1422 *Organometallics* 1990, *9*, 1422-1434

Synthesis, Structure, and Reactivity of (η^4(5e)-Butadienyl)ruthenium Complexes: Crystal Structures of CpRu=C(Ph)-η^3-(C(Ph)C(Ph)CH(Ph)), CpRuC(Ph)=C(Ph)-η^2-(C(Ph)=CH(Ph))P(OMe)$_3$, and CpRu$_2$(μ-(*Z*)-C(Ph)=CH(Ph))(CO)$_2$(η^4-C$_4$Ph$_4$)[1]

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The chemistry of the first example of a η^4(5e)-butadienyl complex is described. Reaction of [CpRu(NCMe)(η^4-C$_4$Ph$_4$)][BF$_4$] with K[BHBu$^s_3$] affords CpRu=C(Ph)-η^3-(C(Ph)C(Ph)CH(Ph)) (**5**), which was structurally identified by single-crystal X-ray crystallography. Compound **5** is triclinic, space group $P\bar{1}$ (No. 2); a = 10.156 (5), b = 10.996 (5), c = 13.145 (6) Å, α = 112.12 (4), β = 101.20 (4), γ = 103.76 (4)°. The molecule contains an open-chain η^4(5e)-butadienyl system, in which the CpRu fragment is double bonded to C(1) (Ru–C(1) = 1.896 (5) Å), the remaining three carbon ruthenium distances Ru–C(2) (2.204 (5) Å), Ru–C(3) (2.152 (4) Å), and Ru–C(4) (2.154 (6) Å) being appropriate for an η^3-allyl system. A mechanism is proposed for the formation of **5** involving conrotatory ring-opening of an η^3-cyclobutenyl intermediate carrying an endo hydrogen, which becomes a pseudo-syn hydrogen on the terminus of the C$_4$ chain. The complex **5** together with the partially characterized (Ru(PPh$_3$)(η^4-C$_4$Ph$_4$))$_x$ is also obtained by reacting [CpRu(PPh$_3$)(η^4-C$_4$Ph$_4$)][BF$_4$] with K[BHBu$^s_3$]. In contrast, the same reaction in the presence of CO or P(OMe)$_3$ affords RuL$_2$(PPh$_3$)(η^4-C$_4$Ph$_4$) (L = CO or P(OMe)$_3$). This is rationalized in terms of the intermediacy of Ru(PPh$_3$)(η^4-C$_4$Ph$_4$)(η^4-C$_5$H$_6$). In support of this the complex Ru(P(OMe)$_3$)(η^4-C$_4$Ph$_4$)(η^4-C$_5$H$_6$) (**9**) is formed as a stable crystalline material by reaction of [CpRu(P(OMe)$_3$)(η^4-C$_4$Ph$_4$)][BF$_4$] with "H$^-$". Thermolysis of **9** affords initially the isomeric complex CpRuC(Ph)=C(Ph)-η^2-(C(Ph)=CH(Ph))P(OMe)$_3$ (**12**), which is also obtained by direct reaction of **5** with P(OMe)$_3$. The solid-state structure of **12** was established by X-ray crystallography. Compound **12** is monoclinic, space group *Cc* (No. 9); a = 18.226 (6), b = 12.190 (4), c = 27.447 (15) Å, α = 90, β = 94.31 (4), γ = 90°. The molecule is an η^3(3e)-butadienyl complex, and significantly, along with the η^4(5e) to η^3(3e) transformation of the bonding mode of the butadienyl ligand, a stereomutation at C(4) has occurred on reaction of **5** with P(OMe)$_3$. Thermolysis of **9** finally leads to the formation of a mixture of η^2-bonded hexatrienyl complexes **10** and **11** formed via an apparent orthometalation reaction. Additionally the reaction of hydride anion sources with [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] (**1**) was examined, leading to the formation of CpRu=C(Ph)-η^3-(C(Ph)C(Ph)C(CHO)Ph) (**15**) together with the X-ray crystallographically identified dinuclear complex CpRu$_2$(μ-CO)(μ-(*Z*)-C(Ph)=CH(Ph))(CO)$_2$(η^4-C$_4$Ph$_4$) (**16**). Compound **16** is monoclinic, space group $P2_1/c$ (No. 14); a = 15.763 (11), b = 15.928 (9), c = 18.914 (9) Å, α = 90, β = 112.58 (5), γ = 90°. The formation of **16** is rationalized in terms of the fragmentation of a cyclobutadiene complex.

Introduction

Relatively little is known about the reactions of nucleophiles with cationic η^4-cyclobutadiene complexes. It has been observed[2] that alkoxide anions react with the cations [CpM(η^4-C$_4$Ph$_4$)]$^+$ (M = Ni, Pd) to form the exo-substituted cyclobutenyl species CpM-η^3-C$_4$Ph$_4$(OR), which is in agreement with the regiochemistry predicted[3] by the Davies, Green, Mingos rules. The only other reports of reactions occurring on the cyclobutadiene ring concern the use of neutral nucleophiles. Thus, the iron cation [Fe(CO)$_2$(NO)(η^4-C$_4$H$_4$)]$^+$ reacts with *N,N*-dimethylaniline or a variety of phosphines to form exo-substituted cyclobutenyl compounds.[4-6] The analogous η^4-benzocyclobutadiene-substituted iron cation also reacts with tertiary phosphines, but in this case, attack at both the ring and the metal was observed.[7] Recently,[8] we described a relatively simple synthetic route to the cationic η^4-bonded tetraphenylcyclobutadiene complex [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$], and in exploring the reactivity of this and related complexes toward sources of "H$^-$" have observed ring-opening reactions leading to the formation of the first η^4(5e)-butadienyl complexes.

Results and Discussion

We have previously shown that the carbonyl ligand, which is present in the cation [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] (**1**), is photolabile and can be replaced by acetonitrile or halide anions.[8] To widen the range of cationic cyclobutadiene complexes available for reactivity studies with nucleophiles, the photoreaction was extended. Ultraviolet irradiation of a solution of [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] and triphenylphosphine or trimethyl phosphite in dichloro-

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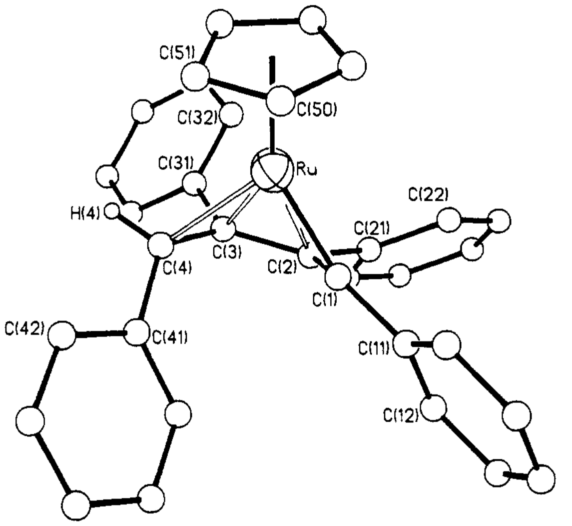


Figure 1. Molecular structure of **5** showing labeling scheme. All phenyl and cyclopentadienyl hydrogen atoms have been omitted for clarity.

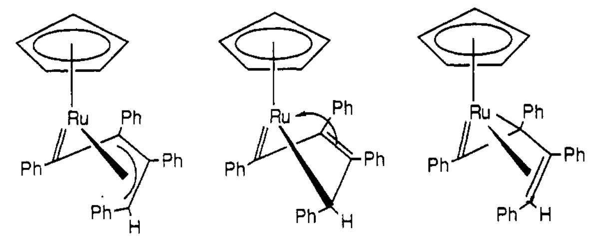
Table I. Selected Bond Lengths (Å) for 5

Ru-C(1)	1.896 (5)	Ru-C(2)	2.206 (5)
Ru-C(3)	2.153 (4)	Ru-C(4)	2.154 (5)
Ru-C(50)	2.188 (6)	Ru-C(51)	2.184 (8)
Ru-C(53)	2.231 (10)	Ru-C(54)	2.203 (8)
Ru-C(52)	2.237 (11)	C(1)-C(2)	1.425 (4)
C(1)-C(11)	1.457 (6)	C(2)-C(3)	1.435 (6)
C(2)-C(21)	1.486 (6)	C(3)-C(4)	1.449 (7)
C(3)-C(31)	1.501 (5)	C(4)-C(41)	1.481 (7)
C(4)-H(4)	0.915 (47)	C(11)-C(12)	1.384 (8)
C(11)-C(16)	1.395 (5)	C(12)-C(13)	1.376 (8)
C(13)-C(14)	1.388 (7)	C(14)-C(15)	1.365 (10)
C(15)-C(16)	1.388 (8)	C(21)-C(22)	1.394 (7)
C(21)-C(26)	1.387 (5)	C(22)-C(23)	1.387 (8)
C(23)-C(24)	1.365 (7)	C(24)-C(25)	1.362 (10)
C(25)-C(26)	1.382 (8)	C(31)-C(32)	1.386 (8)
C(31)-C(36)	1.387 (6)	C(32)-C(33)	1.381 (6)
C(33)-C(34)	1.372 (8)	C(34)-C(35)	1.366 (9)
C(35)-C(36)	1.375 (6)	C(41)-C(42)	1.392 (7)
C(41)-C(46)	1.395 (7)	C(42)-C(43)	1.369 (8)
C(43)-C(44)	1.369 (9)	C(44)-C(45)	1.388 (9)
C(45)-C(46)	1.384 (8)	C(50)-C(51)	1.357 (14)
C(50)-C(54)	1.340 (15)	C(51)-C(52)	1.403 (17)
C(53)-C(54)	1.346 (11)	C(53)-C(52)	1.346 (14)

Table II. Selected Bond Angles (deg) for 5

C(1)-Ru-C(2)	39.8 (1)	C(1)-Ru-C(3)	72.0 (2)
C(2)-Ru-C(3)	38.4 (2)	C(1)-Ru-C(4)	84.5 (2)
C(2)-Ru-C(4)	69.6 (2)	C(3)-Ru-C(4)	39.3 (2)
C(1)-Ru-C(50)	118.1 (2)	C(2)-Ru-C(50)	156.8 (3)
C(3)-Ru-C(50)	161.5 (3)	C(4)-Ru-C(50)	123.2 (3)
C(1)-Ru-C(51)	147.8 (3)	C(2)-Ru-C(51)	166.0 (3)
C(3)-Ru-C(51)	127.6 (3)	C(4)-Ru-C(51)	97.4 (4)
C(50)-Ru-C(51)	36.2 (4)	C(1)-Ru-C(53)	133.9 (3)
C(2)-Ru-C(53)	126.4 (2)	C(3)-Ru-C(53)	126.6 (2)
C(4)-Ru-C(53)	138.5 (3)	C(50)-Ru-C(53)	59.2 (3)
C(51)-Ru-C(53)	59.9 (5)	C(1)-Ru-C(54)	112.3 (3)
C(2)-Ru-C(54)	133.3 (3)	C(3)-Ru-C(54)	158.9 (3)
C(4)-Ru-C(54)	157.1 (3)	C(50)-Ru-C(54)	35.5 (4)
C(51)-Ru-C(54)	59.9 (4)	C(53)-Ru-C(54)	35.3 (3)
C(1)-Ru-C(52)	168.9 (3)	C(2)-Ru-C(52)	139.5 (2)
C(3)-Ru-C(52)	113.1 (2)	C(4)-Ru-C(52)	105.7 (3)
C(50)-Ru-C(52)	60.1 (3)	C(51)-Ru-C(52)	37.0 (4)
C(53)-Ru-C(52)	35.1 (4)	C(54)-Ru-C(52)	59.2 (3)
Ru-C(1)-C(2)	81.9 (3)	Ru-C(1)-C(11)	147.4 (3)
C(2)-C(1)-C(11)	128.5 (4)	Ru-C(2)-C(1)	58.3 (2)
Ru-C(2)-C(3)	68.8 (2)	C(1)-C(2)-C(3)	113.2 (4)
Ru-C(2)-C(21)	135.8 (4)	C(1)-C(2)-C(21)	122.3 (4)
C(3)-C(2)-C(21)	123.9 (3)	Ru-C(3)-C(2)	72.8 (2)
Ru-C(3)-C(4)	70.4 (2)	C(2)-C(3)-C(4)	119.4 (3)
Ru-C(3)-C(31)	125.8 (3)	C(2)-C(3)-C(31)	122.0 (4)
C(4)-C(3)-C(31)	118.6 (4)	Ru-C(4)-C(3)	70.3 (3)
Ru-C(4)-C(41)	117.0 (3)	C(3)-C(4)-C(41)	130.0 (5)
Ru-C(4)-H(4)	111.5 (32)	C(3)-C(4)-H(4)	110.8 (27)
C(41)-C(4)-H(4)	110.8 (32)		

Scheme I



5(i)   5(ii)   5(iii)

methane afforded good yields of the cations $[CpRu(PPh_3)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (**2**) and $[CpRu(P(OMe)_3)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (**3**). In both of these reactions there was no evidence for the formation of products arising from nucleophilic attack by the trivalent phosphorus compound on the cyclobutadiene ring.

In contrast, the reaction of $[CpRu(NCMe)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (**4**) with $K[BHBu^s_3]$ in tetrahydrofuran led to the apparent delivery of "H^-" to the η^4-cyclobutadiene ring.[9] The product **5** was isolated in high yield (85%) by column chromatography and crystallization as an air-sensitive, purple crystalline material. Elemental and mass and NMR spectral analyses suggested that the product had the molecular formula [CpRu(C(Ph)C(Ph)C(Ph)CH(Ph))]. Of particular significance was the $^{13}C\{^1H\}$ NMR spectrum (see Experimental Section), which showed a low-field signal at δ 246.0 characteristic of an alkylidene type carbon and implying the presence of a ruthenium-to-carbon double bond.

