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Synthesis, Structure, and Chemistry of a Dinuclear Tetrahydride-Bridged Complex of Ruthenium, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$. C–H Bond Activation and Coupling Reaction of Ethylene on Dinuclear Complexes

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The tetrahydride-bridged complex $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ (**2**) is synthesized by the reaction of $[(C_5Me_5)RuCl_2]_2$ (**1**) with $LiAlH_4$, which is characterized as a classical hydride complex on the basis of the T_1 value and X-ray diffraction study. In the presence of acid, **2** decomposes to form a coordinatively unsaturated species, which is trapped by the 6-electron ligands to yield the cationic 18-electron complexes. Treatment of **2** with ethylene yields $(C_5Me_5)Ru(CH_2{=}CH_2)(CH{=}CH_2)_2Ru(C_5Me_5)$ (**6**) by way of an intermediary monovinyl complex $(C_5Me_5)Ru(CH_2{=}CH_2)(CH{=}CH_2)(\mu\text{-}H)Ru(C_5Me_5)$ (**8**). The reaction of **2** with dimethyl maleate results in the formation of $(C_5Me_5)Ru(MeOCOCH{=}CHCO_2Me)(MeOCOC{=}CHCO_2Me)(\mu\text{-}H)Ru(C_5Me_5)$ (**9**), structural analogue of the intermediate **8**. Thermolysis of **6** in toluene at 60 °C under 1 atm of ethylene generates a dinuclear ruthenacyclopentadiene complex $(C_5Me_5)Ru(CH_2{=}CH_2)(CMe{=}CHCH{=}CMe)Ru(C_5Me_5)$ (**10**) as a result of the C—C coupling reaction among the coordinated ethylene and two vinyl ligands. The bis(μ-alkylidene) complex $(C_5Me_5)Ru(\mu\text{-}CHMe)[\mu\text{-}CMe(CH{=}CHCOMe)Ru(C_5Me_5)$ (**13**) which seems to be a model compound of the intermediate of the cyclometalation leading to **10** is obtained upon heating a divinyl complex $(C_5Me_5)Ru(CH_2{=}CHCOMe)(CH{=}CH_2)_2Ru(C_5Me_5)$ (**12**) in refluxing toluene. The ethylene molecule coordinated in **10** inserts into the Ru—C bond of the ruthenacyclopentadiene to form $(C_5Me_5)Ru(CMe{=}CHCH{=}CMeCH{=}CH_2)(\mu\text{-}H)Ru(C_5Me_5)$ (**16**) when **10** is heated in toluene at 110 °C. Regioselective insertion of α,β-unsaturated ketones into the Ru—C bond of the ruthenacycle giving $(C_5Me_5)Ru(CMe{=}CHCH{=}CMeCR^1{=}CCOR^2)(\mu\text{-}H)Ru(C_5Me_5)$ (**17**, R^1 = H, R^2 = Me; **18**, R^1, R^2 = $(CH_2)_2$; **19**, R^1, R^2 = $(CH_2)_3$) is demonstrated in the thermolysis of **10** in the presence of methyl vinyl ketone, cyclopentenone, and cyclohexenone. The molecular structures of several of the products are determined by single-crystal X-ray diffraction studies. Crystal data for **2**: space group $P2/a$, a = 12.291(2) Å, b = 8.521(1) Å, c = 10.053(2) Å, β = 108.52(1)°, V = 998.3(3) Å^3, and D_{calcd} = 1.585 g cm^{-3} for Z = 2. Least-squares refinement based on 2391 reflections converged to R = 0.0220 and R_w = 0.0220. Crystal data for **6**: space group P_1, a = 11.335(2) Å, b = 14.315(2) Å, c = 8.401(2) Å, α = 95.09(2)°, β = 117.18(1)°, γ = 94.36(1)°, V = 1197.4(6) Å^3, and D_{calcd} = 1.538 g cm^{-3} for Z = 2. Least-squares refinement based on 2621 reflections converged to R = 0.0900 and R_w = 0.1581. Crystal data for **9**: space group $Pbca$, a = 17.876(2) Å, b = 20.896(2) Å, c = 17.690(2) Å, V = 6608(1) g cm^{-3}, and D_{calcd} = 1.529 g cm^{-3} for Z = 8. Least-squares refinement based on 2186 reflections converged to R = 0.057 and R_w = 0.040. Crystal data for **10**: space group $P2_1/n$, a = 14.882(2) Å, b = 19.718(4) Å, c = 8.794(1) Å, β = 92.30(2)°, V = 2578.5(8) Å^3, and D_{calcd} = 1.496 g cm^{-3} for Z = 4. Least-squares refinement based on 5731 reflections converged to R = 0.044 and R_w = 0.041. Crystal data for **13**: space group $P2_1/a$, a = 17.210(6) Å, b = 9.693(6) Å, c = 16.037(7) Å, β = 100.366(3)°, V = 2632(2) Å^3, and D_{calcd} = 1.506 g cm^{-3} for Z = 4. Least-squares refinement based on 3781 reflections converged to R = 0.037 and R_w = 0.035. Crystal data for **16**: space group $P2_1/a$, a = 18.814(2) Å, b = 9.212(5) Å, c = 15.068(5) Å, β = 100.31(2)°, V = 2569(2) Å^3, and D_{calcd} = 1.501 g cm^{-3} for Z = 4. Least-squares refinement based on 5449 reflections converged to R = 0.048 and R_w = 0.046. Crystal data for **17**: space group $P2_1/n$, a = 17.539(2) Å, b = 14.405(5) Å, c = 10.935(2) Å, β = 102.68(1)°, V = 2695(1) Å^3, and D_{calcd} = 1.535 g cm^{-3} for Z = 4. Least-squares refinement based on 3241 reflections converged to R = 0.037 and R_w = 0.032. Crystal data for **18**: space group P_1, a = 15.012(3) Å, b = 15.365(3) Å, c = 9.240(2) Å, α = 99.99(3)°, β = 90.11(3)°, γ = 137.58(1)°, V = 1388.4(6) Å^3, and D_{calcd} = 1.518 g cm^{-3} for Z = 2. Least-squares refinement based on 6865 reflections converged to R = 0.034 and R_w = 0.045.

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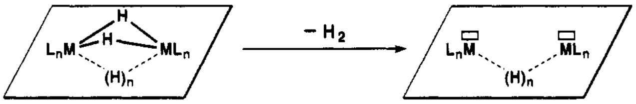
Transition metal polyhydride complexes have been attracting considerable interest as versatile precursors of the active species for C–H activation of alkanes and arenes as well as catalysts for the hydrogenation of unsaturated hydrocarbons. It has been well established that for the mononuclear polyhydride complexes, thermal excitation and/or UV irradiation causes liberation of the hydride ligands as molecular hydrogen to generate a coordinatively unsaturated species.[1] The coordination sites can also be generated via a hydrogen transfer from the hydride complex to an olefin. In such reactions, a bulky, poorly coordinating, metalation-resistant olefin such as *tert*-butylethylene is used as a hydrogen acceptor.[2] If a bimetallic coordinatively unsaturated species which has unsaturated sites on the neighboring two metal centers is generated, the two metal centers seem very likely to cooperate for the activation of a substrate. For this purpose, a dinuclear polyhydride-bridged complex must be one of the most suitable precursors because it possibly gives rise to a pair of coordinatively unsaturated sites on each of the metal centers upon thermal or photochemical excitation or hydrogen transfer to an olefin.



Thus far there have been a few studies of dinuclear transition metal complexes triply or quadruply bridged by hydride ligands[3,4] while there is a vast chemistry of mononuclear polyhydride or dinuclear doubly hydride-bridged complexes. Bau et al. reported an X-ray and neutron diffraction analysis of the structure of $H_8Re_2(PEt_2Ph)_4$ having a formal metal–metal triple bond bridged by four hydrogen atoms.[4a] Triply hydride-bridged complexes of rhenium were derived from the tetrahydride-bridged complex by reaction with phosphite or alternatively by photolysis of $ReH_5(PMe_2Ph)_3$.[3b] As far as ruthenium is concerned, only two examples, $[Ru_2(\mu\text{-}H)_3(PMe_3)_6]BF_4$ and $Ru_2(H)(\mu\text{-}H)_3(N_2)(PPh_3)_4$, were reported prior to our work.[3e,f] The latter was at first identified as a tetrahydride-bridged complex $Ru_2(H)_2(\mu\text{-}H)_4(N_2)(PPh_3)_4$ but was ultimately confirmed to have three bridging hydrides on the basis of the ^1H NMR spectra and an X-ray diffraction study, as well as molecular mechanics calculations.[3g,f]

We were interested in the activation of organic substrates on two or more metal centers tightly bound by a metal–metal bond or bridging hydride, therefore, we intended to synthesize a dinuclear ruthenium complex having four bridging hydrides as a precursor of the active species for *bimetallic activation*. In the preceding communication, we reported briefly the synthesis and structure of a tetrahydride-bridged complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$.[5] Here we describe in full detail the synthesis and structure determination, the bimetallic activation of ethylene which forms a divinyl–ethylene complex, the coupling reaction among the coordinated ethylene and two vinyl ligands yielding a novel class of ruthenacycles, and the carbon chain growth on the dinuclear complex.

Results and Discussion

Synthesis and Structure of Dinuclear Tetrahydride 2. The suspension of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (1)[6] was stirred with $LiAlH_4$ in diethyl ether for 12 h at ambient temperature. After ethanolysis of the yellow intermediate at 197 K, the solvent was removed under reduced pressure. Extraction of the crude product with toluene and purification by column chromatography on Al_2O_3 with toluene followed by recrystallization from toluene/pentane gave a dinuclear tetrahydride-bridged complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (2) in 75% yield as red plates. Complex 2 was also obtained in low yield (13%) by treatment of 1 with $NaBH_4$ in ethanol. Treatment of 1 with $LiAlD_4$ followed by a treatment with either EtOH or EtOD afforded the isotopomer $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}D)_2Ru(\eta^5\text{-}C_5Me_5)$ (2-d_2) or $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ (2-d_4). Isotopomer 2-d_2 can also be obtained when the orange intermediate, derived from the reaction of 1 with $LiAlH_4$, is treated with EtOD. The synthesis of 2, 2-d_2, and 2-d_4 are shown in Scheme 1.

To our knowledge, only two examples have been reported for the dinuclear tetrahydride-bridged complexes $L_nM(\mu\text{-}H)_4ML_n$.[4] Complex 2 is the first dinuclear tetrahydride-bridged complex having no phosphine and arsine ligands. The structure of 2 is unambiguously assigned on the basis of ^1H NMR, ^{13}C NMR, FD-MS, and elemental analysis as well as X-ray crystallographic studies.

The ^1H NMR spectrum of 2 measured at room temperature revealed two sharp singlet peaks at δ 1.87 (C_5Me_5) and −13.99 (Ru–H, $w_{1/2}$ = 2.2 Hz) in the intensity ratio of 15:2. Two resonance signals attributable to the ring and methyl carbons appeared at δ 88.2 and 12.5 in the ^{13}C NMR spectrum of 2.

In 1984, Kubas *et al.* reported the first example of a transition metal hydride complex in which the hydride

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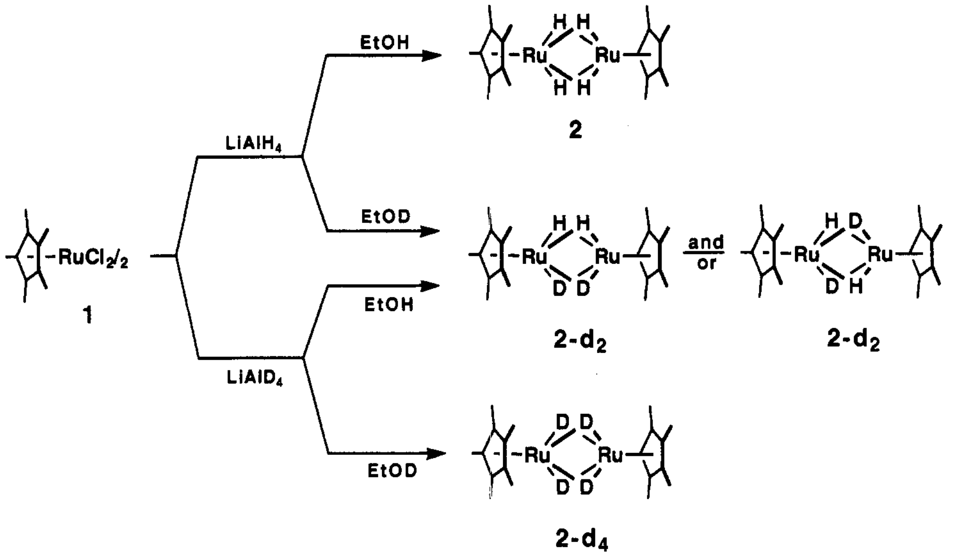
Scheme 1



ligands had bonding interaction in between.[7] Since that time many other examples have been discovered.[8] The T_1 and $^1J_{HD}$ data in ^1H NMR, H–H distances by means of X-ray or neutron diffraction studies, and ν_{HD} data in the IR spectra are adopted as criteria for distinguishing the η^2-H_2 complexes from classical M–H complexes. The proton resonance for the hydride ligands of the isotopomer **2**-d_2 was slightly broadened ($w_{1/2}$ = 6.0 Hz), but the apparent splitting due to the spin coupling with ^2H was not observed. The inversion-recovery T_1 determination for hydride ligands in **2** at 193 K was performed at 500 MHz by using standard JEOL programs. The observed T_1 value of 2.28 s and the J_{HD} data above are deemed to be sufficient to characterize the complex as a classical metal polyhydride.[9]

Complex **2** is soluble in toluene and is slightly soluble in pentane and THF. The molecular structure of tetrahydride **2** was determined on the basis of an X-ray diffraction study. Single crystals of **2** were grown from the mixed solvent of toluene and pentane stored at −15 °C. The results of the single-crystal X-ray diffraction study are displayed in Figure 1 with a numbering scheme, and two views of the Ru_2H_4 core are shown in Figure 2. Table 1 lists some of the relevant bond distances and angles.

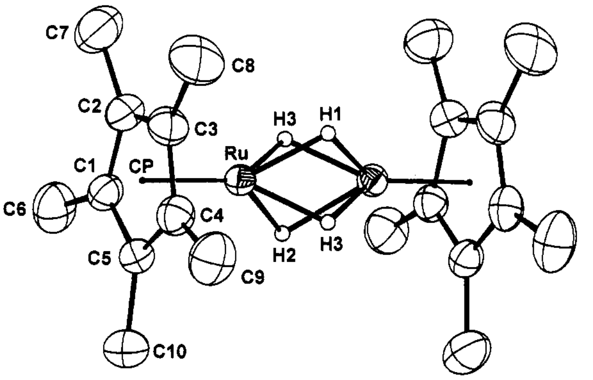


Figure 1. Molecular structure of **2**. The thermal ellipsoids correspond to 30% probability.

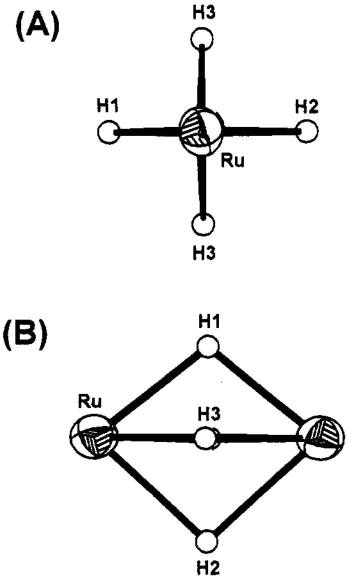


Figure 2. (A) View of the Ru_2H_4 core of the molecule looking along the Ru–Ru axis, showing the approximate square formed by the quartet of bridging hydrogen atoms. (B) Another view of the Ru_2H_4 core.

