oligomerization required a larger (20 equiv) excess of alkyne in these cases. The unsymmetrical alkyne ethyl 2-butynoate (entry 4) produced a nearly 1:1 mixture of regioisomeric phenols despite the large electronic difference between substituents.

The complex of 4-methyl-3-phenylvinylketene (**10b**) was found to be unreactive with alkyl-substituted alkynes. Only dimethyl acetylenedicarboxylate (DMAD) gave a significant yield of phenol (eq 10). Also isolated was the



(10)

η^4-cyclohexa-2,5-dien-1-one complex **20**. The exo methyl stereochemistry indicated for **20** is suggested by a ^1H NOE experiment which showed no enhancement of any indenyl signals upon irradiation of the methyl doublet. Irradiation of the endo hydrogen quartet produced a 5% enhancement of an aromatic multiplet at 7.30 ppm, which contains signals for phenyl and indenyl hydrogens.

This dienone complex is one of two diastereomeric intermediates likely to occur en route to phenol **19**. The endo methyl diastereomer is presumably not isolated because steric strain causes it to convert to **19** more rapidly. However the absence of an exo hydrogen may retard tautomerization/decomplexation of **20**, since no analogous complex was observed in the reaction of **10a** with DMAD. The dienone intermediate in this latter reaction would have hydrogen in both the exo and endo positions and should therefore suffer no greater steric strain than **20**.

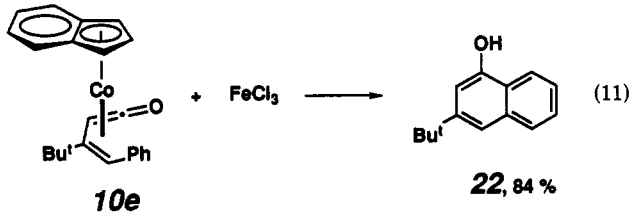
The unreactivity of **10b** with simple alkyl alkynes may be due to steric strain involving the methyl substituent in a metallacyclic intermediate. A potential mechanism for the reaction of simple alkynes with **10a** is shown in Scheme III. Reversible formation of the η^2-vinylketene intermediate **21** is precedented by the addition of CO and PPh_3 to **10a**, producing **11b** and **12** (eq 6). With an alkyne as the incoming ligand, insertion into one of the two metallacycle Co–C bonds can occur from this intermediate leading to a dienone complex and finally phenol. In contrast, analogous η^2-vinylketene complexes were not accessible from **10b** with CO or PPh_3 (vide supra). With an alkyne as the external ligand, formation of an intermediate

(45) Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 739.
(46) Stenstrom, Y.; Klauck, G.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.

metallacycle analogous to **21** is apparently also blocked by the methyl group, preventing insertion and phenol formation. With the extremely electron-deficient alkyne DMAD, phenol formation apparently occurs by a different route which bypasses the η^2-vinylketene intermediate.

The 4-phenylvinylketene complex **10e** represents a type of complex believed to be intermediate in benzannulation reactions of Fischer carbenes with alkynes.[38,39] In these reactions there is evidence that complexed 4-phenylvinylketenes are formed and undergo electrocyclic ring closure and tautomerization to produce the product naphthols. However isolated η^4-4-phenylvinylketene complexes have not previously been shown to give naphthols upon heating or oxidation.[30]

Heating a solution of **10e** to 100 °C led to slow, nonspecific decomposition. But oxidation with $FeCl_3$ produced the naphthol **23** in high yield (eq 11). Cyclization may occur after decomplexation since the reaction is known to occur with the free vinylketenes.[47]



10e **22**, 84 % (11)

Conclusions

Both steps of the proposed phenol synthesis outlined in eq 2 have been realized. $ClRh(PPh_3)_3$ reacted generally with 3-substituted and 2,3-disubstituted cyclobutenones to give metallacyclopentenones which were unreactive with alkynes. $(\eta^5\text{-}C_9H_7)Co(PPh_3)_2$ was found to react with 3-substituted and 3,4-disubstituted cyclobutenones to give predominantly η^4-vinylketene complexes, the latter cases proceeding with kinetic selectivity for anti products.

The 3-phenylvinylketene cobalt complex **10a** was treated with a variety of alkynes producing phenols. In contrast, the 4-methyl-3-phenyl complex **10b** reacted well only with the electron-deficient alkyne DMAD. Thus the possibility of this strategy for a convergent phenol synthesis has been demonstrated, although a practical, general synthesis was not possible with these reagents. Further development has led to the realization of a catalytic system, which has been reported elsewhere.[48]

Experimental Details

General Information. Unless otherwise mentioned, all reactions were performed under an atmosphere of nitrogen or argon and all subsequent filtration, chromatography, and crystallization were carried out in ambient atmosphere. Reaction solvents were purified by distillation from appropriate drying agents under nitrogen or argon. Melting points of metal complexes were measured in capillary tubes sealed under argon; melting points of organic compounds were measured in open capillaries. ^1H NMR chemical shifts are reported in ppm downfield from TMS and are referenced to residual proton peaks of the deuterated solvents. ^{13}C NMR chemical shifts are reported in ppm downfield from TMS and are referenced to deuterated solvent peaks. The vinylketene and metallacycle ligand carbons are numbered sequentially with C1 = CO. ^{31}P NMR shifts are reported in ppm downfield from an external sample of 85% H_3PO_4 and are referenced to the deuterium signal of deuterated solvent.

Alkynes, $ClRh(PPh_3)_3$, and sodium cyclopentadienylide were obtained from commercial suppliers and used as received. $ClCo(PPh_3)_3$ was prepared according to a published procedure[49] and crystallized from acetonitrile. Sodium indenylide solution was prepared by reacting indene with sodium hydride in THF, centrifuging, and decanting the clear red solution. With the exception of 3-*tert*-butyl-4-phenyl-2-cyclobuten-1-one, cyclobutenones and benzocyclobutenones are previously reported compounds prepared according to literature methods.

3-*tert*-Butyl-4-phenyl-2-cyclobuten-1-one. *N,N*-Dimethylphenylacetamide was reacted with 3,3-dimethyl-1-butyne in the presence of 2,4,6-trimethylpyridine and trifluoromethanesulfonic anhydride according to the general procedure described by Ghosez.[50] After hydrolysis, chromatography (silica, 8:1 hexanes/ethyl acetate) gave a 60% yield of a white solid: mp 34–35 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.17 (m, 5 H), 6.18 (s, 1 H), 4.59 (s, 1 H), 1.09 (s, 9 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 191.3, 187.7, 136.3, 134.4, 128.5, 127.7, 127.5, 66.7, 35.5, 27.8; IR (CH_2Cl_2) 2965, 1757 (s), 1570 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$: C, 83.94; H, 8.07. Found: C, 83.79; H, 8.12.

Chlorobis(triphenylphosphine)-3,4-diethylrhodacyclopent-3-en-2-one (4a). A slurry of $ClRh(PPh_3)_3$ (660 mg, 0.713 mmol) and 2,3-diethyl-2-cyclobuten-1-one[51] (104 mg, 0.84 mmol) in chlorobenzene (15 mL) was stirred at 90 °C for 18 h. The solvent was removed under vacuum, the residue redissolved in benzene, and the resulting solution filtered through a coarse frit. Addition of hexanes precipitated the product, which was isolated by filtration, washed with hexanes, and dried under vacuum giving a yellow powder (423 mg, 75%). Recrystallization by diffusion of hexanes into benzene gave yellow crystals of **4a**: mp 192–197 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 7.62 (m, 12 H, PPh_3), 7.38–7.29 (m, 18 H, PPh_3), 2.88 (m, 2 H, C4–H), 1.46 (q, J = 7.6 Hz, 2 H, CH_2CH_3), 1.28 (q, J = 7.7 Hz, 2 H, CH_2CH_3), 0.51 (t, J = 7.6 Hz, 3 H, CH_3), 0.24 (t, J = 7.7 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 222.4 (dt, J_{Rh-C} = 27 Hz, J_{P-C} = 7 Hz, C1), 176.4 (C3), 142.6 (dt, J_{Rh-C} = 6 Hz, J_{P-C} = 3 Hz, C2), 134.8 ("t", J_{P-C} = 6 Hz), 130.8 (t, J_{P-C} = 22 Hz), 130.0, 127.9 ("t", J_{P-C} = 5 Hz, 4 PPh_3), 34.1 (dt, J_{Rh-C} = 34 Hz, J_{P-C} = 6 Hz, C4), 24.9, 19.9, 12.7, 11.4 (4 Et); IR (CH_2Cl_2) 1648, 1622, 1483, 1435, 1097, 819 cm^{-1}. Anal. Calcd for $C_{44}H_{42}ClOP_2Rh$: C, 67.14; H, 5.38; Cl, 4.50. Found: C, 66.95; H, 5.31; Cl, 4.55.