The precise molecular geometry of **5** was elucidated by single-crystal X-ray crystallography and is illustrated in Figure 1 with pertinent bond distances and angles being listed in Tables I and II, respectively. From the structure determination it is immediately apparent that a ring-opening reaction has occurred, a hydrogen atom being located in a pseudo-syn environment on the terminal carbon C(4) of a butadienyl moiety. In contrast with the known η^3(3e)-bonded butadienyl complexes $CpRuC(R)=C(R)C(R')=CH(R')(PPh_3)$ [R = R' = CF_3;[10] R = CO_2Me, R' = CF_3[11]], all four carbon atoms of the C_4 chain present in **5** are bonded to the CpRu fragment. The C_4 chain is near coplanar (torsion angle C(1)C(2)C(3)C(4) = −15.9 (7)°) but differs from the system $CpRuC(CF_3)=C(CF_3)C(CF_3)=C(CF_3)H(PPh_3)$ (∠RuC(1)C(2) 101.1°), in that the ∠RuC(1)C(2) angle is much smaller (81.9 (3)°). In addition the Ru-C(1) bond distance in **5** is significantly shorter (1.896 (5) Å) than those observed[10,11] (2.05 Å, R = R' = CF_3; 2.082 (5) Å, R = CO_2Me, R' = CF_3) in the η^3-(3e)-bonded systems, suggesting that C(1) in **5** is an alkylidene carbon doubly bonded to the ruthenium center. The remaining three carbons of the butadienyl chain have Ru-C(2), Ru-C(3), and Ru-C(4) distances of 2.204 (5), 2.152 (4), and 2.154 (6) Å, respectively, which are appropriate for an η^3-allyl system. In view of the near planarity

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of C(1-4), the π system of this allyl functionality is able to interact with the Ru=C π bond. In agreement with these observations the carbon-carbon distances within the butadienyl moiety are C(1)-C(2), C(2)-C(3), and C(3)-C(4), 1.419 (5), 1.435 (7), and 1.445 (7) Å, respectively.

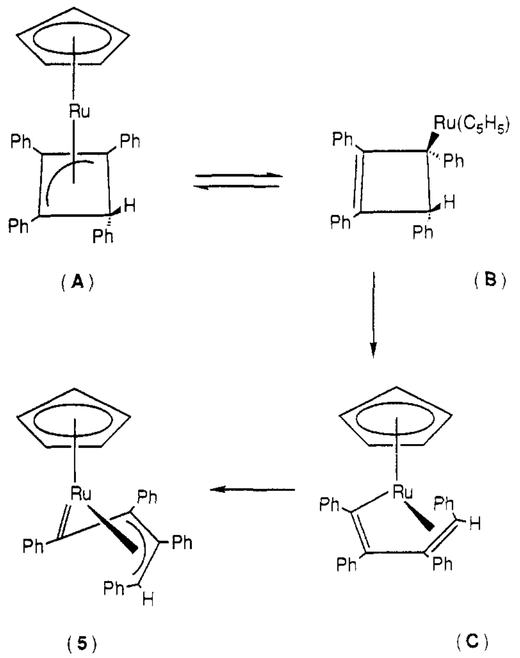
Thus, complex **5** contains an open-chain butadienyl moiety, which bonds to the ruthenium in a novel η^4(5e) bonding mode. As is illustrated in Scheme I three resonance structures can be drawn. The first may be viewed as an allyl-substituted carbene or alkylidene and may be regarded as the next logical progression from η^3(3e) vinyl and η^3(4e) vinyl carbene moieties. The second bonding mode [**5**(ii)] resembles a metallacyclopent-3-ene, i.e., a σ,σ-η^2-bonded 1,3-diene, except that C(1) carries only a phenyl substituent and therefore is double bonded to the ruthenium. The third representation [**5**(iii)] is a vinyl-substituted η^2(3e) vinyl complex.

Subsequent to our initial report[9] on the ruthenium system, two other complexes containing an η^4(5e)-butadienyl ligand have been crystallographically identified. The first complex, $\mathrm{O{=}W{=}C(Ph)}$-η^3-$\mathrm{(C(Ph)C(Ph)CH(Ph))(S_2CNEt_2)}$,[12] was obtained by reaction of $\mathrm{W(PhC_2Ph)_2(S_2CNEt_2)}$ with $\mathrm{HBF_4}$ followed by aqueous $\mathrm{NEt_3}$ and shows bond parameters within the η^4-$\mathrm{C_4Ph_4H}$ ligand similar to those found in **5** with the exception, however, that the ∠MC(1)C(2) angle is opened out to 94.3° in the tungsten system compared to the 81.9 (3)° found for the ruthenium system **5**. It is also interesting to note the variations reported[12] for the J_{CH} parameters for the CHPh group present in the η^4(5e)-$\mathrm{C_4Ph_4H}$ ligand contained in $\mathrm{O{=}W{=}C(Ph)}$-η^3-$\mathrm{(C(Ph)C(Ph)CH(Ph))(S_2CNEt_2)}$ (136 and 144 Hz, two isomers) and the precursor cation $\mathrm{[W{=}C(Ph)}$-η^3-$\mathrm{(C(Ph)C(Ph)CH(Ph))(S_2CNEt_2)][BF_4]}$ (154 Hz) and to compare these with the value observed for **5**, i.e., J_{CH} = 147.6 Hz. Clearly one might expect variations in the bonding mode of the η^4(5e)-butadienyl ligand with the environment of the metal, and this is possibly reflected in J_{CH}. In this context it is interesting that in the third structurally characterized η^4(5e)-butadienyl complex $\mathrm{CpW}(\eta^4$-$\mathrm{C(CF_3)C(CF_3)C(Me)C(Me)SPr^i})(\eta^2$-$\mathrm{CF_3C_2CF_3})$[13] the X-ray data have been interpreted as requiring a major contribution from a structure analogous to **5**(ii) in Scheme I.

Ring-opening reactions of η^3-cyclobutenylpalladium(II) complexes have previously[14,15] been invoked to explain the formation of η^3(3e)-butadienyl species, and it is reasonable to propose that a related reaction is involved in the formation of **5**. It is suggested that the immediate precursor of **5** is a 16-electron η^3(3e)-bonded butadienyl complex (C, Scheme II). To accommodate the unsaturation at the metal center, both a geometrical (closing up of the ∠RuC(1)C(2) bond angle) and an electronic redistribution occur so that the butadienyl fragment can function as a η^4(5e) system. In a sense, the η^3(3e) to η^4(5e) switch in bonding mode masks and therefore stores the unsaturation at the metal center. This process can be related to an η^1(1e) to η^2(3e) change in the bonding mode of a vinyl ligand.[16]

If it is assumed that the stereochemistry of **5** is kinetically controlled, then since the hydrogen substituent at the end of the $\mathrm{C_4}$ chain adopts an outside or pseudo-syn position it is plausible that the butadienyl fragment is formed by a conrotatory ring-opening reaction of an η^3-cyclobutenyl complex (A, Scheme II), in which the hydrogen substituent is on the same face of the $\mathrm{C_4}$ ring as the ruthenium, i.e., an endo configuration. If this is correct, then the hydrogen atom must, therefore, initially reside on the ruthenium before being transferred to the $\mathrm{C_4}$ ring. Such a Ru-H-containing species could be formed either by direct capture of an unsaturated ruthenium cation by "H$^-$" or alternatively by initial exo-attack by "H$^-$" on the cyclopentadienyl ring followed by an endo-hydrogen transfer from the resulting $\mathrm{C_5H_6}$ ligand to the metal.

Scheme II



An insight into the relative importance of these two possibly competing pathways was provided by a study of the reaction of the phosphorus-ligand-substituted cyclobutadiene cations **2** and with sources of "H$^-$". Addition of $\mathrm{K[BHBu^s_3]}$ to a suspension of $\mathrm{[CpRu(PPh_3)}(\eta^4$-$\mathrm{C_4Ph_4)][BF_4]}$ (**2**) in tetrahydrofuran at -78 °C resulted in a rapid reaction. Chromatographic workup afforded the purple crystalline η^4(5e)-butadienyl complex **5** (45% yield) together with a yellow solid, **6** (50% yield), which was analyzed and showed ^{1}H and ^{13}C{^{1}H} NMR spectra consistent with the cluster $(\mathrm{Ru(PPh_3)}(\eta^4$-$\mathrm{C_4Ph_4}))_x$. Particularly significant was the absence of spectral features characteristic of η^5-cyclopentadienyl or η^4-cyclopentadiene ligands. It was also observed that when **2** was treated with $\mathrm{K[BHBu^s_3]}$ at -78 °C in the presence of excess $\mathrm{P(OMe)_3}$ or CO, the formation of **5** and the cluster $(\mathrm{Ru(PPh_3)}(\eta^4$-$\mathrm{C_4Ph_4}))_x$ was completely suppressed, and instead the Ru(0) complexes $[\mathrm{Ru(PPh_3)(P(OMe)_3)_2}(\eta^4$-$\mathrm{C_4Ph_4})]$ (**7**) and $[\mathrm{Ru(PPh_3)(CO)_2}(\eta^4$-$\mathrm{C_4Ph_4})]$ (**8**) were formed respectively in good yield.

These observations can be understood if it is assumed that "H$^-$" is delivered by $\mathrm{K[BHBu^s_3]}$ to the exo face of the η^5-cyclopentadienyl ring of **2**, thus forming the intermediate Ru(0) complex D (Scheme III). Then, either this species can dissociatively lose $\mathrm{C_5H_6}$ to form the cluster complex $(\mathrm{Ru(PPh_3)}(\eta^4$-$\mathrm{C_4Ph_4}))_x$ or alternatively loss of $\mathrm{PPh_3}$ promoted by capture by $\mathrm{BBu^s_3}$ followed by transfer of an endo-hydrogen to the $\mathrm{C_4}$ ring via the metal could lead to the formation of the η^4(5e)-butadienyl complex **5**. In the presence of CO or $\mathrm{P(OMe)_3}$ displacement of $\mathrm{C_5H_6}$ and formation of the Ru(0) complexes **7** and **8** override cluster

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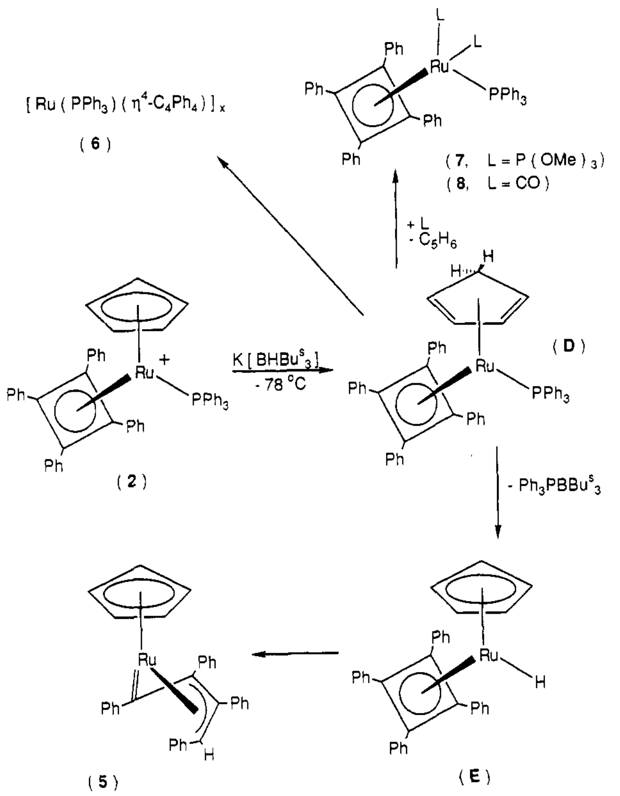
Scheme III



formation or hydrogen transfer. Consistent with this rationale, it was observed that reaction of **2** with $Li[BDEt_3]$ in the absence of CO or $P(OMe)_3$ led to the formation of **5**, in which deuterium was incorporated into only the cyclopentadienyl ring.

Additional support for this mechanistic proposal came from a study of the reaction of $K[BHBu^s_3]$ with the cation $[Ru(P(OMe)_3)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ (**3**). Treatment with $K[BHBu^s_3]$ or $Li[BHEt_3]$ in tetrahydrofuran at −78 °C afforded an almost quantitative yield of the yellow crystalline η^4-cyclopentadiene complex $Ru(P(OMe)_3)(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)$ (**9**), which was characterized by elemental analysis, MS, and NMR spectroscopy. Reaction of **3** with $Li[BDEt_3]$ under the same conditions afforded **9** with deuterium incorporated into only the exo position of the η^4-cyclopentadiene ligand. It is interesting to note that this result is not consistent with the Davies, Green, Mingos rules,[3] which predict regioselective nucleophilic attack on the C_4 ring.

If one refers back to Scheme III, then it is clear that compound **9** is analogous to the postulated intermediate, D and therefore it was interesting to examine its thermal stability. Of course, it must be remembered that it was suggested that the transformation of D into **5** was assisted by capture of PPh_3 by BBu^s_3, and thus there would be no such assistance to the dissociation of $P(OMe)_3$ from **9**. When a solution of **9** in tetrahydrofuran was heated (80 °C) for 5 h in a sealed tube, a smooth isomerization reaction occurred. Examination of the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra (see Experimental Section) of the product, which was isolated by column chromatography as a yellow crystalline material, indicated that this was a mixture (1:1) of two complexes, **10** and **11**, both isomeric with **9**. To gain additional insight into this process, the reaction was monitored by ^1H NMR using toluene-d_8 as solvent. The signals due to **9** decreased smoothly in intensity over 0.5 h. Although signals due to the isomeric mixture of products were observed almost immediately, a third set of signals was also observed which could be attributed to an intermediate. The intensity of the NMR signals due to the intermediate initially increased during the first 0.5 h and then decreased. Interestingly, close examination of the spectra suggested that the intermediate was a further isomer of **9**, and a valuable insight into the thermolysis reaction was obtained when it was realized that the intermediate was identical with the crystalline adduct formed by the room-temperature reaction of **5** with $P(OMe)_3$.[17]

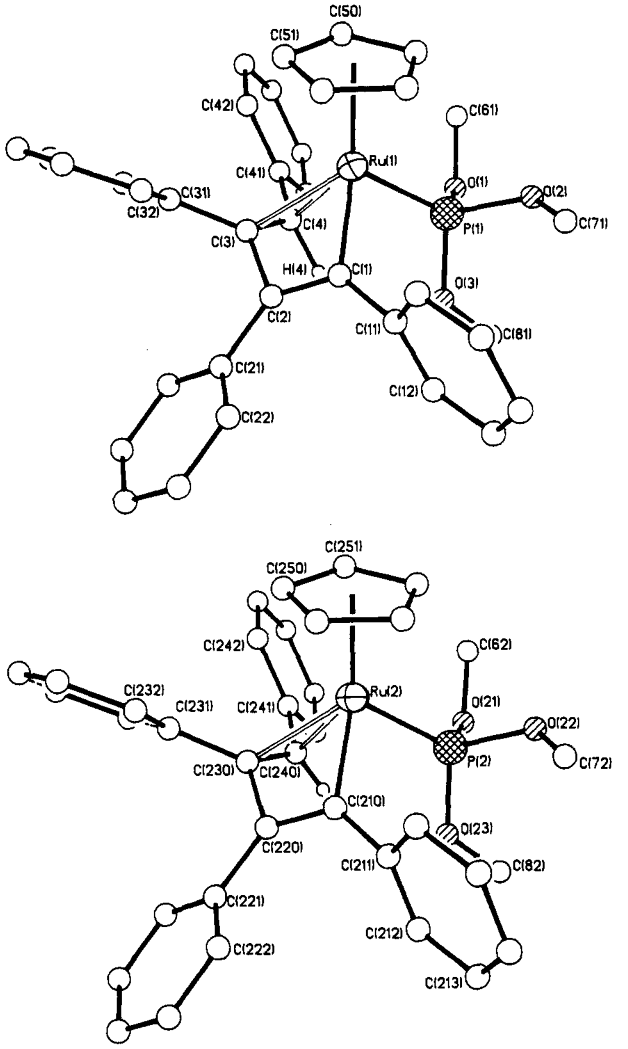


Figure 2. Molecular structure of **12** showing labeling scheme for the two independent molecules present in the crystal structure. All methyl, phenyl and cyclopentadienyl hydrogen atoms have been omitted for clarity.

