Coordination Modes and Catalytic Carbonylative [4 + 1] Cycloaddition of Vinylallenes

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(Vinylallene)rhodium complexes with three kinds of coordination modes, that is, η^2-coordination of the terminal π-bond of the allenyl group, η^4-coordination of the conjugated diene skeleton, and planar σ^2-coordination, were synthesized by ligand substitution of RhCl-(PPh$_3$)$_3$ with vinylallenes of specific substitution patterns. Their structures were determined by X-ray crystallography. Coordination preferences can be explained in terms of spatial interactions between the vinylallene substituents and the phosphine ligands as well as effective delocalization of the π-electrons of the endo- and exocyclic double bonds. The structural studies were extended to the development of the rhodium-catalyzed carbonylative [4 + 1] cycloaddition reaction of vinylallenes, affording five-membered carbocycles. With a nonsymmetrical vinylallene, face-selective η^4-coordination from the less hindered side of the allenyl group was observed. The achievement of [4 + 1] carbonylation can be attributed to (i) the substantial facility of substituted vinylallenes for η^4-coordination and (ii) the significant contribution of a metallacyclo-3-pentene resonance form to the intermediate complex. A platinum(0) complex also catalyzed the [4 + 1] cycloaddition of vinylallenes as efficiently as rhodium.

Introduction

The structures of conjugated-diene—transition-metal complexes have attracted considerable attention owing to the great diversity of their binding modes. For example, most middle-transition-metal— and late-transition-metal—diene complexes assume conventional π^2-bonded structures.[1] Early transition metals prefer the bent σ^2,π-bonded metallacyclo-3-pentene form.[2] On the other hand, planar σ^2-bonded metallacyclic complexes are rare.[3–5] s-*trans* binding has been also reported.[6]

Conjugated dienes which are extended with a cumulated double bond, such as vinylketenes (1; X = O), also furnish η^4-complexes with interesting structures[7] and reactivities.[8] Although vinylallenes (2; X = C) are further examples of such cumulated-diene systems, their complexes have been rare; key examples have been

π^2-bonded complex

bent σ^2,π-bonded complex

planar σ^2-bonded complex

s-*trans* complex
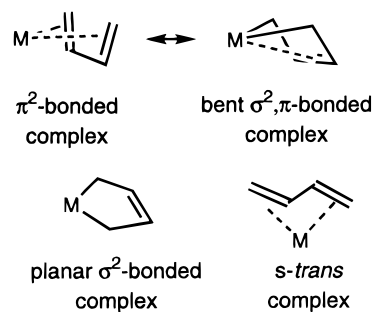
limited to η^4-iron carbonyl complexes prepared directly from a vinylallene[9] and a phenylallene[10] or indirectly via η^4-vinylketene complexes.[11]

In the course of our synthetic study of vinylallenes,[12] we were struck by the paucity of vinylallene complexes

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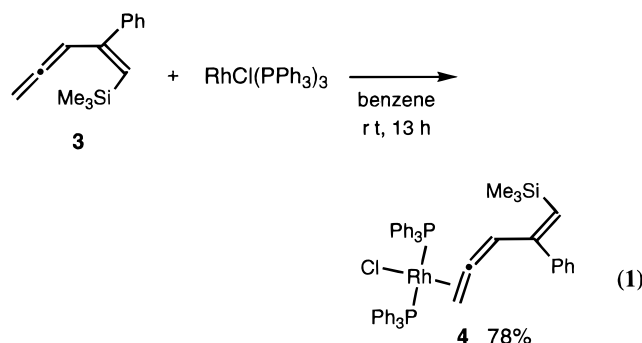(11) Saberi, S. P.; Thomas, S. E. *J. Chem. Soc., Perkin Trans. 1* **1992**, 259.

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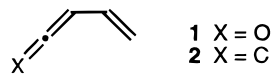
of transition metals. This paper describes the synthesis of (vinylallene)rhodium complexes with three coordination modes, i.e., η^2-coordination of the terminal π-bond of the allenyl group, η^4-coordination of the conjugated diene system, and planar σ^2-coordination. A planar σ^2-complex was also synthesized with platinum. Studies of the coordination modes of vinylallenes revealed a strong σ-bond character of the η^4-bound vinylallene complexes. A new catalytic carbonylative [4 + 1] cycloaddition reaction of vinylallenes, forming five-membered carbocycles, was developed on the basis of the structural studies on the vinylallene complexes.[13]

η^2-Complex Coordinated at the Terminal Allenic π-Bond

Vinylallene **3**, having no substituents at the terminal allenic carbon,[14] was treated with RhCl(PPh₃)₃ in benzene at room temperature. In a manner analogous to that for a simple allene,[15] **3** displaced one molecule of PPh₃ on rhodium to afford **4** in 78% isolated yield (eq 1). Recrystallization from CH₂Cl₂/hexane generated air-

stable yellow crystals. The molecular structure, characterized by X-ray crystallographic analysis, depicts η^2-coordination at the terminal allenic π-bond (Figure 1; bond distances and angles are given in Table 1). The rhodium has a square-planar geometry. The terminal allenic π-bond binds to rhodium from its less hindered side, and the *trans* site is occupied by the chlorine atom. The η^2-bound π-bond axis lies perpendicular to the square plane. As a consequence of η^2-coordination, the allenyl group is distorted from linearity ($\angle$C(8)−C(9)−C(10) = 149.6(9)°), and the η^2-bound π-bond is longer (C(9)−C(10) = 1.393(15) Å) than the free C(8)−C(9) π-bond (1.314(13) Å). As was observed previously,[15] the distance from rhodium to the central allenic carbon atom (C(9)−Rh(1) = 2.015(9) Å) is shorter than the distance to the terminal allenic carbon (C(10)−Rh(1) = 2.115(10) Å), probably reflecting higher s character in orbital hybridization on C(9).

(13) Preliminary communications: (a) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2691. (b) *J. Am. Chem. Soc.* **1996**, *118*, 11672.

(14) Attempted ligand substitution with a vinylallene unsubstituted at both of the vinyl and allenyl terminals failed, because such a vinylallene readily underwent oligomerization.[15b]

(15) (a) Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1231. (b) Otsuka, S.; Tani, K.; Nakamura, A. *J. Chem. Soc. A* **1969**, 312. (c) Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kukudo, M. *J. Chem. Soc., Chem. Commun.* **1969**, 317.
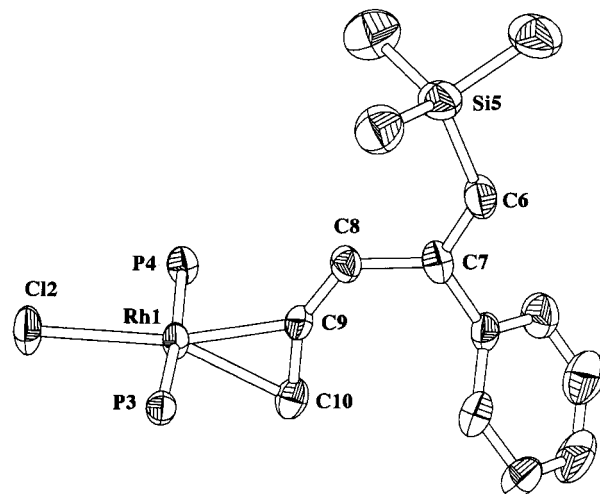
Figure 1. Molecular structure of **4** with the hydrogen atoms and the solvated methanol omitted for clarity (40% probability thermal ellipsoids).

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Complex 4

Rh(1)−P(3)	2.326(3)	Rh(1)−P(4)	2.316(3)
Rh(1)−Cl(2)	2.376(3)	Rh(1)−C(9)	2.015(9)
Rh(1)−C(10)	2.115(10)	C(7)−C(6)	1.346(16)
Si(5)−C(6)	1.875(12)	C(9)−C(8)	1.314(13)
C(9)−C(10)	1.393(15)	C(8)−C(7)	1.466(12)
P(3)−Rh(1)−P(4)	174.4(1)	P(3)−Rh(1)−Cl(2)	90.1(1)
P(3)−Rh(1)−C(9)	91.2(3)	P(3)−Rh(1)−C(10)	92.6(3)
P(4)−Rh(1)−Cl(2)	86.8(1)	P(4)−Rh(1)−C(9)	90.7(3)
P(4)−Rh(1)−C(10)	92.2(3)	Cl(2)−Rh(1)−C(9)	166.7(3)
Cl(2)−Rh(1)−C(10)	153.7(4)	C(9)−Rh(1)−C(10)	39.3(4)
Rh(1)−C(9)−C(8)	136.2(7)	Si(5)−C(6)−C(7)	129.8(8)
Rh(1)−C(9)−C(10)	74.2(6)	C(8)−C(9)−C(10)	149.6(9)
C(9)−C(8)−C(7)	126.2(9)	C(8)−C(7)−C(6)	121.1(9)
Rh(1)−C(10)−C(9)	66.5(5)		

η^4-Complexes Coordinated at Two Conjugated π-Bonds

Vinylallene **5**, having two methyl groups at the allenic terminus, was reacted with RhCl(PPh₃)₃ at room temperature for 20 h. In marked contrast to the case for **3**, two molecules of PPh₃ were displaced by **5** to yield the (η^4-vinylallene)rhodium(I) complex **6** as a mixture of *endo* and *exo* isomers, which were isolated in 44% and 19% yields, respectively, by chromatography (eq 2).
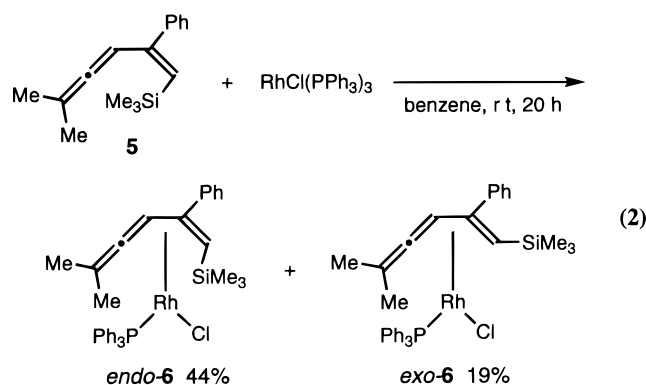
Orange single crystals of *endo*-**6** were obtained from CH₂Cl₂/hexane, and the structure was determined by X-ray crystallography (Figure 2). The rhodium(I) atom has a distorted-square-planar geometry with the two *cis*
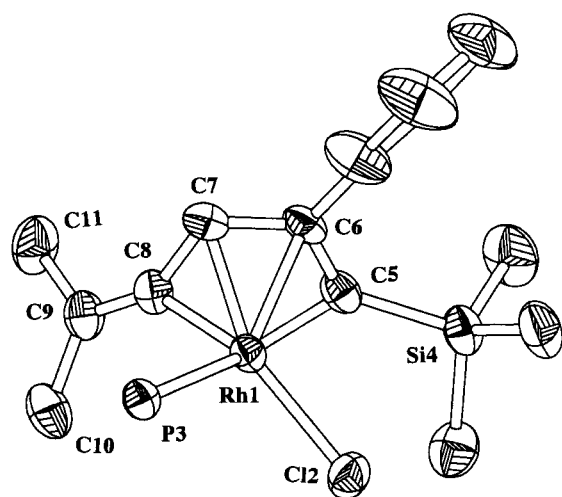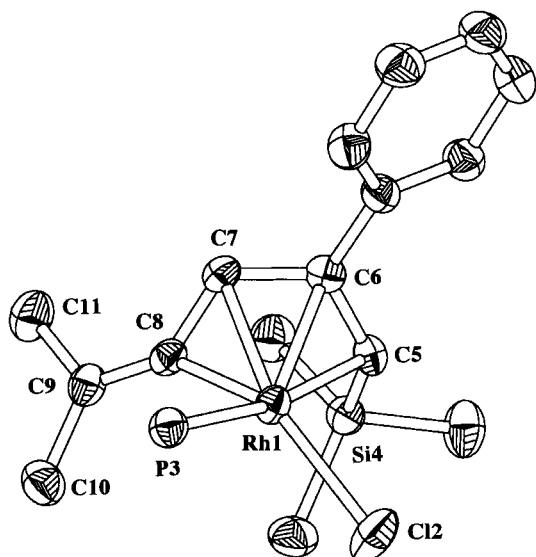
Figure 2. Molecular structures of *endo*-**6** (upper) and *exo*-**6** (lower). The phenyl groups on the phosphorus atoms, the hydrogen atoms, and the solvated CH_2Cl_2 of *exo*-**6** are omitted for clarity (40% probability thermal ellipsoids).