Chlorobis(triphenylphosphine)-4-butylrhodacyclopent-3-en-2-one (4b). A slurry of $ClRh(PPh_3)_3$ (188 mg, 0.203 mmol) and 3-butyl-2-cyclobuten-1-one[52] (29 mg, 0.23 mmol) in chlorobenzene (5 mL) was stirred at 90 °C for 5 h. The resulting suspension was filtered through a coarse frit and the solvent removed under vacuum. The residue was redissolved in benzene (3 mL). Addition of hexanes precipitated the product, which was isolated by filtration, washed with hexanes, and dried under vacuum, giving a yellow powder (113 mg, 71%). Recrystallization from diethyl ether gave yellow crystals of **4b**: mp 170 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (m, 12 H, PPh_3), 7.41–7.26 (m, 18 H, PPh_3), 4.55 (s, 1 H, C2–H), 2.59 (m, 2 H, C4–H), 1.14 (t, J = 7.9 Hz, 2 H, C3–CH_2), 0.91 (m, 2 H, Bu), 0.67 (t, J = 7.3 Hz, 3 H, CH_3), 0.61 (m, 2 H, Bu); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 220.3 (dt, J_{Rh-C} = 26 Hz, J_{P-C} = 6 Hz, C1), 184.1 (C3), 134.9 ("t", J_{P-C} = 6 Hz), 130.5 (t, J_{P-C} = 23 Hz), 130.0 (3 PPh_3), 128.5 (m, C2), 128.0 ("t", J_{P-C} = 5 Hz, PPh_3), 33.8 (dt, J_{Rh-C} = 31 Hz, J_{P-C} = 6 Hz, C4), 33.5, 29.5, 22.4, 13.7 (4 Bu); IR (CH_2Cl_2) 1646, 1484, 1436, 1098 cm^{-1}. Anal. Calcd for $C_{44}H_{42}ClOP_2Rh$: C, 67.14; H, 5.38; Cl, 4.50. Found: C, 66.88; H, 5.44; Cl, 4.60.

Chlorobis(triphenylphosphine)-4-phenylrhodacyclopent-3-en-2-one (4c). A slurry of $ClRh(PPh_3)_3$ (800 mg, 0.864 mmol) and 3-phenyl-2-cyclobuten-1-one[53] (128 mg, 0.89 mmol) in benzene (20 mL) was stirred at 60 °C for 18 h. The resulting orange solution was filtered through a coarse frit. Addition of hexanes caused formation of a precipitate which was isolated by filtration, washed with hexanes, and dried under vacuum to give a yellow powder of **4c** containing a small amount of benzene which

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(51) Ammann, A. A.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1987**, *70*, 321. A higher yield was obtained using the procedure described for 3-*n*-butyl-2-cyclobuten-1-one (ref 52).
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could not be removed (602 mg, 87%): mp (CH_2Cl_2) 175 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 12 H, PPh_3), 7.33–7.23 (m, 18 H, PPh_3), 7.11 ("t", J = 7.4 Hz, 1 H, Ph), 7.02 ("t", J = 7.8 Hz, 2 H, Ph), 6.75 ("d", J = 7.4 Hz, 2 H, Ph), 5.01 (t, J = 0.6 Hz, 1 H, C2–H), 3.15 (m, 2 H, C4–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 220.7 (dt, J_{Rh-C} = 26 Hz, J_{P-C} = 6 Hz, C1), 175.3 (d, J_{Rh-C} = 1 Hz, C3), 135.4 (Ph), 134.7 ("t", J_{P-C} = 6 Hz), 130.3 (t, J_{P-C} = Hz), 130.1 (3 PPh_3), 128.6 (Ph), 128.3 (m, C2), 128.1 ("t", J_{P-C} = 5 Hz, PPh_3), 127.3, 127.0 (2 Ph), 30.8 (dt, J_{Rh-C} = 30 Hz, J_{P-C} = 6 Hz, C4); IR ($CHCl_3$) 1643, 1572 (w), 1482, 1435, 1098, 696, 683 cm^{-1}.

Chlorobis(triphenylphosphine)-4-ethoxyrhodacyclopent-3-en-2-one (4d). A slurry of $ClRh(PPh_3)_3$ (310 mg, 0.335 mmol) and 3-ethoxy-2-cyclobuten-1-one[54] (43 mg, 0.38 mmol) in benzene (5 mL) was stirred at 60 °C for 5 h, during which time a bright yellow precipitate formed. After the addition of hexanes (4 mL), the product was isolated by filtration, washed with hexanes, and dried under vacuum, giving **4d** as an analytically pure yellow powder (238 mg, 92%): mp (THF/hexanes) 190 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (m, 12 H, PPh_3), 7.40–7.30 (m, 18 H, PPh_3), 3.96 (d, J_{Rh-C} = 1.8 Hz, 1 H, C2–H), 2.91 (q, J = 7.1 Hz, 2 H, OCH_2), 2.23 (m, 2 H, C4–H), 0.91 (t, J = 7.1 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 210.1 (dt, J_{Rh-C} = 23 Hz, J_{P-C} = 6 Hz, C1), 190.2 (C3), 134.8 ("t", J_{P-C} = 6 Hz), 130.5 (t, J_{P-C} = 23 Hz), 130.0, 128.0 ("t", J_{P-C} = 5 Hz, 4 PPh_3), 104.3 (m, C2), 67.3 (OCH_2), 22.4 (dt, J_{Rh-C} = 31 Hz, J_{P-C} = 6 Hz, C4), 14.1 (CH_3); IR (CH_2Cl_2) 1648, 1587, 1485, 1438, 1322, 1233, 1129, 1100, 1033, 686 cm^{-1}. Anal. Calcd for $C_{42}H_{38}ClOP_2Rh$: C, 65.07; H, 4.95; Cl, 4.57. Found: C, 65.04; H, 5.00; Cl, 4.62.

Chlorobis(triphenylphosphine)-4-benzoylrhodacyclopent-3-en-2-one (4e). A slurry of $ClRh(PPh_3)_3$ (185 mg, 0.20 mmol) and 3-benzoyl-2-cyclobuten-1-one[55] (38 mg, 0.22 mmol) in benzene (5 mL) was stirred at 60 °C for 5 h. Addition of hexanes to the dark solution produced an orange precipitate, which was isolated by filtration, washed with hexanes, and dried under vacuum, giving an orange-brown powder (149 mg, 89%). Recrystallization by diffusion of hexanes into benzene gave orange prisms of **4e** containing a nonstoichiometric amount of benzene: mp 140 °C dec; ^1H NMR (360 MHz, $CDCl_3$) δ 7.69 (m, 12 H, PPh_3), 7.39–7.31 (m, 19 H, PPh_3 + Ph), 7.19 (m, 2 H, Ph), 6.89 (m, 2 H, Ph), 4.91 (s, 1 H, C2–H), 3.28 (m, 2 H, C4–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 224.2 (dt, J_{Rh-C} = 28 Hz, J_{P-C} = 7 Hz, C1), 191.4 (COPh), 168.7 (C3), 140.1 (m, C2), 137.6 (Ph), 134.7 ("t", J_{P-C} = 6 Hz, PPh_3), 131.9 (Ph), 130.3, 130.0 (t, J_{P-C} = 23 Hz, 2 PPh_3), 128.5 (Ph), 128.3 (PPh_3), 127.7 (Ph), 30.7 (dt, J_{Rh-C} = 30 Hz, J_{P-C} = 6 Hz, C4); IR (CH_2Cl_2) 3064, 1649, 1483, 1437, 1323, 1096, 1042, 1024 cm^{-1}.

X-ray Data Collection and Structural Analysis of 4e. Yellow crystals of **4e**·THF were grown by vapor diffusion of hexanes into a THF solution of the complex. A suitable crystal was mounted on a glass fiber. All measurements were made on a Nicolet R3mV diffractometer with Mo Kα radiation (λ = 0.71073 Å). Cell parameters and an orientation matrix were obtained from a least-squares analysis of the setting angles of 50 carefully centered reflections in the range $28.16 < 2\theta < 37.47°$. The space group $P\bar{1}$ was determined on the basis of a statistical analysis of intensity distribution and was confirmed by successful refinement of the structure.

The data were collected at a temperature of 21 ± 1 °C using the ω-2θ scan technique. Scans of 0.60° below $K\alpha_1$ to 0.60° above $K\alpha_2$ were made at speeds ranging from 2.09 to 14.65°/min (in ω). Stationary crystal, stationary counter background counts were measured at each end of the scan for half of the total scan time.

The intensities of three representative reflections, measured after every 100 reflections, declined by approximately 14% over the course of the data collection; a linear correction was applied to the data to account for this decomposition. The data were corrected for Lorentz and polarization effects.

The structure could not be solved in the centrosymmetric space group $P\bar{1}$. Structure solution by direct methods in the acentric space group $P1$ yielded an enantiomeric pair of molecules. Translation of this pair so that their center of gravity coincided with an inversion center of the centrosymmetric space group $P\bar{1}$ revealed that they were indeed related by inversion symmetry. Subsequent refinement of one of these molecules in space group $P\bar{1}$ yielded a satisfactory result. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the rhodium complex were located by standard difference Fourier techniques (those of the THF molecule were not located) and were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å) and allowed to ride on the atom to which they were bonded. An isotropic group thermal parameter (U_{iso} = 0.073 (4) Å^2) was refined for all of the hydrogens. The final cycle of full-matrix least-squares refinement was based on 5080 observed reflections ($I > 3\sigma(I)$) and 491 variable parameters and converged (largest parameter shift was 0.01 times its esd) with final residual values of R = 0.0594, R_w = 0.0898, and S = 3.06. The weighting scheme was based on counting statistics and included a factor (p = 0.0005) to downweight the intense reflections. An analysis of the variance of reflections based on $(\sin\theta)/\lambda$, magnitude of F, and parity class showed no unusual trends. Peaks on the final difference map ranged from −0.98 to +1.45e/Å^3, and were located in the vicinity of the disordered THF molecule. A summary of the crystal data and data collection parameters is provided in Table II. The atomic coordinates and thermal parameters for core non-hydrogen atoms are provided in Table III. Selected bond lengths and angles are collected in Table IV, and additional information is available as supplementary material.