The core of the molecule consists of four bridging hydrogen atoms tightly clustered around the ruthenium–ruthenium vector, and four hydride ligands are essentially arrayed at the vertices of an approximate square put perpendicularly to the Ru–Ru bond. The average H–H

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 2

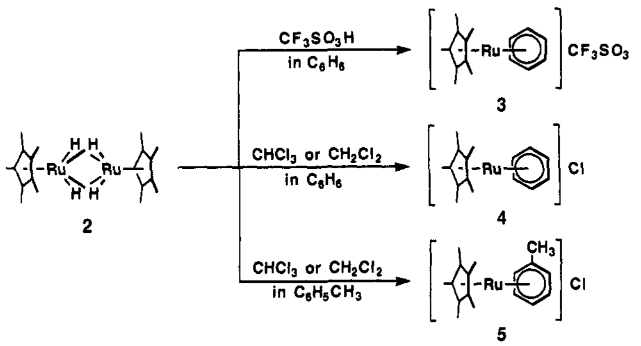
Ru–Ru	2.4630(5)		
Ru–C(1)	2.171(2)	Ru–C(2)	2.180(2)
Ru–C(3)	2.192(2)	Ru–C(4)	2.191(2)
Ru–C(5)	2.179(2)	Ru–H(1)	1.62(3)
Ru–H(2)	1.73(3)	Ru–H(3)	1.67(5)
C(1)–C(2)	1.436(3)	C(1)–C(6)	1.497(3)
C(2)–C(3)	1.429(3)	C(2)–C(7)	1.497(3)
C(3)–C(4)	1.434(3)	C(3)–C(8)	1.505(3)
C(4)–C(5)	1.440(3)	C(4)–C(9)	1.503(3)
C(5)–C(1)	1.439(3)	C(5)–C(10)	1.498(3)
H(1)–H(3)	1.49(5)	H(2)–H(3)	1.63(5)
H(1)–H(2)	2.26(6)	H(3)–H(3)	2.15(6)
Ru–H(1)–Ru	99(2)	Ru–H(2)–Ru	91(2)
Ru–H(3)–Ru	98(2)	H(1)–Ru–H(2)	54(1)
H(1)–Ru–H(3)	85(2)	H(2)–Ru–H(3)	57(1)
H(3)–Ru–H(3)	82(2)	C(2)–C(1)–C(5)	108.0(2)
C(2)–C(1)–C(6)	126.5(2)	C(5)–C(1)–C(6)	125.3(2)
C(1)–C(2)–C(3)	108.0(2)	C(1)–C(2)–C(7)	125.5(2)
C(3)–C(2)–C(7)	126.4(2)	C(2)–C(3)–C(4)	108.5(2)
C(2)–C(3)–C(8)	126.2(2)	C(4)–C(3)–C(8)	125.3(2)
C(3)–C(4)–C(5)	107.8(2)	C(3)–C(4)–C(9)	126.4(2)
C(5)–C(4)–C(9)	125.7(2)	C(4)–C(5)–C(1)	107.8(2)
C(4)–C(5)–C(10)	127.0(2)	C(1)–C(5)–C(10)	125.1(2)

distance of 1.46 Å is shorter than that observed in the quadruply hydride-bridged rhenium complex $[ReH_2(PEt_2Ph)]_2(\mu-H)_4$ [1.956(8) Å][4a] obtained from neutron diffraction analysis, but much longer than the values of 0.75(16) (X-ray) and 0.84 Å (neutron) found in the complex $W(\eta^2-H_2)(CO)_3[P(i-Pr)_3]_2$,[7] 0.80(6) Å (X-ray) in (P-N)-$(\eta^2-H_2)Ru(\mu-H)(\mu-Cl)_2Ru(H)(PPh_3)$,[8j] P-N = $Fe[\eta^5-C_5H_3-(CHMeNMe_2)P(i-Pr)_2-1,2](\eta^5-C_5H_5)$, 0.89(11) Å (X-ray) in *trans*-$[Fe(\eta^2-H)_2)(H)(Ph_2PCH_2CH_2PPh_2]BF_4$,[8g] 0.87(3) (X-ray) and 0.816 (16) Å (neutron) in *trans*-$[Fe(\eta^2-H_2)(H)(Ph_2PCH_2CH_2PPh_2]BPh_4$,[8l] and 1.08(5) Å in $[Re(\eta^2-H_2)H_4(Cyttp)]SbF_6$,[8f] Cyttp = $PhP[CH_2CH_2PCy_2]_2$. These results strongly indicate that there are no bonding interactions among the hydride ligands in 2. Although X-ray crystallography is not the best way to determine H–H distances, the results obtained here are well consistent with those based on the T_1 and $^1J_{HD}$ data. We can therefore conclude that complex 2 is not a η^2-H_2 complex but a classical σ-bonded metal hydride complex.

The Ru–Ru distances of 2.463(1) Å is shorter than the Re–Re bond [2.538(4) Å] in $[ReH_2(PEt_2Ph)]_2(\mu-H)_4$ which was formally termed a triple bond.[4a] In a previous communication,[5] we proposed a structure having a Ru–Ru triple bond for complex 2 on the basis of its having an extremely short Ru–Ru distance and the electron-counting considerations. However, a theoretical study performed by Professors K. Morokuma and N. Koga by using the *ab initio* MO method showed that there was no direct metal–metal bond between two ruthenium atoms and that the short Ru–Ru distance could be due to four 2e–3c M–H–M bonds.[10]

Formation of Cationic Arene– or Triene–Ruthenium Complexes. Hydride ligands which exhibit an acidic character in polar solvents can undergo intermolecular hydrogen-exchange reactions with hydroxylic solvents. The exchange is usually detected by means of isotopic labeling with deuterium. The reaction of 2 with C_2H_5OD was monitored by means of ^1H and ^2H NMR spectroscopy. However, the formation of the deuterated complex and C_2H_5OH could not be observed probably due to low acidity of the hydride ligands in 2 when the solution of 2 in C_2H_5OD was stirred for 2 days at ambient temperature. It was further confirmed by FD-mass spectrometry that deuterium was not incorporated in the complex recovered from the reaction mixture.

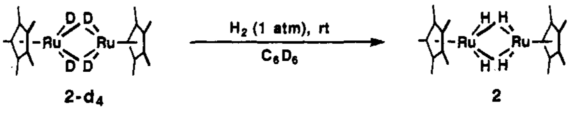
Scheme 2



In the presence of acid or halogenated hydrocarbon, complex 2 decomposed to generate a coordinatively unsaturated species which was immediately trapped by an arene or a triene ligand to yield a stable cationic 18-electron complex (Scheme 2).

Treatment of 2 with 1.1 equiv of CF_3SO_3H in benzene quantitatively afforded a mononuclear cationic arene complex $[(\eta^5-C_5Me_5)Ru(\eta^6-C_6H_6)](CF_3SO_3)$ (3) with the evolution of dihydrogen. Cationic arene–ruthenium complexes 4 and 5 were also obtained in 99 and 91% yields, respectively, by reacting 2 with arene in a halogenated solvent such as $CHCl_3$ or CH_2Cl_2. Cationic arene complexes are usually synthesized by way of halogen abstraction reaction using silver(I) salt.[11] We previously reported a new method for the preparation of $(\eta^5-C_5Me_5)Ru(arene)^+$ starting from $[(\eta^5-C_5Me_5)Ru(\mu-RCO_2)(\mu-H)]_2$.[12] But the present method has the advantage of permitting a free choice of the counteranions because a wide variety of acids are applicable to this reaction.

H/D Exchange Reaction of 2-d_4 with Hydrogen. The hydride ligands of metal hydride complexes can undergo an intermolecular exchange reaction with dihydrogen under mild conditions. We attempted the exchange reaction of deuteride ligands in 2-d_4 with dihydrogen. The reaction of 2-d_4 with atmospheric pressure dihydrogen in C_6D_6 at ambient temperature was monitored by means of ^1H NMR spectroscopy (Figure 3). Exposure of a toluene solution of 2-d_4 to atmospheric pressure dihydrogen results in the exchange of the deuteride ligands for hydride (eq 1), and the progressive increase in the intensity of the resonance signal for bridging hydrides at δ −13.99 was observed. The H/D exchange reaction was completed after 34 h. The complex recovered from the solution was confirmed to be tetrahydride 2 on the basis of ^1H NMR and FD-mass spectra and analytical data. The mechanisms shown in Scheme 3 possibly account for the H/D exchange reaction of the deuteride ligands in 2-d_4 with H_2.

 (1)

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[10] Koga, N.; Morokuma, K. The 36th Symposium on Organometallic Chemistry, Japan, Tokyo, 1989; Abstract, PA203. Koga, N.; Morokuma, K. *J. Mol. Struct.* **1993**, *300*, 181.

[11] For example, see: Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698 and references cited therein.

[12] Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 283.

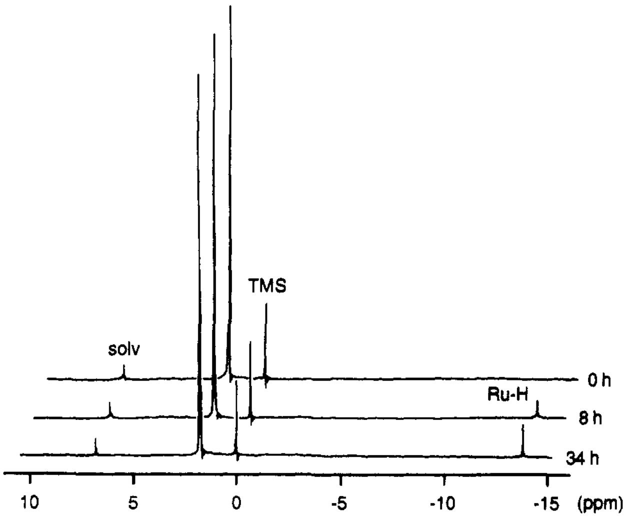
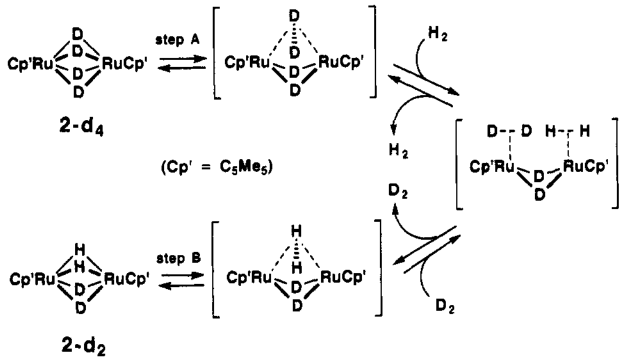


Figure 3. ^1H NMR spectra monitoring the reaction of **2**-d_4 with H_2 in C_6D_6.

Scheme 3



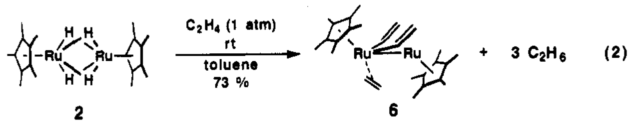
Although the fluxionality of the bridging hydrides in complex **2** was not observable by ^1H NMR over the temperature range +25 to −80 °C, the mechanism presumably involves a dihydride–dihydrogen equilibrium (steps A and B). With regard to the chemistry of η^2-dihydrogen complexes, such an equilibrium is proposed on the basis of variable-temperature ^1H NMR studies.[8a,i,l,n-p,10,13]

Activation of the C–H Bond of Ethylene. Transition metal polyhydride complexes have been shown to be of importance as the precursors of the active species for the alkane C–H bond activation reaction since they have the potential for creating coordinative unsaturation by eliminating molecular hydrogen upon thermal or photochemical excitation. While there exists a fair amount of examples of C–H bond cleavage of both alkanes and arenes with low valent complexes of late transition metals,[14] there are only several reported examples of intermolecular activation of the vinylic C–H bond of alkenes with metal polyhydride complexes.[15]

In the case using a mononuclear complex as a precursor of the active intermediate, relatively extreme conditions, such as UV irradiation or high temperatures, are required for the C–H activation reaction. On the other hand, the C–H bond activation under milder conditions can often be realized by using di- and trinuclear complexes owing to the cooperative effect of the multimetallic centers.

While dinuclear tetrahydride complex **2** is stable under UV irradiation, it causes a coordinatively highly unsaturated species under thermal conditions or treatment with hydrogen acceptors such as olefins. In the course of a study on the reaction of **2** with a number of olefins, we found that a C–H bond of ethylene was facilely cleaved under mild conditions to give a novel dinuclear divinyl complex. In the preceding communication, we briefly reported the synthesis, characterization, and ligand exchange reaction of the divinyl complex.[16]

Treatment of **2** in a toluene solution with atmospheric pressure ethylene at 20 °C for 1 day, followed by chromatographic purification on neutral Al_2O_3 with toluene afforded a deep red crystalline material formulated as (η^5-C_5Me_5)Ru(CH_2=CH_2)(CH=CH_2)$_2$Ru(η^5-C_5Me_5) (**6**) in a 73% isolated yield (eq 2). The yield of **6** determined



on the basis of the ^1H NMR spectrum reached ca. 90%. The complex has been characterized by ^1H and ^{13}C NMR, FD-mass spectrometry, infrared spectroscopy, and elemental analysis.

In the field-desorption mass spectrum of **6**, intensities of the obtained isotopic peaks for $C_{26}H_{40}Ru_2$ were in agreement with the calculated values within the experimental error.

The ^1H NMR spectrum of **6** revealed the coordination of an ethylene molecule and two magnetically equivalent vinyl groups. Characteristic resonances for the vinyl ligands were observed at δ 1.99, 3.65, and 9.98 as an ABX pattern in a 2:2:2 ratio. They were attributed to H_β (*trans* to H_α), H_β (*cis* to H_α), and H_α, respectively, by means of homodecoupling experiments. Resonances for the protons of the coordinated ethylene appeared at δ 1.86 and 1.58 as doublet (J_{HH} = 11.0 Hz) peaks. These shifts lie within the reance of those for ethylene complexes of middle and late transition metals. The gated ^{13}C NMR spectrum showed that there were three sets of equivalent vinyl and ethylene carbons at δ 188.5 (d, J_{CH} = 156.9 Hz, vinyl C_α), 54.5 (dd, J_{CH} = 146.1 and 160.1 Hz, vinyl C_β), and 48.9 (dd, J_{CH} = 157.0 and 151.2 Hz, ethylene). The characteristic chemical shifts for H_α and C_α of the vinyl ligand are consistent with values obtained for related transition metal μ-σ,π-divinyl complexes (Table 2).[17]

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[13] Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.

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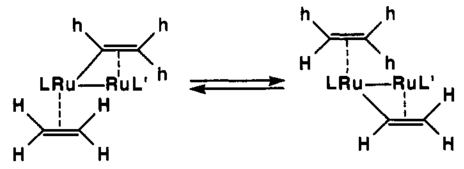
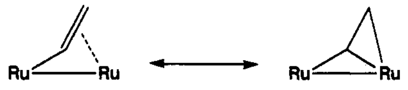
Table 2. NMR Parameters for the Hα and Cα of Vinyl Groups in the Related μ-$\sigma_1\pi$-Vinyl Complexes

complex	δ_{H_α} (ppm)	$^3J_{H_\alpha H_\beta}$ (Hz)	δ_{C_α} (ppm)	$^1J_{CH}$ (Hz)	ref
$(Cp'TaBr_2)_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)$	9.31	8.7, 11.7	214.7	144	15a
$[(CpMo)_2(CO)_3(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$	8.99	9.0, 13.0			15b
$W_2(PMe_2Ph)_2Cl_3(\mu\text{-}CH_2NMe)(\mu\text{-}NMe_2)(NMe_2)(\mu\text{-}CH{=}CH_2)$	14.8	6.5, 8.3	208.0	150	15c
$Mn_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH_2)$	9.27	9.3, 14.6	178.3	160.2	15d
$Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)$	7.18	10.9, 17.2			15e
$[(CpFe)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$	12.57	7, 12	185.8		15f
$[(CpRu)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$					
cis	11.22	7, 12	163.6		15f
trans	10.32	7, 11			15f
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)$	7.58	9.7, 14.9			15g
$Rh_2(dppe)_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)$	9.48	11.4, 18.6	195.6	127	15g
$(Cp'Ru)_2(CO)(\mu\text{-}CH{=}CH_2)_2$					
cis	9.04	6.4, 9.2	176.6	152.2	14
trans	9.50	6.3, 9.4	177.3	162.0	14
$(Cp'Ru)_2(PMe_3)(\mu\text{-}CH{=}CH_2)_2$	9.31	6.8, 10.8	174.2		14
$(Cp'Ru)_2(CH_2CH_2)(\mu\text{-}CH{=}CH_2)_2$ (6)	9.98	6.7, 9.2	188.5	156.9	this work

Scheme 4



While ^{13}C resonances for the vinyl ligand in mononuclear vinyl complexes are often observed in the range δ 120–145, those for the vinyl ligand in 6 appeared at δ 54.5 and 188.5, respectively. An upfield shift of the C_β signal in 6 strongly suggests the coordination of the vinyl group to another ruthenium center in a π mode. On the other hand, a downfield shift of the C_α resonance implied the contribution of a μ-carbene-like resonance hybrid **B**.



A **B**

A ^1H NMR spin saturation transfer experiment carried out for complex 6 reveals an ethylene–vinyl ligand exchange process illustrated in Scheme 4. The experiment was performed at 40 °C by using a JEOL EX-90 instrument. Irradiation at the resonance position for the coordinated ethylene (δ 1.58) resulted in a ca. 15% decrease in the intensities of the proton signals for the vinyl ligands at δ 3.65 and 9.98.

Additional support for the ethylene–vinyl ligand exchange process is provided in the reaction of $(C_5Me_5)Ru(PMe_3)(CH{=}CH_2)_2Ru(C_5Me_5)$ (7)[16] with ethylene-d_4. There exists an exchange equilibrium between the divinyl complex 6 and 7.[18] Especially in the presence of CuCl, PMe_3 coordinated in 7 is completely substituted by ethylene. According to this procedure, deuterium-labeled complex 6-d_4 can be obtained by the reaction of 7 with ethylene-d_4 in toluene. However, the ^2H and ^{13}C NMR spectra of 6-d_4 show that deuterium atoms scrambled to some extent among coordinated ethylene and the two vinyl ligands even at room temperature. Figure 4 shows that the characteristic 1:1:1 triplet peak coupled with deuterium appeared beside the resonance for the α-carbon of the vinyl group at δ 188.5.

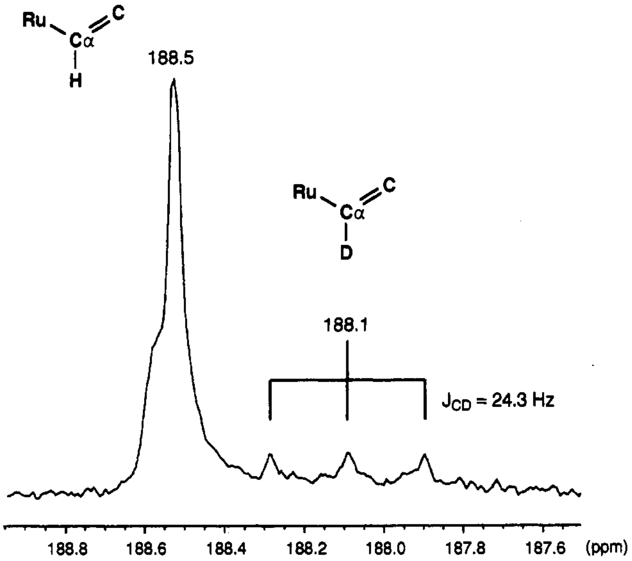


Figure 4. ^{13}C NMR spectrum (125 MHz) of partially deuterated divinyl complex 6-d_n.