This reaction was examined because it was thought that the η^4(5e)-butadienyl complex **5** might behave as a latent or stored coordinatively unsaturated η^3(3e)-butadienyl complex and therefore ought to react with donor ligands. Indeed treatment of **5** (CH_2Cl_2, room temperature) with $P(OMe)_3$ or PPh_3 afforded high yields of the orange–red crystalline materials **12** and **13**. Elemental analysis and mass spectral data indicated that both products were simple 1:1 adducts. The ^1H NMR spectra of the complexes were similar, containing resonances due to phenyl and cyclopentadienyl protons, together with a one-proton doublet at approximately δ 4.10 ($J_{PC} \sim 10$ Hz). Significantly, the $^{13}C\{^1H\}$ NMR spectra did not contain a low-field

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(17) Brammer, L.; Crocker, M.; Dunne, B. J.; Green, M.; Morton, C. E.; Nagle, K. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1226–1228.

Table III. Selected Bond Lengths (Å) for 12

Ru(1)–P(1)	2.215 (2)	Ru(1)–C(1)	2.067 (7)
Ru(1)–C(4)	2.251 (7)	Ru(1)–C(50)	2.304 (5)
Ru(1)–C(51)	2.310 (5)	Ru(1)–C(52)	2.252 (5)
Ru(1)–C(53)	2.208 (5)	Ru(1)–C(54)	2.241 (5)
Ru(1)–C(3)	2.252 (7)	P(1)–O(1)	1.598 (6)
P(1)–O(2)	1.596 (7)	P(1)–O(3)	1.593 (6)
O(1)–C(61)	1.420 (12)	O(2)–C(71)	1.440 (13)
O(3)–C(81)	1.427 (11)	C(1)–C(2)	1.314 (9)
C(1)–C(11)	1.495 (8)	C(4)–C(3)	1.407 (9)
C(4)–C(41)	1.503 (8)	C(4)–H(4)	1.133 (69)
C(2)–C(3)	1.522 (9)	C(2)–C(21)	1.498 (8)
C(3)–C(31)	1.501 (8)	P(2)–O(21)	1.598 (6)
P(2)–O(22)	1.605 (7)	P(2)–O(23)	1.582 (6)
O(21)–C(62)	1.408 (12)	O(22)–C(72)	1.435 (14)
O(23)–C(82)	1.429 (11)	C(210)–C(220)	1.346 (9)
C(210)–C(211)	1.480 (8)	C(220)–C(230)	1.495 (10)
C(220)–C(221)	1.488 (8)	C(23)–C(240)	1.429 (10)
C(230)–C(231)	1.517 (8)	C(240)–C(241)	1.485 (8)
C(240)–H(240)	0.841 (46)		

Table IV. Selected Bond Angles (deg) for 12

P(1)–Ru(1)–C(1)	87.8 (2)	P(1)–Ru(1)–C(4)	81.1 (2)
C(1)–Ru(1)–C(4)	83.0 (2)	P(1)–Ru(1)–C(50)	113.5 (1)
C(1)–Ru(1)–C(50)	156.7 (2)	C(4)–Ru(1)–C(50)	108.5 (2)
P(1)–Ru(1)–C(51)	149.2 (1)	C(1)–Ru(1)–C(51)	121.9 (2)
C(4)–Ru(1)–C(51)	108.6 (2)	P(1)–Ru(1)–C(52)	142.8 (1)
C(1)–Ru(1)–C(52)	96.9 (2)	C(4)–Ru(1)–C(52)	136.1 (2)
P(1)–Ru(1)–C(53)	106.1 (1)	C(1)–Ru(1)–C(53)	105.3 (2)
C(4)–Ru(1)–C(53)	169.0 (2)	P(1)–Ru(1)–C(54)	91.8 (1)
C(1)–Ru(1)–C(54)	140.2 (2)	C(4)–Ru(1)–C(54)	136.2 (2)
P(1)–Ru(1)–C(3)	109.6 (2)	C(1)–Ru(1)–C(3)	63.1 (3)
C(4)–Ru(1)–C(3)	36.4 (2)	C(50)–Ru(1)–C(3)	114.4 (2)
C(51)–Ru(1)–C(3)	92.8 (2)	C(52)–Ru(1)–C(3)	105.3 (2)
C(53)–Ru(1)–C(3)	141.6 (2)	C(54)–Ru(1)–C(3)	150.5 (2)
Ru(1)–P(1)–O(1)	119.9 (2)	Ru(1)–P(1)–O(2)	118.6 (2)
O(1)–P(1)–O(2)	96.0 (3)	Ru(1)–P(1)–O(3)	115.1 (2)
O(1)–P(1)–O(3)	98.9 (3)	O(2)–P(1)–O(3)	104.9 (3)
P(1)–O(1)–C(61)	121.7 (6)	P(1)–O(2)–C(71)	121.3 (6)
P(1)–O(3)–C(81)	124.1 (6)	Ru(1)–C(1)–C(2)	102.7 (5)
Ru(1)–C(1)–C(11)	128.6 (4)	C(2)–C(1)–C(11)	128.7 (6)
Ru(1)–C(4)–C(3)	71.8 (4)	Ru(1)–C(4)–C(41)	114.6 (4)
C(3)–C(4)–C(41)	130.7 (6)	Ru(1)–C(4)–H(4)	107.3 (39)
C(3)–C(4)–H(4)	108.2 (37)	C(41)–C(4)–H(4)	114.8 (39)
Ru(1)–C(50)–C(51)	72.3 (1)	Ru(1)–C(50)–C(54)	69.4 (1)
Ru(1)–C(51)–C(50)	71.8 (1)	Ru(1)–C(51)–C(52)	69.6 (1)
Ru(1)–C(52)–C(51)	74.1 (1)	Ru(1)–C(52)–C(53)	69.8 (1)
Ru(1)–C(53)–C(52)	73.1 (1)	Ru(1)–C(53)–C(54)	72.7 (1)
Ru(1)–C(54)–C(50)	74.2 (1)	Ru(1)–C(54)–C(53)	70.1 (1)
C(1)–C(2)–C(3)	105.8 (5)	C(1)–C(2)–C(21)	132.0 (6)
C(3)–C(2)–C(21)	122.1 (5)	Ru(1)–C(3)–C(4)	71.8 (4)
Ru(1)–C(3)–C(2)	88.4 (4)	C(4)–C(3)–C(2)	116.4 (6)
Ru(1)–C(3)–C(31)	120.8 (4)	C(4)–C(3)–C(31)	126.6 (6)
C(2)–C(3)–C(31)	115.6 (5)	C(1)–C(11)–C(12)	119.3 (3)
C(1)–C(11)–C(16)	120.5 (3)	C(2)–C(21)–C(22)	119.9 (3)
C(2)–C(21)–C(26)	120.1 (3)	Ru(2)–P(2)–O(21)	119.7 (2)
Ru(2)–P(2)–O(22)	117.1 (3)	O(21)–P(2)–O(22)	96.6 (4)
Ru(2)–P(2)–O(23)	115.3 (2)	O(21)–P(2)–O(23)	99.0 (3)
O(22)–P(2)–O(23)	106.1 (3)	P(2)–O(21)–C(62)	123.0 (7)
P(2)–O(22)–C(72)	120.8 (6)	P(2)–O(23)–C(82)	123.4 (6)
Ru(2)–C(210)–C(220)	101.3 (4)	Ru(2)–C(210)–C(211)	129.1 (4)
C(220)–C(210)–C(211)	129.6 (5)	C(210)–C(220)–C(230)	105.9 (5)
C(210)–C(220)–C(221)	130.3 (6)	C(230)–C(220)–C(221)	123.7 (5)
Ru(2)–C(230)–C(220)	89.4 (4)	Ru(2)–C(230)–C(240)	71.9 (4)
C(220)–C(230)–C(240)	116.0 (6)	Ru(2)–C(230)–C(231)	122.0 (4)
C(220)–C(230)–C(231)	116.1 (5)	C(240)–C(230)–C(231)	125.8 (6)
Ru(2)–C(240)–C(230)	71.0 (4)	Ru(2)–C(240)–C(241)	115.5 (4)
C(230)–C(240)–C(241)	129.6 (5)	Ru(2)–C(240)–H(240)	99.5 (32)
C(230)–C(240)–H(240)	110.8 (33)	C(241)–C(240)–H(240)	116.4 (33)
Ru(2)–C(250)–C(251)	72.1 (2)	Ru(2)–C(250)–C(254)	69.9 (2)
Ru(2)–C(251)–C(250)	71.7 (2)	Ru(2)–C(251)–C(252)	70.1 (1)
Ru(2)–C(252)–C(251)	73.4 (1)	Ru(2)–C(252)–C(253)	70.2 (2)
Ru(2)–C(253)–C(252)	72.7 (2)	Ru(2)–C(253)–C(254)	72.3 (1)
Ru(2)–C(254)–C(250)	73.5 (1)	Ru(2)–C(254)–C(253)	70.5 (1)
C(210)–C(211)–C(212)	119.1 (3)	C(210)–C(211)–C(216)	120.7 (3)
C(220)–C(221)–C(222)	120.4 (3)	C(220)–C(221)–C(226)	119.6 (3)
C(230)–C(231)–C(232)	119.0 (3)	C(230)–C231)–C(236)	120.9 (3)
C(240)–C(241)–C(242)	123.8 (3)	C(240)–C(241)–C246)	116.0 (3)

signal characteristic of a carbene complex.

To determine the structural identities of these adducts and to understand the thermolysis of **9**, a single-crystal X-ray study was carried out on **12**. As shown by Figure 2 and the bond lengths and angles listed in Tables III and IV, molecules of **12** (of which there are two, a and b, which are crystallographically distinct but chemically similar) in the solid state consist of a ruthenium atom coordinated by η^5-C_5H_5, $P(OMe)_3$, and η^3-butadienyl ligands. In contrast to **5** the butadienyl ligand binds via σ-vinyl and η^2-alkene functions in **12**. The σ-bonding of the butadienyl ligand to the metal is reflected in the Ru–C(1) bond distance (average 2.067 (2) Å), while C(3) and C(4) comprise an olefinic unit bound to the metal with Ru–C(3) and Ru–C(4) distances of 2.252 (7) and 2.251 (7) Å, respectively. These values compare with Ru–C(3) and Ru–C(4) distances of 2.185 (5) and 2.171 (6) Å in the related η^3-butadienyl complex $\mathrm{Cp\overline{RuC(CO_2Me){=}C(CO_2Me)C(CF_3){=}C}(CF_3)H(PPh_3)}$,[11] the somewhat tighter binding of the metal to C(3) and C(4) in this latter complex resulting from the presence of strongly electron withdrawing groups. The terminal butadienyl carbon C(4) in **12** bears H and Ph substituents in pseudo-anti and -syn positions, respectively. Lengthening of the C(3)–C(4) double bond arising from coordination to the metal is reflected in the C(3)–C(4) bond distance of 1.406 (10) Å, as compared to that of 1.314 (9) Å for the noncoordinated C(1)–C(2) double bond. The asymmetric manner in which the butadienyl unit is bound to the ruthenium is demonstrated by the respective Ru–C(1)–C(2) and Ru–C(4)–C(3) angles of 102.7 (5) and 71.8 (4)°.

Thus, reaction of **5** with $P(OMe)_3$ or PPh_3 involves a change in the bonding mode of the butadienyl fragment from η^4(5e) to η^3(3e), which accommodates the attacking ligand at the ruthenium center. Of particular significance is the change in the stereochemistry of the substituents on the terminal carbon of the butadienyl chain. Whereas in the precursor **5** the hydrogen substituent occupies a pseudo-syn position, the structure determination of **12** shows this stereochemistry to be reversed, with the hydrogen now in the pseudo-anti position, and the phenyl substituent in the pseudo-syn site.

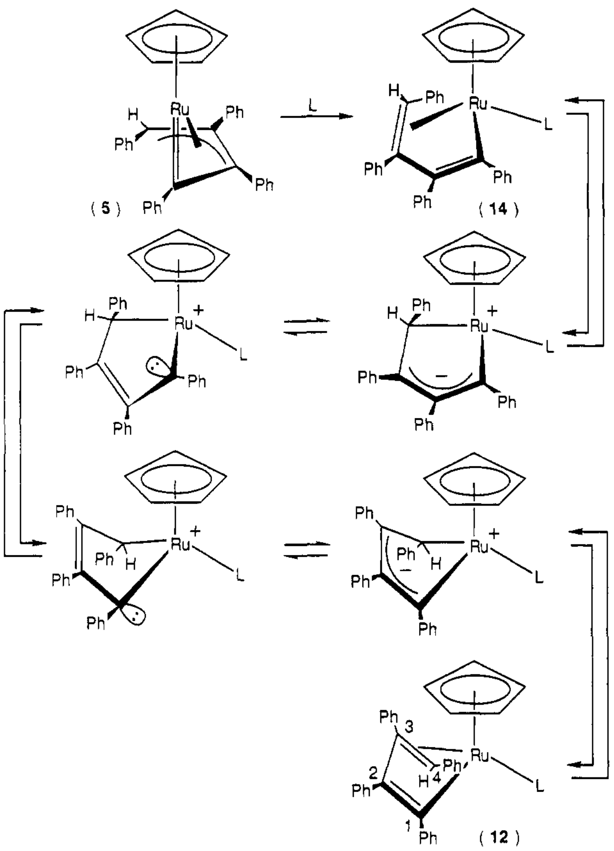
It is suggested that stereomutation of the substituents on carbon 4 occurs after initial formation of the 1:1 adduct **14** (Scheme IV). The stereomutation is thermodynamically driven and occurs via a pathway related to a mechanism suggested by Maitlis[15] to rationalize the products formed in a ring-opening reaction of certain cyclobutenylpalladium complexes. Thus, it is proposed that addition of the donor ligand to **5** results in a switch in the bonding mode of the butadienyl fragment from η^4(5e) to η^3(3e). Ring closure with charge separation then sets things up for a ring-flip process which affects the stereomutation process.