sites occupied by the internal allenic π-bond and the vinylic π-bond. The former π-bond is *trans* to the chlorine atom. The two π-bonds are cisoid and lie in a plane, constituting η^4-coordination. The silicon atom, while staying in the *endo* position, deviates from this plane away from the metal with the torsion angle Si(4)−C(5)−C(6)−C(7) of 52.7°. The Rh−C(8) bond is the shortest of all the metal−carbon bonds (Table 2), presumably due to the difference in hybridization of the orbitals.

On the other hand, recrystallization of *exo*-**6** from CH_2Cl_2/hexane afforded yellow crystals suitable for an X-ray diffraction study, which confirmed an *exo* orientation of the trimethylsilyl group (Figure 2; bond distances and angles are given in Table 3). Interestingly, the C(5)−Si(4) bond is approximately coplanar with the η^4-coordinating skeleton or, rather, slightly bent toward the metal center (torsion angle Si(4)−C(5)−C(6)−C(7) = 170.3°). Otherwise, *exo*-**6** exhibits structural features analogous to those of *endo*-**6**.

Notably, isolated *endo*-**6** underwent gradual isomerization to *exo*-**6** ($t_{1/2}$ = 22.5 h) on standing at 70 °C in

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complex *endo*-6

Rh(1)−P(3)	2.312(2)	Rh(1)−Cl(2)	2.346(2)
Rh(1)−C(6)	2.196(5)	Rh(1)−C(7)	2.131(5)
Rh(1)−C(8)	2.019(5)	Rh(1)−C(5)	2.227(5)
Si(4)−C(5)	1.880(5)	C(6)−C(7)	1.448(7)
C(6)−C(5)	1.415(7)	C(7)−C(8)	1.405(7)
C(8)−C(9)	1.326(6)		
P(3)−Rh(1)−Cl(2)	93.3(1)	P(3)−Rh(1)−C(6)	132.4(2)
P(3)−Rh(1)−C(7)	103.3(2)	P(3)−Rh(1)−C(8)	94.5(2)
P(3)−Rh(1)−C(5)	169.5(2)	Cl(2)−Rh(1)−C(6)	123.4(2)
Cl(2)−Rh(1)−C(7)	162.1(2)	Cl(2)−Rh(1)−C(8)	146.8(2)
Cl(2)−Rh(1)−C(5)	93.8(2)	C(6)−Rh(1)−C(7)	39.1(2)
C(6)−Rh(1)−C(8)	71.6(2)	C(6)−Rh(1)−C(5)	37.3(2)
C(7)−Rh(1)−C(8)	39.5(2)	C(7)−Rh(1)−C(5)	68.9(2)
Rh(1)−C(5)−C(6)	70.2(3)	Rh(1)−C(6)−C(7)	68.0(3)
Rh(1)−C(6)−C(5)	72.6(3)	C(7)−C(6)−C(5)	119.0(4)
Rh(1)−C(7)−C(6)	72.9(3)	Rh(1)−C(8)−C(7)	74.6(3)
Rh(1)−C(7)−C(8)	65.9(3)	C(6)−C(7)−C(8)	119.9(5)
Rh(1)−C(8)−C(9)	142.2(4)	C(7)−C(8)−C(9)	142.1(5)
Rh(1)−C(5)−Si(4)	113.4(3)	Si(4)−C(5)−C(6)	130.2(4)
C(8)−Rh(1)−C(5)	83.7(2)		

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Complex *exo*-6

Rh(1)−Cl(2)	2.333(1)	Rh(1)−P(3)	2.300(1)
Rh(1)−C(8)	2.030(3)	Rh(1)−C(6)	2.183(3)
Rh(1)−C(7)	2.093(3)	Rh(1)−C(5)	2.296(3)
Si(4)−C(5)	1.885(3)	C(6)−C(5)	1.395(4)
C(8)−C(7)	1.411(4)	C(8)−C(9)	1.321(5)
C(6)−C(7)	1.434(5)		
Cl(2)−Rh(1)−P(3)	90.6(1)	Cl(2)−Rh(1)−C(8)	153.8(1)
Cl(2)−Rh(1)−C(6)	120.0(1)	Cl(2)−Rh(1)−C(7)	158.7(1)
Cl(2)−Rh(1)−C(5)	96.7(1)	P(3)−Rh(1)−C(8)	95.5(1)
P(3)−Rh(1)−C(6)	137.5(1)	P(3)−Rh(1)−C(7)	105.5(1)
P(3)−Rh(1)−C(5)	172.6(1)	C(8)−Rh(1)−C(6)	70.3(2)
C(8)−Rh(1)−C(7)	40.0(2)	C(8)−Rh(1)−C(5)	78.5(2)
C(6)−Rh(1)−C(7)	39.1(2)	C(6)−Rh(1)−C(5)	36.2(1)
Rh(1)−C(5)−Si(4)	124.1(2)	Rh(1)−C(7)−C(8)	67.6(2)
Rh(1)−C(8)−C(7)	72.4(2)	Rh(1)−C(8)−C(9)	139.2(3)
C(7)−C(8)−C(9)	148.2(3)	Rh(1)−C(6)−C(7)	67.1(2)
Rh(1)−C(6)−C(5)	76.3(2)	Rh(1)−C(5)−C(6)	67.5(2)
C(7)−C(6)−C(5)	118.4(3)	Si(4)−C(5)−C(6)	132.0(3)
Rh(1)−C(7)−C(6)	73.8(2)	C(8)−C(7)−C(6)	117.1(3)
C(7)−Rh(1)−C(5)	67.1(2)		

C_6D_6. In contrast, *exo*-**6** failed to undergo isomerization,[16] indicating that *exo*-**6** is thermodynamically favored, presumably due to steric reasons. A ring-flipping (flip-envelope) mechanism[17] for this thermal *endo*−*exo* isomerization is shown in Scheme 1. Decomplexation of the double bond of the bent metallacyclic form of *endo*-**6** and a subsequent flip through the planar σ^2-bonded metallacycle **7** generates the η^4-complex with an *exo* orientation of the trimethylsilyl group. It is likely that, in the reaction of **5** with RhCl(PPh$_3$)$_3$, simple ligand substitution results in the initial formation of *endo*-**6** with the original orientation of the silyl group retained together with free PPh$_3$. A ring-flipping isomerization, which may be accelerated by the liberated PPh$_3$, subsequently occurs to furnish a mixture of the two isomers. The observed structural fluxionality of **6** in solution suggests a considerable contribution from the rhodacyclo-3-pentene resonance form.

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(16) Heating of *exo*-**6** for a prolonged time caused decomposition instead.

(17) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (b) Krüger, C.; Müller, G.; Erker, G.; Dolf, U.; Engel, K. *Organometallics* **1985**, *4*, 215. (c) Eaton, B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359. (d) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549. (e) Bürgi, H.-B.; Doubler-Steudle, K. C. *J. Am. Chem. Soc.* **1988**, *110*, 4953.

Scheme 1[a]

bent metallacycle

planar
σ^2-metallacycle
7

bent metallacycle
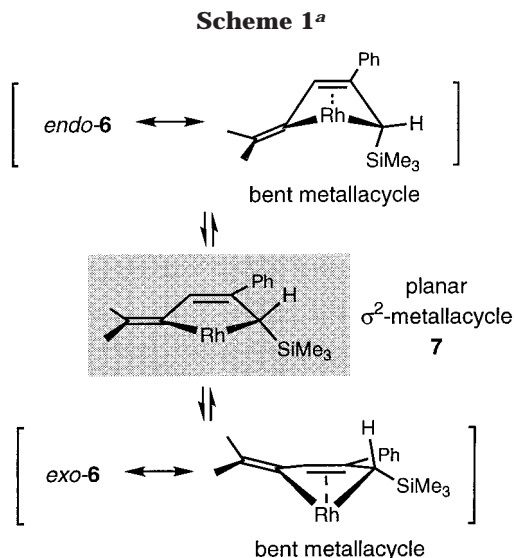
[a] The ligands on rhodium are omitted for clarity.