Divinyl complex 6 is soluble in toluene but is sparingly soluble in pentane. Dark purple-red crystals of 6 were obtained from a mixed solvent of toluene and pentane, but the shapes of the crystals were like thin plates. Preliminary X-ray examination of the crystals of 6 revealed they were not suitable for diffraction study. Although the full-matrix least-squares refinement did not sufficiently converge (R = 0.090, R_w = 0.158), the X-ray data sufficiently elucidates the atom connectivity of the structure. The resulting structure of 6 shown in Figure 5 is fully consistent with the data obtained from ^1H and ^{13}C NMR spectroscopy and FD-MS spectrometry. The two C_5Me_5 rings are mutually *trans* with respect to the Ru–Ru vector, and the two ruthenium atoms are bridged by two μ-σ,π-C_2H_3 fragments, the terminal carbons of which are σ-bonded to Ru(1).

The following two processes P-1 and P-2 can be suggested for the generation of the coordinatively unsaturated sites on 2 at the initial step of the reaction of 2 with ethylene; (P-1) dissociation of hydrides as molecular hydrogen; (P-2) hydride transfer to the ethylene molecule (i.e. ethylene hydrogenation) forming ethane and the coordinatively

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[18] The coordinated ethylene in 6 is easily exchanged with PMe_3, CO, and electron-deficient olefins to give the corresponding divinyl complexes, $(\eta^5\text{-}C_5Me_5)Ru(CH{=}CH_2)_2(L)Ru(\eta^5\text{-}C_5Me_5)$ (L = PMe_3, CO, or electron-deficient olefin).[16] While the CO ligand in $(\eta^5\text{-}C_5Me_5)Ru(CH{=}CH_2)_2(CO)Ru(\eta^5\text{-}C_5Me_5)$ is resistant to the substitution by ethylene, the PMe_3 coordinated in 7 can be replaced again by ethylene. Treatment of 7 in toluene with 1 atm of ethylene for 24 h at room temperature gave the 1:1.3 mixture of 7 and 6. Trimethylphosphine in 7 can be completely substituted by ethylene when 1 equiv of CuCl is added to the reaction mixture as a phosphine-trapping agent.

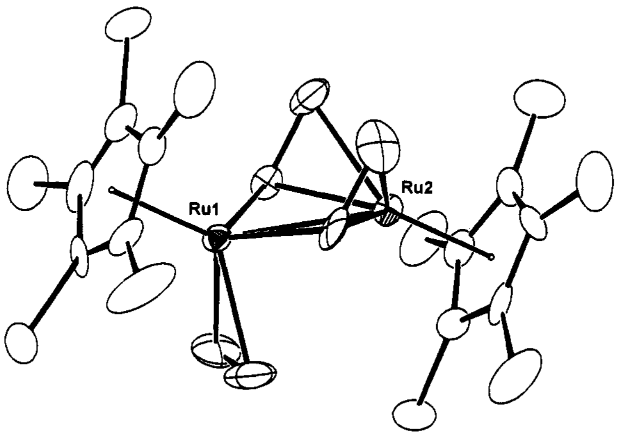


Figure 5. Molecular structure of **6**, with thermal ellipsoids at the 30% probability level.

unsaturated sites. The two processes, P-1 and P-2, can be distinguished by analyzing gases formed during the reaction. The GLC analysis of the gas phase of the reaction revealed the formation of ca. 270 mol % of ethane together with small amounts of 1-butene.

These results suggest that the coordinatively unsaturated sites are generated on the bimetallic complex **2** by way of a hydride transfer from ruthenium to ethylene, i.e. hydrogenation of ethylene.

To elucidate the mechanism for the formation of divinyl complex **6**, the reaction of **2** with ethylene in toluene-d_8 at room temperature was monitored by means of ^{1}H NMR spectroscopy. The signals for tetrahydride **2** disappeared after ca. 40 min, and at the same time the formation of an intermediate **8** in a 92% yield was observed.

Although intermediate **8** could not be isolated in analytically pure form, it was characterized on the basis of ^{1}H and ^{13}C NMR spectra, its ^{1}H–^{13}C HSC spectrum, and FD-MS spectra.

The resonance peaks for the hydride, ethylene, and C_5Me_5 ligands were observed at δ −16.37, 0.69, 0.99, 1.52, and 1.75, respectively, in a 1:2:2:15:15 ratio. Signals for vinyl ligands appeared at δ 7.36 (dd, J = 8.4 and 12.0 Hz, H_α) and 3.89 (d, J = 8.4 Hz, H_β, *cis* to H). These shifts are consistent with those reported for protons of μ-σ,π-vinyl ligands. The ^{1}H–^{13}C HSC spectrum showed that the resonance for one of the protons on the β-carbon was obscured by the resonance of C_5Me_5 at δ 1.75. In the gated decouple ^{13}C NMR spectrum recorded at −78 °C, doublet and doublets of doublet peaks assignable to C_α and C_β of the vinyl ligand were observed at δ 189.4 and 53.5 besides resonances assigned to the C_5Me_5 ligands and two triplets at δ 34.2 and 34.5 for the coordinated ethylene. The values of δ 189.4 and 53.5 are also well consistent with the reported chemical shifts for μ-σ,π-vinyl ligands.

With the reaction time, a progressive increase in the intensities of the signals for **6** and a significant decrease in those for **8** were observed. After 10 h at room temperature, **8** converted to the vinyl complex **6**, and the yield of **6** reached 92%. Time–conversion curves are shown in Figure 6. These results obviously indicate that divinyl complex **6** is formed by way of an intermediary monovinyl complex **8** (Scheme 5).

The monovinyl complex **8** is highly reactive owing to coordinative unsaturation at the ruthenium centers and can readily be converted to divinyl complex **6** in the presence of excess amounts of ethylene. We, therefore, attempted to isolate an intermediary monovinyl complex through the reaction of **2** with an olefin having substituents which could be coordinated to the unsaturated ruthenium center intramolecularly.

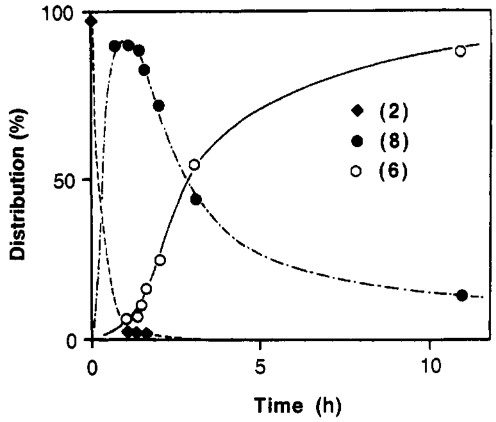
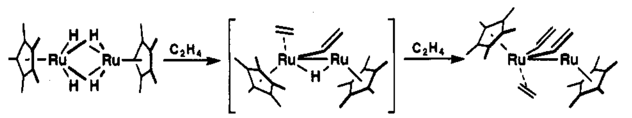


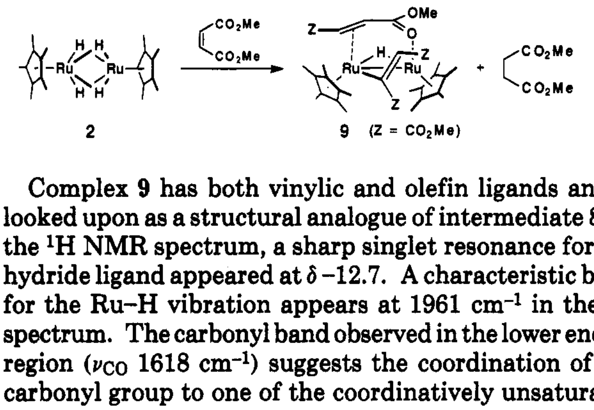
Figure 6. Distribution of **2**, **8**, and **6** *vs* time from integrated ^{1}H NMR spectra.

Scheme 5



2 **8** **6**

The reaction of **2** with an excess amount of dimethyl maleate resulted in the formation of a dinuclear complex **9** in a 46% yield together with 2 equiv of dimethyl succinate which was the hydrogenation product of dimethyl maleate (eq 3). An excess of dimethyl maleate added to **2** completely isomerized to dimethyl fumarate.



(3)

2 **9** (Z = CO_2Me)

Complex **9** has both vinylic and olefin ligands and is looked upon as a structural analogue of intermediate **8**. In the ^{1}H NMR spectrum, a sharp singlet resonance for the hydride ligand appeared at δ −12.7. A characteristic band for the Ru–H vibration appears at 1961 cm^{-1} in the IR spectrum. The carbonyl band observed in the lower energy region (ν_{CO} 1618 cm^{-1}) suggests the coordination of the carbonyl group to one of the coordinatively unsaturated ruthenium centers.

Single-crystal X-ray structural analysis of the dark red prisms of **9** confirmed the proposed structure. The molecular structure is shown in Figure 7, and relevant geometrical bond distances and angles are given in Tables 3. The C_5Me_5 groups are mutually *cis* to the Ru–Ru vector and Ru(1) coordinates a dimethyl fumarate molecule instead of the dimethyl maleate. Although the position of a hydrogen atom σ-bonded to ruthenium could not be determined by the difference Fourier synthesis, we believe a hydride bridges the two ruthenium atoms and is most likely to be located on the opposite side of C(6) with respect to the Ru–Ru vector.

The 18-electron rule applied to complex **9** requires a metal–metal single bond between ruthenium centers and the interatomic distances between ruthenium atoms is 2.924(2) Å, corresponding to a Ru—Ru single bond. Two ruthenium atoms are bridged by a μ-σ,π-C(CO_2Me)CHCO_2-

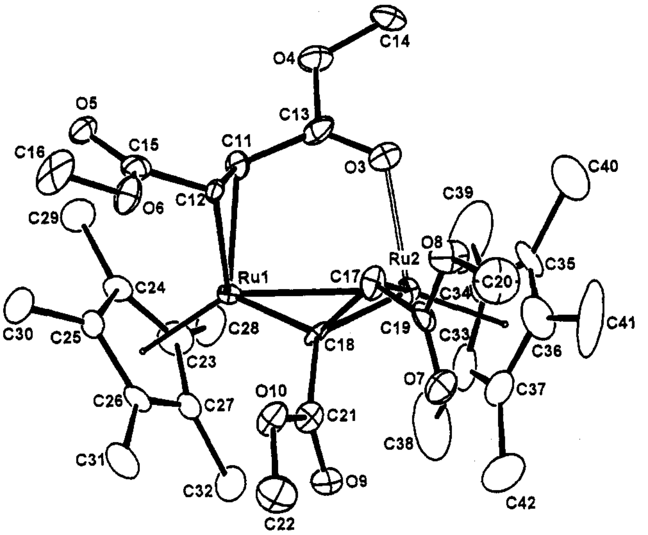


Figure 7. Molecular structure of 9, with thermal ellipsoids at the 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 9[a]

Ru(1)–Ru(2)	2.922(2)		
Ru(1)–C(1)	2.12(2)	Ru(2)–O(8)	2.22(1)
Ru(1)–C(12)	2.18(1)	Ru(2)–C(17)	2.20(2)
Ru(1)–C(18)	2.06(1)	Ru(2)–C(18)	2.14(2)
Ru(1)–C(23)	2.18(2)	Ru(2)–C(33)	2.16(2)
Ru(1)–C(24)	2.24(1)	Ru(2)–C(34)	2.18(2)
Ru(1)–C(25)	2.31(1)	Ru(2)–C(35)	2.15(2)
Ru(1)–C(26)	2.30(2)	Ru(2)–C(36)	2.19(2)
Ru(1)–C(27)	2.21(2)	Ru(2)–C(37)	2.21(2)
C(11)–C(12)	1.43(2)	C(11)–C(13)	1.44(2)
C(12)–C(15)	1.46(2)	C(13)–O(3)	1.20(2)
C(15)–O(5)	1.22(2)	C(13)–O(4)	1.37(2)
C(15)–O(6)	1.34(2)	O(4)–C(14)	1.40(2)
O(6)–C(16)	1.41(2)	C(17)–C(18)	1.47(2)
C(17)–C(19)	1.47(2)	C(18)–C(21)	1.47(2)
C(19)–O(7)	1.21(2)	C(21)–O(9)	1.21(2)
C(19)–O(8)	1.33(2)	C(21)–O(10)	1.37(2)
O(8)–C(20)	1.43(2)	O(10)–C(22)	1.42(2)
CP(1)–Ru(1)–C(18)	180.6(4)	CP(2)–Ru(2)–C(18)	139.3(4)
CP(1)–Ru(1)–C(11)	121.7(5)	CP(2)–Ru(2)–C(17)	130.9(4)
CP(1)–Ru(1)–C(12)	126.3(4)	CP(2)–Ru(2)–O(3)	117.3(3)
Ru(2)–Ru(1)–C(11)	85.2(4)	Ru(2)–Ru(1)–C(12)	95.3(4)
Ru(2)–Ru(1)–C(18)	47.1(4)	C(11)–Ru(1)–C(12)	39.3(6)
C(11)–Ru(1)–C(18)	106.9(6)	C(12)–Ru(1)–C(18)	86.7(6)
Ru(1)–Ru(2)–O(3)	81.1(3)	Ru(1)–Ru(2)–C(17)	74.8(4)
Ru(1)–Ru(2)–C(18)	44.9(3)	O(3)–Ru(2)–C(17)	84.3(5)
O(3)–Ru(2)–C(18)	101.9(5)	C(17)–Ru(2)–C(18)	39.4(5)
Ru(2)–O(3)–C(13)	120(1)	C(12)–C(11)–C(13)	118(1)
C(11)–C(12)–C(15)	120(1)	O(3)–C(13)–O(4)	116(1)
O(3)–C(13)–C(11)	130(1)	O(4)–C(13)–C(11)	112(1)
C(18)–C(17)–C(19)	121(1)	Ru(1)–C(18)–Ru(2)	88(5)
Ru(1)–C(18)–C(17)	126(1)	C(17)–C(18)–C(21)	113(1)

[a] CP(1) and CP(2) are the centroids of the C_5Me_5 ligands.

Me fragment in which two ester groups array in *cis* configuration. The Ru(1)—C(18) distance of 2.073(15) Å is consistent with a Ru–C single bond. The Ru—C(11) and Ru(1)—C(12) distances of 2.144(16) and 2.146(14) Å lie within the range of those between Ru and π-bonded carbon atoms, as are the Ru(2)—C(17) and Ru(2)—C(18) bond lengths of 2.237(16) and 2.129(16) Å. This shows that Ru(1) and Ru(2) are π-bonded to the fumaric acid ester and the vinylic ligand, respectively. The structural feature of 9 is the proximity of one of the carbonyl oxygens in the fumaric acid ester to the Ru(2) center. The O(3)—Ru(2) distance of 2.234(11) Å is comparable with the value of 2.246(7) Å in $(Ph_3P)_3RuH\{CH{=}C(CH_3)CO_2C_4H_9\}$, in which the carbonyl oxygen is coordinated to ruthenium,[19] but is longer than the values for Ru—O σ-bonds. This result indicates the intramolecular coordination of the carbonyl oxygen O(3) to Ru(2). The 18-electron configuration around the Ru(2) center led by the coordination of O(3) should stabilize complex 9 compared to intermediate 8.

Formation of the monovinyl–olefin–hydride complex 9, the structural analogue of intermediate 8, together with 2 equiv of dimethyl succinate in the reaction of 2 with dimethyl maleate suggests the mechanism shown in Scheme 6 for the reaction of 2 with ethylene forming the divinyl complex 6.

Initial coordination and insertion of ethylene into a Ru–H bond yields a dinuclear ethylruthenium species **B**, which undergoes the coordination of ethylene and reductive elimination of ethane to generate **C**. The C–H bond activation of ethylene giving a σ,π-vinyl fragment and the coordination and insertion of ethylene, followed by the addition of ethylene and elimination of ethane would give intermediate 8 by way of **D** and **E**. It is also conceivable that the reaction of **C** with ethylene proceeds alternatively to give 8 by way of intermediate **F**. In this mechanism, the formation of 8 would be accompanied by the hydrogenation of 2 mol of ethylene to yield ethane. The formation of 9, corresponding to 8, and 2 equiv of dimethyl succinate in the reaction of 2 with dimethyl malonate is well consistent with this mechanism. The addition of ethylene to 8 forming **G** followed by the activation of a vinylic C–H bond would lead to the formation of **H**. As mentioned above, small amounts of 1-butene were formed in the reaction of 2 with ethylene. Formation of 1-butene is explicable according to this mechanism. From **G** and/or **H**, 1-butene could arise via a reductive coupling between the ethyl and vinyl ligands. Reductive elimination of ethane from **H** and the subsequent addition of ethylene would afford 6. The formation of 3 equiv of ethane in the reaction of 2 with ethylene can be reasonably interpreted on the basis of this mechanism.

The reaction of tetradeuteride complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ (2-d_4) with atmospheric ethylene in toluene afforded 6 and ethane. It is noteworthy that the isotopomers of ethane detected in this reaction were C_2H_2 and C_2H_5D in a (2.2–2.8):1 ratio and that the formation of $C_2H_4D_2$ was not observed at all. Another important feature of this reaction is the formation of ethylene-*d* in the initial stage of the reaction. These results strongly suggest that scrambling of deuterium between 2-d_4 and large excess amounts of ethylene yielding tetrahydride 2 and ethylene-*d* proceeds much faster than reductive elimination of ethane-d_2 from an intermediate **B**-d_4 (Scheme 7). The $CHD{=}CH_2$ formed by the scrambling in the initial stage of the reaction is then hydrogenated to ethane-*d* in the reaction with 2.