Chlorobis(triphenylphosphine)-2-rhodaindanone (6a) and Chlorobis(triphenylphosphine)-1-rhodaisoindanone (7a). A slurry of $ClRh(PPh_3)_3$ (157 mg, 0.170 mmol) and benzocyclobutenone[56] (22 mg, 0.19 mmol) in chlorobenzene (4 mL) was heated to reflux for 24 h. Addition of hexanes to the cooled solution precipitated the product, which was isolated by filtration, washed with hexanes, and dried under vacuum giving a 1:3 mixture of isomers **6a** and **7a** as an analytically pure yellow powder (97 mg, 71%): ^1H NMR (300 MHz, $CDCl_3$) (**7a**) δ 7.49 (m, 30 H, PPh_3), 6.98 (m, 1 H, aryl), 6.74 (m, 1 H, aryl), 6.48 (m, 1 H, aryl), 6.31 (m, 1 H, aryl), 1.93 (s, 2 H, C2–H); ^1H NMR (300 MHz, $CDCl_3$) (**6a**) δ 7.54 (m, 6 H, PPh_3), 7.49–7.16 (m, 24 H, PPh_3), 6.74 (m, 1 H, aryl), 6.68 (m, 1 H, aryl), 6.60 (m, 1 H, aryl), 6.40 (m, 1 H, aryl), 3.45 (m, 2 H, C4–H); IR (CH_2Cl_2) 1693 (s), 1662, 1653, 1482 (s), 1435 (s), 1098 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{36}ClOP_2Rh$: C, 67.65; H, 4.65; Cl, 4.54. Found: C, 67.48; H, 4.70; Cl, 4.64.

Chlorobis(triphenylphosphine)-6,7-(methylenedioxy)-2-rhodaindanone (6b) and Chlorobis(triphenylphosphine)-6,7-(methylenedioxy)-1-rhodaisoindanone (7b). A slurry of $ClRh(PPh_3)_3$ (194 mg, 0.210 mmol) and 5,6-(methylenedioxy)-benzocyclobutenone[57] (39 mg, 0.24 mmol) in chlorobenzene (5 mL) was stirred at reflux for 5 h. Addition of hexanes to the resulting orange solution caused precipitation of the product. Filtration, washing with hexanes, and drying under vacuum gave a 1:2 mixture of isomers **6b** and **7b** as an analytically pure yellow powder (88 mg, 50%): ^1H NMR (300 MHz, $CDCl_3$) (**6b**) δ 7.62 (m, 6 H, PPh_3), 7.44–7.21 (m, 24 H, PPh_3), 6.21 (d, J = 7.9 Hz, 1 H, aryl), 6.00 (d, J = 7.9 Hz, 1 H, aryl), 5.68 (s, 2 H, OCH_2O), 3.58 (m, 2 H, C4–H); ^1H NMR (300 MHz, $CDCl_3$) (**7b**) 7.44–7.20 (m, 30 H, PPh_3), 6.22 (d, J = 7.7 Hz, 1 H, aryl), 5.84 (d, J = 7.7 Hz, 1 H, aryl), 5.02 (s, 2 H, OCH_2O), 2.18 (s, 2 H, C2–H); IR (CH_2Cl_2) 1697 (s), 1660, 1651, 1485 (s), 1470, 1437 (s), 1246 (s), 1100 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{36}ClO_3P_2Rh$: C, 65.50; H, 4.41; Cl, 4.30. Found: C, 65.53; H, 4.60; Cl, 4.20.

Chlorobis(triphenylphosphine)-6,7-(methylenedioxy)-1-rhodaisoindanone (7b). A glass tube was charged with 5,6-(methylenedioxy)benzocyclobutenone[57] (39 mg, 0.24 mmol), $ClRh(PPh_3)_3$ (194 mg, 0.210 mmol), and chlorobenzene (5 mL). The mixture was degassed with three freeze–pump–thaw cycles. The tube was sealed with a Teflon needle valve and heated in an oil bath at 125–135 °C for 5 days, resulting in an orange solution with yellow precipitate. After addition of hexanes (30 mL) to complete precipitation, the product was collected by filtration, washed with hexanes, and dried under vacuum giving a 30:1 mixture of **7b** and **6b** (111 mg, 64%). A second precipitation from chlorobenzene with hexanes gave a pure sample of **7b**: mp 253

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°C dec; IR (CH_2Cl_2) 1696 (s), 1610 (w), 1486, 1438 (s), 1245 (s), 1100 (s), 1053 cm^{-1}. Anal. Calcd for $C_{45}H_{36}ClO_3P_2Rh$: C, 65.50; H, 4.41; Cl, 4.30. Found: C, 65.29; H, 4.44; Cl, 4.45.

Isomerization of Chlorobis(triphenylphosphine)-2-rhodaindanone (6a) to Chlorobis(triphenylphosphine)-1-rhodaisoindanone (7a). An NMR tube was loaded with a mixture of **6a** and **7a** (8 mg), ferrocene (0.4 mg), and PhCl-d_5 (0.5 mL). The contents were degassed with three freeze–pump–thaw cycles, and the tube was sealed under vacuum. ^1H NMR spectroscopy of the solution showed a 1:1.25 ratio of **6a** to **7a**. The tube was submerged in an oil bath maintained at 130 °C. After 48 h, ^1H NMR analysis showed a new ratio of 1:4.8 (**6a** to **7a**). Integration against the ferrocene standard indicated that 97% of the mixture remained as **6a** and **7a** and that the amount of **7a** had increased to 140%.

Isomerization of Chlorobis(triphenylphosphine)-6,7-(methylenedioxy)-2-rhodaindanone (6b) to Chlorobis(triphenylphosphine)-6,7-(methylenedioxy)-1-rhodaisoindanone (7b). The experiment was set up as in the previous experiment substituting 8 mg of a mixture of **6b,7b** for **6a,7a**. ^1H NMR analysis revealed a 1:1 ratio of isomers. After 10 h at 130 °C, the ratio was found to be 1:13 (**6b** to **7b**). Integration against the ferrocene standard indicated that 74% of the mixture remained as **6b** and **7b** and that the amount of **7b** had increased to 145%.

(η^5-Indenyl)(triphenylphosphine)-3,4-diethylrhodacyclopent-3-en-2-one (8a). To a stirring yellow solution of **4a** (250 mg, 0.318 mmol) in benzene (8 mL) was added a 2 M THF solution of sodium indenylide (0.8 mL, 1.6 mmol). After 60 min, the red reaction mixture was quenched with a few drops of water, filtered through alumina(II) using THF, and evaporated to dryness. The residue was dissolved in hexanes/ethyl acetate (~2:1) and chromatographed on silica with 15:1 hexanes/ethyl acetate. The yellow product band was stripped to an orange oil (158 mg, 82%). Crystallization from acetonitrile gave pale yellow needles of **8a**: mp 149–150 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 1 H, Ind), 7.33–7.10 (m, 9 H, PPh_3), 7.13 (m, 1 H, Ind), 6.96–6.89 (m, 6 H, PPh_3), 6.76 (m, 1 H, Ind), 6.43 (m, 1 H, Ind), 5.94 (m, 1 H, Ind), 5.35 (m, 1 H, Ind), 5.09 (m, 1 H, Ind), 3.51 (ddd, J = 15.4, 4.2, 0.6 Hz, 1 H, C4–H), 2.09 (m, 1 H, CH_2CH$_3$), 1.94–1.76 (m, 2 H, CH_2CH$_3$ + C4–H), 1.64 (m, 2 H, CH_2CH C3), 0.82 (t, J = 7.6 Hz, 3 H, CH_3), 0.57 (t, J = 7.5 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 230.3 (dd, J_{Rh-C} = 33 Hz, J_{P-C} = 11 Hz, C1), 176.6 (C3), 149.0 (d, J = 8 Hz, C2), 133.6 (d, J_{P-C} = 11 Hz), 133.0 (d, J_{P-C} = 45 Hz), 129.6, 127.6 (d, J_{P-C} = 10 Hz, 4 PPh_3), 124.0, 123.3, 120.1, 119.8, 119.0, 118.2, 107.5 (d, J = 4 Hz), 84.4, 68.7 (dd, J = 16, 5 Hz, 9 Ind), 26.3 (CH_2CH$_3$), 24.7 (dd, J_{Rh-C} = 32 Hz, J_{P-C} = 10 Hz, C4), 19.6 (CH_2CH$_3$), 13.6, 12.5 (2 CH_3); IR (CH_2Cl_2) 1644, 1617 (s), 1481, 1437, 1320, 1168, 1095, 819 cm^{-1}. Anal. Calcd for $C_{35}H_{34}OPRh$: C, 69.52; H, 5.68. Found: C, 69.66; H, 5.67.