As was mentioned earlier, the final product of the thermolysis of **9** is a mixture of the two isomeric complexes **10** and **11**. A more careful study of solvent and reaction conditions confirmed the intermediacy of **12** and established the variations in isomer ratio listed in Table V. At 80 °C, the reaction is complete in a few hours, and in both toluene-d_8 or tetrahydrofuran-d_8 the isomer ratio is approximately 1:1. At lower temperatures, the reaction takes considerably longer, having only gone to about 75% completion after 24 h at 58 °C and taking 12 days to get to the same stage at 40 °C. At these lower temperatures, one isomer is favored over the other. In toluene, the ratio is approximately constant at 2:1, while in tetrahydrofuran it is somewhat more variable. It was also found that addition of 0.3 mol equiv of $P(OCD_3)_3$ to a solution of **9** in toluene-d_8 followed by thermal rearrangement did not result in any incorporation of deuterium into **10**, **11**, or **12**.

Table V. Thermolysis of 9

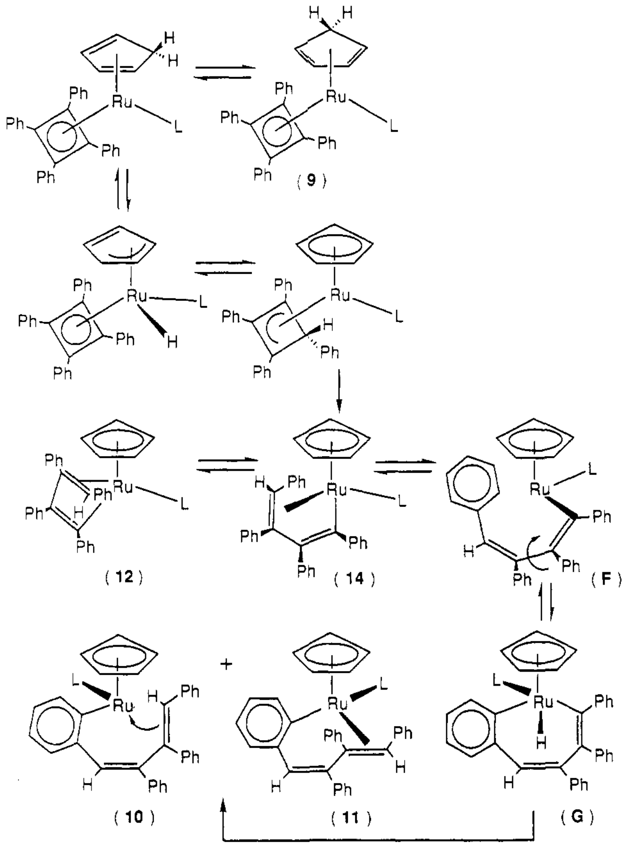
solvent	temp, °C	reaction time	composition, % 9	12	10	11	ratio 10:11
toluene-d_8	80	24 h	0	0	46	54	1:1.2
toluene-d_8	58	24 h	9	17	51	23	2.2:1
toluene-d_8	40	5 days	11	26	41	22	1.9:1
toluene-d_8	40	12 days	15	8	51	26	2.0:1
tetrahydrofuran-d_8	80	24 h	0	0	49	51	1:1
tetrahydrofuran-d_8	58	31 h	10	13	47	30	1.6:1
tetrahydrofuran-d_8	40	6 days	17	31	34	18	1.9:1

Scheme IV[a]



[a] L = P(OMe)$_3$.

Scheme V[a]



[a] L = P(OMe)$_3$.

Detailed examination of the ^{1}H NMR spectrum of the mixture of **10** and **11** showed a broad aromatic region, together with two cyclopentadienyl resonances and two sets of doublets resulting from trimethylphosphite ligands. In addition there were two other resonances for each isomer that integrated as one proton each. One set, occurring at δ 4.31 and 4.20, showed phosphorus coupling of 10.0 and 11.2 Hz, respectively, while the other set at δ 6.18 and 6.37 showed no phosphorus coupling. Consideration of this observation along with the other data relating to **10** and **11** suggested that these isomeric complexes carry an η^2-bonded hexatrienyl ligand as shown in Scheme V.

Thus, it is suggested[18] that on thermolysis of **9** an initial η^4-to-η^2 slippage of the C_5H_6 ligand followed by transfer of an endo-hydrogen onto the ruthenium accesses an η^3-cyclobutenyl complex, which undergoes the conrotatory ring-opening to form **14** which is in equilibrium with **12**. If the coordinated double bond of **14** now lifts off the metal in order to relieve steric crowding, a 16-electron σ-butadienyl species (F) can be formed. A small rotation around the adjacent C–C single bond then brings the ortho hydrogen of the terminal phenyl ring into bonding distance with the metal and allows oxidative addition (orthometalation) with formation of an intermediate metallocycloheptatriene (G). Reductive elimination, with the hydrogen being delivered to the original α-carbon, affords the final products **10** and **11**, containing a σ-bonded phenyl group as part of a σ,η^2-hexatrienylruthenium fragment (Scheme V). The two isomers arise from different orientations of the hexatrienyl chain around the ruthenium atom.

Further support for these suggestions was derived from deuterium-labeling experiments. When **3** is reacted with Li[BDEt$_3$], Ru(P(OMe)$_3$)(η^4-C$_4$Ph$_4$)(η^4-C$_5$H$_5$D) is formed with deuterium incorporated only in the exo position of the cyclopentadiene ring. Thermolysis of a solution of **9**-D afforded **10**-D and **11**-D, which ^{1}H and ^{2}H NMR spectroscopy showed had deuterium only in the cyclopentadienyl ring. Reaction of [CpRu(NCMe)(η^4-C$_4$Ph$_4$)][BF$_4$] (**4**) with Li[BDEt$_3$] and subsequent addition of P(OMe)$_3$ afforded **12**-D, containing 1 mol equiv of deuterium, which was divided between the cyclopentadienyl ring (85%) and the proton on the butadienyl chain (15%). This indicates, of course, that two competing pathways are in operation in the reaction with hydride

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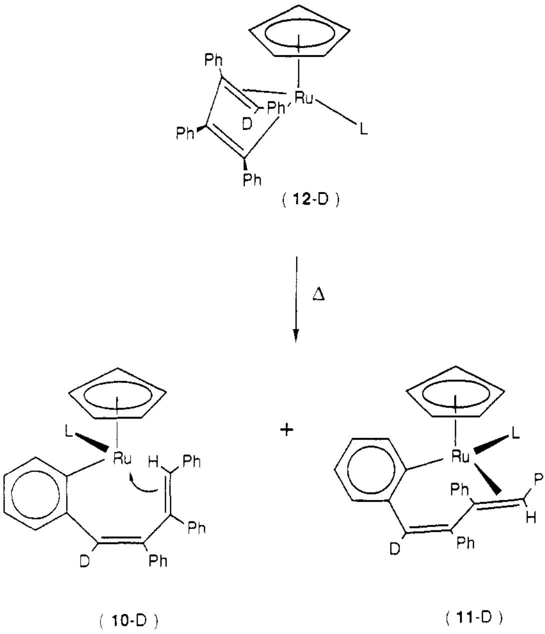
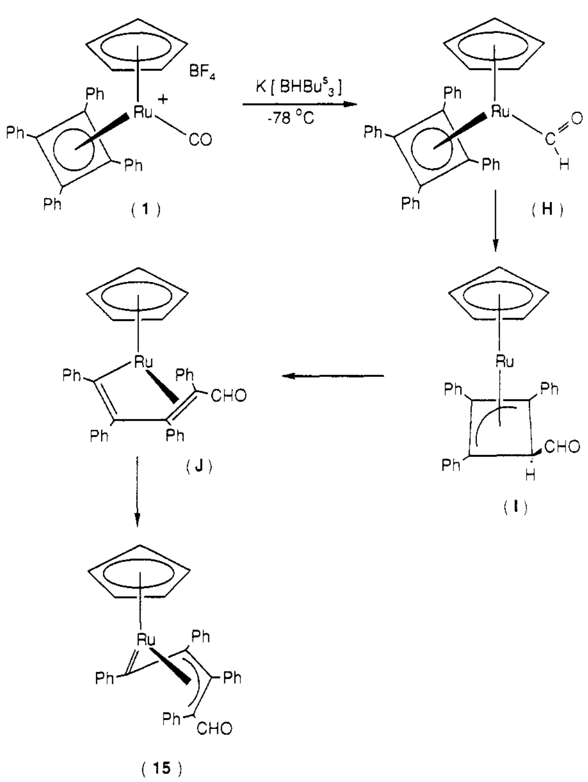
[18] The absence of exchange with P(OCD$_3$)$_3$ argues against a reaction path analogous to that shown in Scheme III where dissociative loss of P(OMe)$_3$ leads to hydrogen transfer from C$_5$ to C$_4$.

Scheme VI[a]



[a] L = P(OMe)$_3$.

Scheme VII



anion. The major one is attack of the nucleophile on the cyclopentadienyl ring, while the minor one must involve attack at the ruthenium center followed by migration to the endo face of the cyclobutadiene ring. On thermolysis of 12-D, ^{1}H and ^{2}H NMR spectroscopy showed that the deuterium was divided, in the same ratio, between the cyclopentadienyl ring and the non-phosphorus-coupled proton position (Scheme VI). Thus, the terminal alkene proton of **10** and **11** does not originate from the terminal proton of **12**, and since the cyclopentadienyl ring, trimethyl phosphite, and solvent can all be ruled out as its source, it must be derived from a phenyl ring.

Attention was next turned to the reaction of hydride anion sources with [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] (**1**). Two products were formed on reaction with K[BHBu$^s_3$] and were isolated as dark green **15** and orange crystalline **16**. Elemental analysis together with IR and NMR spectroscopy suggested the illustrated structure for **15** (Scheme VII), the ^{13}C{^{1}H} NMR spectrum showing a characteristic low-field signal at δ 255.2, and the presence of a CHO group being indicated by a strong band in the IR spectrum at 1643 cm^{-1}. This structural feature was confirmed by a proton-coupled ^{13}C NMR spectrum, which showed a doublet at δ 192.0 (CHO, J_{CH} = 176.4 Hz), the corresponding spectrum of the deuterio analogue obtained from reaction of [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] with Li[BDEt$_3$] exhibiting a triplet at δ 189.2 (CDO, J_{CD} = 25.6 Hz). Thus, **15** is also an η^4(5e)-butadienyl complex, structurally related to **5**, where the C*H*Ph substituent is replaced by a CHO group in the analogous pseudo-syn position. Clearly, the formation of **15**, and in particular of the CHO moiety within the molecule, arises from attack by "H$^-$" at the coordinated CO of [CpRu(CO)(η^4-C$_4$Ph$_4$)][BF$_4$]. Initially, this would lead to the generation of a neutral formyl complex (H). Intramolecular migration of the formyl group onto the endo face of the C$_4$ ring, followed by conrotatory ring-opening of the resultant η^3-cyclobutadenyl ligand (I), would then afford via J the green complex **15**.

Table VI. Selected Bond Lengths (Å) for 16•OEt$_2$

Ru(1)–Ru(2)	2.802 (2)	Ru(1)–C(1)	2.058 (11)
Ru(1)–C(3)	1.887 (12)	Ru(1)–C(4)	2.375 (9)
Ru(1)–C(5)	2.157 (9)	Ru(1)–C(6)	2.165 (11)
Ru(1)–C(7)	2.346 (10)	Ru(1)–C(8)	2.313 (10)
Ru(1)–C(9)	2.366 (9)	Ru(2)–C(1)	2.066 (11)
Ru(2)–C(2)	1.853 (11)	Ru(2)–C(8)	2.073 (11)
Ru(2)–C(16)	2.248 (17)	Ru(2)–C(17)	2.286 (13)
Ru(2)–C(18)	2.297 (13)	Ru(2)–C(19)	2.279 (14)
Ru(2)–C(20)	2.226 (16)	O(1)–C(1)	1.178 (11)
O(2)–C(2)	1.155 (14)	O(3)–C(3)	1.141 (15)
O(4)–C(2a)	1.388 (28)	O(4)–C(2b)	1.229 (36)
C(4)–C(5)	1.497 (15)	C(4)–C(7)	1.450 (15)
C(4)–C(41)	1.461 (15)	C(5)–C(6)	1.506 (14)
C(5)–C(51)	1.480 (13)	C(6)–C(7)	1.471 (16)
C(6)–C(61)	1.475 (17)	C(7)–C(71)	1.473 (14)
C(8)–C(9)	1.414 (15)	C(8)–C(81)	1.489 (12)
C(9)–H(9)	0.912 (67)	C(9)–C(91)	1.501 (15)
C(81)–C(86)	1.386 (13)	C(81)–C(82)	1.374 (15)
C(83)–C(84)	1.332 (17)	C(83)–C(82)	1.424 (15)
C(86)–C(85)	1.401 (16)	C(71)–C(76)	1.410 (17)
C(71)–C(72)	1.417 (17)	C(85)–C(84)	1.329 (19)
C(16)–C(17)	1.386 (19)	C(16)–C(20)	1.406 (17)
C(17)–C(18)	1.379 (19)	C(18)–C(19)	1.400 (15)
C(19)–C(20)	1.414 (21)	C(52)–C(51)	1.379 (12)
C(52)–C(53)	1.411 (16)	C(51)–C(56)	1.373 (15)
C(54)–C(55)	1.369 (15)	C(54)–C(53)	1.367 (18)
C(55)–C(56)	1.381 (16)	C(62)–C(63)	1.424 (20)
C(62)–C(61)	1.405 (16)	C(63)–C(64)	1.363 (14)
C(66)–C(61)	1.389 (13)	C(66)–C(65)	1.377 (19)
C(64)–C(65)	1.379 (17)	C(43)–C(42)	1.428 (18)
C(43)–C(44)	1.371 (18)	C(45)–C(46)	1.387 (16)
C(45)–C(44)	1.343 (16)	C(46)–C(41)	1.391 (15)
C(41)–C(42)	1.404 (15)	C(74)–C(73)	1.386 (19)
C(74)–C(75)	1.374 (19)	C(76)–C(75)	1.396 (15)
C(73)–C(72)	1.385 (15)	C(93)–C(94)	1.369 (16)
C(93)–C(92)	1.408 (17)	C(94)–C(95)	1.357 (19)
C(96)–C(91)	1.397 (14)	C(96)–C(95)	1.384 (18)
C(91)–C(92)	1.400 (16)	C(2a)–C(2c)	1.430 (33)
C(2b)–C(2d)	1.454 (36)		

Characterization of **16**, the other product isolated from the reaction, proved more difficult. ^{1}H and ^{13}C{^{1}H} NMR spectra of the material were complex, while an IR spectrum showed the presence of terminal and bridging carbonyl ligands, indicative of a polynuclear complex. In consequence a single-crystal X-ray study was required to establish the nature of **16**.