Coupling Reaction among Coordinated Ethylene and Two Vinyl Ligands on a Dinuclear Ruthenium Complex. Although a number of examples of C–H bond activation of alkenes by soluble transition metal compounds exist, successful examples of functionalization of resulting metal bound alkenyl groups are scarce. We have so far demonstrated the activation of organic substrates on the dinuclear complex in which two ruthenium centers are bound with bridging hydride. Dinuclear complexes should activate the substrates more effectively than

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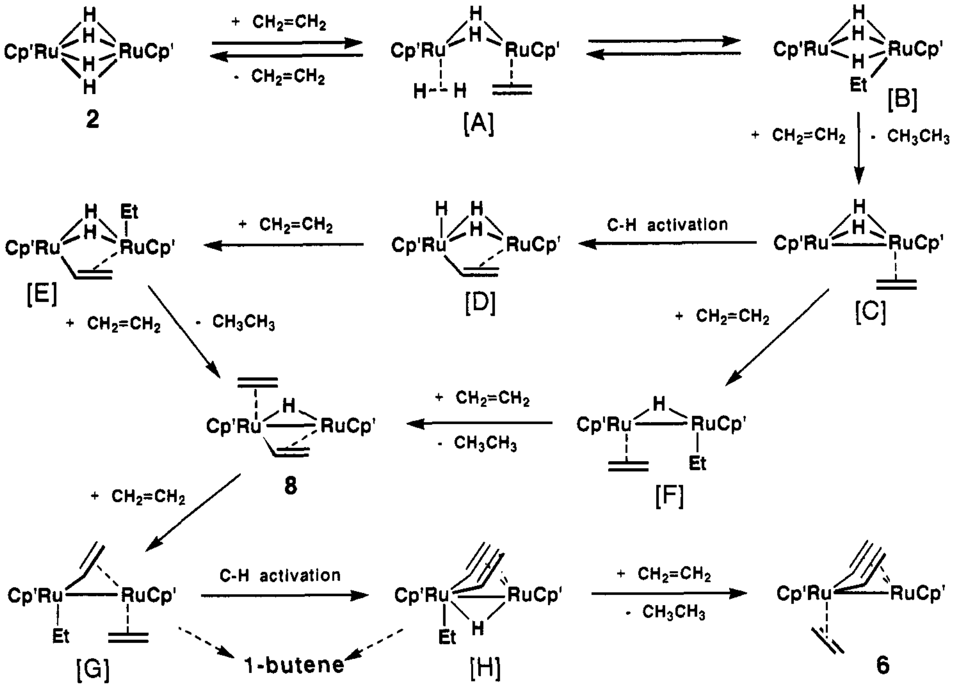
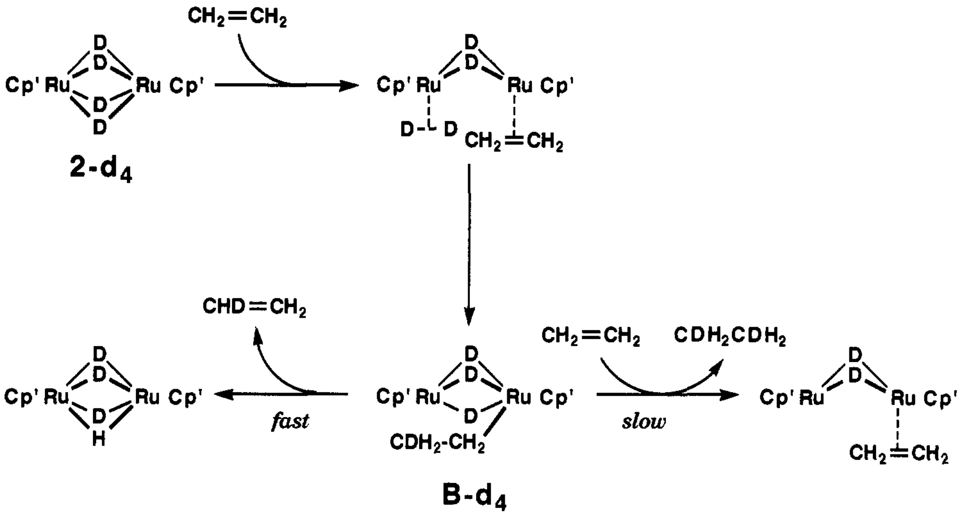
[19] Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874.

Scheme 6

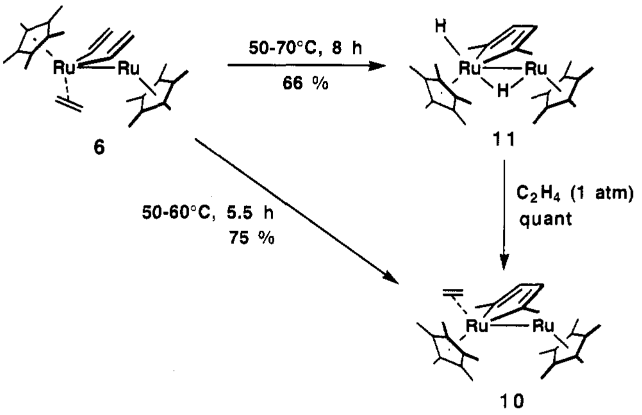


Scheme 7



mononuclear ones because the electron density at the metal centers can be modified by the electron exchange between metal centers through a metal–metal bond or bridging ligand.

Scheme 8



The reaction of the divinyl complex **6** with atmospheric pressure ethylene in toluene at 60 °C for 5.5 h affords a 2,5-dimethylruthenacyclopentadiene complex **10** in a 75% yield together with a small amount of ethane and 1-butene (22%) (Scheme 8). Crystallization from toluene/pentane gives analytically pure **10** as orange prisms. When **6** is heated in benzene in the absence of ethylene, analogous 2,5-dimethylruthenacyclopentadiene complex **11** is formed, which is isolated as an orange oily substance after purification by column chromatography on neutral alumina with hexane/acetone. We have examined the possibility that complex **11** plays a role as an intermediate in the formation of **10**. Exposure of the solution of **11** in toluene to atmospheric pressure ethylene at ambient temperature resulted in the quantitative conversion of **11** to **10**, and an equimolar amount of ethane formed in this reaction was detected and quantified by means of gas chromatography. From these results we can conclude that complex **10** was formed by way of **11** and the C_6 framework of the metallacycle **10** originated from the two vinyl groups and the ethylene ligand coordinated in **6**. An ethylene molecule added to **6** was never incorporated in the

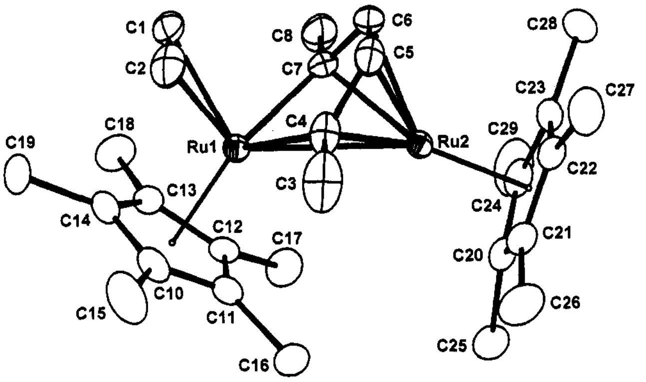


Figure 8. Molecular structure of **10**, with thermal ellipsoids at the 30% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 10[a]

Ru(1)-Ru(2)	2.867(1)		
Ru(1)-C(1)	2.182(7)	Ru(2)-C(4)	2.128(6)
Ru(1)-C(2)	2.188(9)	Ru(2)-C(5)	2.128(7)
Ru(1)-C(4)	2.052(6)	Ru(2)-C(6)	2.131(6)
Ru(1)-C(7)	2.064(6)	Ru(2)-C(7)	2.134(5)
Ru(1)-C(10)	2.293(6)	Ru(2)-C(20)	2.297(5)
Ru(1)-C(11)	2.255(5)	Ru(2)-C(21)	2.254(5)
Ru(1)-C(12)	2.261(5)	Ru(2)-C(22)	2.181(5)
Ru(1)-C(13)	2.297(5)	Ru(2)-C(23)	2.175(5)
Ru(1)-C(14)	2.292(5)	Ru(2)-C(24)	2.248(6)
C(1)-C(2)	1.389(13)	C(3)-C(4)	1.504(9)
C(4)-C(5)	1.419(9)	C(5)-C(6)	1.390(11)
C(6)-C(7)	1.393(9)	C(7)-C(8)	1.528(9)
CP(1)-Ru(1)-C(1)	116.0(2)	CP(2)-Ru(2)-C(4)	142.8(2)
CP(1)-Ru(1)-C(2)	115.4(2)	CP(2)-Ru(2)-C(5)	133.9(2)
CP(1)-Ru(1)-C(4)	134.3(2)	CP(2)-Ru(2)-C(6)	133.6(2)
CP(1)-Ru(1)-C(7)	133.9(2)	CP(2)-Ru(2)-C(7)	142.3(2)
C(4)-Ru(1)-C(7)	77.6(2)	C(3)-C(4)-C(5)	120.7(6)
C(3)-C(4)-Ru(1)	124.4(5)	C(5)-C(4)-Ru(1)	111.8(4)
Ru(1)-C(4)-Ru(2)	86.6(2)	C(4)-C(5)-C(6)	115.0(6)
C(5)-C(6)-C(7)	115.0(6)	C(6)-C(7)-C(8)	120.3(5)
C(6)-C(7)-Ru(1)	112.5(5)	C(8)-C(7)-Ru(1)	124.3(4)
Ru(1)-C(7)-Ru(2)	86.1(2)		

[a] CP(1) and CP(2) are the centroids of the C_5Me_5 ligands.

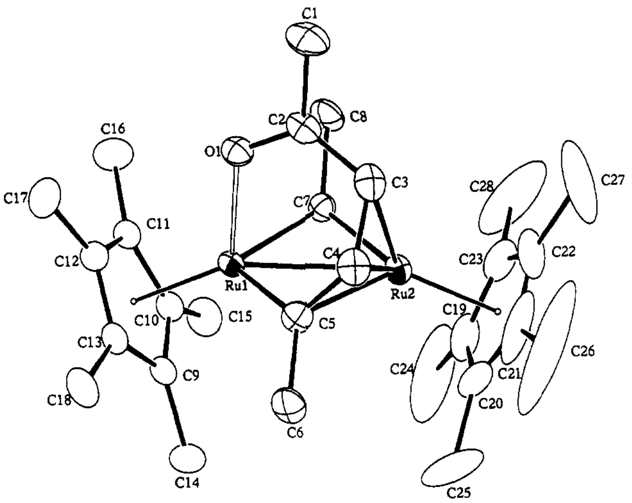
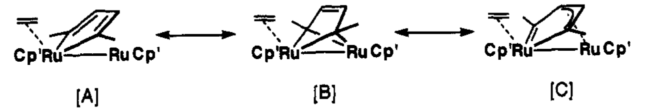


Figure 9. Molecular structure of **13**, with thermal ellipsoids at the 30% probability level.

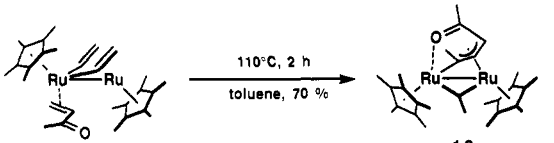
Scheme 9



metallacycle **10**. To our knowledge, such a type of C–C bond forming reaction among the three C_2 units is unprecedented.

Complexes **10** and **11** are characterized on the basis of the ^1H and ^{13}C NMR and ^1H–^{13}C COSY spectra. The molecular structure of **10** was determined by the X-ray diffraction studies. The results are displayed in Figure 8 with a numbering scheme. Table 4 lists some of the relevant bond distances and angles. Figure 8 clearly establishes the structural identity of **10**.

The interatomic distance between the ruthenium atoms is 2.867(1) Å, corresponding to a Ru—Ru single bond. The two ruthenium atoms are bridged by a $\eta^2{:}\eta^4$-μ-C_6H_8 fragment. The values of 2.052(6) and 2.064(6) Å for the Ru(1)—C(4) and Ru(1)—C(7) distances, respectively, indicate that the ends of the bridging C_6 fragments, C(4) and C(7), are σ-bonded to Ru(1). The Ru(2)—C(4) and Ru(2)—C(7) distances of 2.128(6) and 2.134(5) Å, respectively, are significantly longer than those for Ru(1)—C(4) and Ru(1)—C(7) and consistent with the Ru—C π-bonds. The C(5)—C(6) distance is very similar to that of the coordinated ethylene, C(1)—C(2) = 1.389(13) Å, and slightly shorter than those of C(4)—C(5) and C(6)—C(7), C(5)—C(6) = 1.390(11) Å vs C(4)—C(5) = 1.419(9) and C(6)—C(7) = 1.393(9) Å. The unusually short C(5)—C(6) distance may be in terms of the resonance represented in Scheme 9. When we monitored the conversion of **6** into metallacycle **11** by ^1H NMR spectroscopy to elucidate the mechanism for metallacycle formation, no indications of the existence of a stable intermediate were recognized. To elucidate the mechanism for the formation of metallacycle **10**, the thermal transformation of divinyl complex **12** was attempted. When the solution of divinyl complex (η^5-C_5Me_5)Ru($CH{=}CH_2$)$_2$($CH_2{=}CHC(O)CH_3$)Ru(η^5-C_5Me_5) (**12**) in toluene was heated at 110 °C for 5 h, a novel dinuclear μ-alkylidene complex **13** was obtained as a purple microcrystalline solid in an isolated yield of 70% (eq 4).



12 13 (4)

Complex **13** was characterized on the basis of the ^1H NMR, ^{13}C NMR, ^1H–^{13}C COSY, IR, and FD-MS spectra and analytical data. A characteristic resonance peak for the μ-alkylidene carbon appears at δ 182.2 (d, J_{CH} = 133 Hz) in the ^{13}C NMR spectrum. The infrared spectrum of **13** reveals a strong absorption ascribed to the CO stretching at 1557 cm^{-1}. The red-shift of the stretching vibration of the carbonyl group suggests the intramolecular coordination of carbonyl oxygen to one of the ruthenium centers. A *cis*-disposition of the conjugated olefin moiety (J_{HH} = 6 Hz) is also indicative of the intramolecular coordination.

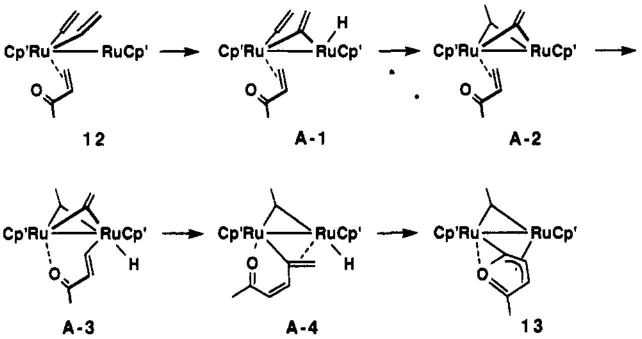
The molecular structure of **13** was established by X-ray diffraction studies by using single crystals obtained from tetrahydrofuran. The molecular structure is shown in Figure 9, and the relevant geometrical parameters are given in Table 5.

The 18-electron formalism applied to **13** requires that complex **13** has a single ruthenium–ruthenium bond. Indeed, the Ru(1)–Ru(2) distance of 2.738(1) Å lies within the range of those observed for a ruthenium–ruthenium single bond. The short Ru(1)–O(1) distance of 2.110(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) for 13

Ru(1)–Ru(2)	2.738(1)	Ru(2)–C(23)	2.224(5)
Ru(1)–O(1)	2.110(3)	Ru(2)–C(24)	2.119(5)
Ru(1)–C(25)	2.034(5)	Ru(2)–C(25)	2.185(5)
Ru(1)–C(27)	2.075(5)	Ru(2)–C(27)	2.092(5)
Ru(1)–C(1)	2.238(5)	Ru(2)–C(11)	2.209(6)
Ru(1)–C(2)	2.226(5)	Ru(2)–C(12)	2.196(7)
Ru(1)–C(3)	2.232(5)	Ru(2)–C(13)	2.195(8)
Ru(1)–C(4)	2.235(5)	Ru(2)–C(14)	2.182(7)
Ru(1)–C(5)	2.257(5)	Ru(2)–C(15)	2.213(6)
O(1)–C(22)	1.259(6)	C(21)–C(22)	1.521(8)
C(22)–C(23)	1.421(8)	C(23)–C(24)	1.445(8)
C(24)–C(25)	1.404(7)	C(25)–C(26)	1.506(7)
C(27)–C(28)	1.512(7)		
C(25)–Ru(1)–C(27)	100.9(2)	C(25)–Ru(2)–C(27)	95.6(2)
O(1)–Ru(1)–C(25)	88.0(2)	O(1)–Ru(1)–C(27)	82.5(2)
Ru(1)–C(25)–Ru(2)	80.8(2)	Ru(1)–C(27)–Ru(2)	82.2(2)
Ru(1)–C(25)–C(26)	124.7(4)	Ru(1)–C(27)–C(28)	123.9(4)
Ru(2)–C(25)–C(26)	125.4(4)	Ru(2)–C(27)–C(28)	123.4(4)
Ru(1)–C(25)–C(24)	119.9(4)	C(24)–C(25)–C(26)	115.2(5)
C(23)–C(24)–C(25)	121.3(5)	C(22)–C(23)–C(24)	119.6(5)
C(21)–C(22)–C(23)	119.2(5)	O(1)–C(22)–C(21)	117.4(5)
O(1)–C(22)–C(23)	123.4(5)		

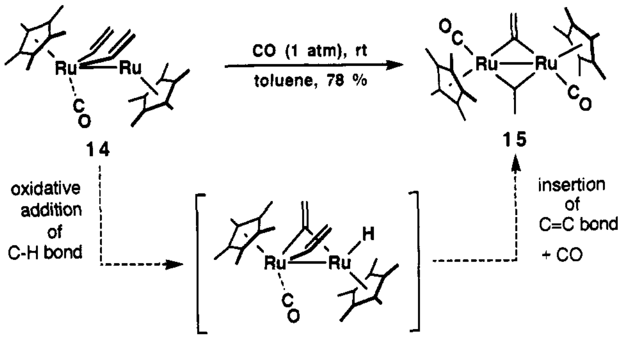
Scheme 10



Å is compatible with the intramolecular coordination of carbonyl oxygen suggested by the red-shift of the ν_{CO} band in the IR spectrum. The alkylidene carbon C(27) bridges two ruthenium centers and the values of 2.075(5) and 2.092(5) Å for Ru(1)–C(27) and Ru(2)–C(27), respectively, correspond with the ruthenium–carbon σ-bond. The values of 2.224(5), 2.119(5), and 2.185(5) Å for Ru(2)–C(23), Ru(2)–C(24), and Ru(2)–C(25), respectively, are significantly longer than the ruthenium–carbon σ-bond, and indicate that the C_3 moiety, C(23)–C(24)–C(25), is coordinated to Ru(2) as a η^3-allyl ligand. An important feature of the structure is that branch C(24)–C(23)–C(22)-{O(1)}–C(21) originates from the methyl vinyl ketone initially coordinated in **12**. Although no intermediary species could be detected by ^{1}H NMR, we can propose several possible reaction paths leading to the formation of **13**. One of the plausible reaction paths is shown in Scheme 10, which involves an initial oxidative addition of a C–H bond at the α-carbon of the vinyl ligand, followed by the insertion of the remaining vinyl group into a Ru–H bond.