Planar σ^2-Bonded Complexes

Vinylallene **8**, lacking substituents at the vinylic terminus, was treated with $RhCl(PPh_3)_3$ in benzene at room temperature. The vinylallene **8** displaced one molecule of PPh_3 on the rhodium to afford metallacycle **9** as a solid in 92% isolated yield, for which satisfactory analytical data were obtained (eq 3).
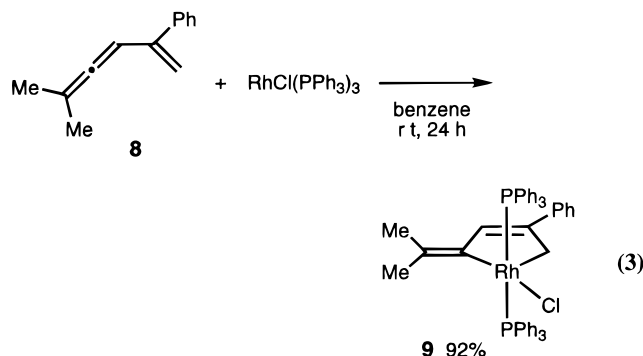
Recrystallization from CH_2Cl_2/methanol gave air-stable orange crystals as a methanol solvate. The solid-state structure of **9** was determined by a single-crystal X-ray diffraction study. An ORTEP diagram of the molecule is shown in Figure 3; bond distances and angles are given in Table 4. The most notable feature of the structure is that the five-membered rhodacyclo-3-pentene ring constitutes an almost perfect plane. The maximum deviation from the mean plane is only 0.018 Å. There is no interaction between the C(6)−C(7) double bond and rhodium. The arrangement of the pentacoordinated rhodium atom can be considered as a flat square pyramid, or as a distorted-octahedral geometry with one vacant site over which the C(10) methyl group at the allenic terminus hangs. The chlorine atom sits *trans* to the sp^2 carbon atom (C(8); Cl(2)−Rh(1)−C(8) = 163.1(2)°), and the two PPh$_3$ ligands are also *trans*. The C(5)−C(6) and C(7)−C(8) linkages (1.510(5) and 1.452(6) Å, respectively) are longer than C(6)−C(7) (1.332(6) Å), reflecting the bond order. The dihedral angle C(6)−C(7)−C(8)−C(9) is 179.2°. Comparison with the corresponding dihedral angles of *endo*-**6** (140.6°) and
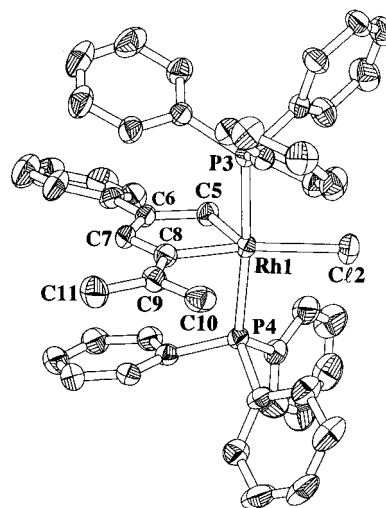

Figure 3. Molecular structure of **9** with the hydrogen atoms and the solvated methanol omitted for clarity (40% probability thermal ellipsoids).

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Complex 9

Rh(1)−Cl(2)	2.458(1)	Rh(1)−P(3)	2.339(1)
Rh(1)−P(4)	2.374(1)	Rh(1)−C(5)	2.024(4)
Rh(1)−C(8)	2.025(4)	P(3)−C(18)	1.835(4)
C(5)−C(6)	1.510(5)	C(6)−C(7)	1.332(6)
C(7)−C(8)	1.452(6)	C(8)−C(9)	1.362(6)
Cl(2)−Rh(1)−P(3)	92.9(1)	Cl(2)−Rh(1)−P(4)	92.2(1)
Cl(2)−Rh(1)−C(5)	114.9(2)	Cl(2)−Rh(1)−C(8)	163.1(2)
P(3)−Rh(1)−P(4)	174.8(1)	P(3)−Rh(1)−C(5)	89.2(1)
P(3)−Rh(1)−C(8)	87.5(2)	P(4)−Rh(1)−C(5)	89.7(1)
P(4)−Rh(1)−C(8)	87.3(2)	C(5)−Rh(1)−C(8)	82.0(2)
Rh(1)−C(5)−C(6)	111.8(3)	C(5)−C(6)−C(7)	115.7(3)
C(6)−C(7)−C(8)	117.4(3)	Rh(1)−C(8)−C(7)	113.1(3)
Rh(1)−C(8)−C(9)	119.6(3)	C(7)−C(8)−C(9)	127.3(4)

exo-**6** (127.8°) infers that the most effective conjugation is between the endocyclic (C(6)−C(7)) and exocyclic (C(8)−C(9)) double bonds of **9**. In fact, the C(7)−C(8) distance is significantly shorter than the C(5)−C(6) distance, probably due to the conjugation. This is consistent with the lengthening of the exocyclic C(8)−C(9) double bond (1.362(6) Å) as compared with the corresponding exocyclic double-bond distances in the η^4-bound complexes *endo*-**6** (1.326(6) Å) and *exo*-**6** (1.321(5) Å). The sp^2-carbon−metal distance (C(8)−Rh(1) = 2.025(4) Å) is identical with the sp^3-carbon−metal distance (C(5)−Rh(1) = 2.024(4) Å), suggesting little contribution of metal to olefin π*-back-bonding.[18]

The most effective delocalization of the π-electrons of the endo- and exocyclic double bonds can be relevant to the observed preference for the planar structure with the vinylallene ligand. In the case of vinylallene **8**, the absence of substituents at the vinylic terminus renders possible *trans* coordination of two bulky PPh$_3$ molecules to rhodium. As a consequence, the 16-electron complex with a planar structure is formed without coordination of the C(6)−C(7) double bond. In the case of vinylallene **5**, the steric bulk of the trimethylsilyl group at the vinylic terminus hampers *trans* coordination of two PPh$_3$ molecules to rhodium. Instead, formation of the 16-electron complex as a stable species requires internal coordination of the C(6)−C(7) double bond, leading to the observed η^4-coordination.

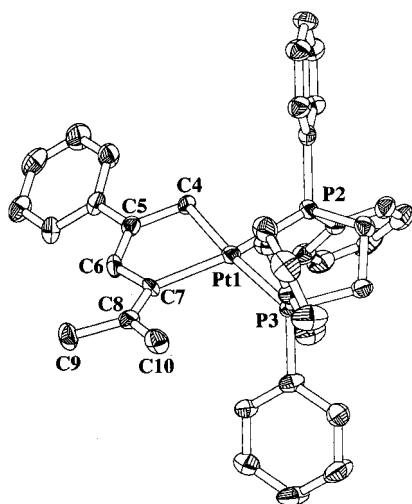(18) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.

Figure 4. Molecular structure of **10** with the hydrogen atoms and the solvated CH_2Cl_2 omitted for clarity (40% probability thermal ellipsoids).

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for Complex 10

Pt(1)−P(2)	2.288(2)	Pt(1)−P(3)	2.298(2)
Pt(1)−C(4)	2.099(8)	Pt(1)−C(7)	2.132(8)
C(4)−C(5)	1.50(1)	C(5)−C(6)	1.34(1)
C(6)−C(7)	1.45(1)	C(7)−C(8)	1.37(1)
P(2)−Pt(1)−P(3)	84.45(8)	P(2)−Pt(1)−C(4)	89.3(2)
P(2)−Pt(1)−C(7)	169.9(2)	P(3)−Pt(1)−C(4)	173.4(2)
P(3)−Pt(1)−C(7)	105.6(3)	C(4)−Pt(1)−C(7)	80.6(3)
Pt(1)−C(4)−C(5)	110.9(6)	C(4)−C(5)−C(6)	116.5(8)
C(4)−C(5)−C(11)	121.1(8)	C(6)−C(5)−C(11)	122.3(9)
C(5)−C(6)−C(7)	119.9(8)	Pt(1)−C(7)−C(6)	110.0(6)
Pt(1)−C(7)−C(8)	131.8(7)	C(6)−C(7)−C(8)	118.0(8)

An equimolar reaction of the vinylallene **8** with a platinum(0) complex was also examined using Pt(cod)$_2$ (cod = 1,5-cyclooctadiene). Facile replacement of the cod ligand with **8** occurred at room temperature to afford a Pt(vinylallene)(cod) complex. Sequential treatment with dppe (1,2-bis(diphenylphosphino)ethane) gave the Pt(vinylallene)(dppe) complex **10**, from which colorless crystals suitable for X-ray crystallography were obtained (eq 4). The crystal structure shown in Figure 4
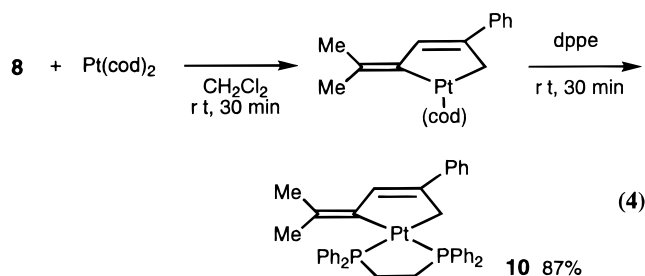
(bond distances and angles are given in Table 5) depicts planar σ^2-coordination of **8**, in which the platinum possesses a square-planar geometry. Similarly to the rhodium complex **9**, the C(4)−C(5) and C(6)−C(7) linkages (1.50(1) and 1.45(1) Å, respectively) are longer than C(5)−C(6) (1.34(1) Å), reflecting the bond order.

Stereochemical fluxionality of s-*cis*-diene−transition metal complexes has been often observed and can be explained by a ring-flipping mechanism.[17] Although implicated as a transitory species in the ring flipping, examples of thermodynamically stable planar σ^2-bonded

complexes remain rare[3−5] and are mostly limited to perfluoro-1,3-butadiene[4] and vinylketene complexes.[5] The planar vinylallene complexes **9** and **10** provide new examples, and their isolation lends direct evidence to the involvement of a planar metallacyclopentene complex in the ring flipping of a η^4-diene complex.

[4 + 1] Cycloaddition of Vinylallenes with Carbon Monoxide

Five-membered carbocycles are common structural features of a broad range of natural products. A variety of [3 + 2] cycloaddition reactions have been developed, providing a versatile synthetic tool for the preparation of these skeletons.[19] The Pauson−Khand reaction presents another viable synthetic protocol for [2 + 2 + 1] assemblies.[20] Although [4 + 1] cycloaddition is also a potential means to construct five-membered carbocycles,[21] there are only a few examples of [4 + 1] cycloaddition reactions catalyzed by transition metals.[22,23]

The structural fluxionality observed with the (η^4-vinylallene)rhodium complex **6** suggests a considerable contribution from the rhodacyclo-3-pentene form. Isolation of the stable planar σ^2-bonded complex **9** provides further inference of the significant metallacyclic character of (η^4-vinylallene)rhodium complexes. One important ramification of these findings is that incorporation of carbon monoxide into the conjugated diene skeleton may possibly result from migratory insertion of carbon monoxide into the C−Rh σ-bond of the rhodacyclo-3-pentene species, leading to a [4 + 1] assembly. Moreover, occurrence of η^4-coordination of a vinylallene to rhodium through direct ligand exchange is particularly attractive because it would offer access to a catalytic cycle.