(η^5-Indenyl)(triphenylphosphine)-4-phenylrhodacyclopent-3-en-2-one (8b). To a stirring yellow slurry of **4c** (100 mg, 0.124 mmol) in benzene (3 mL) was added a 2 M THF solution of sodium indenylide (0.4 mL, 0.8 mmol). After 60 min, the red reaction mixture was quenched with a few drops of water, filtered through alumina(II) using THF, and evaporated to dryness. The residue was dissolved in toluene and chromatographed on silica with 4:1 hexanes/ethyl acetate. The broad yellow product band was stripped to give a pale yellow solid (54 mg, 70%). Recrystallization from a THF/hexanes mixture gave yellow crystals of **8b**: mp 175 °C dec; ^1H NMR (360 MHz, $CDCl_3$) δ 7.48 (br d, J = 8.1 Hz, 1 H), 7.36–7.17 (m, 15 H), 6.95–6.90 (m, 6 H), 6.86 (br t, J = 7.5 Hz, 1 H), 6.54 (br d, J = 7.9 Hz, 1 H, 24 PPh_3 + Ph + Ind), 6.02 (br s, 1 H), 5.55 (br s, 1 H), 5.31 (br s, 1 H), 5.25 (m, 1 H, 3 Ind + C2–H), 3.94 (br dd, J = 15.9, 4.2 Hz, 1 H, C4–H), 2.13 (ddd, J = 15.8, 8.6, 2.2 Hz, 1 H, C4–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 230.4 (dd, J_{Rh-C} = 32 Hz, J_{P-C} = 11 Hz, C1), 176.2 (C3), 137.6 (Ph), 135.5 (d, J = 8 Hz, C2), 133.6 (d, J_{P-C} = 11 Hz), 132.6 (d, J_{P-C} = 46 Hz), 129.8 (d, J_{P-C} = 1 Hz, 3 PPh_3), 128.5, 127.9 (2 Ph), 127.8 (d, J_{P-C} = 10 Hz, PPh_3), 127.1 (Ph), 124.4, 123.8, 120.4, 120.3, 119.2, 117.4 (d, J = 3 Hz), 108.1 (d, J = 4 Hz), 85.0 (d, J = 2 Hz), 68.1 (dd, J = 16, 5 Hz, 9 Ind), 20.9 (dd, J_{Rh-C} = 33 Hz, J_{P-C} = 11 Hz, C4); IR (CH_2Cl_2) 1623 (s), 1481, 1435, 1318, 1092 (s), 860, 795 cm^{-1}. Anal. Calcd for $C_{37}H_{30}OPRh$: C, 71.15; H, 4.85. Found: C, 71.00; H, 4.97.

(η^5-Cyclopentadienyl)(triphenylphosphine)-3,4-diethylrhodacyclopent-3-en-2-one (8c). To a stirring yellow solution of **4a** (200 mg, 0.254 mmol) in benzene (6 mL) was added a 2.0 M THF solution of sodium cyclopentadienylide (0.6 mL, 1.2 mmol). After 60 min, the red reaction mixture was quenched with a few drops of water, filtered through alumina(II) using THF, and evaporated to dryness. The residue was chromatographed on silica using 7:1 hexanes/ethyl acetate. The yellow product band was stripped to a yellow-orange oil (120 mg, 85%). Crystallization from Et_2O gave clear yellow prisms of **8c**: mp 163–164 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 7.66–7.43 (m, 15 H, PPh_3), 5.14 (dd, J = 1.3, 0.6 Hz, 5 H, Cp), 3.97 (br dd, J = 15.5, 3.6 Hz, 1 H, C4–H), 2.04 (m, 1 H, CH_2CH$_3$), 1.91 (br dd, J = 15.0, 9.7 Hz, 1 H, C4–H), 1.82 (m, 1 H, CH_2CH$_3$), 1.62 (m, 2 H, CH_2CH$_3$), 0.79 (t, J = 7.6 Hz, 3 H, CH_3), 0.57 (t, J = 7.5 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 238.8 (dd, J_{Rh-C} = 30 Hz, J_{P-C} = 13 Hz, C1), 175.1 (C3), 150.1 (dd, J = 6, 1 Hz, C2), 134.1 (d, J_{P-C} = 47 Hz), 134.0 (d, J_{P-C} = 11 Hz), 129.7 (d, J_{P-C} = 2 Hz), 127.6 (d, J_{P-C} = 10 Hz, 4 PPh_3), 92.2 ("t", J = 3 Hz, Cp), 26.3, 18.9 (2 CH_2CH$_3$), 18.1 (dd, J_{Rh-C} = 31 Hz, J_{P-C} = 11 Hz, C4), 13.6, 12.5 (2 CH_3); IR (CH_2Cl_2) 1636 (w), 1606 (s), 1481, 1434, 1167, 1094, 991, 820, 791 cm^{-1}. Anal. Calcd for $C_{31}H_{32}OPRh$: C, 67.14; H, 5.83. Found: C, 66.92; H, 5.82.

(η^5-Indenyl)bis(triphenylphosphine)cobalt (9). The synthesis is a modification of the procedure reported for (η^5-C_5H_5)Co(PPh_3)$_2$ by Yamazaki and Wakatsuki.[58] A solution of sodium indenylide (5.0 mL of 2.0 M in THF, 10 mmol) was added via syringe to a stirring suspension of $ClCo(PPh_3)_3$ (6.00 g, 6.81 mmol) in benzene (80 mL). The resulting red solution was stirred for 60 min, then quenched with 20 mL of argon-purged water. The mixture was stirred vigorously for 5 min and allowed to separate. The benzene layer was transferred via cannula into an argon-filled flask containing $NaSO_4$ and dried for 30 min. The solution was then filtered under argon through a glass frit and concentrated under vacuum to 25 mL. Argon-purged hexanes (45 mL) was added and the mixture was cooled to −15 °C, giving dark red crystals. The supernatant solution was removed via cannula and the crystals were washed with argon-purged hexanes and dried under vacuum, giving 4.09 g (6.30 mmol, 93%) of air-sensitive red crystals which contained some residual benzene. The material failed to give adequate elemental analysis but was weighed for subsequent reactions as if pure: mp 152–155 °C; ^1H NMR (300 MHz, benzene-d_6) δ 7.45 (br m, 12 H, PPh_3), 6.98 (dd, J = 6.0, 3.0 Hz, 2 H, Ind), 6.93 (br m, 18 H, PPh_3), 6.37 (m, 1 H, Ind), 6.00 (dd, J = 6.0, 3.0 Hz, 2 H, Ind), 4.10 (distorted dt, J = 2.7 Hz, 2.4 Hz, 2 H, Ind); $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6) δ 139.2 (t, J_{P-C} = 18 Hz), 134.2 ("t", J_{P-C} = 5 Hz), 128.2, 127.1 ("t", J_{P-C} = 4 Hz, 4 PPh_3), 121.6, 119.3, 106.4, 89.0, 70.5 (5 Ind); ^{31}P NMR (81 MHz, benzene-d_6) δ 63.0; IR (Nujol) 1577 (w), 1431, 1319 (w), 1229 (w), 1171, 1082 (s), 1021, 883 (w), 844 (w), 793 (w), 743 (s), 698 (s) cm^{-1}. Anal. Calcd for $C_{45}H_{37}CoP_2$: C, 77.35; H, 5.35. Found: C, 74.94; H, 4.79.

(η^5-Indenyl)(η^4-3-phenylbuta-1,3-dienone)cobalt (10a). Toluene (40 mL) was transferred into a flask containing **9** (445 mg, 0.637 mmol) and 3-phenyl-2-cyclobuten-1-one[53] (94 mg, 0.65 mmol). The red mixture was heated to reflux for 1 h, giving a dark brown solution. The solution was cooled to room temperature and exposed to air. THF (20 mL) was added and the mixture filtered through silica and evaporated to a red oil. The residue was dissolved in toluene and chromatographed on silica with 6:1 hexanes/diethyl ether, giving analytically pure orange crystals of **10a** (43 mg, 32%): mp 137–138 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 3 H, Ph), 6.96 (m, 2 H, Ph), 6.87 (br d, J = 8.3 Hz, 1 H, Ind), 6.62 (br d, J = 8.5 Hz, 1 H, Ind), 6.56 (m, 1 H, Ind), 6.34 (m, 1 H, Ind), 6.16 (m, 1 H, Ind), 5.87 (m, 2 H, Ind), 3.30 (br t, J = 2.3 Hz, 1 H), 3.20 (dd, J = 2.5, 1.1 Hz, 1 H, C2–H + syn C4–H), 1.16 (dd, J = 2.0, 1.1 Hz, 1 H, anti C4–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 224.4 (C1), 136.0, 128.7, 127.9, 127.8 (4 Ph), 126.0, 125.4, 121.9, 120.2 (4 Ind), 109.8, 108.3, 104.8 (2 Ind + C3), 93.4, 74.0, 73.4 (3 Ind), 35.3 (C4), 27.4 (C2); IR (CH_2Cl_2) 1770 (s), 1749 (s), 1384, 1321, 965, 818, 668 cm^{-1}. Anal. Calcd for $C_{19}H_{15}CoO$: C, 71.70; H, 4.76. Found: C, 71.75; H, 4.79.

General Procedure for Synthesis of Indenylcobalt η^4-Vinylketene Complexes: (η^5-Indenyl)(η^4-*anti*-3-phenylpenta-1,3-dienone)cobalt (*anti*-10b). A solution of 4-

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methyl-3-phenyl-2-cyclobuten-1-one[59] (39 mg, 0.25 mmol) in toluene (20 mL) was transferred via cannula into a flask containing **9** (173 mg, 0.25 mmol). The resulting red solution was stirred at 100 °C for 60 min and then cooled and filtered through silica with THF. The filtrate was concentrated to 3 mL under reduced pressure and chromatographed on silica with 5:1 hexanes/diethyl ether. The red product band was collected and evaporated to give an orange solid (67 mg, 81%) (95:5 anti to syn). Recrystallization by diffusion of hexanes into benzene gave a pure sample of the anti isomer: mp 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.18 (m, 3 H, Ph), 6.90–6.84 (m, 3 H, Ph + Ind), 6.59 (m, 1 H, Ind), 6.54 (m, 1 H, Ind), 6.31 (m, 1 H, Ind), 6.10 ("t", J = 2.8 Hz, 1 H, Ind), 5.86 (m, 1 H, Ind), 5.72 (m, 1 H, Ind), 4.53 (qd, J = 6.9, 1.9 Hz, 1 H, C4–H), 3.17 (d, J = 1.9 Hz, 1 H, C2–H), 0.84 (d, J = 6.9 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 225.3 (C1), 136.8, 128.4, 128.0, 127.6 (4 Ph), 125.8, 125.3, 121.5, 120.1, 109.4, 109.0 (6 Ind), 104.7 (C3), 93.1, 74.9, 74.7 (3 Ind), 55.4 (C4), 27.8 (C2), 21.6 (CH_3); IR (CH_2Cl_2) 1761 cm^{-1}. Anal. Calcd for $C_{20}H_{17}CoO$: C, 72.28; H, 5.17. Found: C, 72.25; H, 5.19. ^{1}H NOE: presaturation of the CH_3 doublet (δ 0.84) gave only a small enhancement of the C4 hydrogen (δ 4.53, 3%).