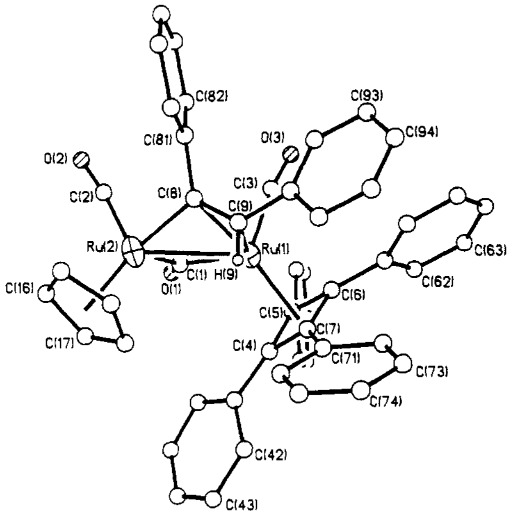


Figure 3. Molecular structure of **16** showing labeling scheme. All phenyl and cyclopentadienyl group hydrogen atoms have been omitted for clarity.

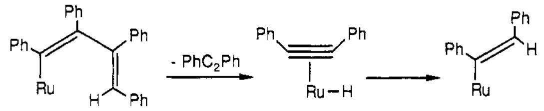
As shown in Figure 3 and by the data listed in Tables VI and VII, the solid-state structure of **16** consists of two ruthenium atoms, Ru(1) and Ru(2), at a single-bond distance of 2.802 (2) Å and bridged by carbonyl and (*Z*)-1,2-diphenylvinyl ligands. Each ruthenium bears a terminal carbonyl ligand, and Ru(1) and Ru(2) are further coordinated by η^4-tetraphenylcyclobutadiene and η^5-cyclopentadienyl ligands, respectively. The $Ru_2(CO)_2(\mu\text{-}CO)$ unit shows cis stereochemistry. The μ-vinyl ligand has phenyl groups as cis substituents, with the CHPh group in a position syn to the cyclopentadienyl group. This latter observation is in contrast to the structure of the cation $[Cp_2Ru_2(CO)_2(\mu\text{-}C(Ph){=}CH(Ph))]^+$, wherein it was observed[19] that the μ-vinyl ligand showed a preference for anti orientation. Also of note is the finding that the tetraphenylcyclobutadiene ligand is somewhat asymmetrically bound to Ru(1). This is reflected in the ruthenium-to-ring carbon distances of 2.375 (9), 2.157 (9), 2.165 (11), and 2.347 (10) Å for C(4), C(5), C(6), and C(7) respectively. Those ring carbons that are furthest from Ru(1) (C(4) and C(7)) are most nearly trans to C(3), the C(3)–Ru(1)–C(ring) angles being 137.3 (4), 99.3 (4), 91.6 (5), and 127.6 (5)° for C(4)–C(7), respectively.

The mechanism of formation of the dinuclear complex **16** is clearly complicated, and detailed speculation is unwarranted. However, two mechanistic observations are justified. The first is that the right-hand side, i.e., the η^4-C_4Ph_4 substituted, of the molecule is presumably formed by initial attack by "H^-" on the exo face of the cyclopentadienyl ring, thus forming the labile Ru(0) species $Ru(CO)(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)$ analogous to **9**. The left-hand side of the molecule poses a more serious problem in that it requires an unprecedented fragmentation of one of the carbon–carbon bonds originally present in the η^4-cyclobutadiene ring. One way of achieving this would be via initial competitive exo attack by "H^-" on the η^4-cyclobutadiene ring of **1** followed by conrotatory ring opening to access a σ-butadienyl species carrying a hydrogen substituent on the inside position. As is illustrated in Scheme VIII a fragmentation reaction initiated by a 1,6-interaction between an unsaturated ruthenium center and the inside hydrogen could lead to the formation of uncoordinated PhC_2Ph and a (*Z*)-1,2-diphenylvinyl ligand. Interaction with the Ru(0) complex with displacement of C_5H_6 could then afford **16**.

Table VII. Selected Bond Angles (deg) for 16•OEt$_2$

Ru(2)–Ru(1)–C(1)	47.3 (3)	Ru(2)–Ru(1)–C(3)	110.8 (4)
C(1)–Ru(1)–C(3)	95.6 (5)	Ru(2)–Ru(1)–C(4)	104.3 (3)
C(1)–Ru(1)–C(4)	90.6 (4)	C(3)–Ru(1)–C(4)	137.3 (4)
Ru(2)–Ru(1)–C(5)	129.1 (3)	C(1)–Ru(1)–C(5)	91.0 (4)
C(3)–Ru(1)–C(5)	99.3 (4)	C(4)–Ru(1)–C(5)	38.2 (4)
Ru(2)–Ru(1)–C(6)	157.6 (3)	C(1)–Ru(1)–C(6)	131.7 (4)
C(3)–Ru(1)–C(6)	91.6 (5)	C(4)–Ru(1)–C(6)	54.9 (4)
C(5)–Ru(1)–C(6)	40.8 (4)	Ru(2)–Ru(1)–C(7)	120.7 (3)
C(1)–Ru(1)–C(7)	125.6 (4)	C(3)–Ru(1)–C(7)	127.7 (5)
C(4)–Ru(1)–C(7)	35.8 (3)	C(5)–Ru(1)–C(7)	55.0 (3)
C(6)–Ru(1)–C(7)	37.8 (4)	Ru(2)–Ru(1)–C(8)	46.6 (3)
C(1)–Ru(1)–C(8)	87.4 (4)	C(3)–Ru(1)–C(8)	86.7 (4)
C(4)–Ru(1)–C(8)	135.8 (4)	C(5)–Ru(1)–C(8)	173.8 (4)
C(6)–Ru(1)–C(8)	140.8 (4)	C(7)–Ru(1)–C(8)	121.7 (3)
Ru(2)–Ru(1)–C(9)	71.3 (3)	C(1)–Ru(1)–C(9)	118.1 (4)
C(3)–Ru(1)–C(9)	99.8 (4)	C(4)–Ru(1)–C(9)	114.2 (3)
C(5)–Ru(1)–C(9)	143.1 (4)	C(6)–Ru(1)–C(9)	107.4 (4)
C(7)–Ru(1)–C(9)	88.5 (3)	C(8)–Ru(1)–C(9)	35.2 (4)
Ru(1)–Ru(2)–C(1)	47.1 (3)	Ru(1)–Ru(2)–C(2)	108.4 (4)
C(1)–Ru(2)–C(2)	84.8 (4)	Ru(1)–Ru(2)–C(8)	54.2 (3)
C(1)–Ru(2)–C(8)	93.9 (4)	C(2)–Ru(2)–C(8)	91.4 (5)
Ru(1)–Ru(2)–C(16)	152.7 (3)	C(1)–Ru(2)–C(16)	120.8 (4)
C(2)–Ru(2)–C(16)	92.4 (5)	C(8)–Ru(2)–C(16)	145.2 (4)
Ru(1)–Ru(2)–C(17)	117.1 (4)	C(1)–Ru(2)–C(17)	96.2 (4)
C(2)–Ru(2)–C(17)	117.5 (5)	C(8)–Ru(2)–C(17)	150.1 (4)
C(16)–Ru(2)–C(17)	35.6 (5)	Ru(1)–Ru(2)–C(18)	96.8 (4)
C(1)–Ru(2)–C(18)	103.4 (4)	C(2)–Ru(2)–C(18)	151.2 (5)
C(8)–Ru(2)–C(18)	115.1 (4)	C(16)–Ru(2)–C(18)	59.5 (5)
C(17)–Ru(2)–C(18)	35.0 (5)	Ru(1)–Ru(2)–C(19)	109.3 (4)
C(1)–Ru(2)–C(19)	136.5 (4)	C(2)–Ru(2)–C(19)	137.4 (5)
C(8)–Ru(2)–C(19)	94.8 (5)	C(16)–Ru(2)–C(19)	60.4 (5)
C(17)–Ru(2)–C(19)	59.1 (5)	C(18)–Ru(2)–C(19)	35.6 (4)
Ru(1)–Ru(2)–C(20)	144.9 (4)	C(1)–Ru(2)–C(20)	155.7 (4)
C(2)–Ru(2)–C(20)	102.0 (5)	C(8)–Ru(2)–C(20)	109.0 (5)
C(16)–Ru(2)–C(20)	36.6 (5)	C(17)–Ru(2)–C(20)	59.9 (5)
C(18)–Ru(2)–C(20)	60.1 (5)	C(19)–Ru(2)–C(20)	36.6 (5)
C(2a)–O(4)–C(2b)	143.3 (21)	Ru(1)–C(1)–Ru(2)	85.6 (4)
Ru(1)–C(1)–O(1)	136.9 (10)	Ru(2)–C(1)–O(1)	137.5 (10)
Ru(2)–C(2)–O(2)	173.5 (12)	Ru(1)–C(3)–O(3)	170.1 (10)
Ru(1)–C(4)–C(5)	63.0 (5)	Ru(1)–C(4)–C(7)	71.1 (5)
C(5)–C(4)–C(7)	90.1 (9)	Ru(1)–C(4)–C(41)	133.0 (8)
C(5)–C(4)–C(41)	130.3 (8)	C(7)–C(4)–C(41)	137.7 (9)
Ru(1)–C(5)–C(4)	78.8 (5)	Ru(1)–C(5)–C(6)	69.9 (5)
C(4)–C(5)–C(6)	88.8 (8)	Ru(1)–C(5)–C(51)	131.0 (7)
C(4)–C(5)–C(51)	132.9 (8)	C(6)–C(5)–C(51)	131.9 (10)
Ru(1)–C(6)–C(5)	69.3 (6)	Ru(1)–C(6)–C(7)	77.8 (6)
C(5)–C(6)–C(7)	89.0 (8)	Ru(1)–C(6)–C(61)	128.6 (6)
C(5)–C(6)–C(61)	131.3 (9)	C(7)–C(6)–C(61)	135.4 (9)
Ru(1)–C(7)–C(4)	73.2 (5)	Ru(1)–C(7)–C(6)	64.4 (5)
C(4)–C(7)–C(6)	92.0 (8)	Ru(1)–C(7)–C(71)	128.2 (6)
C(4)–C(7)–C(71)	133.1 (10)	C(6)–C(7)–C(71)	134.1 (10)
Ru(1)–C(8)–Ru(2)	79.2 (3)	Ru(1)–C(8)–C(9)	74.5 (6)
Ru(2)–C(8)–C(9)	119.6 (7)	Ru(1)–C(8)–C(81)	131.6 (8)
Ru(2)–C(8)–C(81)	120.0 (8)	C(9)–C(8)–C(81)	118.2 (8)
Ru(1)–C(9)–C(8)	70.4 (5)	Ru(1)–C(9)–H(9)	93.6 (38)
C(8)–C(9)–H(9)	124.8 (48)	Ru(1)–C(9)–C(91)	118.2 (7)
C(8)–C(9)–C(91)	128.4 (8)	H(9)–C(9)–C(91)	106.0 (47)

Scheme VIII



A key feature of this rationale is the idea that "H^-" can also be competitively delivered to the exo face of the η^4-cyclobutadiene ring. Support for this came from a study of the reaction between **1** and $NaBH_4$ in tetrahydrofuran. At 0 °C a smooth reaction occurred, leading to the formation of an orange solution. Workup afforded a yellow crystalline solid (**17**, 11% yield), together with an extensive amount of decomposed material. In contrast to the products obtained from the reaction of $[CpRu(CO)(\eta^4$-

---

(19) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426.

Table VIII. Structure Analysis

	5	12	$16 \cdot C_4H_{10}O$
Crystal Data			
formula	$C_{33}H_{26}Ru$	$C_{36}H_{35}O_3PRu$	$C_{54}H_{46}O_4Ru_2$
M_r	523.6	647.7	961.1
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	Cc (No. 9)	$P2_1/c$ (No. 14)
a, Å	10.156 (5)	18.226 (6)	15.763 (11)
b, Å	10.996 (5)	12.190 (4)	15.928 (9)
c, Å	13.145 (6)	27.447 (15)	18.914 (9)
α, deg	112.12 (4)	90	90
β, deg	101.20 (4)	94.31 (4)	112.58 (5)
γ, deg	103.76 (4)	90	90
V, Å^3	1253.4 (9)	6080 (4)	4385 (5)
T, K	295	295	295
Z	2	8	4
D_c, g cm^{-3}	1.39	1.42	1.46
$F(000)$	536	2672	1892
μ(Mo Kα), cm^{-1}	6.3	5.9	7.2
Data Collection and Reduction			
cryst dimens, mm	0.075 × 0.25 × 0.40	0.3 × 0.4 × 0.5	0.5 × 0.2 × 0.2
wavelength, Å	0.71069	0.71069	0.71069
2θ range, deg	4–50	3–50	3–46
scan method	ω–2θ	ω–2θ	ω–2θ
scan width ω, deg	$1.0 + \Delta\alpha_1\alpha_2$	$1.1 + \Delta\alpha_1\alpha_2$	$1.0 + \Delta\alpha_1\alpha_2$
total data	4749	5717	5024
unique data	4315	5448	3884
"obsd" data (NO)	3321	5066	3014
obsd criterion $[F^2 > n\sigma(F^2)]$	2	2	2
cryst faces [dist from origin, mm]		(001) [0.20], $(00\bar{1})$ [0.20], (120) [0.133], (111) [0.266], $(\bar{1}\bar{1}0)$ [0.133], $(\bar{1}10)$ [0.266]	
min, max trans coeff		0.790–0.861	
Refinement			
disordered atoms	none	hexane	none
least-squares variables (NV)	311	409	345
R^a	0.044	0.042	0.054
$R_w{}^a$	0.048	0.053	0.058
S^a	1.21	1.80	1.37
g	0.0005	0.0004	0.0005
final diff map features, e Å^{-3}	+0.55, −0.36	+0.65, −0.47	+0.97, −0.59

[a] $R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum w\Delta^2/\sum wF_o{}^2]^{1/2}$; $S = [\sum w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$; $w = [\sigma_c{}^2(F_o) + gF_o{}^2]^{-1}$, $\sigma_c{}^2(F_o)$ = variance in F_o due to counting statistics.