On the basis of these considerations, we next investigated the [4 + 1] cycloaddition reaction of vinylallenes with carbon monoxide. First, stoichiometric carbonylation reactions were examined. When a solution of the (η^4-vinylallene)rhodium complex (*endo*-**6**) in CH_2Cl_2 was stirred at room temperature under atmospheric pressure of carbon monoxide, a [4 + 1] cycloaddition reaction proceeded cleanly to furnish 2-(alkylidene)cyclopent-3-en-1-one **11** in 98% isolated yield. A plausible mechanism for this [4 + 1] cycloaddition is shown in eq 5. Carbon monoxide is introduced into the coordination sphere of the metal to give a (vinylallene)carbonylrhodium species, which has a contribution from the rhodacyclo-3-pentene form in solution. Migratory insertion of the carbonyl group into the C−Rh σ-bond of the
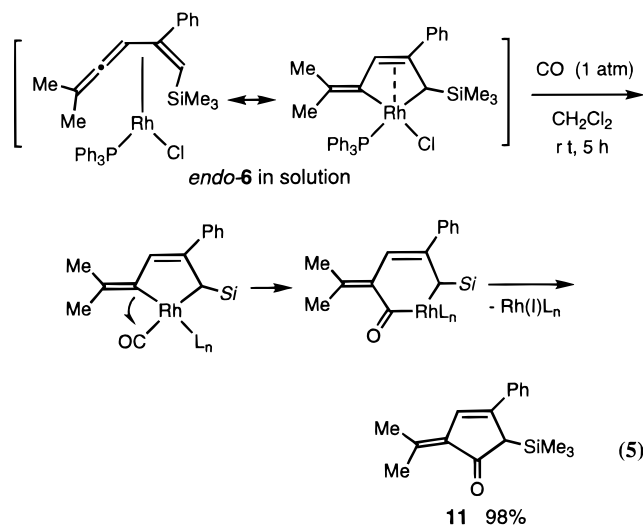
(19) (a) Little, R. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, Chapter 3.1. (b) Chan, D. M. T. In ref 19a, Chapter 3.2.

(20) Schore, N. E. In ref 19a, Chapter 9.1.

(21) (a) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025. (b) Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1991**, *113*, 2127. Nitrogen heterocycles: (c) Rigby, J. H.; Qabar, M. *J. Am. Chem. Soc.* **1991**, *113*, 8975. (d) Rigby, J. H.; Cavezza, A.; Ahmed, G. *J. Am. Chem. Soc.* **1996**, *118*, 12848.

(22) (a) Eaton, B. E.; Rollman, B.; Kaduk, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 6245. (b) Mandai, T.; Tsuji, J.; Tsujiguchi, Y.; Saito, S. *J. Am. Chem. Soc.* **1993**, *115*, 5865. (c) Sigman, M. S.; Eaton, B. E. *J. Am. Chem. Soc.* **1996**, *118*, 11783. (d) Darcel, C.; Bruneau, C.; Dixneuf, P. H. *Synlett* **1996**, 218.

(23) For transition metal-catalyzed [4 + 1] cycloaddition of hetero conjugated systems, such as allenyl ketones and allenyl imines, to give five-membered heterocycles, see: (a) Sigman, M. S.; Kerr, C. E.; Eaton, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 7545. (b) Sigman, M. S.; Eaton, B. E. *J. Org. Chem.* **1994**, *59*, 7488.

decreased back-bonding, than to a neutral complex. The cationic complex [Rh(cod)(MeCN)$_2$]BF$_4$ efficiently catalyzed the [4 + 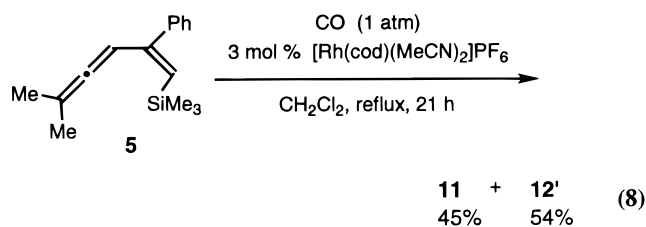1] cycloaddition of **5**. The corresponding 2-alkylidenecyclopent-3-en-1-one **11** was obtained together with 2-alkylidenecyclopent-4-en-1-one **12′** in an excellent combined yield (eq 8). It is likely that the


initial product **11** lost the trimethylsilyl group, located α to both the carbonyl group and the C−C double bond, through hydrolysis by water present in the reaction medium to form **12′**.

When alkyl-substituted vinylallene **13** was used instead of **5**, the corresponding [4 + 1] cycloadduct was obtained as a mixture of 2-alkylidenecyclopent-3-en-4-one **14** and isomerized 2-alkylidenecyclopent-4-en-1-one **14′** in only ca. 30% yield (Table 6, entry 1). In pursuit of a selective and high-yielding catalytic system of wide generality, we examined the effects of a variety of reaction conditions using **13** as a model substrate (Table 6). After much experimentation, it was found that the use of 1,2-bis(diphenylphosphino)benzene (dppbe) as the phosphorus ligand and TfO$^-$ as the counteranion in DME under 10 atm of CO gave the best result (83% conversion, **14**:**14′** = 92:8, entry 10).

Next, the standard set of reaction conditions using the isolated complex [Rh(cod)(dppbe)]OTf was applied to the [4 + 1] cycloaddition of various vinylallenes (Table 7). Carbon monoxide was catalytically incorporated into substituted vinylallenes in a [4 + 1] assembly mode. Bicyclic skeletons were constructed by the reactions of cyclic vinylallenes (entries 8−10).[24] The reactions of **21** and **23** proceeded at lower temperatures. In particular, 0.5 mol % of the catalyst efficiently catalyzed the reaction of **23** (entry 7). It is reasonable to presume that the catalytic cycle consists of binding of a vinylallene in an s-*cis* form to rhodium, then elementary steps analogous to those involved in eq 5, and subsequent rebinding of a new vinylallene molecule to rhodium(I).

Vinylallene **31,** in which the allenyl group is nonsymmetrical, gave only one stereoisomer about the geometry of the exocyclic C=C bond, the structure of which was confirmed by ^{1}H NMR NOE experiments (eq 9). This stereoselectivity can be accounted for by assuming face-selective η^4-coordination from the less hindered side of the vinylallene in an s-*cis* form and the subsequent specific disrotatory motion to a rhodacyclo-3-pentene intermediate. In the case of vinylallene **33**, formation of a small amount of *Z*-**34** was observed (eq 10). The ratio *Z*-**34**:*E*-**34** gradually increased as the reaction proceeded, suggesting that isomerization of the major isomer *E*-**34** to *Z*-**34** took place during the reaction course. In contrast, the vinylallene **3** with an unsubstituted allenyl group failed to undergo cycloaddition.

rhodacyclo-3-pentene form ensues. Although it is unclear which one of the sp^2 or sp^3 carbon atoms migrates, the result reported by Dixneuf et al.[22d] may favor migration of the sp^2 carbon atom. The subsequent reductive elimination of rhodium(I) produces **11**. The complexes *exo*-**6** and **9** also underwent similar carbonylative [4 + 1] cycloaddition on treatment with carbon monoxide (1 atm) in CH$_2$Cl$_2$ (eqs 6 and 7). In the case

of **9**, the conjugated cyclopentenone (**12′**) was produced as the cycloadduct, probably via transposition of C^3−C^4 unsaturation of the primary product (**12**) through rhodium-catalyzed double-bond isomerization. In contrast, the (η^2-vinylallene)rhodium complex **4** afforded no cycloaddition product under analogous conditions, indicating that η^4-coordination is needed for the carbonylative [4 + 1] cycloaddition.

On the basis of the auspicious results in the stoichiometric reactions, we next endeavored to establish a catalytic system of this [4 + 1] cycloaddition. Thus, free vinylallene **5** was treated with a catalytic quantity of RhCl(PPh$_3$)$_3$ under carbon monoxide (1 atm). Even when heated at 70 °C, however, **5** remained unreacted and only a trace amount of **11** was formed. This is possibly due to an irreversible reaction of the nascent catalytic species with carbon monoxide to exclude **5** from the coordination sphere. We next tried the use of a cationic complex with the expectation that carbon monoxide would bind less well to a cationic complex, owing to the

(24) A vinylallene that has a cyclopentenyl group instead of a cyclohexenyl group and is otherwise identical with **25** failed to undergo the [4 + 1] cycloaddition.

Table 6. Rhodium(I)-Catalyzed [4 + 1] Cycloaddition of Vinylallene 13 with CO
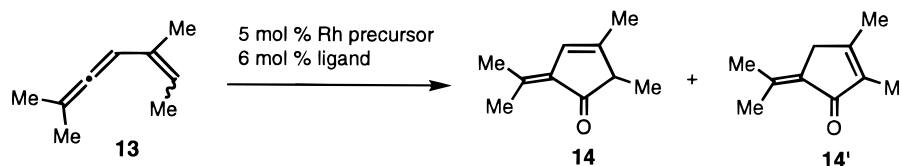
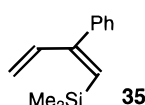| entry no.	Rh precursor	ligand[a]	CO press/atm	solvent	conditions	conversn/%	**14:14′**
1	[Rh(cod)(MeCN)$_2$]BF$_4$		1	toluene	70 °C, 12 h	99[b]	70:30
2	[Rh(cod)$_2$]PF$_6$	dppm	1	toluene	80 °C, 24 h	20	90:10
3	[Rh(cod)$_2$]PF$_6$	dppe	1	toluene	80 °C, 24 h	91	48:52
4	[Rh(cod)$_2$]PF$_6$	dppp	1	toluene	80 °C, 20 h	56	11:89
5	[Rh(cod)$_2$]PF$_6$	dppb	1	toluene	80 °C, 24 h	39	60:40
6	[Rh(cod)$_2$]PF$_6$	dppe	5	toluene	60 °C, 4 h	75	55:45
7	[Rh(cod)$_2$]PF$_6$	dppe	5	DME	60 °C, 4 h	50	90:10
8	[Rh(cod)$_2$]PF$_6$	dppbe	5	toluene	60 °C, 4 h	54	68:32
9	[Rh(cod)$_2$]PF$_6$	dppbe	10	DME	60 °C, 15 h	78	70:30
10	[Rh(cod)$_2$]OTf	dppbe	10	DME	60 °C, 12 h	83	92:8
11	[Rh(cod)$_2$]OTf	dppf	10	DME	60 °C, 12 h	97	38:62
12	[Rh(cod)$_2$]OTf	PMe$_2$Ph (12 mol %)	10	DME	60 °C, 12 h	97	38:62

[a] Abbreviations: dppm = bis(diphenylphosphino)methane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dppbe = 1,2-bis(diphenylphosphino)benzene, dppf = 1,1′-bis(diphenylphosphino)ferrocene. [b] A significant amount of side products was formed.