(η^5-Indenyl)(η^4-*syn*-3-phenylpenta-1,3-dienone)cobalt (*syn*-10b). A solution of pure anti isomer of **10b** (32 mg, 0.10 mmol) in toluene (10 mL) was heated to 100 °C for 22 h. Preparatory thin-layer chromatography on silica with 10:1 hexanes/diethyl ether gave an orange band of starting material (6 mg, 19%) followed by an orange band, which was evaporated to red crystals of *syn*-**10b** (12 mg, 38%): mp 138–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.17 (m, 3 H, Ph), 7.12 (m, 1 H, Ind), 7.02 (m, 1 H, Ind), 6.79 (m, 1 H, Ind), 6.64 (m, 1 H, Ind), 6.56 (m, 2 H, Ph), 6.37 ("t", J = 2.8 Hz, 1 H, Ind), 5.84 (m, 1 H, Ind), 5.12 (m, 1 H, Ind), 2.76 (d, J = 1.0 Hz, 1 H, C2–H), 2.03 (qd, J = 6.4, 1.0 Hz, 1 H, C4–H), 1.69 (d, J = 6.4 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 225.1 (C1), 135.0, 129.7, 128.0, 127.7 (4 Ph), 126.3, 124.5, 120.5, 119.7, 111.0, 110.4 (6 Ind), 104.7 (C3), 95.0, 79.2, 72.7 (3 Ind), 48.9 (C4), 27.4 (C2), 18.9 (CH_3); IR (CH_2Cl_2) 1783 (sh), 1762 cm^{-1}. Anal. Calcd for $C_{20}H_{17}CoO$: C, 72.28; H, 5.17. Found: C, 72.39; H, 5.19. ^{1}H NOE: presaturation of the CH_3 doublet (δ 1.69) caused enhancement of one phenyl multiplet (δ 6.56, 12%) and two indenyl multiplets (δ 5.12, 15%; δ 6.79, 12%).

(η^5-Indenyl)(η^4-3-(trimethylsilyl)penta-1,3-dienone)cobalt (10c). Reaction of 4-methyl-3-(trimethylsilyl)-2-cyclobuten-1-one[50] (54 mg, 0.35 mmol) with **9** (250 mg, 0.36 mmol) in toluene (20 mL) was carried out according to the general procedure. Chromatography on silica with 9:1 hexanes/diethyl ether gave a 3.5:1 mixture of anti and syn isomers of **10c** as an analytically pure red solid (93 mg, 81%) which was characterized as the mixture: ^{1}H NMR (300 MHz, $CDCl_3$, major isomer) δ 7.15–6.89 (m, 4 H, Ind), 6.06 ("t", J = 2.8 Hz, 1 H, Ind), 5.76 (m, 1 H, Ind), 5.59 (m, 1 H, Ind), 4.28 (qd, J = 6.8, 1.1 Hz, 1 H, C4–H), 2.62 (d, J = 1.1 Hz, 1 H, C2–H), 0.59 (d, J = 6.8 Hz, 3 H, C4–CH_3), −0.14 (s, 9 H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, major isomer) δ 228.9 (C1), 124.9, 124.4, 122.9, 121.1, 109.7 (5 Ind), 106.0 (C3), 105.3, 94.1, 76.0, 74.6 (4 Ind), 59.2 (C4), 28.4, 21.9 (C2 + C4–CH_3), −1.8 ($Si(CH_3)_3$); IR (CH_2Cl_2) 1759 (s), 1322, 1241, 842 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{21}CoOSi$: C, 62.18; H, 6.45. Found: C, 62.08; H, 6.49.

(η^5-Indenyl)(η^4-*anti*-3-*tert*-butylpenta-1,3-dienone)cobalt (10d). Reaction of 3-*tert*-butyl-4-methyl-2-cyclobuten-1-one[50] (50 mg, 0.36 mmol) with **9** (254 mg, 0.36 mmol) in toluene (20 mL) was carried out according to the general procedure. Chromatography on silica with 10:1 hexanes/ethyl acetate gave an orange solid, which crystallized upon trituration with hexanes (47 mg, 42%): mp 102–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–6.90 (m, 4 H, Ind), 6.11 ("t", J = 2.8 Hz, 1 H, Ind), 5.72 (m, 1 H, Ind), 5.62 (m, 1 H, Ind), 4.41 (qd, J = 6.8, 1.9 Hz, 1 H, C4–H), 2.92 (d, J = 1.9 Hz, 1 H, C2–H), 0.74 (s, 9 H, $C(CH_3)_3$), 0.61 (d, J = 6.8 Hz, 3 H, C4–CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 227.3 (C1), 125.9 (C3), 125.0, 124.6, 122.8, 121.1, 110.6, 106.9, 95.1, 74.5, 74.0 (9 Ind), 49.6 (C4), 34.6 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 27.2, 22.3 (C2 + C4–CH_3); IR (CH_2Cl_2) 2950, 1756 (s), 1354, 1322, 1031, 994, 822 cm^{-1}. Anal. Calcd for $C_{18}H_{21}CoO$: C, 69.22; H, 6.79. Found: C, 69.30; H, 6.81.

(η^5-Indenyl)(η^4-*anti*-3-*tert*-butyl-4-phenylbuta-1,3-dienone)cobalt (10e). Reaction of 3-*tert*-butyl-4-phenyl-2-cyclobuten-1-one (61 mg, 0.30 mmol) with **9** (211 mg, 0.30 mmol) in toluene (20 mL) was carried out according to the general procedure. Chromatography on silica with 11:1 hexanes/ethyl acetate gave a red solid (19 mg, 17%). Cooling a solution in hexanes gave dark red crystals of **10e**: mp 154–155 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.31 (m, 1 H, Ind), 7.04–6.94 (m, 6 H, Ind + Ph), 6.70 (m, 2 H, Ph), 5.99 (t, J = 2.8 Hz, 1 H, Ind), 5.78 (m, 1 H, Ind), 5.63 (m, 2 H, Ind + C4–H), 3.03 (d, J = 1.8 Hz, 1 H, C2–H), 0.88 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 225.8 (C1), 144.2 (C3), 128.4, 126.1, 125.4, 125.3, 124.4, 123.0, 121.3, 120.1 (4 Ph + 4 Ind), 110.4, 107.2, 95.6, 76.6, 73.8 (5 Ind), 53.7 (C4), 34.6 ($C(CH_3)_3$), 29.4 ($C(CH_3)_3$), 27.6 (C2); IR (CH_2Cl_2) 2955, 1777 (s), 1760 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{23}CoO$: C, 73.78; H, 6.20. Found: C, 73.69; H, 6.29. ^{1}H NOE: presaturation of the *tert*-butyl singlet (δ 0.88) produced enhancement of the C2 vinyl signal (δ 3.03, 35%) and multiplet for the C4 vinyl and one indenyl proton (δ 5.63, 29%).

(η^5-Indenyl)(triphenylphosphine)-4-ethoxycobaltacyclopent-3-en-2-one (11a). A solution of 3-ethoxy-2-cyclobuten-1-one[54] (39 mg, 0.35 mmol) in toluene (20 mL) was transferred via cannula into a flask containing **9** (163 mg, 0.23 mmol), and the resulting red solution was stirred at 60 °C for 105 min. The solution was then filtered through silica with THF, concentrated to 3 mL under reduced pressure, and chromatographed on silica. Eluting with 4:1 hexanes/ethyl acetate gave fast-moving brown and orange bands followed by the broad orange product band. Evaporation of the solvent under reduced pressure gave **11a** as an orange solid (33 mg, 0.060 mmol, 26%). Recrystallization by diffusion of hexanes into benzene gave orange needles of **11a**: mp 190–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (br d, J = 8.2 Hz, 1 H, Ind), 7.34–7.19 (m, 10 H, PPh_3 + Ind), 6.95 (m, 6 H, PPh_3), 6.81 (br t, J = 7.5 Hz, 1 H, Ind), 6.32 (br d, J = 8.4 Hz, 1 H, Ind), 5.59 (m, 1 H, Ind), 4.91 (m, 1 H, Ind), 4.38 (d, J = 3.0 Hz, 1 H), 4.37 (m, 1 H, Ind + C2–H), 3.56 (m, 1 H, OCH_2), 3.27 (m, 1 H, OCH_2), 2.88 (d, J = 15.3 Hz, 1 H, C4–H), 1.28 (dd, J = 15.3, 9.7 Hz, 1 H, C4–H), 1.18 (t, J = 7.0 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 241.7 (d, J_{P-C} = 22 Hz, C1), 193.2 (d, J_{P-C} = 2 Hz, C3), 133.8 (d, J_{P-C} = 10 Hz), 133.0 (d, J_{P-C} = 42 Hz), 129.6, 127.5 (d, J_{P-C} = 13 Hz, 4 PPh_3), 125.9, 125.2, 123.1, 121.6, 113.8, 112.2 (6 Ind), 111.5 (d, J_{P-C} = 7 Hz, C2), 106.9, 78.2, 69.2 (d, J_{P-C} = 9 Hz, 3 Ind), 66.6 (OCH_2), 14.6 (CH_3), 10.5 (d, J_{P-C} = 20 Hz, C4); IR (CH_2Cl_2) 1609, 1581, 1433, 1311, 1207, 1094, 912 cm^{-1}. Anal. Calcd for $C_{33}H_{30}CoO_2P$: C, 72.25; H, 5.52. Found: C, 72.11; H, 5.55.