$C_4Ph_4)][BF_4]$ (1) with $K[BHBu^s{}_3]$, the IR spectrum of 17 showed the presence of one terminal band at 1935 cm^{-1}. The ^1H NMR spectrum contained resonances (δ 7.59–6.98) due to phenyl protons (20 H) and cyclopentadienyl protons at δ 4.66 (s, 5 H) as well as a one-proton singlet at δ 4.02. That hydride anion attack had occurred at the cyclobutadiene ligand was confirmed by $^{13}C\{^1H\}$ NMR, the single resonance for the cyclobutadiene ring being replaced by resonances at δ 76.1 and 73.3, which are ascribed to the coordinated olefinic carbons of the butadienyl unit (C(3) and C(4)), while C(1) and C(2) lie in the phenyl regions of the spectrum. Comparison of the chemical shift of the C*H*Ph proton at the end of the butadienyl chain with that observed in 12 suggests that it also occupies an inside position. Such an arrangement would arise by exo attack by "H$^-$" on the C_4 ring followed by a conrotatory ring-opening reaction as shown in Scheme IX. The thermolysis of 17 led to extensive decomposition.

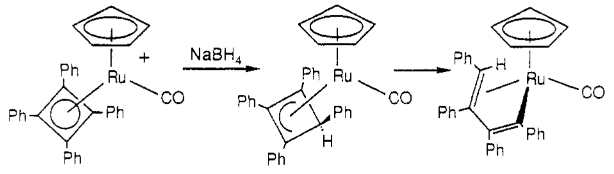
Conclusion

A study of ring-opening reactions of cyclobutadiene ruthenium complexes has established the structural identity of a new organic ligand, viz., the η^4(5e)-butadienyl fragment. Experiments are described that show that this species may be viewed as a masked or latent coordinatively unsaturated η^3(3e)-butadienyl ligand.

Experimental Section

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL FX 200 or Bruker WH-360 spectrometers. Data are given for room-temperature measurements unless otherwise stated. Chemical shifts are positive to high frequency of the reference $SiMe_4$ for ^{13}C and ^1H, and H_3PO_4 (85% external) for ^{31}P. IR spectra were recorded on Perkin-Elmer 257 and 983G spectrophotometers. All reactions were carried out in Schlenk tubes under atmospheres of dry oxygen-free nitrogen, using freshly distilled and degassed solvents. Neutral alumina was used.

Scheme IX

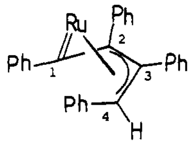


(1) (17)

Preparation of $[CpRu(PPh_3)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (2). A solution of $[CpRu(CO)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (1, 0.25 g, 0.29 mmol) and triphenylphosphine (0.30 g, 1.15 mmol) in dichloromethane (35 mL) contained in a water-cooled quartz reactor was irradiated with UV light (500-W lamp) for 16 h. Volatile material was removed in vacuo, and the residue redissolved in CH_2Cl_2 (5 mL) and filtered. Addition of Et_2O gave an orange precipitate, which was collected and recrystallized (0 °C) from CH_2Cl_2/Et_2O (4:1) to give orange crystals of 2 (0.25 g, 73%). Anal. Calcd for $C_{51}H_{40}BF_4PRu$: C, 70.21; H, 4.63. Found: C, 70.26; H, 4.85. ^1H NMR (CD_3NO_2) δ 7.54–7.07 (complex m, 35 H, Ph), 5.10 (d, 5 H, J_{HP} = 1.3 Hz, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 136.2–129.1 (Ph), 93.3 (C_5H_5), 87.6 (C_4Ph_4); $^{31}P\{^1H\}$ (acetone-d_6) δ 40.1 (PPh_3).

Preparation of $[CpRu(P(OMe)_3)(\eta^4\text{-}C_4Ph_4)][BF_4]$ (3). Similarly, irradiation (16 h) of a solution of 1 (0.25 g, 0.29 mmol) and trimethyl phosphite (0.4 mL, 34 mmol) in dichloromethane (150 mL) afforded on recrystallization (0 °C) from CH_2Cl_2/Et_2O (4:1) orange crystals of **3** (0.90 g, 78%). Anal. Calcd for $C_{36}H_{34}BF_4O_3PRu$: C, 58.90; H, 4.67. Found: C, 58.90; H, 4.62. ^1H NMR (CD_3NO_2) δ 7.37 (m, 20 H, Ph), 5.35 (s, 5 H, $C_5\mathit{H}_5$), 3.51 (d, 9 H, J_{HP} = 12.0 Hz, $POC\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 132.6 (Ph), 131.8 (Ph), 130.3 (Ph), 129.7 (Ph), 91.7 (C_5H_5), 87.6 (C_4Ph_4), 55.7 (d, J_{CP} = 7.8 Hz, $POCH_3$); $^{31}P\{^1H\}$ NMR (CD_3NO_2) δ 137.6 (s, $\mathit{P}OCH_3$).

Preparation of CpRu=C(Ph)-η^3-(C(Ph)C(Ph)CH(Ph)) (5). A solution of K[$BHBu^s_3$] (1.45 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of [CpRu(NCMe)(η^4-C_4Ph_4)][BF_4] (**4**, 0.95 g, 1.45 mmol) in tetrahydrofuran (18 mL). After stirring for 15 min at this temperature, the mixture was allowed to warm slowly to room temperature, whereupon a purple solution rapidly formed. The volatile material was removed in vacuo, and the residue extracted into diethyl ether/hexane (2:1) (10 mL) and chromatographed on an alumina-packed column. Elution with diethyl ether/hexane (1:5) afforded a purple band, which was collected and recrystallized (-78 °C) from hexane to give purple crystals of **5** (0.65 g, 85%). Anal. Calcd for $C_{36}H_{26}Ru$: C, 75.69; H, 5.00. Found: C, 76.07; H, 5.14. ^1H NMR (C_6D_6) δ 7.56–6.42 (m, 20 H, Ph), 6.43 (s, 1 H, $C\mathit{H}Ph$), 4.89 (s, 5 H, $C_5\mathit{H}_5$); $^{13}C\{^1H\}$ NMR ($C_6D_6CD_3$) δ 246.0 (C_1), 151.5–123.3 (Ph), 97.5 (C_3), 95.0 (C_2), 82.6 (C_5H_5), 55.1 (C_4); ^1H-coupled ^{13}C NMR (C_6D_6) δ 248.8 (t, C_1, $^3J_{CH}$ = 4.6 Hz), 142.7–122.0 (m, Ph), 100.1 (t, C_3, $^3J_{CH}$ = 4.1 Hz), 97.9 (t, C_2, $^3J_{CH}$ = 4.1 Hz), 85.1 (m, C_5H_5, $^1J_{CH}$ = 175.7, $^2J_{CH}$ = 6.6 Hz), 57.8 (d, C_4, $^1J_{CH}$ = 147.6 Hz); MS, m/z 523 (M^+).



5

Reaction of 2 with K[$BHBu^s_3$]. To a suspension of **2** (0.70 g, 0.80 mmol) in tetrahydrofuran (15 mL), K[$BHBu^s_3$] (0.80 mmol) was added at -78 °C. On warming to room temperature, a slow reaction occurred. After stirring for 10 min, volatiles were removed in vacuo; the residue was extracted into dichloromethane (5 mL) and chromatographed on alumina. Elution with hexane/diethyl ether (10:1) afforded a purple band, which was collected and recrystallized, being identified by NMR as **5** (0.19 g, 45%). Further elution with hexane/diethyl ether (3:1) gave a yellow band, which on recrystallization (-78 °C) from CH_2Cl_2/hexane (1:2) afforded yellow microcrystals of [Ru(PPh_3)(η^4-C_4Ph_4)]$_x$ (**6**, 0.28 g, 49%). Anal. Calcd for $C_{46}H_{35}RuP$: C, 76.77; H, 4.876. Found: C, 76.31; H, 4.54. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 139.1–121.0 (Ph), 79.3 (C_4Ph_4); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 62.1 (PPh_3).

Preparation of Ru(P(OMe)$_3$)$_2$(PPh$_3$)(η^4-C$_4$Ph$_4$) (7). A solution of K[$BHBu^s_3$] (0.26 mmol) was added to a stirred and cooled (-78 °C) solution of **2** (0.43 g, 0.49 mmol) and $P(OMe)_3$ (1.5 g, 12.1 mmol) in tetrahydrofuran (12 mL). The reaction mixture was allowed to warm to room temperature, the volatiles were removed in vacuo, and the residue was extracted into diethyl ether (10 mL) and chromatographed on an alumina-packed column. Elution with hexane/diethyl ether (1:2) gave a yellow band, which was collected and recrystallized (-78 °C) from hexane/diethyl ether to give bright yellow crystals of **7** (0.23 g, 48%). Anal. Calcd for $C_{52}H_{53}RuO_6P_3$: C, 64.52; H, 5.52. Found: C, 64.61; H, 6.02. ^1H NMR ($CDCl_3$) δ 7.45–6.95 (m, 35 H, Ph), 3.08 (br s, 18 H, POMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 138.2–123.9 (Ph), 74.3 (C_4Ph_4), 51.9 (POMe); $^{31}P\{^1H\}$ ($CDCl_3$) δ 151.2 (d, J_{PP} = 45.2 Hz, $\mathit{P}(OMe)_3$), 57.4 (t, J_{PP} = 45.2 Hz, $\mathit{P}Ph_3$).

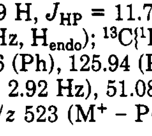
Preparation of Ru(PPh$_3$)(CO)$_2$(η^4-C$_4$Ph$_4$) (8). Similarly, CO was passed through a cooled (-78 °C) suspension of **2** (0.225 g, 0.26 mmol) in tetrahydrofuran (12 mL) for 10 min, to which K[$BHBu^s_3$] (0.26 mmol) was then added. After stirring at this temperature for 15 min, the mixture was allowed to warm to room temperature, CO being bubbled continuously through the mixture during this time. Volatiles were then removed in vacuo, and the residue was extracted into diethyl ether (10 mL) and chromatographed. Elution with hexane/diethyl ether (1:2) afforded a yellow band, which was then reduced in volume in vacuo and cooled to -78 °C to yield pale yellow crystals of **8** (0.18 g, 91%). Anal. Calcd for $C_{48}H_{35}O_2PRu$: C, 74.31; H, 4.55. Found: C, 73.96; H, 4.53. IR (CH_2Cl_2) ν_{CO} 1905(s) cm^{-1}.

Table IX. Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for 5

	x	y	z	U^a
Ru	4462 (1)	645 (1)	2701 (1)	46 (1)
C(1)	3124 (4)	1489 (4)	3179 (3)	43 (2)
C(2)	2136 (4)	210 (4)	2253 (3)	38 (2)
C(3)	2568 (4)	-218 (4)	1234 (3)	39 (2)
C(4)	3673 (5)	784 (4)	1119 (4)	43 (2)
C(11)	2839 (5)	2553 (4)	4088 (3)	45 (2)
C(12)	1482 (5)	2625 (5)	3999 (4)	54 (2)
C(13)	1224 (7)	3645 (6)	4853 (5)	69 (3)
C(14)	2358 (7)	4637 (6)	5824 (5)	80 (3)
C(15)	3711 (7)	4604 (6)	5925 (4)	78 (3)
C(16)	3966 (6)	3567 (5)	5066 (4)	62 (2)
C(21)	919 (4)	-683 (4)	2409 (3)	40 (2)
C(22)	1064 (5)	-775 (5)	3451 (4)	53 (2)
C(23)	-105 (6)	-1535 (5)	3618 (5)	65 (3)
C(24)	-1404 (6)	-2193 (5)	2776 (5)	68 (3)
C(25)	-1552 (5)	-2121 (5)	1750 (4)	58 (2)
C(26)	-408 (5)	-1361 (5)	1564 (4)	49 (2)
C(31)	1965 (4)	-1698 (4)	305 (3)	40 (2)
C(32)	1963 (5)	-2833 (5)	531 (4)	52 (2)
C(33)	1411 (5)	-4174 (5)	-357 (4)	61 (3)
C(34)	839 (5)	-4396 (5)	-1473 (4)	58 (2)
C(35)	806 (5)	-3294 (5)	-1710 (4)	54 (2)
C(36)	1370 (5)	-1956 (5)	-831 (4)	47 (2)
C(41)	3780 (4)	2191 (4)	1214 (3)	40 (2)
C(42)	4933 (5)	2928 (4)	1007 (4)	47 (2)
C(43)	5094 (5)	4224 (5)	1059 (4)	56 (2)
C(44)	4099 (6)	4838 (5)	1311 (4)	64 (3)
C(45)	2928 (6)	4135 (5)	151 (4)	62 (3)
C(46)	2767 (5)	2823 (5)	1458 (4)	50 (2)
C(50)	6699 (6)	1657 (8)	3795 (8)	110 (5)
C(51)	6661 (7)	917 (13)	2692 (9)	155 (8)
C(53)	5644 (7)	-545 (8)	3317 (7)	106 (5)
C(54)	6062 (7)	765 (9)	4165 (6)	92 (4)
C(52)	6006 (8)	-499 (10)	2396 (6)	142 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. See pp 314–316 in ref 22.

Preparation of Ru(P(OMe)$_3$)(η^4-C$_4$Ph$_4$)(η^4-C$_5$H$_6$) (9). To **3** (0.40 g, 0.55 mmol), in tetrahydrofuran (30 mL) at -78 °C, was added K[$BHBu^s_3$] (0.55 mmol). After stirring at this temperature for 30 min, the mixture was allowed to warm to room temperature, when the volatiles were removed in vacuo. The residue was extracted into CH_2Cl_2 (2 mL), and chromatographed on alumina. Elution with diethyl ether/hexane (1:4) afforded a single yellow band, which was collected, and the volume was reduced in vacuo to 2 mL, affording a yellow crystalline material, which was washed with hexane and dried in vacuo to give crystals of **9** (0.30 g, 85%). Anal. Calcd for $C_{36}H_{35}O_3PRu$: C, 66.70; H, 5.45. Found: C, 66.60; H, 5.23. ^1H NMR ($C_6D_5CD_3$) δ 7.5–7.35 (m, 8 H, o-Ph), 7.17–6.9 (m, 12 H, m,p-Ph), 4.58 (br s, 2 H, H_1), 3.97 (br s, 2 H, H_2), 3.37 (m, 1 H, H_{exo}), 3.21 (d, 9 H, J_{HP} = 11.7 Hz, $POC\mathit{H}_3$), 3.03 (d, 1 H, $J(H_{exo}H_{endo})$ = 12.7 Hz, H_{endo}); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 138.03 (Ph), 129.97 (Ph), 127.76 (Ph), 125.94 (Ph), 88.90 (C_4Ph_4), 74.21 (C_1), 61.63 (d, C_2, J_{CP} = 2.92 Hz), 51.08 ($PO\mathit{C}H_3$), 46.28 (d, C_3, J_{CP} = 16.1 Hz); MS, m/z 523 (M^+ - $P(OCH_3)_3$).