Activation of a C(sp^2)–H bond at the α-carbon of the vinyl group can be expected to yield the μ-vinylidene species **A1**, which would undergo insertion of the remaining vinyl group into a Ru–H bond to give the μ-ethylidene–μ-vinylidene intermediate **A2**. The occurrence of two important elementary steps, i.e., vinylic C–H activation at the α-carbon and insertion of the vinyl group into a metal–H bond, are supported on the basis of precedent results. There have been several reported examples of the transformation of the μ-σ,π-vinyl ligand to a μ-vinylidene one.[20] Insertion of the vinyl group into a metal–H bond to generate a μ-ethylidene complex has also been well established.[20a] In the reaction of carbonyl divinyl complex **14** with carbon monoxide, an analogous μ-ethylidene–μ-vinylidene complex **15** was also obtained via the activation of a C(α)–H bond and the subsequent insertion of a vinylic C=C bond into a resulting Ru–H bond (Scheme 11).[21] This result strongly supports the reaction path leading to intermediate **A2**.

Scheme 11



The oxidative addition of a C–H bond at the terminal position of the coordinated methyl vinyl ketone followed by the reductive coupling of the resulting 3-oxobut-1-en-1-yl ligand with the vinylidene ligand can yield an intermediate **A4** by way of **A3**. Finally, insertion of a vinylic carbon–carbon double bond into a Ru–H bond would give the μ-alkylidene complex **13**.

The formation of ruthenacycle complex **11** or **10** in the thermal reaction of **6** could be reasonably interpreted if we assumed that the reaction of **6** proceeded similarly to that of methyl vinyl ketone complex **12**. Scheme 12 represents a possible route to ruthenacycle **10**.

A μ-ethylidene intermediate **B5**, which corresponds to complex **13** in Scheme 11, is provided via the intermediary complexes **B1**–**B4**. The actual structure of **B5** can be represented as a resonance hybrid somewhere among three extremes, **B5**, **B5′**, and **B5″**. Contributions of such resonance hybrids for the μ-propenylidene complexes of ruthenium and iron have already been pointed out by Knox et al. (Scheme 13).[22]

Reductive C–C coupling at the Ru2 center should yield a ruthenacyclopentene **B6**. Activation of an allylic C–H bond followed by H abstraction at C(α') afforded ruthenacyclopentadiene **11**. In the presence of ethylene, **11** is converted to **10** with the formation of ethane.

According to this mechanism, the ethylene molecule coordinated in **6** should be incorporated in the ruthenacycle **10** as a C(3) and C(4) moiety. Furthermore, C(2) and C(5) of the metallacycle, and two methyl groups attached to

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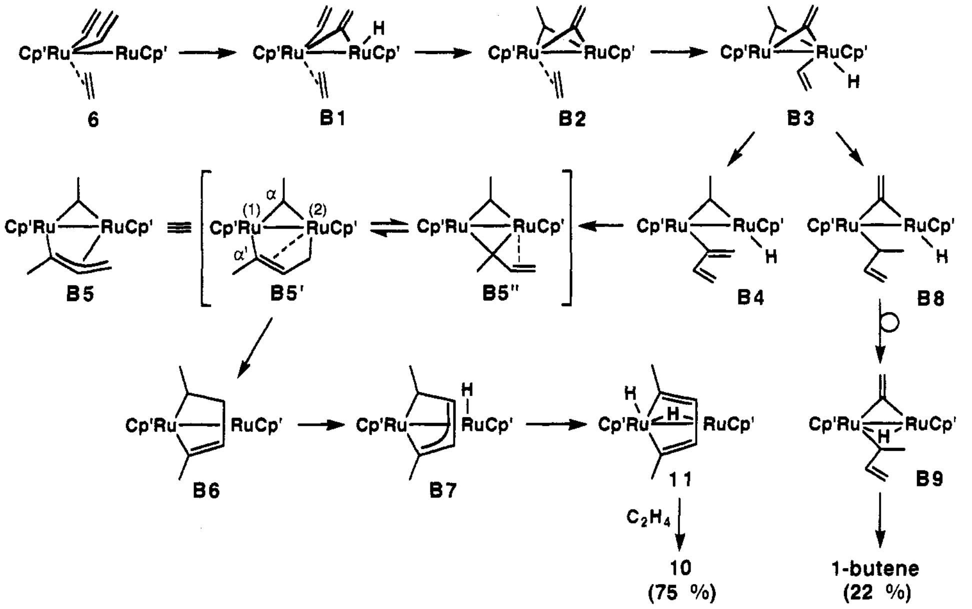
[20] (a) Brain, F. G. J.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 547. (b) Casey, C. P.; Marder, S. P.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700. (c) Delgodo, E.; Hein, J.; Jeffery, J. C.; Rathermann, A. L.; Stone, F. G. A.; Farrugia, L. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1191. (d) Green, M.; Orpen, A. G.; Schaverin, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 14333.

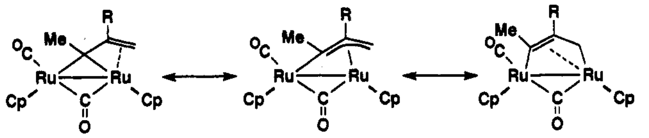
[21] Fukushima, M.; Suzuki, H.; Moro-oka, Y. *Abstracts, 38th Symposium on Organometallic Chemistry, Japan*, Kyoto, October 1991; PA111.

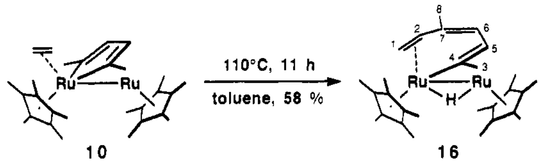
[22] (a) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1985**, 1935. (b) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297. (d) Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J. *J. Chem. Soc., Chem. Commun.* **1981**, 537. (e) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803.

Scheme 12



Scheme 13





(5)

C(2) and C(5) must be originating from the two vinyl ligands coordinated in **6**. An experiment using ethylene-d_4 was attempted to verify the mechanism shown in Scheme 13. However, the attempt was in vain because the labeled complex (η^5-C_5Me_5)Ru(CD_2=CD_2)(CH=CH_2)$_2$-Ru(η^5-C_5Me_5) (**6**-d_4) could not be obtained in pure form owing to the ethylene–vinyl ligand exchange process (*vide supra*). Moreover, at high temperatures (~50 °C), scrambling of deuterium due to the ethylene–vinyl ligand exchange proceeds predominantly over the metallacycle formation.

As shown in Scheme 8, pyrolysis of **6** in the presence of ethylene affords 1-butene in a 22% yield together with ruthenacycle **10** (75%). Scheme 12 also reasonably accounts for the formation of 1-butene. Reductive C–C coupling between an ethylidene ligand and a vinyl ligand in intermediate **B3** should lead to **B8**. The β-H elimination from **B9**, a positional isomer of **B8**, gives 1-butene. This mechanism involving two competitive reductive coupling paths for the intermediate **B3**, the coupling of μ-vinylidene with a vinyl ligand *vs* coupling between μ-ethylidene and a vinyl ligand, is well consistent with the fact that the sum of the yields of complex **10** and 1-butene is almost 100%. At this stage, we have no direct evidence for the mechanism shown in Scheme 12; however, the isolation of μ-vinylidene complex **13** in the pyrolysis of **12** and the detection of 1-butene strongly suggest the validity of this mechanism.

Carbon Chain Growth on the Dinuclear Ruthenacyclopentadiene Complexes. Insertion of Coordinated Olefin into a Ru–C Bond. Heating ruthenacycle **10** in refluxing toluene for 11 h followed by chromatographic purification on neutral alumina with pentane affords a dinuclear μ-η^2:η^2:η^2-5-methylhepta-2,4,6-trien-2-yl complex **16** in a 58% yield as an orange microcrystalline solid (eq 5). Complex **16** is also derived directly from tetrahydride **2** in the reaction with an excess of ethylene (50 atm) in an autoclave at 110 °C.

The structure of **16** has been unequivocally determined on the basis of ^1H and ^{13}C NMR, ^1H–^{13}C COSY, and IR spectra.

The ^{13}C NMR spectrum reveals eight signals except for those for two sets of the C_5Me_5 group at δ 10.9 (1), 11.2 (q), 89.1 (s), and 92.8 (s). Signals for two quaternary carbons, C(4) and C(7), appear at δ 163.1 and 67.9, respectively. The shift of δ 163.1 ppm is comparable to those for the α-carbon of the μ-σ,π-vinyl group (*vide supra*, Table 3). Two quartets observed at δ 26.8 (q, J_{CH} = 125.2 Hz) and 37.7 (q, 122.6 Hz) are assignable to the methyl carbons bound to C(4) and C(7). The resonance for the terminal carbon atom C(1) appears at δ 32.0 as a doublet of doublets (J_{CH} = 151.2 and 157.5 Hz). Three resonances for the olefin carbons C(2), C(6), and C(5) are found at δ 44.5, 85.4, and 96.9, respectively.

The hydride ligand can be observed by NMR and IR. In the ^1H NMR spectrum a hydride resonance of intensity 1 relative to each C_5Me_5 group is found at δ −16.0. In the IR spectrum a weak absorption at 1848 cm^{-1} can be assigned to the stretching vibration of Ru–H. The red-shift of the Ru–H band is consistent with the bridging hydride.

Complex **6** is soluble in aromatic solvents and a single crystal of **16** suitable for an X-ray diffraction study was obtained from a mixed solvent of toluene and pentane. Figure 10 displays the molecular structure of **16**, and Table 6 lists the bond distances and angles.

The structure shown in Figure 11 is fully consistent with the spectral data. The complex contains an η^6-bound C_8H_6 ligand in which one of the three double bonds is bound to Ru(1) in an η^2-fashion and the remaining two double bonds are coordinated to Ru(2) in an η^4-fashion. The Ru(1)–C(4) distance of 2.019(5) Å is compatible with the existence of the σ-bond between them. Ru(1) is bound to C(1) and C(2) in the π-mode [Ru–C_{av} = 2.200(6) Å].

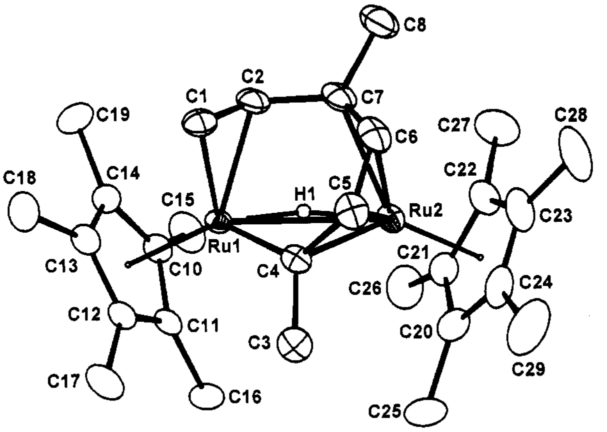


Figure 10. Molecular structure of **16**, with thermal ellipsoids at the 30% probability level.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 16[a]

Ru(1)–Ru(2)	2.905(1)		
Ru(1)–C(1)	2.155(6)	Ru(2)–C(4)	2.223(5)
Ru(1)–C(2)	2.144(6)	Ru(2)–C(5)	2.175(6)
Ru(1)–C(4)	2.019(5)	Ru(2)–C(6)	2.149(6)
Ru(1)–C(10)	2.248(5)	Ru(2)–C(7)	2.279(6)
Ru(1)–C(11)	2.248(5)	Ru(2)–C(20)	2.231(6)
Ru(1)–C(12)	2.261(5)	Ru(2)–C(21)	2.232(6)
Ru(1)–C(13)	2.244(6)	Ru(2)–C(22)	2.225(6)
Ru(1)–C(14)	2.258(6)	Ru(2)–C(23)	2.194(8)
Ru(1)–H(1)	1.62(6)	Ru(2)–C(24)	2.173(6)
C(1)–C(2)	1.411(10)	Ru(2)–H(1)	1.64(6)
C(3)–C(4)	1.531(8)	C(2)–C(7)	1.465(10)
C(5)–C(6)	1.430(9)	C(4)–C(5)	1.415(8)
C(7)–C(8)	1.528(10)	C(6)–C(7)	1.395(10)
CP(1)–Ru(1)–C(1)	118.1(2)	CP(2)–Ru(2)–C(4)	188.8(1)
CP(1)–Ru(1)–C(2)	130.7(2)	CP(2)–Ru(2)–C(5)	134.0(2)
CP(1)–Ru(1)–C(4)	135.8(2)	CP(2)–Ru(2)–C(6)	132.5(2)
C(1)–C(2)–C(7)	122.5(6)	C(3)–C(4)–C(5)	112.9(5)
C(4)–C(5)–C(6)	122.5(6)	C(5)–C(6)–C(7)	124.2(6)
C(2)–C(7)–C(6)	120.5(6)	C(6)–C(7)–C(8)	118.7(6)
C(2)–C(7)–C(8)	115.0(6)	Ru(1)–C(4)–Ru(2)	86.3(2)
Ru(1)–H(1)–Ru(2)	126(4)		

[a] CP(1) and CP(2) are the centroids of the C_5Me_5 ligands.

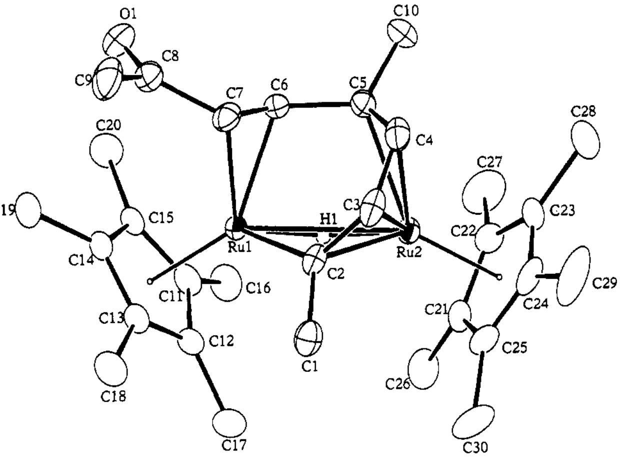


Figure 11. Molecular structure of **17**, with thermal ellipsoids at the 30% probability level.

Significantly long distances (average 2.207 Å) for Ru(2)–C(4–7) bonds are comparable of those between Ru and π-bonded carbon. Two C_5Me_5 rings are mutually *cis* with respect to the Ru–Ru vector. Although the 18-electron formalism requires that complex **16** have a double ruthenium–ruthenium bond, the observed Ru–Ru distance of 2.905(1) Å is much longer than that for metal–metal double bond and corresponds to a singly bonded metal–metal distance. The hydride ligand equally bridges the two ruthenium atoms. The average Ru–H distance of 1.63(6) Å in **16** lies in the range of the metal–hydrogen distances in the transition metal hydride complexes.[23]

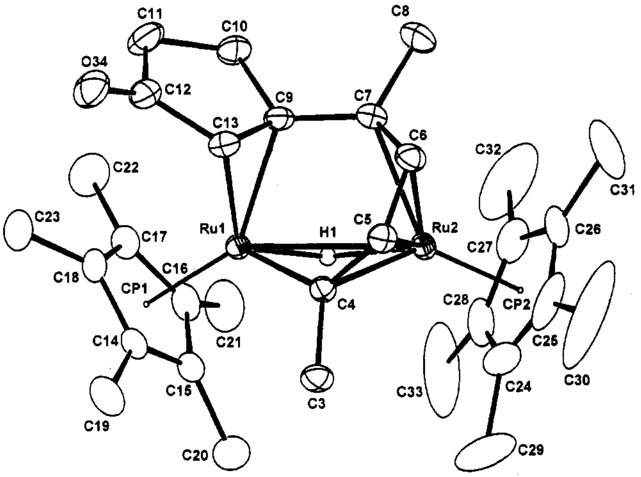
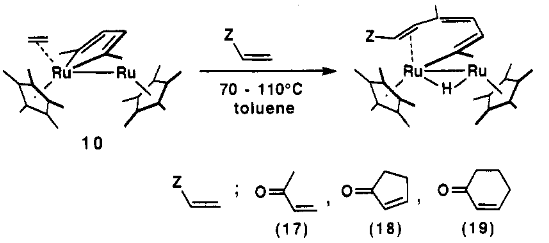


Figure 12. Molecular structure of **18**, with thermal ellipsoids at the 30% probability level.

The formation of **16** can be reasonably elucidated by the mechanism involving an insertion of the coordinated ethylene into one of the ruthenium–carbon σ-bonds of ruthenacyclopentadiene **10** at the initial stage of the reaction. Subsequent β-H elimination from the resulting intermediary ruthenacycloheptadiene yields complex **16**.

Electron-deficient olefin such as methyl vinyl ketone, cyclopentanone, or cyclohexenone is efficiently and regioselectively introduced into the carbon skeleton instead of ethylene when **10** is heated in toluene in the presence of such electron-deficient olefins (eq 6).