(η^5-Indenyl)(triphenylphosphine)-4-phenylcobaltacyclopent-3-en-2-one (11b). Triphenylphosphine (943 mg, 3.60 mmol) and **10a** (37 mg, 0.12 mmol) were dissolved in toluene (15 mL) in a glass tube. The solution was degassed with three freeze–pump–thaw cycles. The tube was then closed with a Teflon screw valve and heated in an oil bath at 100 °C for 45 h. The solvent was removed under reduced pressure and the residue chromatographed on silica with 4:1 hexanes/ethyl acetate. The starting complex was eluted first (22 mg, 0.069 mmol, 59%) followed by a second orange band of **11b** (11 mg, 0.019 mmol, 16%): mp 163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (br d, J = 8.2 Hz, 1 H, Ind), 7.47–7.44 (m, 2 H, Ph), 7.33–7.16 (m, 13 H, PPh_3 + Ph + Ind), 6.94–6.85 (m, 7 H, PPh_3 + Ind), 6.37 (br d, J = 8.0 Hz, 1 H, Ind), 5.57 (m, 1 H, Ind), 5.50 (m, 1 H), 4.80 (m, 1 H), 4.48 (br s, 1 H, 2 Ind + C2–H), 3.63 (d, J = 15.8 Hz, 1 H, C4–H), 2.04 (dd, J = 15.8, 9.5 Hz, C4–H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 253.4 (d, J_{P-C} = 24 Hz, C1), 178.7 (C3), 137.9 (Ph), 135.0 (d, J_{P-C} = 8 Hz, C2), 133.7 (d, J_{P-C} = 10 Hz), 133.0 (d, J_{P-C} = 42 Hz), 129.6 (3 PPh_3), 128.4, 128.0 (2 Ph), 127.6 (d, J_{P-C} = 10 Hz, PPh_3), 126.9 (Ph), 125.9, 125.3, 123.1, 121.9, 113.6, 112.5, 106.4, 79.6, 68.8 (d, J_{P-C} = 8 Hz, 9 Ind), 18.6 (d, J_{P-C} = 20 Hz, C4); IR (CH_2Cl_2) 1605 (s), 1475, 1426, 1320, 1089 (s) cm^{-1}. Anal. Calcd for $C_{37}H_{30}CoOP$: C, 76.54; H, 5.22. Found: C, 76.67; H, 5.26.

(η^5-Indenyl)carbonyl-4-phenylcobaltacyclopent-3-en-2-one (12). A glass pressure bottle was charged with **10a** (39 mg, 0.12 mmol) and acetone (10 mL). The orange solution was degassed with three freeze–pump–thaw cycles, and the bottle was filled

(59) The reported procedure (ref 50) gave a mixture of the desired compound and 2-methyl-3-phenyl-2-cyclobuten-1-one which was not readily separated. Pure material was obtained using the procedure employed for 3-phenyl-2-cyclobuten-1-one (ref 53).

with carbon monoxide to 80 psi. Within 1 h the solution had turned yellow. After 4 h the pressure was released and the solution was evaporated under reduced pressure without warming and dried under vacuum protected from light, giving **12** as an orange, analytically pure oil (43 mg, 0.12 mmol, 100%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.44 ("d", J = 8.4 Hz, 1 H), 7.39–7.23 (m, 5 H), 7.16 ("t", J = 7.3 Hz, 1 H, Ph + Ind), 6.05 (br s, 1 H, Ind), 6.01 (d, J = 1.6 Hz, 1 H, C2–H), 5.39 ("t", J = 3.0 Hz, 1 H, Ind), 5.23 (br s, 1 H, Ind), 3.55 (dd, J = 14.5, 1.6 Hz, 1 H, C4–H), 2.14 (d, J = 14.5 Hz, C4–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 234.4 (C1), 179.9 (C3), 136.6 (Ph), 134.0 (C2), 129.5, 128.4 (2 Ph), 127.5 (Ind), 127.1 (Ph), 126.3, 123.6, 121.9, 111.6, 108.6, 106.6, 77.4, 73.9 (8 Ind), 23.7 (C4); IR (CH_2Cl_2) 2000 (s), 1639, 1074 cm^{-1}. Anal. Calcd for $C_{20}H_{15}CoO_2$: C, 69.37; H, 4.38. Found: C, 69.13; H, 4.46.

(η^5-Indenyl)(triphenylphosphine)-4-phenylcobaltacyclopent-4-en-2-one (13a). A solution of 3-phenyl-2-cyclobuten-1-one[53] (34 mg, 0.24 mmol) in toluene (5 mL) was added via cannula to a flask containing **9** (115 mg, 0.16 mmol) and $ZnCl_2$ (65 mg, 0.48 mmol). After stirring for 60 min, the resulting red-brown mixture was diluted with THF (5 mL), filtered through silica, and concentrated to 4 mL under reduced pressure. Chromatography on silica with 10:1 hexanes/ethyl acetate gave the orange product band overlapping with recovered 3-phenyl-2-cyclobuten-1-one. Mixed fractions were stripped, redissolved in toluene, and chromatographed again. The combined pure product fractions were stripped to a light orange solid (33 mg, 36%). Diffusion of hexanes into a benzene solution gave orange crystals of **13a**: mp 184–185 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.74 (dd, J = 2.9, 0.9 Hz, 1 H, C4–H), 7.42 (br d, J = 8.2 Hz, 1 H, Ind), 7.30–6.78 (m, 22 H, PPh_3 + Ind + Ph), 6.54 (br d, J = 8.1 Hz, 1 H, Ind), 5.62 (m, 1 H, Ind), 4.80 (m, 1 H, Ind), 4.66 (m, 1 H, Ind), 3.60 (ddd, J = 20.2, 3.2, 1.1 Hz, 1 H, C2–H), 2.54 (d, J = 20.2 Hz, 1 H, C2–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 265.6 (d, J_{P-C} = 23 Hz, C1), 150.7 (d, J_{P-C} = 30 Hz, C4), 142.4 (C3), 136.8 (d, J_{P-C} = 4 Hz, Ph), 133.8 (d, J_{P-C} = 10 Hz), 132.8 (d, J_{P-C} = 44 Hz), 129.7 (d, J_{P-C} = 2 Hz, 3 PPh_3), 128.0 (Ph), 127.5 (d, J_{P-C} = 10 Hz, PPh_3), 126.0, 125.7, 124.7, 124.2, 123.6, 122.1 (4 Ind + 2 Ph), 113.6, 112.0, 105.9, 81.1, 68.5 (d, J_{P-C} = 8 Hz, 5 Ind), 64.9 (d, J_{P-C} = 9 Hz, C2); IR (CH_2Cl_2) 1660 (s), 1652 (s), 1480, 1435, 1092, 989, 819, 680 cm^{-1}. Anal. Calcd for $C_{37}H_{30}CoOP$: C, 76.54; H, 5.22. Found: C, 76.77; H, 5.28.

(η^5-Indenyl)(triphenylphosphine)-4-butylcobaltacyclopent-4-en-2-one (13b). A solution of 3-butyl-2-cyclobuten-1-one[52] (36 mg, 0.29 mmol) in benzene (6 mL) was reacted with **9** (131 mg, 0.19 mmol) and $ZnCl_2$ (82 mg, 0.6 mmol) as described for **13a**. Chromatography on silica with 10:1 hexanes/ethyl acetate gave an orange solid (40 mg, 0.071 mmol, 38%). Recrystallization from hexanes gave an analytically pure sample of **13b**: mp 148–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (br d, J = 8.3 Hz, 1 H, Ind), 7.36–7.20 (m, 10 H, PPh_3 + Ind), 7.02–6.96 (m, 6 H, PPh_3), 6.86 (br t, J = 7.5 Hz, 1 H, Ind), 6.39 (br d, J = 8.1 Hz, 1 H, Ind), 5.67 (m, 1 H), 5.41 (m, 1 H), 4.82 (m, 1 H), 4.47 (br s, 1 H, 3 Ind + C4–H), 2.94 (ddd, J = 20.6, 3.4, 0.9 Hz, 1 H, C2–H), 1.99 (m, 2 H, Bu), 1.76 (d, J = 20.6 Hz, 1 H, C2–H), 1.26 (m, 4 H, Bu), 0.87 (m, 3 H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 268.6 (d, J_{P-C} = 23 Hz, C1), 143.6 (C3), 135.5 (d, J_{P-C} = 32 Hz, C4), 133.8 (d, J_{P-C} = 10 Hz), 133.4 (d, J_{P-C} = 43 Hz), 129.5, 127.4 (d, J_{P-C} = 10 Hz, 4 PPh_3), 125.3, 125.2, 123.5, 122.1, 112.7, 111.8, 104.8, 80.3, 69.0 (d, J_{P-C} = 8 Hz, 9 Ind), 66.5 (d, J_{P-C} = 9 Hz, C2), 34.2 (d, J = 2 Hz), 30.7, 22.6, 14.0 (4 Bu); IR (CH_2Cl_2) 1641 (br, s), 1484, 1428, 1319, 1088, 980, 905, 809 cm^{-1}. Anal. Calcd for $C_{35}H_{34}CoOP$: C, 74.98; H, 6.13. Found: C, 74.87; H, 6.14.