Reaction of 2 with Li[BDEt$_3$]. To **2** (0.16 g, 0.18 mmol) in tetrahydrofuran (10 mL) at -78 °C, was added Li[$BDEt_3$] (0.18 mmol). The mixture was allowed to warm to room temperature, when volatiles were removed in vacuo. The residue was extracted into CH_2Cl_2 (2 mL) and chromatographed on alumina. Elution with hexane/diethyl ether (10:1) afforded first a purple band, which was collected and recrystallized (-78 °C) from hexane to give purple crystals (0.04 g 40%) of **5**-D: ^1H NMR (C_6D_6) δ 7.56–6.5 (m, 20 H, Ph), 6.42 (s, 1 H, $C\mathit{H}Ph$), 4.90 (s, 4 H, $C_5\mathit{H}_4D$);

Table X. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 12

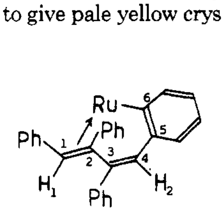
	x	*y*	*z*	*U*^{a}		*x*	*y*	*z*	*U*^{a}
Ru(1)	0	1114 (1)	0	32 (1)*	Ru(2)	9519 (1)	6455 (1)	2452 (1)	37 (1)*
P(1)	860 (1)	1062 (2)	614 (1)	43 (1)*	P(2)	8671 (1)	6537 (2)	1827 (1)	45 (1)*
O(1)	689 (3)	1535 (4)	1137 (2)	55 (2)*	O(21)	8853 (3)	6070 (5)	1306 (2)	65 (2)*
O(2)	1600 (3)	1743 (6)	569 (2)	60 (2)*	O(22)	7931 (3)	5843 (6)	1873 (3)	68 (2)*
O(3)	1127 (3)	−137 (4)	777 (2)	48 (2)*	O(23)	8417 (3)	7733 (5)	1667 (2)	54 (2)*
C(71)	2071 (5)	1533 (9)	180 (4)	69 (4)*	C(210)	9149 (3)	7968 (5)	2676 (2)	33 (2)*
C(1)	380 (4)	−392 (5)	−218 (2)	36 (2)*	C(220)	9741 (4)	8603 (5)	2621 (2)	36 (2)*
C(4)	−596 (4)	84 (5)	525 (2)	36 (2)*	C(230)	10299 (4)	7872 (6)	2415 (3)	37 (2)*
C(61)	383 (6)	2595 (9)	1190 (4)	76 (4)*	C(240)	10122 (3)	7485 (5)	1928 (2)	37 (2)*
C(81)	1636 (6)	−357 (10)	1186 (4)	85 (4)*	C(62)	9135 (7)	5009 (9)	1240 (5)	83 (4)*
C(50)	−585 (3)	2787 (4)	−86 (2)	49 (2)*	C(72)	7445 (6)	6092 (10)	2246 (5)	90 (4)*
C(51)	−858	2108	−480	49 (2)*	C(82)	7893 (6)	7952 (10)	1265 (4)	85 (4)*
C(52)	−258	1812	−753	55 (3)*	C(250)	10349 (3)	5443 (5)	2929 (3)	61 (3)*
C(53)	387	2307	−529	57 (3)*	C(251)	10072	4771	2534	58 (3)*
C(54)	185	2910	−117	54 (3)*	C(252)	9301	4662	2563	71 (4)*
C(2)	−181 (3)	−1043 (5)	−160 (2)	33 (2)*	C(253)	9101	5266	2975	68 (4)*
C(3)	−764 (4)	−326 (5)	50 (3)	34 (2)*	C(254)	9749	5749	3201	72 (4)*
C(12)	1600 (3)	−1326 (4)	−123 (2)	48 (2)	C(212)	7992 (2)	9038 (4)	2561 (2)	45 (2)
C(13)	2303	−1519	−273	62 (2)	C(213)	7278	9272	2682	56 (2)
C(14)	2513	−1054	−706	63 (2)	C(214)	6990	8740	3075	56 (2)
C (15)	2019	−397	−988	64 (2)	C(215)	7416	7974	3348	50 (2)
C(16)	1317	−204	−838	54 (2)	C(216)	8129	7740	3228	40 (2)
C(11)	1107	−668	−405	39 (2)	C(211)	8417	8272	2834	35 (1)
C(22)	80 (3)	−2723 (4)	−642 (2)	50 (2)	C(222)	9471 (2)	10289 (4)	3096 (2)	44 (2)
C(23)	−48	−3821	−765	60 (2)	C(223)	9602	11387	3215	61 (2)
C(24)	−576	−4417	−535	73 (2)	C(224)	10142	11971	2991	62 (2)
C(25)	−976	−3916	−182	70 (2)	C(225)	10551	11455	2647	66 (2)
C(26)	−848	−2819	−60	53 (2)	C(226)	10420	10356	2528	55 (2)
C(21)	−320	−2222	−290	43 (2)	C(221)	9880	9773	2753	35 (1)
C(32)	−1526 (2)	−367 (4)	−735 (2)	47 (2)	C(232)	11116 (2)	7800 (4)	3192 (2)	46 (2)
C(33)	−2198	−448	−1011	56 (2)	C(233)	11806	7847	3448	56 (2)
C(34)	−2852	−496	−778	67 (2)	C(234)	12438	7958	3195	56 (2)
C(35)	−2833	−464	−269	62 (2)	C(235)	12380	8023	2686	61 (2)
C(36)	−2161	−383	7	50 (2)	C(236)	11690	7976	2430	46 (2)
C(31)	−1507	−335	−226	39 (2)	C(231)	11058	7865	2683	35 (1)
C(42)	−1593 (3)	1474 (4)	683 (2)	46 (2)	C(242)	11104 (3)	6083 (4)	1760 (2)	48 (2)
C(43)	−1969	2096	1011	63 (2)	C(243)	11480	5491	1422	62 (2)
C(44)	−1807	1970	1512	72 (3)	C(244)	11336	5683	923	70 (3)
C(45)	−1271	1222	1686	64 (2)	C(245)	10816	6467	762	66 (3)
C(46)	−896	600	1358	50 (2)	C(246)	10439	7059	1100	53 (2)
C(41)	−1057	726	857	39 (2)	C(241)	10584	6867	1599	39 (2)

[a] Asterisks indicate equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

^{2}H NMR (C_6H_6), δ 4.90 (br s, C_5H_4D). Further elution afforded yellow **6** (0.07 g 45%).

Reaction of 3 with Li[BDEt$_3$]. To a suspension of **3** (0.08 g, 0.10 mmol) in tetrahydrofuran (8 mL), Li[BDEt$_3$] (0.10 mmol) was added at −78 °C. After stirring at this temperature for 15 min, the mixture was allowed to warm slowly to room temperature, whereupon a yellow solution formed. Workup as for **9** afforded yellow crystals of **9**-D (0.06 g, 91%): ^{1}H NMR (C_6D_6) δ 7.49–7.39 (m, 8 H, *o*-Ph), 7.08–6.93 (m, 12 H, *m*,*p*-Ph), 4.58 (m, 2 H, H_1), 3.97 (m, 2 H, H_2) 3.21 (d, 9 H, J_{HP} = 11.7 Hz, POCH_3), 3.04 (m, 1 H, H_{endo}).

Thermolysis of 9. A solution of **9** (0.20 g, 0.31 mmol) in tetrahydrofuran (20 mL) was heated (80 °C), in a sealed tube for 5 h. Volatiles were then removed in vacuo, and the residue was extracted into CH_2Cl_2 (2 mL) and chromatographed on alumina. Elution with hexane/diethyl ether (1:4) afforded a single pale yellow band, which was collected and recrystallized (0 °C) from hexane/diethyl ether to give pale yellow crystals of **10** and **11** (0.17 g, 85%).



Anal. Calcd for $C_{36}H_{35}O_3PRu$: C, 66.80; H, 5.45. Found: C, 67.10; H, 5.60. ^{1}H NMR (CD_2Cl_2) (**10**) δ 7.6–6.6 (m, 20 H, Ph), 6.18 (s, 1 H, H_2), 4.64 (d, 5 H, J_{HP} = 0.98 Hz, C_5H_5), 4.31 (d, 1 H, J_{HP} = 10.0 Hz, H_1), 3.52 (d, 9 H, J_{HP} = 11.0 Hz, POCH_3); (**11**) δ 7.6–6.6 (m, 20 H, Ph), 6.37 (s, 1 H, H_2), 4.58 (d, 5 H, J_{HP} = 1.22 Hz, C_5H_5), 4.20 (d, 1 H, J_{HP} = 11.2 Hz, H_1), 3.32 (d, 9 H, J_{HP} = 10.7 Hz, POCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2) (**10**) δ 160.3–119.6 (Ph), 141.5 (C_4), 91.7 (d, J_{CP} = 3.14 Hz, C_5H_5), 90.64 (C_2), 56.79 (d, J_{CP} = 6.13 Hz, C_1), 51.6 (d, J_{CP} = 6.1 Hz, POCH$_3$); (**11**) δ 160.3–119.6 (Ph), 141.1 (C_4), 91.4 (d, J_{CP} = 3.06 Hz, C_5H_5), 81.27 (C_2), 55.23 (d, J_{CP} = 4.59 Hz, C_1), 51.8 (d, J_{CP} = 6.1 Hz, POCH$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2) (**10**) δ 156.3 (*P*OCH$_3$); (**11**) δ 154.2 (*P*OCH$_3$).

Reaction of 5. (a) With Trimethyl Phosphite. To a solution of **5** (0.13 g, 0.25 mmol) in dichloromethane (10 mL), trimethyl phosphite (0.05 g, 0.40 mmol) was added, and the mixture stirred at room temperature for 1 h. After this time the solution had changed color from purple to dark red. Volatiles were then removed in vacuo, and the residue was dissolved in hexane/diethyl ether (1:1, 5 mL) and chromatographed on alumina. Elution with hexane/diethyl ether (3:1) gave a yellow band, which on collection and cooling (−78 °C) afforded orange crystals of **12** (0.10 g, 63%). Anal. Calcd for $C_{36}H_{35}O_3PRu$: C, 66.80; H, 5.45. Found: C, 66.95; H, 5.46. ^{1}H NMR (C_6D_6) δ 7.95–6.63 (m, 20 H, Ph), 4.65 (s, 5 H, C_5H_5), 4.22 (d, 1 H, J_{HP} = 9.5 Hz, C*H*Ph), 2.86 (d, 9 H, J_{HP} = 11.7 Hz, POCH_3); ^{13}C{^{1}H} NMR (C_6D_6), δ 151.8–124.2 (Ph, C_1, C_2), 87.8 (C_5H_5), 68.4 (d, J_{CP} = 7.4 Hz, C_4), 61.9 (C_3), 50.5 (POCH$_3$); MS, *m/z* 648 (M$^+$).

(b) With Triphenylphosphine. A solution of **5** (0.12 g, 0.23 mmol) and PPh$_3$ (0.08 g, 0.29 mmol) in dichloromethane (10 mL) was stirred at room temperature for 16 h. Subsequent workup (as for **12**) of the resulting red-purple solution afforded deep orange crystals of **13** (0.09 g, 15%). Anal. Calcd for $C_{51}H_{41}RuP$: C, 77.94; H, 5.26. Found: C, 77.76; H, 5.18. ^{1}H NMR (C_6D_6) δ 7.89–6.68 (m, 35 H, Ph), 4.57 (s, 5 H, C_5H_5), 4.08 (d, 1 H, J_{HP} = 12.5 Hz, C*H*Ph); ^{13}C{^{1}H} NMR (C_6D_6) δ 147.6–124.1 (Ph, C_1, C_2), 88.8 (d, J_{CP} = 2.2 Hz, C_5H_5), 69.6 (d, J_{CP} = 3.3 Hz, C_4), 63.4 (C_3); ^{31}P{^{1}H} NMR (C_6D_6) δ 51.7 (PPh$_3$); MS, *m/z* 523 (M − PPh$_3$).

Preparation of CpRu$_2$(μ-CO)(μ-(*Z*)-C(Ph)=CH(Ph))(CO)$_2$(η^4-C$_4$Ph$_4$) (16) and CpRu=C(Ph)-η^3-(C(Ph)C(Ph)C-

(Ph)CHO) (15). A solution of K[BHBu$^s_3$] (0.53 mmol) was added dropwise with stirring (−55 °C) to 1 (0.34 g, 0.53 mmol) dissolved in tetrahydrofuran. After 15 min the stirred reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo, and the residue extracted into toluene (5 mL) and applied to an alumina packed column (1 × 30 cm). Elution with diethyl ether/hexane (1:3) afforded an orange band, which was collected and recrystallized (−78 °C) from hexane to give orange crystals of **16** (0.05 g, 20%). Anal. Calcd for $C_{50}H_{36}O_3Ru_2{\cdot}Et_2O$: C, 67.48; H, 4.82. Found: C, 68.10; H, 5.00. IR (CH_2Cl_2) ν_{CO} 1969 (s), 1933 (s), 1795 (s) cm^{-1}. ^{1}H NMR ($(CD_3)_2(CO)$) δ 7.34–6.63 (m, 30 H, Ph), 4.94 (s, 5 H, C_5H_5), 2.83 (s, 1 H, C*H*Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 208.9 (CO), 201.9 (CO), 189.7 (CO), 156.2 (*C*(Ph)=C), 140.3–125.6 (Ph), 93.3 (C_5H_5). Further elution with diethyl ether gave a green band, which on collection and recrystallization (−78 °C) from hexane afforded green crystals of **15** (0.035 g, 12%). Anal. Calcd for $C_{34}H_{26}ORu$: C, 74.02; H, 4.75. Found: C, 73.93; H, 5.00. IR (CH_2Cl_2) ν_{CO} 1643 (m) cm^{-1}; ^{1}H NMR (CD_3NO_2), δ 9.28 (s, 1 H, C*H*O), 7.41–6.56 (m, 20 H, Ph), 5.44 (s, 5 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ 255.2 (C_1), 192.0 (*C*HO), 147.6–125.1 (m, Ph), 109.5 (C_3), 98.0 (C_2), 86.0 (C_5H_5), 73.8 (C_4); ^{1}H-coupled ^{13}C NMR (CD_3NO_2) δ 253.0 (t, C_1, $^3J_{CH}$ = 3.1 Hz), 192.5 (d, CHO, $^1J_{CH}$ = 176.4 Hz), 148.3–122.0 (m, Ph), 109.9 (t, C_3, $^3J_{CH}$ = 3.3 Hz), 98.4 (t, C_2, $^3J_{CH}$ = 3.3 Hz), 86.5 (m, C_5H_5, $^1J_{CH}$ = 176.6 Hz, $^2J_{CH}$ = 6.6 Hz), 73.6 (t, C_4, $^3J_{CH}$ = 2.8 Hz); MS, *m/z* 552 (M^+), 523 (M^+ − CHO), 356 ($M^+ - C_4Ph_4$).