(6)

Treatment of the ruthenacycle **10** with 1.4 equiv of methyl vinyl ketone in toluene at 70 °C for 4 h affords a dinuclear trienyl complex **17** in 33% isolated yield. Under similar reaction conditions, the olefin adduct **18** or **19** is obtained upon treatment of **10** with cyclopentenone or cyclohexenone. In the IR spectra, characteristic bands ascribed to the stretching vibration of the carbonyl groups appear at 1650, 1632, and 1665 cm^{-1} for **17–19**, respectively. This shows that the carbonyl groups in **17–19** are not coordinated to the ruthenium centers. Resonance signals for the hydride ligands are observed in the region δ −16 to −17 ppm in the ^1H NMR spectra of these complexes.

Results of the X-ray diffraction studies for **17** and **18** are illustrated in Figures 11 and 12, and selected bond lengths and angles are listed in Tables 7 and 8.

Structures shown in Figures 11 and 12 establish the structural identities of **17** and **18**. In each case, electron-

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(23) For example, see: Frenz, B. A.; Ibers, J. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker, Inc.: New York, 1971; Chapter 3.

Table 7. Selected Bond Distances (Å) and Angles (deg) for 17

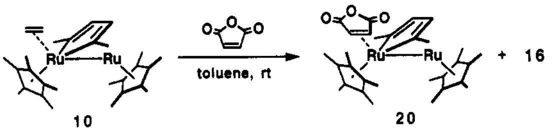
Ru(1)–Ru(2)	2.9096(8)	Ru(2)–C(2)	2.236(6)
Ru(1)–C(2)	2.038(6)	Ru(2)–C(3)	2.156(6)
Ru(1)–C(6)	2.131(6)	Ru(2)–C(4)	2.137(7)
Ru(1)–C(7)	2.171(6)	Ru(2)–C(5)	2.257(6)
Ru(1)–C(11)	2.233(6)	Ru(2)–C(21)	2.248(6)
Ru(1)–C(21)	2.225(6)	Ru(2)–C(22)	2.196(6)
Ru(1)–C(13)	2.252(6)	Ru(2)–C(23)	2.182(6)
Ru(1)–C(14)	2.290(6)	Ru(2)–C(24)	2.177(6)
Ru(1)–C(15)	2.296(6)	Ru(2)–C(25)	2.228(6)
Ru(1)–H(1)	1.73(5)	Ru(2)–II(1)	1.67(5)
C(1)–C(2)	1.497(9)	C(2)–C(3)	1.403(9)
C(3)–C(4)	1.43(1)	C(4)–C(5)	1.39(1)
C(5)–C(6)	1.472(9)	C(5)–C(10)	1.51(1)
C(6)–C(7)	1.40(1)	C(7)–C(8)	1.473(9)
C(8)–C(9)	1.50(1)	O(1)–C(8)	1.224(9)
C(2)–Ru(1)–C(6)	91.2(3)	C(2)–Ru(2)–C(3)	37.2(2)
C(2)–Ru(1)–C(7)	83.6(3)	C(2)–Ru(2)–C(4)	69.7(3)
C(6)–Ru(1)–H(1)	79(2)	C(2)–Ru(2)–C(5)	83.3(2)
C(7)–Ru(1)–H(1)	114(2)	C(3)–Ru(2)–C(4)	38.9(5)
C(6)–Ru(1)–C(7)	38.1(3)	C(3)–Ru(2)–C(5)	68.4(3)
Ru(1)–C(2)–C(1)	121.3(4)	Ru(1)–C(2)–C(3)	124.3(5)
C(1)–C(2)–C(3)	114.0(6)	C(2)–C(3)–C(4)	124.1(6)
C(3)–C(4)–C(5)	123.8(6)	C(4)–C(5)–C(6)	119.6(7)
C(4)–C(5)–C(10)	120.2(6)	C(6)–C(5)–C(10)	113.3(6)
C(5)–C(6)–C(7)	120.7(6)	C(6)–C(7)–C(8)	120.5(7)
C(7)–C(8)–C(9)	115.9(7)	C(7)–C(8)–O(1)	123.7(8)
C(9)–C(8)–O(1)	120.3(7)		

Table 8. Selected Bond Distances (Å) and Angles (deg) for 18

Ru(1)–Ru(2)	2.9204(8)	Ru(2)–C(4)	2.217(3)
Ru(1)–C(4)	2.048(3)	Ru(2)–C(5)	2.181(4)
Ru(1)–C(9)	2.163(3)	Ru(2)–C(6)	2.149(4)
Ru(1)–C(13)	2.172(4)	Ru(2)–C(7)	2.269(4)
Ru(1)–C(14)	2.235(4)	Ru(2)–C(24)	2.221(5)
Ru(1)–C(15)	2.234(4)	Ru(2)–C(25)	2.172(4)
Ru(1)–C(16)	2.273(4)	Ru(2)–C(26)	2.192(4)
Ru(1)–C(17)	2.350(4)	Ru(2)–C(27)	2.212(4)
Ru(1)–C(18)	2.299(1)	Ru(2)–C(28)	2.240(5)
Ru(1)–H(1)	1.73(4)	Ru(2)–H(1)	1.81(4)
C(3)–C(4)	1.514(4)	C(1)–C(5)	1.416(4)
C(5)–C(6)	1.432(5)	C(6)–C(7)	1.422(5)
C(7)–C(8)	1.517(5)	C(7)–C(9)	1.477(5)
C(9)–C(10)	1.532(5)	C(10)–C(11)	1.528(6)
C(11)–C(12)	1.526(6)	C(12)–C(13)	1.466(5)
C(12)–O(34)	1.217(5)	C(13)–C(9)	1.434(5)
C(4)–Ru(1)–C(9)	90.3(1)	C(4)–Ru(2)–C(5)	37.6(1)
C(4)–Ru(1)–C(13)	82.4(1)	C(4)–Ru(2)–C(6)	70.1(1)
C(9)–Ru(1)–H(1)	86(1)	C(4)–Ru(2)–C(7)	83.5(1)
C(13)–Ru(1)–H(1)	121(1)	C(5)–Ru(2)–C(6)	38.6(1)
C(9)–Ru(1)–C(13)	38.6(1)	C(5)–Ru(2)–C(7)	68.4(1)
Ru(1)–C(4)–C(3)	121.1(2)	Ru(1)–C(4)–C(5)	125.4(2)
Ru(1)–C(4)–Ru(2)	86.4(1)	C(3)–C(4)–C(5)	112.8(3)
C(4)–C(5)–C(6)	123.4(3)	C(5)–C(6)–C(7)	122.7(3)
C(6)–C(7)–C(9)	119.7(3)	C(6)–C(7)–C(8)	116.9(3)
C(8)–C(7)–C(9)	116.9(3)	C(7)–C(9)–C(13)	121.5(3)
C(7)–C(9)–C(10)	120.4(3)	C(9)–C(10)–C(11)	105.5(3)
C(9)–C(13)–C(12)	109.7(3)	C(10)–C(11)–C(12)	106.4(3)
C(11)–C(12)–C(13)	108.4(3)	C(11)–C(12)–O(34)	124.4(4)
C(13)–C(12)–O(34)	126.9(7)		

deficient olefin added to 10 is regioselectively incorporated in the carbon skeleton.

Although the coupling reaction of ruthenacyclopentadiene 10 with electron-deficient olefins proceeds smoothly, complex 10 shows a great resistance to the reaction with an electron-rich olefin such as cyclopentene or propene. Treatment of toluene solution of 10 with propene (3 atm) at 100 °C for 5 h in an autoclave forms neither insertion products corresponding to 16 nor an analogue of 10 having a propene ligand but results in the quantitative recovery of 10. On the other hand, the ethylene ligand coordinated in 10 can readily be replaced by added electron-deficient olefin. Treatment of ruthenacycle complex 10 with maleic anhydride in toluene at room temperature affords a substitution product 20 together with the ethylene-insertion product 16 (eq 7).



(7)

On the basis of these results, it can be concluded that the C–C coupling reaction between 10 and electron-deficient olefins shown in eq 6 proceeds by way of a metallacycle intermediate analogous to 20.

Experimental Section

All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques. Toluene, benzene, and pentane were all purified and distilled under argon prior to use according to an established procedure. Benzene-d_6 was dried over molecular sieves 4A under an atmosphere of argon and was vacuum transferred into a storage vessel. Reagents used in this study that were purchased from commercial sources and used without further purification were as follows: trimethylphosphine, methyl vinyl ketone, acrylonitrile, acrolein, methyl acrylate, dimethyl maleate, maleic anhydride, cyclopentene, and cyclohexene. Ethylene and propene were purchased from Takachiho Koeki Co. Ltd. and used without further purification. The neutral alumina (Merck Art. 1097) used for column chromatography was deoxygenated under vacuum.

Infrared spectra were recorded on a Hitachi 260-50 spectrophotometer. ^1H, ^{13}C, and ^1H–^{13}C 2D-COSY spectra were recorded on JEOL GX-270 or GX-500 instruments. Field-desorption mass spectra were measured on a Hitachi GC–MS M80 high resolution mass spectrometer.

Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology. $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ was prepared according to previously published method.[6a]

$(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (2). To a stirred suspension of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (5.04 g, 8.21 mmol) in diethyl ether (50 mL) was added $LiAlH_4$ (1.41 g, 37.1 mmol) at −78 °C. The mixture was then slowly warmed to room temperature and allowed to stir for 5 h. The color of the suspension changed from brown to yellow. The suspension was again cooled to −78 °C. Ethanol (35 mL) was added dropwise to the cooled suspension. After warming to room temperature, the resulting dark brown mixture was allowed to stir for 12 h. Removal of the solvent under reduced pressure gave a black-brown residue. The products were extracted with five portions of 150 mL of degassed toluene and the combined extract was passed through short columns packed with Celite and neutral alumina. The filtrate was concentrated to ca. 100 mL under reduced pressure and purified by column chromatography on alumina (Merck Art. 1097) with toluene afforded 2.57 g (66%) of a red crystalline solid. Anal. Found (calcd) for $C_{20}H_{34}Ru_2$: C, 50.37 (50.39); H, 7.27 (7.18). ^1H NMR (C_6D_6): δ 1.87 (s, 30H, C_5Me_5), −13.99 (s, 4H, Ru-*H*-Ru). ^{13}C NMR (C_6D_6): δ 12.5 (C_5Me_5), 88.2 (C_5Me_5). The field-desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{20}H_{34}Ru_2$ agreed with the calculated values within experimental error.

$(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}D)_2Ru(\eta^5\text{-}C_5Me_5)$ (2-d_2). The preparation of this compound from $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (2.30 g, 3.73 mmol) and $LiAlD_4$ (1.00 g, 23.9 mmol) in diethyl ether (30 mL) proceeded analogously to that of 2. After workup with ethanol and subsequent removal of solvent, the products were extracted with degassed toluene. The combined extract was filtered by passing through Celite and alumina short columns and was purified by column chromatography on alumina with toluene to afford 1.09 g (61%) of 2-d_2 as red crystalline solid. This compound was alternatively prepared by the addition of EtOD to the yellow suspension formed from the reaction of 1 (2.55 g, 4.14 mmol) with $LiAlH_4$ (0.785 g, 20.7 mmol). Procedures analogous to that of 2 gave 1.19 g (60%) of 2-d_2.

$(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ (2-d_4). The reaction of 1 with $LiAlD_4$ in diethyl ether followed by alcoholysis with EtOD gave 2-d_4, which was isolated as red microcrystals in a 63% yield according to the procedure analogous to that of 2.

Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (2) with CF_3SO_3H in Benzene. A 50-mL Schlenk tube was charged with 0.070 g (0.15 mmol) of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (2) and 5 mL of benzene. To the solution was added 0.075 g (0.50 mmol) of CF_3SO_3H, and the reaction mixture was allowed to stir at room temperature. The color of the solution immediately changed to green-brown with evolution of hydrogen. Standing for 5 h at room temperature afforded 0.133 g (97%) of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (3) as colorless prisms. Anal. Found (calcd) for $C_{17}H_{21}F_3O_3SRu$: C, 43.96 (44.06); H, 4.65 (4.57). ^1H NMR (CD_3COCD_3): δ 5.97 (s, 6H, C_6H_6), 2.04 (s, 15H, C_5Me_5). ^{13}C NMR (C_6D_6): δ 9.74 (C_5Me_5), 87.0 (C_6H_6), 96.5 (C_5Me_5).

Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ with Benzene in the Presence of $CHCl_3$. To a solution of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (0.150 g, 0.31 mmol) in 15 mL of benzene was added 4 mL of chloroform at room temperature. After stirring for 12 h at room temperature, 0.203 g (91%) of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)]Cl$ (4) was precipitated as a colorless crystalline solid. Anal. Found (calcd) for $C_{16}H_{21}ClRu$: C, 53.59 (54.93); H, 6.29 (6.05); Cl, 10.92 (10.13). ^1H NMR ($CDCl_3$): δ 2.03 (s, 15 H, C_5Me_5), 5.93 (s, 6H, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 10.8 (q, J_{C-H} = 128.0 Hz, C_5Me_5), 88.5 (d, J_{C-H} = 176.4 Hz, C_6H_6), 98.0 (s, C_5Me_5).

Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ with Toluene in the Presence of CH_2Cl_2. A 50-mL Schlenk tube was charged with 0.189 g (0.40 mmol) of 2 and 15 mL of dichloromethane. After stirring for 10 h at room temperature, the reaction mixture was concentrated to ca. 8 mL under reduced pressure. Then 10 mL of toluene was added. Standing the resulting mixture at room temperature yielded 0.289 g (99%) of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5CH_3)]Cl$ (5) as colorless needles. Anal. Found (calcd) for $C_{17}H_{23}ClRu$: C, 55.85 (56.11); H, 6.41 (6.37); Cl, 9.53 (9.74). ^1H NMR (CD_2Cl_2): δ 2.00 (s, 15 H, C_5Me_5), 2.33 (s, 3H, C_6H_5Me), 5.33–5.52 (m, 2H, aromatic), 5.80–5.95 (m, 3H, aromatic). ^{13}C NMR (CD_2Cl_2): δ 11.1 (q, J_{C-H} = 128.6 Hz, C_5Me_5), 19.0 (q, J_{C-H} = 129.2 Hz, C_6H_5Me), 87.4 (d, J_{C-H} = 176.0 Hz, aromatic), 88.1 (d, J_{C-H} = 151.9 Hz, aromatic), 88.9 (d, J_{C-H} = 171.7 Hz, aromatic), 96.9 (s, C_5Me_5), 100.6 (s, *ipso*).

Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ with H_2. A 300-mL glass autoclave was charged with 15 mg (0.032 mmol) of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ and 1 mL of C_6D_6. The autoclave was evacuated after the solvent was frozen by using a dry ice–methanol bath, and 1 atm of hydrogen was admitted to the autoclave at −78 °C. After stirring for 10 h at room temperature, ca. 0.4 mL of the reaction mixture was transferred by syringe into 5-mm NMR sample tube filled with argon. After measurement of a ^1H NMR spectrum, the sample was put back in the autoclave. Atmospheric pressure hydrogen was admitted again to the autoclave, and the solution was allowed to stir. The ^1H NMR spectra were measured three times at 10-h intervals and, additionally, two times at 2-h intervals. The H/D exchange reaction was completed after stirring for 34 h at room temperature.

$(\eta^5\text{-}C_5Me_5)Ru(CH_2{=}CH_2)(CH{=}CH_2)_2Ru(\eta^5\text{-}C_5Me_5)$ (6). A 50-mL Schlenk tube was charged with 0.445 g (0.93 mmol) of 2 and 15 mL of toluene. The Schlenk tube was evacuated after the solvent was frozen by using liquid nitrogen. Then the solution was warmed to room temperature, and a rubber baloon filled with 1 atm of ethylene was connected to the Schlenk tube. The color of the solution changed from red to red-purple after stirring under an atmosphere of ethylene for 24 h at room temperature. Removal of the solvent under reduced pressure gave a red-purple residue. Purification by column chromatography on alumina with toluene followed by recrystallization from toluene–pentane afforded 0.372 g (73%) of 6 as red-purple plates. IR (KBr, cm^{-1}): 3046, 2965, 2934, 2896, 1447, 1374, 1235, 1175, 1022, 776, 485. Anal. Found (calcd) for $C_{26}H_{40}Ru_2$: C, 56.02 (56.29); H, 7.33 (7.27). ^1H NMR (C_6D_6): δ 1.49 (s, 15H, C_5Me_5), 1.57 (s, 15H, C_5Me_5), 1.58 (d, J = 11.0 Hz, 2H, CHH=CHH), 1.86 (d, J = 11.0 Hz, 2H, CHH=CHH), 1.99 (dd, J = 9.2 and 1.2 Hz, 2H, Ru—CH=CHH), 3.65 (dd, J = 6.7 and 1.2 Hz, 2H, Ru—CH=CHH), 9.98 (dd, J = 9.2 and 6.7 Hz, 2H, Ru—CH=CHH). ^{13}C NMR (C_6D_6): δ 9.74 (q, J_{C-H} = 126.1 Hz, C_5Me_5), 10.34 (q, J_{C-H} = 126.8 Hz, C_5Me_5), 48.9 (dd, J_{C-H} = 157.0 and 151.2 Hz, $CH_2{=}CH_2$), 54.5 (dd, J_{C-H} = 146.1 and 160.1 Hz, Ru—CH=CH_2), 91.1 (s, C_5Me_5), 95.4 (s, C_5Me_5), 188.5 (d, J_{C-H} = 156.9 Hz, Ru—CH=CH_2). Field-desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{26}H_{40}Ru_2$ agreed with the calculated values within experimental error.

Analysis of Gases Formed during the Reaction of 2 with Ethylene. A 50-mL Schlenk tube equipped with a septa (sleeve stopper) was charged with 0.080 g (0.168 mmol) of 2 and 2 mL of toluene. The Schlenk tube was evacuated after the solvent was frozen by using a dry ice–methanol bath, and atmospheric pressure argon was admitted to the reactor. Then the solution was warmed to room temperature, and 20 mL of ethylene (1 atm) was charged through the septa by using a gastight syringe. After stirring at the temperature for 6 h, 2 mL (1 atm) of propane was added as a internal standard for GLC analysis. GLC analysis (column, 3 m × 3 mm; Porapack-Q; column temperature, 100 °C; injection temperature, 110 °C; N_2 flow rate, 20 mL/min; detector, FID) of the gas phase shows the formation of ethane (0.46 mmol, 270 mol % based on 2) and small amounts of 1-butene. Dihydrogen was not detected at all in both the gas phase and liquid phase.