(η^5-Indenyl)(triphenylphosphine)-2-cobaltaindanone (14) and (η^5-Indenyl)(triphenylphosphine)-1-cobaltaisoindanone (15). A solution of benzocyclobutenone[56] (22 mg, 0.19 mmol) in toluene (20 mL) was transferred into a flask containing **9** (113 mg, 0.16 mmol). The red mixture was heated to reflux for 1 h. The resulting red solution was filtered through silica using THF and concentrated to 5 mL under reduced pressure. Chromatography on silica with 10:1 hexanes/ethyl acetate gave orange needles, which were washed with hexanes and dried under vacuum. ^{1}H NMR showed the product to be a 2:1 mixture of **14** and **15** (53 mg, 0.096 mmol, 60%). Repeated crystallization by diffusion of hexanes into benzene and manual separation of the light orange needles of **14** from the dark red crystals of **15** gave pure samples of each isomer. **14**: mp 205–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (br d, J = 8.3 Hz, 1 H), 7.34–6.71 (m, 21 H), 6.32 (br d, J = 8.1 Hz, 1 H), 5.52 (m, 1 H, Ind), 4.77 (m, 1 H, Ind), 4.59 (m, 1 H, Ind), 3.80 (d, J = 14.5 Hz, 1 H, C4–H), 2.30 (dd, J = 14.5, 11.5 Hz, 1 H, C4–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.1 (C3), 149.9 (d, J_{P-C} = 8 Hz, C2), 133.6 (d, J_{P-C} = 10 Hz), 132.7 (d, J_{P-C} = 42 Hz), 129.6 (3 PPh_3), 129.5 (aryl), 127.4 (d, J_{P-C} = 10 Hz, PPh_3), 126.4, 125.9, 125.4, 123.6, 123.4, 122.0, 117.4 (3 aryl + 4 Ind), 113.7, 112.6, 106.1, 79.7, 69.4 (d, J_{P-C} = 8 Hz, 5 Ind), 17.1 (d, J_{P-C} = 19 Hz, C4); IR (CH_2Cl_2) 1624 (s), 1432, 1095, 912, 861, 818 cm^{-1}. Anal. Calcd for $C_{35}H_{28}CoOP$: C, 75.80; H, 5.10. Found: C, 75.63; H, 5.13. **15**: mp 207–208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–6.54 (m, 23 H), 5.50 (dt, J = 1.2, 2.9 Hz, 1 H, Ind), 4.91 (m, 1 H, Ind), 4.71 (m, 1 H, Ind), 3.69 (br d, J = 20.7 Hz, 1 H, C2–H), 2.51 (d, J = 20.7 Hz, 1 H, C2–H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 266.8 (d, J_{P-C} = 24 Hz, C1), 147.5 (d, J_{P-C} = 1 Hz, C3), 140.4 (d, J_{P-C} = 2 Hz, aryl), 133.7 (d, J_{P-C} = 10 Hz), 132.4 (br d, J_{P-C} = 43 Hz), 129.8, 127.4 (d, J_{P-C} = 10 Hz, 4 PPh_3), 126.9, 125.1, 124.8, 123.8 (d, J_{P-C} = 2 Hz), 122.5, 121.5, 120.6 (d, J_{P-C} = 2 Hz, 3 aryl + 4 Ind), 117.5, 111.7, 104.7, 78.6, 70.8 (d, J_{P-C} = 8 Hz, 5 Ind), 65.6 (d, J_{P-C} = 8 Hz, C2); IR (CH_2Cl_2) 1662 (s), 1426, 1085, 1012, 972 cm^{-1}. Anal. Calcd for $C_{35}H_{28}CoOP$: C, 75.80; H, 5.10. Found: C, 75.93; H, 5.14.

General Procedure for Reaction of 10 with Alkynes. 4,5-Diethylbiphenyl-3-ol (17a). A glass tube was charged with **10a** (50 mg, 0.16 mmol), cyclooctadiene (37 μL, 32 mg, 0.30 mmol), 3-hexyne (91 μL, 66 mg, 0.80 mmol), and toluene (3 mL). The solution was degassed with three freeze–pump–thaw cycles. The tube was refilled with argon to 0.75 atm, sealed with a Teflon screw valve, and heated in an oil bath at 100 °C for 19 h. After cooling, the solution was concentrated to 1 mL by rotary evaporation and chromatographed on silica with 10:1 hexanes/ethyl acetate giving **17a** as a pale yellow oil (23 mg, 65%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.40 (m, 2 H), 7.30 (m, 1 H), 7.01 (d, J = 1.4 Hz, 1 H), 6.84 (d, J = 1.4 Hz, 1 H), 4.79 (s, 1 H, OH), 2.69 (q, J = 7.6 Hz, 4 H), 1.25 (t, J = 7.6 Hz, 3 H), 1.20 (t, J = 7.6 Hz, 3 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.8, 143.9, 140.9, 139.6, 128.6, 127.3, 127.1, 126.9, 120.0, 111.6, 26.0, 18.9, 15.8, 14.2; IR (CH_2Cl_2) 3590, 2975, 2940, 2880, 1573, 1486, 1412, 1166, 1110, 937 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.90; H, 8.03. Found: C, 84.66; H, 8.08.

5-Butylbiphenyl-3-ol (17b) and 4-Butylbiphenyl-3-ol (18b). 1-Hexyne (85 μL, 61 mg, 0.74 mmol) was reacted with **10a** (47 mg, 0.15 mmol) in the presence of cyclooctadiene (37 μL, 32 mg, 0.30 mmol) and toluene (3 mL) for 17 h. After concentration, the mixture was chromatographed on silica with 10:1 hexanes/ethyl acetate. Eluted first was an impure sample of **18b**, which was purified by radial chromatography on silica with 15:1 hexanes/ethyl acetate (6 mg, 18%). Cooling a solution in hexanes gave white crystals of **18b**: mp 73–74 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.40 (m, 2 H), 7.31 (m, 1 H), 7.17 (d, J = 7.8 Hz, 1 H), 7.10 (dd, J = 7.8, 1.8 Hz, 1 H), 6.99 (d, J = 1.8 Hz, 1 H), 4.83 (s, 1 H, OH), 2.63 (t, J = 7.7 Hz, 2 H), 1.63 (m, 2 H), 1.40 (m, 2 H), 0.95 (t, J = 7.3 Hz, 3 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.7, 140.7, 140.3, 130.5, 128.7, 127.6, 126.9, 119.5, 113.9, 32.0, 29.4, 22.6, 14.0; IR (CH_2Cl_2) 3595, 3400 (br, w), 2965, 2935, 2870, 1488, 1414, 1229, 1176, 1126 cm^{-1}; HRMS calcd for $C_{16}H_{18}O$ 226.13575, found 226.1352. Further elution gave **17b** as a colorless oil (15 mg, 45%). Cooling a solution in hexanes gave white needles: mp 47–48 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.56 (m, 2 H), 7.41 (m, 2 H), 7.32 (m, 1 H), 6.98 ("t", J = 1.5 Hz, 1 H), 6.87 (dd, J = 2.4, 1.6 Hz, 1 H), 6.64 (dd, J = 2.3, 1.6 Hz, 1 H), 4.81 (s, 1 H, OH), 2.61 (t, J = 7.7 Hz, 2 H), 1.62 (m, 2 H), 1.37 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.7, 145.2, 142.7, 140.9, 128.7, 127.3, 127.1, 120.1, 114.3, 111.4, 35.6, 33.5, 22.4, 14.0; IR (CH_2Cl_2) 3580, 2960, 2930, 2860, 1597 (s), 1452, 1181, 1152, 855 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.90; H, 8.03. Found: C, 84.71; H, 8.05.

Dimethyl 5-Hydroxybiphenyl-3,4-dicarboxylate (17c). Dimethyl acetylenedicarboxylate (368 μL, 426 mg, 3.00 mmol) was reacted with **10a** (47 mg, 0.15 mmol) in the presence of cyclooctadiene (37 μL, 32 mg, 0.30 mmol) and toluene (3 mL) for 20 h. Chromatography on silica with 4:1 hexanes/ethyl acetate gave **17c** as a colorless oil (19 mg, 45%). Cooling a solution in hexanes gave white needles: mp 118–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.70 (s, 1 H, OH), 7.58 (m, 2 H), 7.46–7.39 (m, 3 H),

7.29 (d, J = 1.8 Hz, 1 H), 7.18 (d, J = 1.8 Hz, 1 H), 3.92 (s, 3 H), 3.90 (s, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.4, 169.2, 161.5, 147.6, 138.5, 135.9, 129.0, 128.9, 127.1, 118.1, 117.6, 108.6, 52.9, 52.7; IR (CH_2Cl_2) 3200 (br, w), 2950 (w), 1730 (s), 1675 (s), 1615, 1564, 1439, 1360 (sh), 1345, 1284, 1258 (sh), 1206 (s), 1175, 1120, 1019 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.94. Found: C, 66.98; H, 4.95.