(9)

32:32′ = 96:4

(10)

7 h   65%   *E*-34:*Z*-34 = 95:5
24 h   80%   *E*-34:*Z*-34 = 92:8
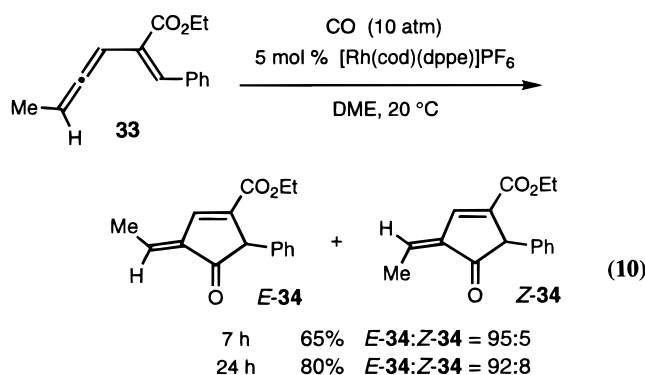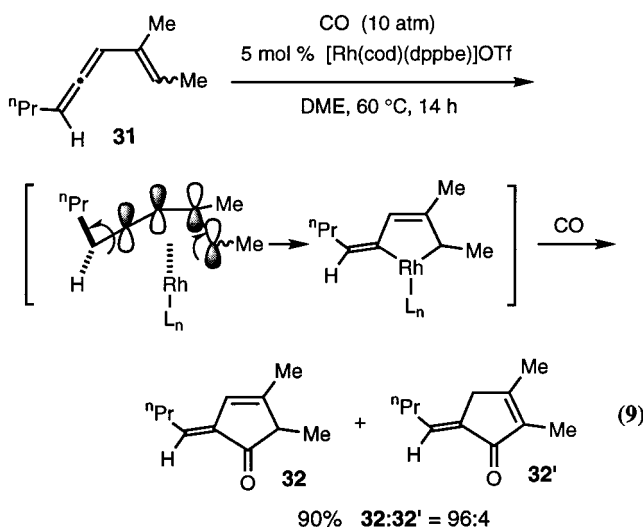
These results can be explained in terms of the preference for η^4- vs η^2-coordination (vide supra).

It is of interest to compare the reactivities of vinylallenes with those of ordinary conjugated dienes. In the case of 35, which is the butadiene analogue of vinyl-

allene 5, neither RhCl(PPh$_3$)$_3$ nor cationic Rh(I) complexes catalyzed a similar carbonylation reaction. All the attempted catalytic carbonylation reactions of other dienes, including 2,3-dimethyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene, and 1,4-diphenyl-1,3-butadiene, were unsuccessful. Next, 35 was treated with a stoichiometric amount of RhCl(PPh$_3$)$_3$ under conditions similar to those used for the synthesis of the (η^4-vinylallene)rhodium complex 6. However, no ligand displacement with 35 was observed by ^{1}H NMR. This finding suggests that the achievement of the [4 + 1] carbonylation mentioned above can be primarily attributed to the substantial facility of substituted vinylallenes for η^4-coordination through ligand displacement. The significant contribution from a metallacyclo-3-pentene resonance form is also relevant to the enhanced reactivity of the vinylallene system. This is probably also the case for the reported examples of [4 + 1] carbonylation of conjugated systems containing an allenyl group.[22,23]
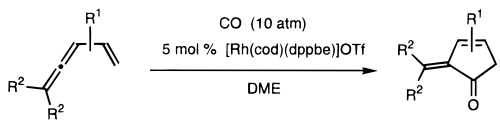
The use of transition metals other than rhodium was briefly examined. When [Ir(cod)(dppe)]PF$_6$ was used as the catalyst in the reaction of 13 at 60 °C in DME, only 4% of 14 was produced after 15 h. In contrast, a platinum(0) complex prepared from Pt(cod)$_2$ and dppbe efficiently catalyzed the [4 + 1] cycloaddition of vinylallenes (eqs 11 and 12).[25]

(11)

(12)
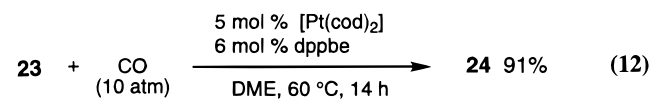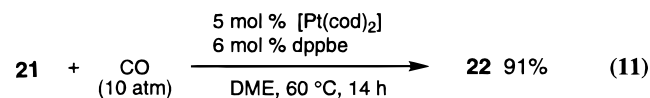
Conclusion

In conclusion, three (vinylallene)rhodium complexes with different coordination modes were directly synthesized by simple ligand displacement of RhCl(PPh$_3$)$_3$ with

(25) Although the reason is unclear, no reaction took place when Pt(dibenzylideneacetone)$_2$ was used instead of Pt(cod)$_2$.

Table 7. Rhodium-Catalyzed [4 + 1] Cycloaddition of Vinylallenes with CO

entry	vinylallene	conditions	product	isolated yield / %[a]	isomers ratio[b]
1	**13**	60 °C 15 h	**14**	85	91:9
2	**15**	60 °C 14 h	**16**	90	94:6
3	**17**	60 °C 15 h	**18**	80	88:12
4	**19**	60 °C 22 h	**20**	89	92:8
5	**21**	40 °C 16 h	**22**	93	>99:1
6	**23**	20 °C 16 h	**24**	94	>99:1
7	**23**	40 °C 41 h	**24**	90[c]	>99:1
8	**25**	60 °C 14 h	**26**	92	96:4
9	**27**	60 °C 14 h	**28**	85	93:7
10	**29**	60 °C 14 h	**30**	95	99:1

[a] Isolated yield of 2-alkylidenecyclopent-3-en-1-one. [b] The ratio of 2-alkylidenecyclopent-3-en-1-one and 2-alkylidenecyclopent-4-en-1-one was determined by ^{1}H NMR and GC analysis of the reaction mixture. [c] 0.5 mol % of [Rh(cod)(dppbe)]OTf was used.

vinylallenes, and their structures were determined. Vinylallene ligands demonstrated a preference for the planar structure, presumably maximizing delocalization of the π-electrons of the endo- and exocyclic double bonds. The spatial interactions between the substituents of the vinylallene and phosphine ligands dictate the coordination modes. Although this steric effect may be amplified in the present case, since RhCl(PPh$_3$)$_3$ has sterically demanding phosphine ligands, it is reasonable to suppose that a similar determinant operates generally in ligand substitution reactions with vinylallenes. The present study lends direct evidence to the ring flipping of a η^4 complex via a planar metallacyclopentene complex. The structural findings were rationally extended to the development of a new synthetic reaction. The catalytic carbonylative [4 + 1] cycloaddition of

vinylallenes demonstrated the potential reactivities of vinylallenes toward transition-metal catalysts by way of η^4-coordination.[26]

Experimental Section

General Considerations. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran was distilled under N$_2$ from sodium diphenylketyl. Toluene, 1,2-dimethoxyethane (DME), and CH$_2$Cl$_2$ were distilled from CaH$_2$. Pt(cod)$_2$ was prepared according to the literature procedure.[27]

NMR spectra were recorded on Varian VXR-200, Varian GEMINI-2000, and JEOL JNM-A400 spectrometers. Unless otherwise noted, ^{1}H, ^{31}P, and, ^{13}C NMR spectra were acquired in chloroform-d at 200, 80, and 50 MHz, respectively. Optical rotation was measured with a Perkin-Elmer 243 polarimeter. Mass spectra were recorded with a JEOL JMS-D300 spectrometer. Column chromatography was performed with Wakogel C-200 (Wako Pure Chemical Co.; 200 mesh). Preparative thin-layer chromatography was performed with silica gel 60 PF254 (E. Merck, Darmstadt, Germany).

Preparation of Vinylallenes. (*E*)-5-Methyl-2-phenyl-1-(trimethylsilyl)-1,3,4-hexatriene (5). To a mixture of PhCH$_2$-PdCl(PPh$_3$)$_2$ (155 mg, 0.21 mmol) and CuI (82 mg, 0.43 mmol) in DMF (20 mL) were successively added 3-bromo-3-methyl-1-butyne (6.0 g, 40.8 mmol) and 1-phenyl-1-(tributylstannyl)-2-(trimethylsilyl)ethene (9.5 g, 20.4 mmol). The reaction mixture was stirred at room temperature for 21 h. Et$_2$O (50 mL) and a saturated aqueous solution of potassium fluoride (20 mL) were added to the mixture, which was vigorously stirred for 2 h. The resulting precipitate of tributyltin fluoride was removed by filtration through Celite. The organic layer was separated, washed with brine, and dried over MgSO$_4$. The product was purified by column chromatography (silica gel, hexane) to afford **5** (2.93 g, 60%) as a pale yellow oil: ^{1}H NMR δ 0.23 (s, 9 H), 1.61 (t, J = 2.9 Hz, 6 H), 5.62 (d, J = 0.7 Hz, 1 H), 6.1−6.2 (m, 1 H), 7.2−7.4 (m, 5 H); ^{13}C{^{1}H} NMR δ 0.8, 20.5, 93.8, 97.9, 127.7, 128.0, 128.3, 131.1, 143.7, 152.7, 205.9. Anal. Calcd for C$_{16}$H$_{22}$Si: C, 79.27; H, 9.15. Found: C, 79.18; H, 9.15.

Vinylallenes (**3**, **21**, **23**, and **33**) were prepared by the palladium-catalyzed cross-coupling reactions of the corresponding (organostannyl)alkenes with propargylic bromides or chlorides according to a procedure analogous to that for **5**.

2,5-Dimethyl-2,3,5-heptatriene (13). A solution of 2-bromo-2-butene (3 mL, 29.5 mmol) in THF (8 mL) was added dropwise to a suspension of Mg (0.717 g, 29.5 mmol) in refluxing THF (20 mL). The reaction mixture was stirred for 1 h and then cooled to room temperature. Tetrakis(triphenylphosphine)-palladium(0) (1.00 g, 0.87 mmol) and 3-bromo-3-methyl-1-butyne (4.34 g, 29.5 mmol) were added successively. The reaction mixture was stirred for 1 h and poured into a saturated aqueous solution of NH$_4$Cl (50 mL). The aqueous phase was extracted with pentane. The combined extracts were washed with cold water and dried over MgSO$_4$. The pentane was carefully removed by distillation, and the product was purified by column chromatography (silica gel, hexane) to afford **13** (3.1 g, 86%) as an unstable colorless liquid: ^{1}H NMR δ 1.68 (br s, 3 H), 1.71 (br s, 3 H), 1.74 (d, J = 2.9 Hz, 6 H), 5.20−5.40 (m, 1 H), 6.00−6.10 (m, 1 H); ^{13}C{^{1}H} NMR δ 13.5, 21.0, 21.6, 90.4, 97.5, 121.9, 131.0, 204.5.

(26) [4 + 2] cycloaddition: (a) Siegel, H.; Hopf, H.; Germer, A.; Binger, P. *Chem. Ber.* **1978**, *111*, 3112. (b) Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7687. (c) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7163. (d) Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2248. [4 + 4] cycloaddition: (e) Murakami, M.; Itami, K.; Ito, Y. *Synlett*, in press. [4 + 4 + 1] cycloaddition: (f) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3418.

(27) Spencer, J. L. *Inorg. Synth.* **1979**, *12*, 213.