$(\eta^5\text{-}C_5Me_5)Ru(CH_2{=}CH_2)(\mu\text{-}H)(CH{=}CH_2)Ru(\eta^5\text{-}C_5Me_5)$ (8). The solution of 2 (0.118 g, 0.25 mmol) in 5 mL of toluene was stirred under 1 atm of ethylene at room temperature. After stirring for 0.5 h, the color of the solution changed to yellow. Then the solvent and excess ethylene were immediately removed under reduced pressure. To a yellow-brown residue was added 1 mL of toluene, and the product was extracted. Removal of the solvent under reduced pressure afforded 8 as a yellow semisolid. The ^1H and ^{13}C NMR spectra were measured at −78 °C. ^1H NMR ($C_6D_5CD_3$): δ −16.37 (s, 1H, Ru—H—Ru), 0.69 (m, 2H, $CH_2{=}CH_2$), 0.99 (m, 2H, $CH_2{=}CH_2$), 1.52 (s, 15H, C_5Me_5), 1.75 (s, 15H, C_5Me_5), 1.75 (1H, Ru—CH=CHH′, obscured by resonance of C_5Me_5 at 1.75 ppm), 3.89 (d, J = 8.4 Hz, 1H, Ru—CH=CHH′), 7.36 (dd, J = 8.4 and 12.0 Hz, 1H, Ru—CH=CHH′). ^{13}C NMR ($C_6D_5CD_3$): δ 9.7 (q, J = 127.7 Hz, C_5Me_5), 10.4 (q, J = 125.2 Hz, C_5Me_5), 34.2 (t, J = 155.0 Hz, $CH_2{=}CH_2$), 34.5 (t, J = 161.2 Hz, $CH_2{=}CH_2$), 53.5 (dd, J = 154.0 and 153.0 Hz, Ru—CH=CHH′), 93.0 (s, C_5Me_5), 95.0 (s, C_5Me_5), 189.4 (d, J = 140.0 Hz, Ru—CH=CHH′). The field-desorption mass spectrum was recorded, and the intensities of the obtained isotopic peaks for $C_{24}H_{38}Ru_2$ agreed with the calculated values within experimental error.

$(\eta^5\text{-}C_5Me_5)Ru(MeOCOCH{=}CHCO_2Me)(\mu\text{-}H)[CH(CO_2Me){=}CHCO_2Me]Ru(\eta^5\text{-}C_5Me_5)$ (9). A 50-mL Schlenk tube was charged with 0.168 g (0.35 mmol) of 2, 0.252 g (1.75 mmol) of dimethyl maleate, and 10 mL of toluene. The mixture was stirred at 60–70 °C for 2 h. The color of the solution turned from red to orange. Removal of the solvent under reduced pressure gave a red-orange residue. Purification by column chromatography on alumina with toluene/acetone followed by crystallization from cold (−20 °C) pentane afforded 0.124 g (46%) of 9 as red-yellow prisms. Dimethyl succinate formed in this reaction was identified and quantified by means of GC–MS. Dp: 185 °C. IR (KBr, cm^{-1}): 2939, 2890, 1961, 1697, 1618, 1457, 1433, 1315, 1276, 1214, 1175, 1128, 1032. Anal. Found (calcd) for $C_{32}H_{46}O_8Ru_2$: C, 50.28 (50.52); H, 6.33 (6.09). ^1H NMR (C_6D_6): δ −12.7 (s, 1H, Ru—H—Ru), 1.54 (s, 15H, C_5Me_5), 1.74 (s, 15H, C_5Me_5), 2.05 (d, J = 9.8 Hz, 1H, MeO_2C—CH=CH—CO_2Me), 2.57 (d, J = 9.8 Mz, 1H, MeO_2C—CH=CH—CO_2Me), 2.91 (s, 3H, -OMe), 3.36 (s, 3H, -OMe), 3.55 (s, 3H, -OMe), 3.86 (s, 3H, -OMe). ^{13}C NMR (C_6D_6): δ 9.41 (q, J = 127.1 Hz, C_5Me_5), 10.3 (q, J = 127.2 Hz, C_5Me_5), 40.5 (d, J = 157.0 Hz, MeO_2C—CH=CH—CO_2Me), 49.9

(q, *J* = 144.8 Hz, -O*Me*), 50.5 (q, *J* = 145.3 Hz, -O*Me*), 50.5 (d, *J* = 152.5 Hz, MeO$_2$C—CH=CH—CO$_2$Me), 51.7 (q, *J* = 144.8 Hz, -O*Me*), 53.2 (q, *J* = 147.2 Hz, -O*Me*), 66.5 (d, 157.0 Hz, Ru—C(CO$_2$Me)=CHCO$_2$Me), 89.2 (s, *C*$_5$Me$_5$), 97.5 (s, *C*$_5$Me$_5$), 171.3 (s, -*C*O$_2$Me), 173.7 (s, -*C*O$_2$Me), 176.6 (s, -*C*O$_2$Me), 179.4 (s, -*C*O$_2$Me), 191.5 (s, Ru—*C*(CO$_2$Me)=CHCO$_2$Me). The field-desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{32}H_{46}O_8Ru_2$ agreed with the calculated values within experimental error.

Pyrolysis of 6 in the Presence of Ethylene. Synthesis of Metallacycle Complex 10. A 300-mL glass autoclave was charged with 0.300 g (0.540 mmol) of **6** and 10 mL of toluene. The autoclave was evacuated after the solution was cooled by using a dry ice–methanol bath, and 1 atm of ethylene was admitted the autoclave. The mixture was then stirred for 5.5 h at 50–60 °C. The color of the reaction mixture changed from red to brownish yellow. Removal of the solvent under reduced pressure gave a brown residue. Purification by column chromatography on alumina with toluene afforded 0.234 g (75%) of **10** as red-yellow prisms. Single crystals for the X-ray diffraction study were obtained from toluene–pentane at -20 °C. Mp: 168 °C dec. IR (KBr, cm^{-1}): 3048, 2961, 2861, 1493, 1468, 1418, 1373, 1256, 1189, 1106, 1063, 1021, 1006, 877, 799, 526, 424, 381. Anal. Found (calcd) for $C_{28}H_{42}Ru_2$: C, 57.60 (57.91); 7.09 (7.29). ^{1}H NMR (C$_6$D$_6$): δ 0.84 (d, *J* = 11.9 Hz, 2H, C*H*H'=C*H*H'), 1.47 (d, *J* = 11.9 Hz, 2H, CH*H'*=CH*H'*), 1.64 (s, 15H, C$_5$*Me*$_5$), 1.68 (s, 15H, C$_5$*Me*$_5$), 2.83 (s, 6H, -C(*Me*)=), 3.93 (s, 2H, -(Me)C=C*H*C*H*=C(Me)-). ^{13}C NMR (C$_6$D$_6$): δ 10.6 (q, *J* = 126.2 Hz, C$_5$*Me*$_5$), 11.2 (q, *J* = 126.2 Hz, C$_5$*Me*$_5$), 30.3 (q, *J* = 123.3 Hz, -C(*Me*)=), 45.3 (dd, *J* = 160.4 and 151.5 Hz, *C*HH'=*C*HH'), 87.3 (s, *C*$_5$Me$_5$), 93.5 (d of quintet, *J* = 157.5 and 5.9 Hz, -C(Me)=*C*H-), 95.3 (s, *C*$_5$Me$_5$), 170.0 (s, -*C*(Me)=CH-). The field-desorption mass spectrum was recorded, and the intensities of the obtained isotopic peaks for $C_{28}H_{42}Ru_2$ agreed with the calculated values within experimental error.

Pyrolysis of 6 in the Absence of Ethylene. Synthesis of Metallacycle Complex 11. A 300-mL glass autoclave was charged with 0.210 g (0.44 mmol) of **6** and 10 mL of toluene. The autoclave was evacuated after the solution was cooled by using a dry ice–methanol bath. The solution was then heated at 50–70 °C for 8 h, and the color of the solution turned from red to brownish yellow. Removal of the solvent under reduced pressure followed by purification of a residue by column chromatography on alumina with hexane–acetone gave 0.130 g (66%) of **11** as a yellow oily substance. ^{1}H NMR (C$_6$D$_6$): δ -10.34 (s, 1H, Ru-*H*), -9.92 (s, 1H, Ru-*H*-Ru), 1.65 (s, 15H, C$_5$*Me*$_5$), 1.66 (d, *J* = 1.9 Hz, 6H, -C(*Me*)=), 2.02 (s, 15H, C$_5$*Me*$_5$), 4.63 (q, *J* = 1.9 Hz, 2H, -C(Me)=C*H*C*H*=C(Me)-). ^{13}C NMR (C$_6$D$_6$): δ 10.9 (q, *J* = 125.8 Hz, C$_5$*Me*$_5$), 12.3 (q, *J* = 126.4 Hz, C$_5$*Me*$_5$), 27.9 (q, *J* = 124.5 Hz, -C(*Me*)=), 87.7 (s, *C*$_5$Me$_5$), 88.5 (s, *C*$_5$Me$_5$), 94.9 (d of quintet, *J* = 161.2 and 4.8 Hz, -C(Me)=*C*H*C*H=C(Me)-), 111.9 (d of quintet, *J* = 42.1 and 4.8 Hz, -*C*(Me)=CHCH=*C*(Me)-). The field-desorption mass spectrum was recorded, and the intensities of the obtained isotopic peaks for $C_{28}H_{40}Ru_2$ agreed with the calculated values within experimental error.

(η^5-C$_5$Me$_5$)Ru(CH=CH$_2$)$_2$(CH$_2$=CHC(O)CH$_3$)Ru(η^5-C$_5$Me$_5$) (12). To a stirred solution of **6** (0.240 g, 0.43 mmol) in toluene (5 mL) was added methyl vinyl ketone (166 μL, 2 mmol) at ambient temperature, and the mixture was allowed to stir for 12 h. Removal of the solvent under reduced pressure afforded a dark-purple residue. Purification by column chromatography on alumina with toluene/acetone gave 0.187 g (73%) of **12** as purple powder. Dp: 152 °C. IR (KBr, cm^{-1}): 3033, 2938, 2902, 1654, 1461, 1376, 1237, 1223, 1198, 1169, 1066, 1021, 973, 949, 921, 898, 881, 806, 774, 634, 598, 479. Anal. Found (calcd) for $C_{28}H_{42}ORu_2$: C, 56.05 (56.35); H, 7.19 (7.09). ^{1}H NMR (C$_6$D$_6$): δ 1.43 (s, 30H, C$_5$*Me*$_5$), 1.76 (d, *J* = 7.1 Hz, 1H, C*H*H'=CHCOMe), 1.83 (d, *J* = 8.8 Hz, Ru—CH=C*H*H'), 2.17 (s, 3H, CHH'=CHCO*Me*), 2.29 (d, *J* = 9.4 Hz, 1H, Ru—CH=C*H*H'), 2.81 (d, *J* = 10.4 Hz, 1H, CH*H'*=CHCOMe), 2.94 (dd, *J* = 10.4 and 7.1 Hz, 1H, CHH'=C*H*COMe), 3.46 (d, *J* = 6.6 Hz, 1H, Ru—CH=CH*H'*), 3.58 (d, *J* = 6.6 Hz, 1H, Ru—CH=CH*H'*), 10.19 (dd, *J* = 9.4 and 6.6 Hz, 1H, Ru—C*H*=CHH'), 10.23 (dd, *J* = 8.8 and 6.6 Hz, 1H, Ru—C*H*=CHH'). ^{13}C NMR (C$_6$D$_6$): δ 9.48 (q, *J* = 126.3 Hz, C$_5$*Me*$_5$), 9.98 (q, *J* = 127.0 Hz, C$_5$*Me*$_5$), 30.5 (q, *J* = 125.6 Hz, CH$_2$=CHCO*Me*), 52.1 (dd, *J* = 148.2 and 164.7 Hz, Ru—CH=*C*H$_2$), 52.4 (t, *J* = 157.0 Hz, *C*H$_2$=CHCOMe), 56.0 (dd, *J* = 159.3 and 144.9 Hz, Ru—CH=*C*H$_2$), 58.8 (d, *J* = 156.5 Hz, CH$_2$=*C*HCOMe), 91.2 (s, *C*$_5$Me$_5$), 96.5 (s, *C*$_5$Me$_5$), 188.2 (d, *J* = 156.5 Hz, Ru—*C*H=CH$_2$), 192.2 (d, *J* = 157.6 Hz, Ru—*C*H=CH$_2$), 202.7 (d, *J* = 4.4 Hz, CH$_2$=CH*C*OMe).

Pyrolysis of 12. Synthesis of Bis(μ-alkylidene) Complex 13. A 50-mL glass autoclave was charged with 0.120 g (0.20 mmol) of **12** and 5 mL of toluene. The mixture was heated at 110 °C for 5 h. Removal of solvent from the resulting purple solution followed by chromatographic purification on alumina with toluene gave 0.082 g (70%) of **13** as a purple microcrystalline solid. Mp: 51 °C. IR (KBr, cm^{-1}): 2970, 2895, 1562, 1428, 1370, 1256, 1194, 1095, 1020. Anal. Found (calcd) for $C_{28}H_{42}ORu_2$: C, 56.62 (56.35); H, 7.16 (7.09). ^{1}H NMR (C$_6$D$_6$): δ 1.57 (s, 15H, C$_5$*Me*$_5$), 1.72 (s, 15H, C$_5$*Me*$_5$), 1.77 (s, 3H, *Me*), 2.55 (d, *J* = 6.1 Hz, 1H, -CH=C*H*—COMe), 2.57 (d, *J* = 7.1 Hz, 3H, Ru—CH(*Me*)—Ru), 3.02 (s, 3H, *Me*), 4.27 (d, *J* = 6.1 Hz, 1H, -C*H*=CH—COMe), 10.73 (q, *J* = 7.1 Hz, 1H, Ru—C*H*(Me)—Ru). ^{13}C NMR (C$_6$D$_6$): δ 9.7 (q, *J* = 126.7 Hz, C$_5$*Me*$_5$), 10.3 (q, *J* = 125.6 Hz, C$_5$*Me*$_5$), 29.7 (q, *J* = 126.7 Hz, *Me*), 30.6 (q, *J* = 122.3 Hz, Ru—CH(*Me*)—Ru), 34.8 (q, *J* = 124.5 Hz, *Me*), 58.4 (d, *J* = 152.0 Hz, -CH=*C*H—COMe), 80.5 (d, *J* = 160.9 Hz, -*C*H=CH—COMe), 88.4 (s, *C*$_5$Me$_5$), 89.5 (s, *C*$_5$Me$_5$), 170.8 (s, Ru—*C*(CH=CHCOMe)—Ru), 182.2 (d, *J* = 133.3 Hz, Ru—*C*H(Me)—Ru), 212.1 (s, -CH=CH*C*OMe). The field-desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{28}H_{42}ORu_2$ agreed with the calculated values within experimental error. Recrystallization from tetrahydrofuran afforded purple prisms suitable for X-ray diffraction study.

Pyrolysis of 10. Insertion of Ethylene into a Ruthenium–Carbon Bond. A 50-mL glass autoclave was charged with 0.112 g (0.19 mmol) of **10** and 5 mL of toluene. The mixture was heated at 110 °C for 11 h. Solvent was then removed under reduced pressure, and residual solid was purified by column chromatography on alumina with toluene to afford 0.066 g (58%) of **16** as a yellow solid. Mp. 189 °C dec. IR (KBr, cm^{-1}): 3040, 2964, 2897, 1477, 1424, 1373, 1361, 1231, 1083, 1020, 1001, 880, 638, 527, 463. Anal. Found (calcd) for $C_{28}H_{42}Ru_2$: C, 57.47 (57.91); H, 7.43 (7.29). ^{1}H NMR (C$_6$D$_6$): δ -16.00 (s, 1H, Ru—*H*), 0.50 (d, *J* = 9.8 Hz, 1H, -C(Me)CHCHC(Me)CHC*H*H'), 0.74 (d, *J* = 7.3 Hz, 1H, -C(Me)CHCHC(Me)CHCH*H'*), 1.50 (dd, *J* = 7.3 and 9.8 Hz, 1H, -C(Me)CHCHC(Me)C*H*CHH'), 1.57 (s, 3H, Ru—C(Me)CHCHC(*Me*)-), 1.63 (s, 15H, C$_5$*Me*$_5$), 1.80 (s, 15H, C$_5$*Me*$_5$), 2.45 (s, 3H, Ru—C(*Me*)CHCH-), 3.41 (d, *J* = 6.1 Hz, 1H, Ru—C(Me)CHC*H*-), 4.81 (d, *J* = 6.1 Hz, 1H, Ru—C(Me)C*H*CH-). ^{13}C NMR (C$_6$D$_6$): δ 10.9 (q, *J* = 126.7 Hz, C$_5$*Me*$_5$), 11.2 (q, *J* = 125.6 Hz, C$_5$*Me*$_5$), 26.8 (q, *J* = 125.2 Hz, Ru—C(Me)CHCHC(*Me*)-), 32.0 (dd, *J* = 151.2 and 157.5 Hz, -C(Me)CH*C*HH'), 37.7 (q, *J* = 122.6 Hz, Ru—C(*Me*)CHCH-), 44.5 (d, *J* = 156.5 Hz, -C(Me)*C*HCHH'), 67.9 (s, -*C*(Me)CHCHH'), 85.4 (d, *J* = 157.7 Hz, -C(Me)CH*C*HC(Me)-), 89.1 (s, *C*$_5$Me$_5$), 92.8 (s, *C*$_5$Me$_5$), 96.9 (d, *J* = 153.1 Hz, Ru—C(Me)*C*HCH-), 163.1 (s, Ru—*C*(Me)CHCH-). The field-desorption mass spectrum was measured, and the intensities of obtained isotopic peaks for $C_{28}H_{42}Ru_2$ agreed with the calculated values within experimental error. Recrystallization from the mixed solvent of toluene and pentane gave orange prisms suitable for the X-ray diffraction study.