Ethyl 3-Hydroxy-5-methylbiphenyl-4-carboxylate (17d) and Ethyl 5-Hydroxy-4-methylbiphenyl-3-carboxylate (18d). Ethyl 2-butynoate (350 μL, 336 mg, 3.00 mmol) was reacted with **10a** (50 mg, 0.16 mmol) in the presence of cyclooctadiene (37 μL, 32 mg, 0.30 mmol) and toluene (3 mL) for 21.5 h. Chromatography on silica with 10:1 hexanes/ethyl acetate gave **17d** as a pale yellow oil (17 mg, 42%). Cooling a solution of hexanes gave pale yellow crystals: mp 75–76 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 11.47 (s, 1 H, OH), 7.59 (m, 2 H), 7.56–7.45 (m, 3 H), 7.07 (d, J = 1.7 Hz, 1 H), 6.95 (d, J = 1.7 Hz, 1 H), 4.44 (q, J = 7.1 Hz, 2 H), 2.61 (s, 3 H), 1.43 (t, J = 7.1 Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 171.7, 163.2, 146.6, 141.7, 139.6, 128.8, 128.3, 127.1, 121.8, 113.8, 111.1, 61.6, 24.4, 14.2; IR (CH_2Cl_2) 3000 (br, w), 2980 (w), 2935 (w), 1658 (s), 1614, 1554, 1393, 1374, 1353, 1320, 1223, 1210, 1112, 870, 811 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.97; H, 6.30. Found: C, 74.92; H, 6.33. Further elution gave a 3.9:1 mixture of the alkyne trimer triethyl 3,5,6-trimethyl-1,2,4-benzenetricarboxylate[60] and **18d** (123 mg; yield of **18d** 0.078 mmol, 50%). A pure sample was obtained with low mass recovery by extracting into 1 N NaOH, neutralizing and extracting into Et_2O, and chromatographing again, yielding a pale yellow oil: ^1H NMR (360 MHz, $CDCl_3$) δ 7.63 (d, J = 1.9 Hz, 1 H), 7.54 (m, 2 H), 7.41 (m, 2 H), 7.33 (m, 1 H), 7.15 (d, J = 1.9 Hz, 1 H), 5.10 (s, 1 H), 4.37 (q, J = 7.1 Hz, 2 H), 2.47 (s, 3 H), 1.39 (t, J = 7.1 Hz, 3 H); IR (CH_2Cl_2) 3590, 3450 (br), 2936, 1715 (s), 1372, 1337, 1237 (s), 1053 (s) cm^{-1}; HRMS calcd for $C_{16}H_{16}O_3$ 256.1099, found 256.1100.

Reaction of 10b with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (184 μL, 213 mg, 1.50 mmol) was reacted with **10b** (50 mg, 0.15 mmol) in the presence of cyclooctadiene (27 μL, 20 mg, 0.18 mmol) and toluene (2 mL) for 15 h. Chromatography on silica with 4:1 hexanes/ethyl acetate gave a small amount of recovered **10b** followed by a colorless, fluorescent band which was evaporated to a yellow oil: dimethyl 5-hydroxy-2-methylbiphenyl-3,4-dicarboxylate (**19**) (20 mg, 43%). An analytically pure sample was obtained by preparatory thin-layer chromatography on silica with 10:1 hexanes/diethyl ether. ^1H NMR (300 MHz, $CDCl_3$) δ 10.80 (s, 1 H, OH), 7.35 (m, 3 H), 7.24 (m, 2 H), 6.94 (s, 1 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 2.04 (s, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.7, 169.1, 159.3, 150.2, 140.0, 135.6, 128.6, 128.3, 127.8, 123.6, 120.0, 108.1, 52.9, 52.4, 16.5; IR (CH_2Cl_2) 3050 (br, w), 2960, 1728 (s), 1674 (s), 1594, 1560, 1436 (s), 1349 (s), 1226 (s), 1200 (s), 1111, 1040 (s), 930, 802 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.98; H, 5.38. Found: C, 67.92; H, 5.38. Further elution with 20:1 ethyl acetate/methanol gave a broad orange band, which was evaporated to give **20** as an orange film (12 mg, 16%). Recrystallization by diffusion of hexanes into benzene gave analytically pure red-orange crystals of (η^5-indenyl)(η^4-dimethyl 6-methyl-3-oxo-5-phenylcyclohexa-1,4-diene-1,2-dicarboxylate)cobalt (**20**): mp 142–143 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 7 H), 7.09 (m, 1 H), 6.06 (br d, J = 8.5 Hz, 1 H), 5.47 (br s, 1 H), 5.40 (m, 1 H), 5.02 (m, 1 H), 4.90 (m, 1 H), 3.92 (s, 3 H), 3.83 (s, 3 H), 3.18 (br q, J = 6.5 Hz, 1 H), 0.37 (d, J = 6.5 Hz, 3 H); IR (CH_2Cl_2) 1723, 1701, 1596, 1435, 1238, 1089, 1041 cm^{-1}. Anal. Calcd for $C_{26}H_{23}CoO_5$: C, 65.81; H, 4.90. Found: C, 65.97; H, 4.96. ^1H NOE: presaturation of the methyl doublet (δ 0.37) produced only a small enhancement of the signal for the hydrogen coupled to it (3.18, 4%). Presaturation of the latter signal produced a small enhancement of one aromatic signal (7.30, 5%).

3-*tert*-Butyl-1-naphthol (22).[61] To a solution of **10e** (51 mg, 0.14 mmol) in diethyl ether (5 mL) was added anhydrous $FeCl_3$ (33 mg, 0.20 mmol), and the mixture was stirred 20 min. Dilute aqueous HCl was added, and the mixture was separated. The ether layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica with 10:1 hexanes/ethyl acetate giving **22** as a pale yellow solid (23 mg, 84%). Cooling a solution in hexanes gave pale yellow crystals: mp 80–81 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 8.07 (m, 1 H), 7.76 (m, 1 H), 7.43 (m, 2 H), 7.36 (br s, 1 H), 6.90 (d, J = 1.4 Hz, 1 H), 5.17 (s, 1 H, OH), 1.37 (s, 9 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 151.3, 149.1, 134.6, 127.7, 126.3, 124.5, 122.8, 121.2, 115.6, 107.7, 34.8, 31.1; IR (CH_2Cl_2) 3580, 3290 (br), 2970, 2910, 2875, 1639, 1604, 1580, 1517, 1484, 1469, 1405, 1395, 1297, 1246, 1202, 1187, 1152, 1112, 1069, 1026, 947, 885, 855, 782, 677, 627 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$: C, 83.94; H, 8.07. Found: C, 83.75; H, 8.12.

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Registry No. **4a**, 128191-18-4; **4b**, 128191-19-5; **4c**, 128191-20-8; **4d**, 128216-92-2; **4e**, 137365-47-0; **4e**·THF, 137365-48-1; **5** (R^1 = R^2 = H), 3469-06-5; **5** (R^1, R^2 = OCH_2O), 118112-19-9; **6a**, 128191-23-1; **6b**, 128191-22-0; **7a**, 128191-24-2; **7b**, 128191-25-3; **8a**, 137365-49-2; **8b**, 137365-50-5; **8c**, 137365-51-6; **9**, 130196-88-2; **10a**, 130196-89-3; *anti*-**10b**, 130196-90-6; *syn*-**10b**, 130196-91-7; *anti*-**10c**, 130196-92-8; *syn*-**10c**, 130196-93-9; **10d**, 137365-52-7; **10e**, 130196-96-2; **11a**, 137365-53-8; **11b**, 137365-54-9; **12**, 137365-55-0; **13a**, 137365-56-1; **13b**, 137365-57-2; **14**, 137365-58-3; **15**, 137365-59-4; **17a**, 108191-73-7; **17b**, 130196-83-7; **17c**, 130196-85-9; **17d**, 130196-86-0; **18b**, 130196-84-8; **18d**, 130196-87-1; **19**, 130196-98-4; **20**, 130196-99-5; **22**, 57985-68-9; $ClRh(PPh_3)_3$, 14694-95-2; $ClCo(PPh_3)_3$, 26305-75-9; 3-*tert*-butyl-4-phenyl-2-cyclobuten-1-one, 130196-82-6; *N,N*-dimethylphenylacetamide, 18925-69-4; 2,3-diethyl-2-cyclobuten-1-one, 110655-92-0; 3-butyl-2-cyclobuten-1-one, 38425-48-8; 3-phenyl-2-cyclobuten-1-one, 38425-47-7; 3-ethoxy-2-cyclobuten-1-one, 4683-54-9; 3-benzoyl-2-cyclobuten-1-one, 137365-46-9; triethyl 3,5,6-trimethyl-1,2,4-benzenetricarboxylate, 91620-94-9; 3,3-dimethyl-1-butyne, 917-92-0; sodium indenide, 23181-84-2; sodium cyclopentadienide, 4984-82-1; 4-methyl-3-phenyl-2-cyclobuten-1-one, 95904-83-9; 4-methyl-3-(trimethylsilyl)-2-cyclobuten-1-one, 95904-87-3; 3-*tert*-butyl-4-methyl-2-cyclobuten-1-one, 95904-84-0; 3-hexyne, 928-49-4; 1-hexyne, 693-02-7; dimethyl acetylenedicarboxylate, 762-42-5; ethyl 2-butynoate, 4341-76-8.

Supplementary Material Available: Textual presentation of details of the data collection and structure solution for **4e**·THF and full listings of structure determination data, atomic coordinates and thermal parameters, bond distance and angle data, and least-squares planes (16 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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