Vinylallenes (**8**,[28] **25**, and **31**) were prepared by the palladium-catalyzed cross-coupling reactions of the corresponding vinylic Grignard reagents with propargylic bromides or chlorides according to a procedure analogous to that for **13**.

1-(5,6-Benzo-1-cyclohexenyl)-3-methyl-1,2-butadiene (27). To a solution of tetrakis(triphenylphosphine)palladium-(0) (239 mg, 0.207 mmol) in THF (20 mL) were successively added (5,6-benzo-1-cyclohexenyl)boronic acid (1.20 g, 6.89 mmol), 1,1-dimethyl-2-propynyl methyl carbonate (1.47 g, 10.3 mmol), $K_3PO_4 \cdot H_2O$ (439 mg, 2.07 mmol), and THF (30 mL). The mixture was stirred at reflux for 3 h. The cooled reaction mixture was passed through a short column of Florisil and eluted with hexane. The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane) to afford **27** (815 mg, 60%) as a yellow oil: ^1H NMR δ 1.91 (d, $J = 3.1$ Hz, 6 H), 2.34–2.48 (m, 2 H), 2.86 (t, $J = 7.8$ Hz, 2 H), 6.00–6.10 (m, 1 H), 6.17 (t, $J = 4.8$ Hz, 1 H), 7.20–7.40 (m, 3 H), 7.60–7.70 (m, 1 H); $^{13}C\{^1H\}$ NMR δ 20.6, 23.5, 28.4, 90.4, 96.9, 123.9, 126.1, 126.8, 127.3, 127.5, 132.3, 134.0, 137.0, 203.3.

Vinylallenes (**15**, **17**, **19**, and **29**) were prepared by the palladium-catalyzed cross-coupling reactions of the corresponding vinylboronic acids or esters with 1,1-dimethyl-2-propynyl methyl carbonate according to a procedure analogous to that for **27**.[29]

Synthesis of Complex 4. To a solution of (*E*)-4-phenyl-5-(trimethylsilyl)-1,2,4-pentatriene (**3**; 25 mg, 0.12 mmol) in benzene (3 mL) at room temperature was added RhCl(PPh₃)₃ (129 mg, 0.139 mmol). After the mixture was stirred for 13 h, the solvent was removed under vacuum. The residue was subjected to column chromatography (silica gel, CH_2Cl_2:hexane = 3:1) to afford **4** (80 mg, 78%) as a yellow powder: ^1H NMR δ 0.07 (s, 9 H), 5.03 (s, 1 H), 6.07 (d, $J = 7.0$ Hz, 2 H), 6.67–6.82 (m, 2 H), 6.92 (t, $J = 7.0$ Hz, 1 H), 7.3–7.8 (m, 33 H); $^{31}P\{^1H\}$ NMR δ 35.1 (d, $J_{Rh-P} = 127.5$ Hz); $^{13}C\{^1H\}$ NMR δ 0.39, 113.8 (d, $J_{Rh-C} = 2.7$ Hz), 125.9, 126.0, 127.9, 128.0, 128.1, 128.3, 128.5, 128.7, 129.9, 131.2, 131.6, 132.0, 132.3, 135.0, 135.1, 135.2, 143.2, 153.4 (d, $J_{Rh-C} = 3.0$ Hz).

Crystallographic Analysis of 4. Crystal data: $C_{50}H_{48}ClP_2$-RhSi, $M_r = 877.3$, monoclinic, space group $P2_1/a$, $a = 23.49(1)$ Å, $b = 10.677(4)$ Å, $c = 19.31(1)$ Å, $\beta = 112.55(4)°$, $U = 4472-(4)$ Å³, $Z = 4$, $D_c = 1.30$ g/cm³, $\mu = 49.04$ cm⁻¹. Intensity data were measured on a Mac Science MXC³ diffractometer using the $\omega-2\theta$ scan technique with graphite-monochromated Cu Kα radiation ($\lambda = 1.541\ 78$ Å). A total of 7137 unique reflections within $3 \leq 2\theta \leq 125°$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares procedure to $R = 0.054$ ($R_w = 0.059$) for 3981 reflections ($I > 2.5\sigma(I)$), using the Crystan GM package program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms on C(6), C(8), and C(10) were found on a difference Fourier map and refined isotropically. All other hydrogen atoms were included in the refinement at calculated distances (0.96 Å) with a general isotropic temperature factor.

Synthesis of Complexes endo-6 and exo-6. To a solution of (*E*)-5-methyl-2-phenyl-1-(trimethylsilyl)-1,3,4-hexatriene (**5**; 40 mg, 0.165 mmol) in benzene (4 mL) at room temperature was added RhCl(PPh₃)₃ (153 mg, 0.165 mmol). After the mixture was stirred for 20 h, the solvent was removed under vacuum. The residue was subjected to preparative thin-layer chromatography (silica gel, CH_2Cl_2:hexane = 3:1) to afford *endo*-**6** (47 mg, 44%, orange powder) and *exo*-**6** (20 mg, 19%, yellow powder). *endo*-**6**: ^1H NMR (400 MHz) δ 0.11 (s, 9 H), 1.49 (s, 3 H), 1.59 (s, 3 H), 3.48 (s, 1 H), 4.11 (d, $J_{Rh-H} = 3.0$ Hz, 1 H), 6.8–7.7 (m, 20 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 29.6 (d, $J_{Rh-P} = 167.6$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz) δ 1.63, 21.51, 25.35, 59.07 (d, $J_{Rh-C} = 3.8$ Hz), 116.76, 128.01, 128.11, 128.32,

128.40, 128.52, 128.56, 129.02, 130.01, 130.04, 131.88, 131.91, 132.01, 132.11, 134.15, 134.26, 141.15, 149.14 (d, $J_{P-C} = 28.9$ Hz). *exo*-**6**: ^1H NMR δ −0.05 (s, 9 H), 1.47 (s, 3 H), 1.51 (s, 3 H), 2.26 (d, $J_{Rh-H} = 5.4$ Hz, 1 H), 2.81 (s, 1 H), 7.0–7.6 (m, 20 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 33.8 (d, $J_{Rh-P} = 180.4$ Hz); $^{13}C\{^1H\}$ NMR δ 0.3, 20.0, 24.1, 59.4 (d, $J_{Rh-C} = 5.2$ Hz), 116.7 (d, $J_{Rh-C} = 2.5$ Hz), 127.8, 127.9, 128.1, 128.4, 129.1, 130.0 (d, $J_{Rh-C} = 2.4$ Hz), 132.3, 133.1, 133.7, 133.8, 134.1, 134.3, 140.0, 145.4 (dd, $J_{Rh-C} = 6.4$ Hz, $J_{P-C} = 22.1$ Hz).

Crystallographic Analysis of endo-6. Crystal data: $C_{34}H_{37}$-ClPRhSi, $M_r = 643.1$, monoclinic, space group $C2/c$, $a = 44.189$ Å, $b = 8.242$ Å, $c = 17.782$ Å, $\beta = 105.456°$, $U = 6242$ Å³, $Z = 8$, $D_c = 1.37$ g/cm³, $\mu = 7.33$ cm⁻¹. Intensity data were collected on a Mac Science DIP2000 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 70$ Å), using an imaging plate area detector with an oscillation mode. From a total of 21 987 observations, 5427 unique reflections were processed by a MAC-DENZO program. The structure was solved by a direct method and refined by the full-matrix least-squares procedure to $R = 0.040$ ($R_w = 0.042$) for 4217 reflections ($I > 2.0\sigma(I)$), using a Crystan GM package program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms on C(5) and C(7) were found on a difference Fourier map and refined isotropically. All other hydrogen atoms were included in the refinement at calculated positions (0.96 Å) with a general isotropic temperature factor.

Crystallographic Analysis of exo-6. Crystal data: $C_{35}H_{39}$-Cl₃PRhSi (*exo*-**6** + CH_2Cl_2), $M_r = 728.0$, triclinic, space group $P\bar{1}$, $a = 9.809(2)$ Å, $b = 13.398(3)$ Å, $c = 14.489(3)$ Å, $\alpha = 88.75-(2)°$, $\beta = 78.18(2)°$, $\gamma = 74.50(2)°$, $U = 1795.0(6)$ Å³, $Z = 2$, $D_c = 1.19$ g/cm³, $\mu = 69.59$ cm⁻¹. Intensity data were measured on a Mac Science MXC³ diffractometer using the $\omega-2\theta$ scan technique with graphite-monochromated Cu Kα radiation ($\lambda = 1.541\ 78$ Å). A total of 5993 unique reflections within $3 \leq 2\theta \leq 130°$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares procedure to $R = 0.062$ ($R_w = 0.068$) for 5348 reflections ($I > 3.0\sigma(I)$), using the Crystan GM package program. The crystal contains one molecule of *exo*-**6** and one molecule of CH_2Cl_2 in an asymmetric unit. The non-hydrogen atoms, except those of CH_2Cl_2, were refined anisotropically. Hydrogen atoms on C(5) and C(7) were found on a difference Fourier map and refined isotropically. All other hydrogen atoms were included in the refinement at calculated distances (0.96 Å) with isotropic temperature factors.

Synthesis of Complex 9. To a solution of 5-methyl-2-phenyl-1,3,4-hexatriene (**8**; 430 mg, 2.53 mmol) in benzene (20 mL) at room temperature was added RhCl(PPh₃)₃ (2.00 g, 2.16 mmol). After the mixture was stirred for 24 h, the solvent was removed under vacuum. Addition of ether to the residue afforded **9** (1.65 g, 92%) as an orange powder. As frequently observed with five-coordinate complexes,[30] **9** became stereochemically nonrigid in solution to present complicated NMR spectra. The data for the predominant isomer, which are consistent with the planar crystal structure, are given below: ^1H NMR (C_6D_6, 400 MHz) δ 1.41 (s, 3 H), 1.66 (s, 3 H), 4.25–4.33 (br, 2 H), 5.35 (s, 1 H), 6.80–8.10 (m, 35 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz) δ 19.6, 25.7, 31.1 (d, $J_{Rh-C} = 32.8$ Hz), 120–145 (m); $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 26.5 (d, $J_{Rh-P} = 126.2$ Hz). Anal. Calcd for $C_{49}H_{44}ClP_2Rh$: C, 70.64; H, 5.32. Found: C, 70.91; H, 5.48.