Pyrolysis of 6 in the Presence of Ethylene. Direct Synthesis of 16 from 6. A 50-mL glass autoclave was charged with 0.226 g (0.41 mmol) of **6** and 10 mL of toluene. The vessel was evacuated after the solvent was cooled by a dry ice–methanol bath, and ethylene (50 atm) was then admitted to the reactor. The mixture was heated at 110 °C for 11 h. Removal of the solvent followed by chromatographic purification of the yellow-brown residue on alumina with toluene afforded 0.140 g (59%) of **16** as a yellow microcrystalline solid.

Pyrolysis of 10 in the Presence of Methyl Vinyl Ketone. Insertion of Methyl Vinyl Ketone into a Ruthenium–Carbon Bond. A 50-mL glass autoclave was charged with 0.240 g (0.41 mmol) of **10**, 0.037 g (0.57 mmol) of methyl vinyl ketone, and 5 mL of toluene. The mixture was heated at 70 °C for 4 h. The color of the solution changed from red to brown. After removal of solvent under reduced pressure, the dark brown residual solid was purified by column chromatography on alumina with the mixed solvent of toluene and acetone to give 0.083 g (35%) of **17** as a yellow-orange solid. Mp: 146 °C. IR (KBr, cm^{-1}): 2945, 2868, 1650, 1480, 1448, 1422, 1371, 1345, 1205, 1079, 1016, 878, 856, 637, 601, 525, 465. Anal. Found (calcd) for $C_{30}H_{41}ORu_2$: C, 57.66 (57.85); 6.83 (6.67). ^1H NMR (C_6D_6): δ −16.9 (s, 1H, Ru—*H*), 1.39 (d, *J* = 8.5 Hz, 1H, -CH=C*H*—CO—Me), 1.51 (s, 15H, $C_5\mathit{Me}_5$), 1.52 (s, 3H, Ru—C(Me)=CH—CH=C(*Me*)-), 1.85 (s, 15H, $C_5\mathit{Me}_5$), 1.88 (s, 3H, -CH=CH—CO—*Me*), 2.42 (s, 3H, Ru—C(*Me*)=CH-), 2.85 (d, *J* = 8.5 Hz, 1H, -C*H*=CH—CO—Me), 3.43 (d, *J* = 4.9 Hz, 1H, Ru—C(Me)=CH—C*H*=C(Me)-), 4.54 (d, *J* = 4.9 Hz, 1H, Ru—C(Me)=C*H*—CH=C(Me)-). ^{13}C NMR (C_6D_6): δ 10.8 (q, *J* = 126.4 Hz, 2 $C_5\mathit{Me}_5$), 26.1 (qd, *J* = 126.4 and 3.6 Hz, Ru—C(Me)=CH—CH=C(*Me*)-), 33.1 (q, *J* = 126.4 Hz, -CH=CH—CO—*Me*), 37.1 (qd, *J* = 124.1 and 3.6 Hz, Ru—C(*Me*)=CH-), 43.5 (d, *J* = 159.9 Hz, -*C*H=CH—CO—Me), 46.8 (d, *J* = 153.3 Hz, -CH=*C*H—CO-Me), 68.8 (s, Ru—C(Me)=CH—CH=*C*(Me)-), 84.8 (d, *J* = 158.6 Hz, Ru—C(Me)=H—*C*H=C(Me)-), 90.0 (s, C_5-Me_5), 95.1 (s, C_5Me_5), 96.4 (d, *J* = 170.7 Hz, Ru—C(Me)=*C*H-), 164.9 (d, *J* = 8.1 Hz, Ru—*C*(Me)=CH-), 208.0 (s, -CH=CH—*C*O—Me). The field-desorption mass spectrum was measured, and the intensities of obtained isotopic peaks for $C_{30}H_{41}$-ORu_2 agreed with the calculated values within experimental error. Recrystallization from toluene–pentane afforded yellow-orange prisms suitable for the X-ray diffraction study.

Pyrolysis of 10 in the Presence of Cyclopentenone. Insertion of Cyclopentenone into a Ruthenium–Carbon Bond. A 50-mL glass autoclave was charged with 0.116 g (0.20 mmol) of **10**, 0.035 g (0.43 mmol) of cyclopent-2-en-1-one, and 5 mL of toluene. The mixture was heated at 60 °C for 13 h. The color of the solution changed from red to yellow-brown. After removal of solvent under reduced pressure, the brown residual solid was purified by column chromatography on alumina with the mixed solvent of toluene and acetone to give 0.082 g (65%) of **18** as red solid. Dp: 207 °C. IR (KBr, cm^{-1}): 2960, 2895, 1665, 1447, 1423, 1372, 1311, 1281, 1254, 1200, 1160, 1028, 632. Anal. Found (calcd) for $C_{31}H_{44}ORu_2$: C, 58.80 (58.65); H, 6.71 (6.99). ^1H NMR (C_6D_6): δ −16.7 (s, Ru—*H*), 1.46 (s, 3H, Ru—C(*Me*)=CH-), 1.52 (m, 1H, -C=CH—CO—$CH_2C\mathit{H}H'$-), 1.52 (s, 15H, $C_5\mathit{Me}_5$), 1.65 (s, 15H, $C_5\mathit{Me}_5$), 1.75 (s, 1H, -C=C*H*—CO—CH_2CH_2-), 1.94 (m, 2H, -C=CH—CO—CH_2CH_2-), 2.31 (s, 3H, Ru—C(*Me*)=CH—CH=C(Me)-), 2.47 (m, 1H, -C=CH—CO—$CH_2CH\mathit{H}'$-), 3.45 (d, *J* = 6.1 Hz, 1H, Ru—C(Me)=CH—C*H*=C(Me)-), 4.38 (d, *J* = 6.1 Hz, 1H, Ru—C(Me)=C*H*—CH=C(Me)-). ^{13}C NMR (C_6D_6): δ 10.7 (q, *J* = 126.3 Hz, $C_5\mathit{Me}_5$), 10.8 (q, *J* = 126.3 Hz, $C_5\mathit{Me}_5$), 24.4 (q, *J* = 123.6 Hz, Ru—C(Me)=CH—CH=C(*Me*)-), 29.0 (t, *J* = 127.4 Hz, -C=CH—CO—$CH_2\mathit{C}H_2$-), 36.1 (t, *J* = 124.6 Hz, -C=CH—CO—$\mathit{C}H_2CH_2$-), 36.9 (q, *J* = 123.6 Hz, Ru—C(*Me*)=CH—CH=C(Me)-), 50.3 (d, *J* = 167.1 Hz, -C=*C*H—CO—CH_2CH_2-), 65.4 (t, *J* = 3.2 Hz, -*C*=CH—CO—CH_2CH_2-), 65.7 (d, *J* = 3.1 Hz, Ru—C(Me)=CH—CH=*C*(Me)-), 86.9 (d, *J* = 162.0 Hz, Ru—C(Me)=CH—*C*H=C(Me)-), 90.3 (s, C_5Me_5), 95.1 (s, C_5-Me_5), 97.6 (d, *J* = 159.0 Hz, Ru—C(Me)=*C*H—CH=C(Me)-), 165.3 (s, Ru—*C*(Me)=CH—CH=C(Me)-), 214.3 (s, -C=CH—*C*O—CH_2CH_2-). The field-desorption mass spectrum was measured, and the intensities of obtained isotopic peaks for $C_{31}H_{44}$-ORu_2 agreed with the calculated values within experimental error. Recrystallization from toluene–ether afforded orange prisms suitable for X-ray diffraction analysis.

Pyrolysis of 10 in the Presence of Cyclohexenone. Insertion of Cyclohexenone into a Ruthenium–Carbon Bond. A 50-mL glass autoclave was charged with 0.209 g (0.36 mmol) of **10**, 0.040 g (0.42 mmol) of cyclohex-2-en-1-one, and 5 mL of toluene. The mixture was heated at 90 °C for 6 h. The color of the solution changed from red to brown. After removal of solvent under reduced pressure, the brown residual solid was purified by column chromatography on alumina with the mixed solvent of ether and acetone to afford 0.067 g (29%) of **19** as red solid. Dp: 183 °C. IR (KBr, cm^{-1}): 2998, 2954, 2886, 1632, 1470, 1442, 1392, 1369, 1262, 1241, 1166, 1021, 514. Anal. Found (calcd) for $C_{32}H_{46}ORu_2$: C, 58.93 (59.24); H, 7.24 (7.15). ^1H NMR (C_6D_6): δ −16.5 (s, Ru—*H*), 1.41 (s, 1H, -C=C*H*—CO—$CH_2CH_2CH_2$-), 1.53 (s, 3H, Ru—C(Me)=CH—CH=C(*Me*)-), 1.54 (s, 15H, C_5-Me_5), 1.65 (s, 15H, $C_5\mathit{Me}_5$), 2.30 (s, 3H, Ru—C(*Me*)=CH—CH=C(Me)-), 3.39 (d, *J* = 5.5 Hz, 1H, Ru—C(Me)=CH—C*H*=C(Me)-), 4.55 (d, *J* = 5.5 Hz, 1H, Ru—C(Me)=C*H*—CH=C(Me)-). Other signals derived from cyclohexenone were obscured by the resonances of C_5Me_5 at δ 1.54 and 1.65. ^{13}C NMR (C_6D_6): δ 10.8 (q, *J* = 125.9 Hz, $C_5\mathit{Me}_5$), 11.1 (q, *J* = 125.9 Hz, $C_5\mathit{Me}_5$), 25.2 (qd, *J* = 125.0 and 5.4 Hz, Ru—C(Me)=CH—CH=C(*Me*)-), 26.6 (t, *J* = 126.1 Hz, -C=CH—CO—$CH_2\mathit{C}H_2CH_2$-), 32.2 (t, *J* = 126.1 Hz, -C=CH—CO—$CH_2CH_2\mathit{C}H_2$-), 37.4 (qd, *J* = 124.1 and 5.7 Hz, Ru—C(*Me*)=CH—CH=C(Me)-), 39.1 (t, *J* = 121.7 Hz, -C=CH—CO—$\mathit{C}H_2CH_2CH_2$-), 47.1 (dd, 154.9 and 2.7 Hz, -C=*C*H—CO—$CH_2CH_2CH_2$-), 54.6 (s, -*C*=CH—CO—$CH_2CH_2CH_2$-), 67.6 (s, Ru—C(Me)=CH—CH=*C*(Me)-), 89.6 (d, *J* = 158.7 Hz, Ru—C(Me)=CH—*C*H=C(Me)-), 89.7 (s, C_5Me_5), 95.9 (s, C_5Me_5), 98.6 (dq, *J* = 153.5 and 5.4 Hz, Ru—C(Me)=*C*H—CH=C(Me)-), 166.2 (s, Ru—*C*(Me)=CH—CH=C(Me)-), 211.1 (s, -C=CH—*C*O—$CH_2CH_2CH_2$-). The field-desorption mass spectrum was measured, and the intensities of obtained isotopic peaks for $C_{32}H_{46}ORu_2$ agreed with the calculated values within experimental error.

Reaction of 10 with Maleic Anhydride. Synthesis of 20. A 50-mL Schlenk tube was charged with 0.094 g (0.161 mmol) of **10**, 0.050 g (0.514 mmol) of maleic anhydride, and 5 mL of toluene. The mixture was stirred for 2 h at room temperature. The color of the solution changed from dark orange to red-orange. After removal of the solvent under reduced pressure, the dark brown residual solid was purified by column chromatography on alumina with toluene–tetrahydrofuran to yield 0.063 g (60%) of **20** as a red crystalline solid together with 0.035 g (37%) of ethylene-insertion product **16**. IR (KBr, cm^{-1}): 2929, 2871, 1815, 1740, 1380, 1238. Anal. Found (calcd) for $C_{30}H_{40}O_3Ru_2$: C, 55.12 (55.37); H, 6.33 (6.20). ^1H NMR (C_6D_6): δ 1.37 (s, 15H, $C_5\mathit{Me}_5$), 1.40 (s, 15H, $C_5\mathit{Me}_5$), 2.47 (s, 2H, maleic anhydride), 2.67 (s, 6H, Ru—C(*Me*)=CH-), 4.46 (s, 2H, Ru—C(Me)=C*H*-). ^{13}C NMR (C_6D_6): δ 10.5 (q, *J* = 127.0 Hz, $C_5\mathit{Me}_5$), 10.7 (q, *J* = 126.6 Hz, $C_5\mathit{Me}_5$), 29.9 (q, *J* = 125.6 Hz, Ru—C(*Me*)=CH-), 40.1 (d, *J* = 169.1 Hz, =*C*H—(CO)—O-), 89.1 (s, C_5Me_5), 97.6 (d, *J* = 163.3 Hz, Ru—C(Me)=*C*H-), 99.2 (s, C_5Me_5), 168.8 (s, Ru—*C*(Me)=CH-), 173.6 (s, =CH—(*C*O)—O-).

X-ray Data Collection and Reduction. X-ray-quality crystals of **2**, **6**, **9**, **10**, **13**, and **16–18** were obtained directly from the preparations described above and mounted on glass fibers. Diffraction experiments were performed on a Rigaku AFC-5 (**2**, **9**, **10**, **16**, and **18**) and AFC-5R (**6**, **13**, and **17**) four-circle diffractometer equipped with graphite-monochromated Mo Ka radiation. The lattice parameters and orientation matrices were obtained and refined from 20 (**2**, **9**, **10**, **16**, and **18**) or 24 (**6**, **13**, and **17**) machine-centered reflections with $20° < 2\theta < 30°$. Intensity data were collected using a ω–2θ scan technique, and three standard reflections were recorded every 100 (**2**, **9**, **10**, **16**, and **18**) or 150 (**6**, **13**, and **17**) reflections. The data of **6**, **9**, **13**, **17**, and **18** were processed using the TEXSAN crystal solution package operating on a Micro VAX II computer. Data processing of **10** and **16** was performed on a FACOM A-70 computer by using the R-CRYSTAN data collection program system, and the data for **2** were processed on a Hitachi HITAC M680 computer

Table 9. Crystallographic Data for 2, 6, 9, 10, 13, 16, 17, and 18

	2	6	9	10	13	16	17	18
formula	$C_{20}H_{34}Ru_2$	$C_{26}H_{40}Ru_2$	$C_{32}H_{46}O_8Ru_2$	$C_{28}H_{42}Ru_2$	$C_{28}H_{42}ORu_2$	$C_{28}H_{42}Ru_2$	$C_{30}H_{44}ORu_2$	$C_{31}H_{44}ORu_2$
mol wt	476.63	554.75	760.86	580.78	596.78	580.78	622.82	634.83
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2/a$	$P\bar{1}$	$Pbca$	$P2_1/n$	$P2_1/a$	$P2_1/a$	$P2_1/n$	$P\bar{1}$
cell constants								
a, Å	12.291(2)	11.335(2)	17.876(2)	14.882(2)	17.210(7)	18.814(2)	17.539(2)	15.012(3)
b, Å	8.521(1)	14.315(2)	20.896(2)	19.718(4)	9.693(6)	9.212(5)	14.405(6)	15.365(3)
c, Å	10.053(2)	8.401(2)	17.690(2)	8.794(1)	16.037(6)	15.068(5)	10.935(2)	9.240(2)
α, deg		95.09(2)						99.99(3)
β, deg	108.52(1)	117.18(1)		92.30(2)	100.36(3)	100.31(2)	102.68(1)	90.11(3)
γ, deg		94.36(1)						137.58(1)
V, Å^3	998.3(3)	1197.4(6)	6608(1)	2578.5(8)	2631(2)	2569(2)	2695(1)	1388.4(6)
Z value	2	2	8	4	4	4	4	2
D_{calcd}, g cm^{-3}	1.585	1.538	1.529	1.496	1.506	1.501	1.535	1.518
temp, °C	−155	25	25	25	23	23	25	25
radiation; λ, Å	Mo Kα; 0.710 68	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 68	Mo Kα; 0.710 69	Mo Kα; 0.710 68	Mo Kα; 0.710 69	Mo Kα; 0.710 69
$2\theta_{max}$, deg	60	45	50	60	50	60	50	60
no. of obsd rflns	2391 ($I > 3\sigma$)	2621 ($I > 6\sigma$)	2186 ($I > 3\sigma$)	5731 ($I > 3\sigma$)	3781 ($I > 3\sigma$)	5449 ($I > 3\sigma$)	3241 ($I > 3\sigma$)	6865 ($I > 3\sigma$)
μ(Mo Kα), cm^{-1}	14.81	12.46	9.41	11.61	11.42	11.66	11.19	10.85
residuals: R; R_w	0.022; 0.022	0.090; 0.158	0.057; 0.040	0.044; 0.041	0.037; 0.035	0.048; 0.046	0.037; 0.032	0.034; 0.045

by using the UNICS III program system.[24] Neutral atom scattering factors were obtained from the standard sources.[25] In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data for each structure.

Structure Solution and Refinement. The Ru atom positions were determined using either Patterson methods (**2**, **10**, and **16**) or direct methods employing the MITHRIL direct-methods routines (**6**, **9**, **13**, **17**, and **18**). In each case, the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In all cases, the non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on F. In the case of **2** and **16**–**18**, the positions of hydrogen atoms bonded to the Ru atoms were located by sequential difference Fourier synthesis and were refined isotropically. However, the positions of the hydrogen atoms bound to the Ru atoms were not located from the difference Fourier map calculations in the case of **9**. Crystal data and results of the analyses are listed in Table 9.

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Supplementary Material Available: Tables giving positional parameters, anisotropic thermal parameters, and listings of bond distances and bond angles for compounds **2**, **6**, **9**, **10**, **13**, **16**, **17**, and **18** (67 pages). Ordering information is given on any current masthead page.

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