Preparation of CpRuC(Ph)=C(Ph)-*η*^{2}-(C(Ph)=CH(Ph))(CO) (17). $Na[BH_4]$ (0.03 g, 0.79 mmol) was added to a stirred suspension (−30 °C) of [CpRu(CO)(η^4-C_4Ph_4)][BF_4] (0.44 g, 0.69 mmol) in tetrahydrofuran (15 mL). After this was stirred for 15 min at this temperature, no reaction was observed and the mixture was allowed to warm slowly to room temperature, whereupon it became deep orange. After 10 min at room temperature the volatile material was removed in vacuo, and the residue extracted into diethyl ether and chromatographed on alumina. Elution with diethyl ether/hexane (1:2) afforded a yellow band, which was collected and recrystallized (−78 °C) from diethyl ether/hexane to give yellow crystals of **17** (0.07 g, 18%). Anal. Calcd for $C_{34}H_{26}ORu$: C, 74.02; H, 4.75. Found: C, 74.20; H, 4.32. IR (CH_2Cl_2) ν_{CO} 1935 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59–6.98 (m, 20 H, Ph), 4.66 (s, 5 H, C_5H_5), 4.02 (s, 1 H, CH(Ph)); $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ 210.7 (CO), 147.0–125.7 (m, Ph, C_1, C_2), 85.5 (C_5H_5), 76.1 (C_3), 73.3 (C_4).

Structure Determination for 5, 12, and 16·OEt$_2$. Many of the details of the structure analyses carried out on **5**, **12**, and **16**·OEt$_2$ are listed in Table VIII. X-ray diffraction measurements were made using Nicolet four-circle P3m diffractomers on single crystals mounted in thin-walled glass capillaries under N_2 at room temperature. Cell dimensions for each analysis were determined from the setting angle values of 15 centered reflections.

For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarization, crystal decay (negligible in each case), and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. For **16**·OEt$_2$, only reflections with intensity above a low threshold were recorded (>12 counts s^{-1} for $2\theta > 40°$). Corrections for X-ray absorption effects were applied for **12** on the basis of the indexed crystal faces and dimensions. The structures were solved by heavy-atom (Patterson and difference Fourier) methods and refined by blocked-cascade least-squares against *F* until all shift/esd values were <0.1. The space group of **12** was determined by successful structure solution and refinement in *Cc* (attempts to solve the structure in *C*2/*c* being unsuccessful). We note that the two independent molecules are in large part related by a pseudo-center of inversion at ca. (0.48,0.38,0.12). The numbering scheme for atoms of the second independent molecule is based on that of the first molecule, with the digit 2 added ahead of the other digits [e.g., C(2*nn*) being equivalent to C(*nn*)] except for atoms Ru(2), P(2), C(62), C(72), and C(82), which are equivalent to Ru(1), P(1), C(6), C(7), and C(8). The phenyl and cyclopentadienyl rings of the two independent molecules of **12** were constrained to idealized symmetries (D_{6h} and D_{5h}, respectively, with C–C 1.395 Å in the phenyl groups, and 1.42 Å in cyclopentadienyl rings). The ether solvent molecule in **16**·OEt$_2$ shows signs of disorder in having large displacement parameters and distorted geometry, but it was not possible to improve significantly on the model used in refinement.

Table XI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 16•OEt$_2$

	x	*y*	*z*	U^a
Ru(1)	2477 (1)	3165 (1)	2086 (1)	34 (1)*
Ru(2)	3909 (1)	2883 (1)	1583 (1)	43 (1)*
O(1)	2200 (5)	1793 (4)	910 (4)	56 (3)*
O(2)	4669 (6)	1142 (5)	2002 (5)	84 (5)*
O(3)	2364 (5))	1895 (5)	3231 (4)	75 (4)*
O(4)	2732 (10)	9489 (13)	2750 (8)	237 (12)*
C(1)	2638 (7)	2329 (6)	1317 (5)	44 (5)*
C(2)	4367 (7)	1812 (7)	1880 (6)	53 (5)*
C(3)	2483 (7)	2346 (7)	2810 (6)	51 (5)*
C(4)	1364 (7)	3923 (6)	1070 (6)	37 (5)*
C(5)	1018 (6)	3233 (6)	1426 (5)	36 (4)*
C(6)	1267 (6)	3759 (6)	2139 (5)	35 (4)*
C(7)	1616 (7)	4410 (6)	1769 (6)	39 (5)*
C(8)	4060 (7)	3179 (6)	2693 (5)	42 (5)*
C(9)	3764 (6)	3972 (6)	2847 (5)	37 (4)*
C(81)	4699 (7)	2684 (6)	3349 (5)	37 (3)
C(83)	5237 (8)	1445 (8)	4141 (7)	73 (4)
C(86)	5510 (7)	3079 (7)	3799 (6)	56 (3)
C(71)	1941 (7)	5278 (6)	1969 (5)	37 (3)
C(85)	6164 (10)	2632 (8)	4400 (8)	84 (4)
C(84)	6012 (9)	1845 (8)	4552 (8)	83 (4)
C(16)	4546 (10)	2964 (8)	709 (7)	70 (7)*
C(17)	3672 (9)	3292 (9)	364 (7)	61 (6)*
C(18)	3599 (8)	4001 (8)	755 (7)	64 (7)*
C(19)	4447 (9)	4140 (8)	1356 (7)	71 (7)*
C(20)	5039 (9)	3482 (9)	1335 (7)	77 (7)*
C(52)	−410 (7)	2715 (7)	426 (6)	47 (3)
C(51)	325 (7)	2563 (6)	1103 (5)	36 (3)
C(54)	−1070 (8)	1371 (8)	503 (7)	69 (4)
C(55)	−339 (8)	1210 (8)	1172 (7)	70 (4)
C(53)	−1116 (8)	2114 (7)	129 (7)	68 (4)
C(56)	354 (8)	1799 (7)	1447 (6)	57 (3)
C(62)	45 (8)	3436 (7)	2625 (7)	56 (3)
C(63)	−283 (8)	3447 (7)	3230 (6)	57 (3)
C(66)	1459 (7)	4042 (7)	3493 (6)	50 (3)
C(61)	931 (7)	3743 (6)	2767 (5)	37 (3)
C(64)	272 (8)	3718 (7)	3941 (7)	62 (3)
C(65)	1146 (7)	4009 (7)	4079 (6)	52 (3)
C(43)	906 (8)	5036 (8)	−789 (7)	69 (4)
C(46)	923 (7)	3568 (7)	−1013 (6)	54 (3)
C(46)	1132 (7)	3411 (7)	−243 (6)	47 (3)
C(41)	1234 (7)	4065 (6)	272 (5)	40 (3)
C(42)	1109 (8)	4896 (7)	5 (7)	58 (3)
C(74)	2465 (8)	6951 (8)	2345 (6)	66 (4)
C(76)	2532 (7)	5681 (7)	1676 (6)	53 (3)
C(73)	1880 (7)	6564 (7)	2636 (7)	58 (3)
C(75)	2803 (8)	6509 (7)	1886 (6)	64 (4)
C(72)	1615 (7)	5737 (7)	2456 (6)	55 (3)
C(93)	3752 (7)	4145 (7)	4864 (6)	58 (3)
C(94)	3758 (8)	5001 (7)	4926 (7)	69 (4)
C(96)	3797 (7)	5177 (7)	32697 (6)	51 (3)
C(91)	3788 (6)	4307 (6)	3596 (5)	35 (3)
C(92)	3773 (7)	3790 (7)	4189 (6)	47 (3)
C(95)	3803 (8)	5519 (8)	4371 (7)	64 (4)
C(44)	821 (8)	4364 (7)	−1265 (7)	67 (4)
C(82)	4558 (8)	1868 (7)	3515 (6)	58 (3)
C(2a)	2408 (16)	9900 (15)	2050 (13)	192 (9)
C(2b)	2546 (17)	9323 (15)	3309 (15)	178 (10)
C(2c)	2670 (11)	9427 (10)	1523 (9)	110 (5)
C(2d)	3179 (22)	9849 (19)	3908 (18)	254 (14)

[a] Asterisks indicate equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

All non-hydrogen atoms were assigned anisotropic displacement parameters with the exception of the phenyl carbons of **12** and the ethyl carbons of **16**·OEt$_2$. All hydrogen atoms were constrained to ideal geometries (with C–H = 0.96 Å), with the exception of H(4) in **5**, H(4) and H(240) in **12**, and H(9) in **16**·OEt$_2$. All hydrogen atoms were assigned isotropic displacement parameters; these were fixed and related to those of their attached carbon atoms for all but H(4) in **5**, H(4) and H(240) in **12**, and H(9) in **16**·OEt$_2$. The absolute structure of the crystal of **12** used was assigned by the Rogers η refinement method[20] (η = 1.08 (9)).

Final difference syntheses showed no chemically significant features, the largest being close to the metal or solvent atoms. Refinements converged smoothly to residuals given in Table VIII. Tables IX–XI report the positional parameters for the non-hydrogen atoms for these structure determinations. Full tables of interatomic distances and bond angles, displacement parameters, hydrogen atomic parameters and observed and calculated structure amplitudes are given in supplementary material (see paragraph at end of paper).

All calculations were made with programs of the SHELXTL[21] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref 22.

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Supplementary Material Available: Tables of interatomic distances and bond angles, displacement parameters, and hydrogen atomic parameters (16 pages); a listing of observed and calculated structure factor amplitudes (68 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Transition Metals and Main-Group Elements. 73.[1a] Synthetic Routes to Rhenium(V) Alkyl and Rhenium(VII) Alkylidyne Complexes. X-ray Crystal Structures of $(\eta^5\text{-}C_5Me_5)Re({=}O)(CH_3)[CH_2C(CH_3)_3]$ and $(\eta^5\text{-}C_5Me_5)(Br)_3Re{\equiv}CC(CH_3)_3$

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Dialkyloxo(η^5-pentamethylcyclopentadienyl)rhenium(V) complexes $(\eta^5\text{-}C_5Me_5)Re({=}O)(CH_3)R'$ [$R' = C_2H_5$, $CH_2Si(CH_3)_3$, $CH_2C(CH_3)_3$], **1c–e**, have become accessible through alkylation of $(\eta^5\text{-}C_5Me_5)Re({=}O)(Cl)(CH_3)$ (**7**) with R′MgCl. **1c–e** are the first rhenium complexes containing different alkyl ligands. The neopentyl derivative **1e** [$R' = CH_2C(CH_3)_3$] crystallizes in the orthorhombic space group *Pbca* with $a = 960.7$ (2), $b = 2844.5$ (4), $c = 1260.7$ (2) pm, and $Z = 8$. The X-ray crystal structure was refined to $R_w = 3.9\%$. The chiral molecule shows a distorted tetrahedral geometry around the rhenium center. The coordination of the aromatic ring ligand is highly unsymmetric due to the pronounced trans influence of the oxo ligand, with the $Re–C_{ring}$ bond distances varying from 217.8 (5) to 249.3 (7) pm. Different products arise from halogenation of $(\eta^5\text{-}C_5Me_5)Re({=}O)(R)_2$ (**1**) with $(\eta^5\text{-}C_5H_5)TiX_3$ (**4**). Chlorination of **1f** ($R = CH_3$) with **4a** ($X = Cl$) results in formation of $(\eta^5\text{-}C_5Me_5)Re(Cl)_2(CH_3)_2$ (**9**). Chlorination of **1a** ($R = C_2H_5$) and **1h** [$R = CH(CH_3)_2$] with 2 equiv of **4a** finally yields the reduced binuclear complexes $[(\eta^5\text{-}C_5Me_5)Re(Cl)_2(\mu\text{-}Cl)]_2$ (**11**) and $[(\eta^5\text{-}C_5Me_5)Re(Cl)(\mu\text{-}Cl)]_2$ (**12**) of rhenium(IV) and rhenium(III), respectively. By way of contrast, chlorination of dialkyl complexes **1** lacking β-hydrogen atoms leads to rhenium alkylidyne complexes. Reaction of **1i** [$R = CH_2C(CH_3)_3$] with 2 equiv of **4** yields the unique *paramagnetic* rhenium(VI) complex $(\eta^5\text{-}C_5Me_5)(X)_2Re{\equiv}CC(CH_3)_3$ (**2**). Carbyne complexes **2** are quantitatively oxidized by a stoichiometric amount of the respective halogen to yield the rhenium(VII) compounds $(\eta^5\text{-}C_5Me_5)(X)_3Re{\equiv}CCMe_3$ (**3**). The tribromide **3b** has been structurally characterized. Brown crystals of **3b** belong to space group $P2_1/c$ with unit cell dimensions $a = 1311.5$ (2), $b = 723.0$ (1), $c = 1901.6$ (2) pm, $\beta = 92.68$ (1)°, and $Z = 4$. The structure refinement yielded a final *R* value of $R_w = 3.3\%$. The structure exhibits a "four-legged piano stool" geometry with no trans influence of the neopentylidyne ligand to the bromine atom. The rhenium–carbyne bond length is 175.5 (6) pm, typical of a rhenium–carbon triple bond. The "carbyne" angle $Re{\equiv}C{-}C$ of 179.1 (5)° corresponds to an ideal "sp geometry". Chlorination of the benzyl derivative **1g** ($R = CH_2C_6H_5$) provides the new binuclear complex $[(\eta^5\text{-}C_5Me_5)ReCl]_2(\mu\text{-}Cl)(\mu\text{-}CC_6H_5)$ (**14a**), formally a rhenium(IV) system.

Introduction

In 1975, Katz postulated that according to the Hérisson–Chauvin olefin metathesis mechanism carbyne complexes should mediate alkyne metathesis.[2a] At that time, however, hardly anything was known about such metal carbyne complexes. While for low-valent carbyne

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