Crystallographic Analysis of 9. Crystal data: $C_{50}H_{48}$-ClOP₂Rh (**9** + MeOH), $M_r = 865.2$, orthorhombic, space group $P2_12_12_1$, $a = 19.33(1)$ Å, $b = 21.74(1)$ Å, $c = 10.13(1)$ Å, $U = 4259.9(4)$ Å³, $Z = 4$, $D_c = 1.349$ g/cm³, $\mu = 48.90$ cm⁻¹. Intensity data were measured on a Mac Science MXC³ diffractometer using the $\omega-2\theta$ scan technique with graphite-monochromated Cu Kα radiation ($\lambda = 1.541\ 78$ Å). A total of 3918 unique

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reflections within $3 \leq 2\theta \leq 130°$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares procedure to $R = 0.063$ ($R_w = 0.067$) for 3616 reflections ($I > 3.0\sigma(I)$), using the Crystan GM package program. The crystal contains one molecule of **9** and one molecule of MeOH in an asymmetric unit. The non-hydrogen atoms, except those of MeOH, were refined anisotropically. Hydrogen atoms were included in the refinement at calculated distances (0.96 Å) with isotropic temperature factors calculated from those of the bonded atoms.

Synthesis of Complex 10. To a solution of Pt(cod)$_2$ (200 mg, 486 μmol) in CH$_2$Cl$_2$ (15 mL) at room temperature was added 5-methyl-2-phenyl-1,3,4-hexatriene (**8**; 91 mg, 535 μmol). After the mixture was stirred for 30 min, dppe (194 mg, 486 μmol) was added. The mixture was stirred for an additional 30 min, and then the solvent was removed under vacuum. The residue was dissolved in a small quantity of CH$_2$Cl$_2$, and the resulting solution was added to a stirred solution of hexane to afford the title complex **10** (357 mg, 87%, beige powder) as a CH$_2$Cl$_2$ solvate. The solvating CH$_2$Cl$_2$ was gradually lost under vacuum: ^{1}H NMR δ 1.59 (s and satellite, $J_{Pt-H} = 10.3$ Hz, 3 H), 1.90–2.40 (m, 4 H), 2.00 (s and satellite, $J_{Pt-H} = 9.5$ Hz, 3 H), 2.84 (dd, $J_{P-H} = 9.3, 8.3$ Hz and satellite, $J_{Pt-H} = 74.5$ Hz, 2 H), 6.97–7.58 (m, 18 H), 7.62–7.76 (m, 4 H), 7.92–8.10 (m, 4 H); ^{31}P{^{1}H} NMR (121 MHz) δ 45.3 (d, $J_{P-P} = 3$ Hz and satellite, $J_{Pt-P} = 1818$ Hz), 50.4 (d, $J_{P-P} = 3$ Hz and satellite, $J_{Pt-P} = 1842$ Hz); selected ^{13}C{^{1}H} NMR resonances (75 MHz) δ 20.1 (d, $J_{P-C} = 8$ Hz and satellite, $J_{Pt-C} = 50$ Hz), 28.1 (m), 31.5 (dd, $J_{P-C} = 89, 5$ Hz and satellite, $J_{Pt-C} = 603$ Hz), 33.6 (m), 34.8 (dd, $J_{P-C} = 7, 5$ Hz and satellite, $J_{Pt-C} = 52$ Hz), 159.0 (dd, $J_{P-C} = 113, 6$ Hz and satellite, $J_{Pt-C} = 926$ Hz); HRMS m/e calcd for C$_{39}$H$_{38}$P$_2$Pt 763.2096, found 763.2099. Anal. Calcd (partially solvated formula C$_{39}$H$_{38}$P$_2$Pt·0.8CH$_2$Cl$_2$): C, 57.47; H, 4.80. Found: C, 57.76; H, 4.90.

Crystallographic Analysis of 10. Crystal data: C$_{40}$H$_{40}$Cl$_2$P$_2$Pt (**10** + CH$_2$Cl$_2$), M_r = 848.7, monoclinic, space group $P2_1/c$, a = 12.2706(9) Å, b = 13.9824(7) Å, c = 21.241(2) Å, β = 104.920(3)°, U = 3521.5 Å^3, Z = 4, D_c = 1.601 g/cm^3, μ = 42.39 cm^{-1}. Intensity data were collected on a Rigaku RAXIS-IV diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å), using an imaging plate area detector with an oscillation mode. A total of 7395 unique reflections were collected. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares procedure to R = 0.061 (R_w = 0.079) for 5504 reflections ($I > 3.0\sigma(I)$), using the teXsan package program. The crystal contains one molecule of **10** and one molecule of CH$_2$Cl$_2$ in an asymmetric unit. The non-hydrogen atoms, except those of CH$_2$Cl$_2$, were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions (0.95 Å) with isotropic temperature factors.

Reaction of Complex 9 with Carbon Monoxide. A solution of **9** (105 mg, 126 μmol) in CH$_2$Cl$_2$ (3 mL) under an atmosphere of carbon monoxide (1 atm) was stirred at room temperature for 18 h. The solvent was removed under vacuum. The residue was subjected to preparative thin-layer chromatography (ether:hexane = 1:7) to afford **12′** (24 mg, 96%) as a white powder: ^{1}H NMR δ 2.06 (s, 3 H), 2.32 (s, 3 H), 3.30 (d, J = 1.7 Hz, 2 H), 7.20–7.50 (m, 6 H); ^{13}C{^{1}H} NMR δ 20.5, 23.8, 44.0, 125.2, 126.7, 128.2, 128.7, 134.8, 135.2, 137.1, 144.0, 204.6; HRMS m/e calcd for C$_{14}$H$_{14}$O 198.1045, found 198.1049.

The reactions of complexes *endo*-**6** and *exo*-**6** with carbon monoxide, affording **11**, were carried out according to the preceding procedure for complex **9**. **11**: ^{1}H NMR δ −0.06 (s, 9 H), 2.03 (s, 3 H), 2.28 (s, 3 H), 3.44 (s, 1 H), 6.91 (s, 1 H), 7.25–7.60 (m, 5 H); ^{13}C{^{1}H} NMR δ −2.0, 20.5, 23.9, 51.7, 123.1, 126.0, 127.8, 128.4, 136.0, 136.5, 141.0, 143.0, 206.0; MS m/e 270 (M$^+$). Anal. Calcd for C$_{17}$H$_{22}$OSi: C, 75.50; H, 8.20. Found: C, 75.38; H, 8.20.

Preparation of [Rh(dppbe)(cod)]OTf. To a solution of [Rh(cod)$_2$]OTf (144 mg, 0.307 mmol) in CH$_2$Cl$_2$ (5 mL) at room temperature was added dropwise a solution of dppbe (146 mg, 0.326 mmol) in CH$_2$Cl$_2$ (4 mL). The reaction mixture was stirred for 30 min and then concentrated to ca. 1 mL under vacuum. Et$_2$O (15 mL) was added, and the resulting precipitates were washed with Et$_2$O to afford [Rh(dppbe)(cod)]OTf (239 mg, 97%) as orange solids: ^{1}H NMR δ 2.24–2.60 (m, 8 H), 5.08 (br s, 4 H), 7.40–7.70 (m, 24 H); ^{31}P{^{1}H} NMR (121 MHz) δ 58.2 (d, J_{Rh-P} = 149 Hz).

Synthesis of 4,5-Dimethyl-2-isopropylidene-3-cyclopentenone (14) by the Rhodium-Catalyzed [4 + 1] Cycloaddition. A mixture of [Rh(cod)(dppbe)]OTf (16.5 mg, 20.5 μmol) and **13** (50.0 mg, 409 μmol) in DME (2 mL) under 10 atm of CO in an autoclave was stirred in an oil bath at 60 °C for 15 h. After the mixture was cooled, the solvent was removed under vacuum. The residue was subjected to preparative thin-layer chromatography (silica gel, ether:hexane = 1:7) to afford **14** (52.2 mg, 85%): ^{1}H NMR δ 1.14 (d, J = 7.6 Hz, 3 H), 1.87 (s, 3 H), 1.90 (s, 3 H), 2.21 (s, 3 H), 2.67 (q, J = 7.6 Hz, 1 H), 6.41 (s, 1 H); ^{13}C{^{1}H} NMR δ 13.8, 15.9, 20.0, 23.4, 50.4, 126.4, 133.1, 140.2, 142.4, 208.9; HRMS m/e calcd for C$_{10}$H$_{14}$O 150.1045, found 150.1053.

2,3-Dimethyl-5-isopropylidene-2-cyclopentenone (14′): ^{1}H NMR δ 1.71 (s, 3 H), 1.85 (s, 3 H), 2.02 (s, 3 H), 2.29 (s, 3 H), 2.96 (s, 2 H); ^{13}C{^{1}H} NMR δ 8.2, 16.3, 19.6, 23.9, 37.4, 128.9, 139.3, 143.8, 159.1, 197.1; MS m/e 150 (M$^+$). Anal. Calcd for C$_{10}$H$_{14}$O: C, 79.96; H, 9.39. Found: C, 80.12; H, 9.11.

The rhodium-catalyzed [4 + 1] cycloaddition reactions for the synthesis of the following compounds were carried out according to the preceding procedure for **14** under conditions specified in Table 7. Compound numbers with a prime designate 2-alkylidene-4-cyclopentenone forms.

4,5-Dipropyl-2-isopropylidene-3-cyclopentenone (16): ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.05–1.40 (m, 2 H), 1.40–1.65 (m, 3 H), 1.70–1.90 (m, 1 H), 1.91 (s, 3 H), 2.10–2.25 (m, 2 H), 2.22 (s, 3 H), 2.76 (t, J = 4.4 Hz, 1 H), 6.46 (d, J = 1.4 Hz, 1 H); ^{13}C{^{1}H} NMR δ 15.3, 15.6, 19.9, 21.2, 21.6, 24.6, 32.0, 33.5, 55.1, 127.4, 134.8, 141.1, 146.3, 210.2; HRMS m/e calcd for C$_{14}$H$_{22}$O 206.1670, found 206.1655.

2,3-Dipropyl-5-isopropylidene-2-cyclopentenone (16′): ^{1}H NMR δ 0.90 (t, J = 7.4 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.20–1.70 (m, 4 H), 1.87 (s, 3 H), 2.20 (t, J = 7.7 Hz, 2 H), 2.31 (s, 3 H), 2.40 (t, J = 7.6 Hz, 2 H), 2.99 (s, 2 H); ^{13}C{^{1}H} NMR δ 14.5, 19.9, 21.4, 22.2, 24.2, 25.7, 30.0, 32.6, 35.1, 129.3, 143.8, 144.2, 163.5, 197.5; HRMS m/e calcd for C$_{14}$H$_{22}$O 206.1670, found 206.1668.

4,5-Dibutyl-2-isopropylidene-3-cyclopentenone (18). ^{1}H NMR δ 0.85 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 6.7 Hz, 3 H), 1.00–1.85 (m, 10 H), 1.91 (s, 3 H), 2.10–2.30 (m, 2 H), 2.22 (s, 3 H), 2.77 (t, J = 4.4 Hz, 1 H), 6.46 (d, J = 1.5 Hz, 1 H); ^{13}C{^{1}H} NMR δ 14.15, 14.21, 20.2, 22.8, 23.3, 23.6, 27.6, 28.4, 29.5, 30.1, 54.1, 126.3, 133.9, 140.1, 145.5, 209.2; HRMS m/e calcd for C$_{16}$H$_{26}$O 234.1982, found 234.1981.

2,3-Dibutyl-5-isopropylidene-2-cyclopentenone (18′): ^{1}H NMR δ 0.85–1.00 (m, 6 H), 1.20–1.60 (m, 8 H), 1.87 (s, 3 H), 2.15–2.30 (m, 2 H), 2.31 (s, 3 H), 2.35–2.48 (m, 2 H), 2.98 (s, 2 H); HRMS m/e calcd for C$_{16}$H$_{26}$O 234.1982, found 234.1980.

4,5-Diethyl-2-(1-ethylpropylidene)-3-cyclopentenone (20): ^{1}H NMR δ 0.72 (t, J = 7.5 Hz, 3 H), 1.02 (t, J = 7.5 Hz, 3 H), 1.07 (t, J = 7.6 Hz, 3 H), 1.13 (t, J = 7.4 Hz, 3 H), 1.54–1.73 (m, 1 H), 1.78–1.96 (m, 1 H), 2.10–2.40 (m, 4 H), 2.55–2.83 (m, 3 H), 6.48 (d, J = 1.6 Hz, 1 H); ^{13}C{^{1}H} NMR δ 9.5, 11.6, 12.9, 13.3, 21.5, 23.3, 24.1, 27.8, 55.0, 125.5, 132.8, 146.8, 151.8, 209.1; HRMS m/e calcd for C$_{14}$H$_{22}$O 206.1670, found 206.1667.

2,3-Diethyl-5-(1-ethylpropylidene)-2-cyclopentenone (20′): ^{1}H NMR δ 1.00 (t, J = 7.6 Hz, 3 H), 1.07 (t, J = 7.5 Hz, 3 H), 1.08 (t, J = 7.6 Hz, 3 H), 1.14 (t, J = 7.7 Hz, 3 H), 2.19

(q, $J = 7.6$ Hz, 2 H), 2.23 (q, $J = 7.5$ Hz, 2 H), 2.44 (q, $J = 7.7$ Hz, 2 H), 2.81 (q, $J = 7.6$ Hz, 2 H), 3.00 (s, 2 H); $^{13}C\{^1H\}$ NMR δ 12.3, 12.6, 13.2, 13.6, 16.7, 23.3, 23.5, 28.3, 33.9, 128.0, 144.5, 155.5, 164.3, 197.0.

4,5-Diphenyl-2-isopropylidene-3-cyclopentenone (22): ^1H NMR δ 2.12 (s, 3 H), 2.28 (s, 3 H), 4.46 (d, $J = 1.3$ Hz, 1 H), 7.20−7.40 (m, 8 H), 7.40−7.50 (m, 2 H), 7.51 (d, $J = 1.3$ Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 21.2, 24.5, 60.0, 126.6, 127.6, 128.4, 128.5, 128.9, 129.1, 129.3, 133.5, 134.9, 137.6, 140.1, 146.3, 203.8; HRMS m/e calcd for $C_{20}H_{18}O$ 274.1357, found 274.1363.

4-(Ethoxycarbonyl)-2-isopropylidene-5-phenyl-3-cyclopentenone (24): ^1H NMR δ 1.16 (d, $J = 7.1$ Hz, 3 H), 2.15 (s, 3 H), 2.32 (s, 3 H), 4.06−4.22 (m, 2 H), 4.28 (d, $J = 1.6$ Hz, 1 H), 7.10−7.20 (m, 2 H), 7.20−7.40 (m, 3 H), 7.90 (d, $J = 1.6$ Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 14.3, 21.3, 24.6, 58.4, 60.7, 127.3, 127.8, 128.8, 132.7, 132.8, 137.2, 141.5, 154.8, 164.6, 202.5; HRMS m/e calcd for $C_{17}H_{18}O_3$ 270.1255, found 270.1252.

8-Isopropylidenebicyclo[4.3.0]non-1(9)-en-7-one (26): ^1H NMR δ 0.80−1.50 (m, 4 H), 1.80−2.40 (m, 3 H), 1.92 (s, 3 H), 2.22 (s, 3 H), 2.45−2.70 (m, 2 H), 6.36 (s, 1 H); $^{13}C\{^1H\}$ NMR δ 20.0, 23.5, 25.3, 27.3, 28.9, 29.8, 52.8, 122.6, 133.4, 140.6, 145.0, 208.3; MS m/e 176 (M$^+$). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.92; H, 9.38.

8-Isopropylidenebicyclo[4.3.0]non-1(6)-en-7-one (26′): ^1H NMR δ 1.60−1.80 (m, 4 H), 1.84 (s, 3 H), 2.10−2.25 (m, 2 H), 2.25−2.50 (m, 2 H), 2.29 (s, 3 H), 2.95 (s, 2 H); $^{13}C\{^1H\}$ NMR δ 19.5, 20.2, 21.8, 22.3, 23.9, 27.6, 35.9, 129.3, 141.9, 143.8, 162.8, 196.5. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.85; H, 9.36.

2,3-Benzo-8-isopropylidenebicyclo[4.3.0]non-1(9)-en-7-one (28): ^1H NMR δ 1.45−1.70 (m, 1 H), 2.05 (s, 3 H), 2.31 (s, 3 H), 2.40−2.53 (m, 1 H), 2.90−3.14 (m, 3 H), 7.00 (t, $J = 2.3$ Hz, 1 H), 7.12−7.28 (m, 3 H), 7.60−7.70 (m, 1 H); $^{13}C\{^1H\}$ NMR δ 20.5, 23.8, 24.3, 30.0, 51.5, 122.1, 123.9, 126.4, 128.1, 129.4, 131.4, 134.6, 137.2, 139.0, 143.2, 206.9; HRMS m/e calcd for $C_{16}H_{16}O$ 224.1201, found 224.1199.

4,5-Benzo-8-isopropylidenebicyclo[4.3.0]non-1(6)-en-7-one (28′): ^1H NMR δ 1.97 (s, 3 H), 2.38 (s, 2 H), 2.47−2.62 (m, 2 H), 2.93 (t, $J = 8.2$ Hz, 2 H), 3.38 (s, 2 H), 7.20−7.45 (m, 4 H); $^{13}C\{^1H\}$ NMR δ 18.4, 20.0, 24.3, 28.1, 31.0, 124.2, 126.9, 128.4, 130.0, 130.3, 131.9, 138.7, 141.5, 145.6, 156.1, 195.5; HRMS m/e calcd for $C_{16}H_{16}O$ 224.1201, found 224.1184.

9-Isopropylidenebicyclo[5.3.0]dec-1(10)-en-9-one (30): ^1H NMR δ 1.40−1.55 (m, 3 H), 1.55−1.85 (m, 4 H), 1.91 (s, 3 H), 1.90−2.20 (m, 1 H), 2.21 (s, 3 H), 2.45−2.60 (m, 2 H), 2.75−2.90 (m, 1 H), 6.40−6.50 (m, 1 H); $^{13}C\{^1H\}$ NMR δ 20.1, 23.4, 28.0, 28.6, 30.2, 30.9, 31.7, 56.3, 126.0, 133.7, 139.8, 147.4, 208.5; HRMS m/e calcd for $C_{13}H_{18}O$ 190.1358, found 190.1366.

9-Isopropylidenebicyclo[5.3.0]dec-1(7)-en-9-one (30′): ^1H NMR δ 1.45−1.70 (m, 4 H), 1.70−1.90 (m, 2 H), 1.86 (s, 3 H), 2.25−2.40 (m, 2 H), 2.30 (s, 3 H), 2.40−2.55 (m, 2 H), 3.00 (s, 2 H); $^{13}C\{^1H\}$ NMR δ 19.7, 23.9, 24.1, 26.8, 27.0, 31.5, 33.1, 37.6, 129.5, 144.2, 145.4, 166.1, 196.4; HRMS m/e calcd for $C_{13}H_{18}O$ 190.1358, found 190.1338.

(E)-2-Butylidene-4,5-dimethyl-3-cyclopentenone (32): ^1H NMR δ 0.93 (t, $J = 7.3$ Hz, 3 H), 1.18 (d, $J = 7.6$ Hz, 3 H), 1.40−1.58 (m, 2 H), 1.93 (s, 3 H), 2.21 (q, $J = 7.9$ Hz, 2 H), 2.74 (q, $J = 7.6$ Hz, 1 H), 6.11 (t, $J = 7.9$ Hz, 1 H), 6.45 (s, 1 H); $^{13}C\{^1H\}$ NMR δ 13.6, 13.9, 16.2, 22.3, 31.2, 49.4, 124.7, 129.1, 138.3, 146.8, 208.0. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.17; H, 10.02.

(E)-2-Butylidene-4,5-dimethyl-4-cyclopentenone (32′): ^1H NMR δ 0.92 (t, $J = 7.3$ Hz, 3 H), 1.49 (sextet, $J = 7.3$ Hz, 2 H), 1.75 (s, 3 H), 2.06 (s, 3 H), 2.10−2.21 (m, 2 H), 2.99 (s, 2 H), 6.52 (t, $J = 7.6$ Hz, 1 H); $^{13}C\{^1H\}$ NMR δ 8.3, 13.9, 16.7, 21.9, 31.6, 35.2, 133.2, 134.9, 138.3, 162.3, 196.5. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 10.03.

(E)-4-(Ethoxycarbonyl)-2-ethylidene-5-phenyl-3-cyclopentenone (E-34): ^1H NMR (300 MHz) δ 1.16 (t, $J = 7.2$ Hz, 3 H), 2.08 (d, $J = 7.5$ Hz, 3 H), 4.06−4.22 (m, 2 H), 4.34 (d, $J = 1.5$ Hz, 1 H), 6.71 (q, $J = 7.5$ Hz, 1 H), 7.10−7.40 (m, 5 H), 7.89 (s, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz) δ 13.9, 15.6, 57.3, 60.7, 127.3, 127.7, 128.7, 136.2, 136.6, 136.8, 138.4, 164.1, 201.2; HRMS m/e calcd for $C_{16}H_{16}O_3$ 256.1098, found 256.1099.

Synthesis of 24 by the Platinum-Catalyzed [4 + 1] Cycloaddition. A mixture of Pt(cod)$_2$ (3.4 mg, 8.3 μmol), dppbe (4.4 mg, 9.9 μmol), and **23** (40.0 mg, 165 μmol) in DME (2 mL) under 10 atm of CO in an autoclave was stirred in an oil bath at 60 °C for 14 h. After the mixture was cooled, the solvent was removed under vacuum. The residue was subjected to preparative thin-layer chromatography (silica gel, ether: hexane = 1:3) to afford **24** (40.6 mg, 91%).

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and bond angles for **4**, *endo*-**6**, *exo*-**6**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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