5572 *Organometallics* **1997,** *16,* 5572−5584

Synthesis and Reactivity of Labile MeCN Adducts of Diruthenium Bis(μ-methylene) Species, Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(CO)$_n$(MeCN)$_{2-n}$ (n = 1, 2): Reaction with H Sources, H−X (X = SiR$_3$, SnR$_3$, H), and C−C Coupling with Alkynes and Diazoalkanes

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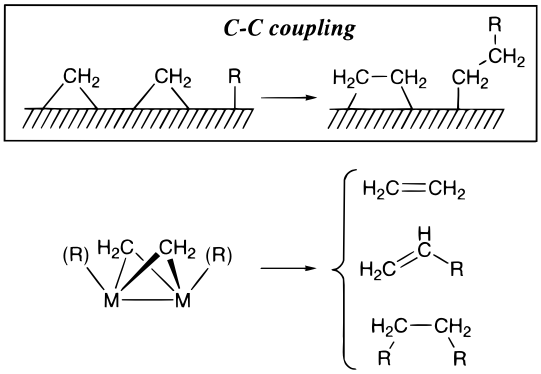
Irradiation of the diruthenium bis(μ-methylene) complex Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(CO)$_2$ (**1**), in acetonitrile gives the mono- and bis(acetonitrile) species Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(CO)(MeCN) (**2**) and Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(MeCN)$_2$ (**3**) in a successive manner. The mono-MeCN species **2** has been characterized spectroscopically and crystallographically, but the bis-MeCN species **3** is too unstable to be fully characterized. Reaction of **2** with hydrosilanes and hydrostannanes results in oxidative addition of the H−Si and H−Sn bond to give hydrido−μ-methylene complexes, Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(H)(mR$_3$)(CO) (m = Si (**7**), Sn (**9**)). In the case of the reactions with dihydrosilane, phenylsilane, and triphenylstannane, one of the two methylene bridges is eliminated as methane (and benzene from phenylsilane) to give μ-methylene−μ-silylene complexes, Cp$_2$Ru$_2$(μ-CH$_2$)(μ-SiR$_2$)(H)(SiR$_3$)(CO) (**8**), and a tristannyl−μ-methylene complex, Cp$_2$Ru$_2$(μ-CH$_2$)(μ-H)(SnPh$_3$)$_3$(CO) (**10**). Treatment of **2** with alkynes (R^{1}C≡CR^2) and diphenyldiazomethane produces the metallacyclic products Cp$_2$Ru$_2$[μ-η^3-C(R^1)C(R^2)═CH$_2$](μ-CH$_2$)(CO) (**12**), and the vinylidene complex Cp$_2$Ru$_2$(μ-C═CPh$_2$)(μ-η^3-CPh$_2$) (**14**), respectively, via C−C coupling. In contrast to **2**, corresponding reactions of the bis-MeCN species **3** are sluggish and only the simple MeCN replacement reaction proceeds in a selective manner.

Introduction

A polynuclear complex containing more than two bridging alkylidene units is one of the attractive candidates which may be able to reproduce the multiple C−C coupling process occurring on a heterogeneous catalyst surface (Scheme 1).[1] However, only a few reports have appeared so far, mainly because examples of polynuclear poly(alkylidene) complexes are limited. Maitlis and his co-workers reported that a successful C−C coupling was observed upon thermolysis or oxidation of a bis(μ-methylene)dimethyldirhodium complex, Cp*$_2$Rh$_2$(μ-CH$_2$)$_2$(CH$_3$)$_2$, where coupling of the two CH$_2$ units and one methyl group led to the formation of a C$_3$ product, propene.[2] In contrast to the case for the rhodium system, it was reported that C−C coupling of bis(μ-alkylidene)diruthenium complexes, Cp$_2$Ru$_2$(μ-CR$_2$)$_2$(CO)$_2$, was sluggish under thermolysis conditions[3] and a low-yield mixture of products was merely obtained, as reported by Knox et al. In a previous paper, we reported the synthesis of the bis(μ-methylene) complex Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(CO)$_2$ (**1**) via deoxygenative reduction of a simple carbonyl complex, Cp$_2$Ru$_2$(CO)$_4$, with hydrosilane.[4] However, its thermolysis also produced very small amounts of methane and C$_2$ hydrocarbons, although complex **1** contained bridging alkylidene ligands which did not bear a β-hydrogen atom.

Scheme 1



In order to introduce a component which may induce C−C coupling with a bridging alkylidene ligand, replacement of a CO ligand by a labile "lightly stabilizing" ligand has been studied.[5] In the case of the mono(μ-methylene) diruthenium system Cp$_2$Ru$_2$(μ-CH$_2$)(CO)$_3$ (**4**) (Scheme 2), conversion to the MeCN adduct Cp$_2$Ru$_2$(μ-CH$_2$)(CO)$_2$(MeCN) (**5**)[6] resulted in successful coupling

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

[1] Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley-Interscience: New York, 1994.

[2] (a) Saez, I. M.; Andrews, D. G.; Maitlis, P. M. *Polyhedron* **1988**, *7*, 827. (b) Maitlis, P. M. *J. Organomet. Chem.* **1995**, *500*, 239. (c) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *J. Chem. Soc., Chem. Commun.* **1996**, 1.

[3] Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1799.

[4] (a) Akita, M.; Oku, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1031. (b) Akita, M.; Hua, R.; Oku, T.; Moro-oka, Y. *Organometallics* **1996**, *15*, 2548.

[5] Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19.

[6] Doherty, N. M.; Howard, J. A. K.; Knox, S. A. R.; Terril, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 638.

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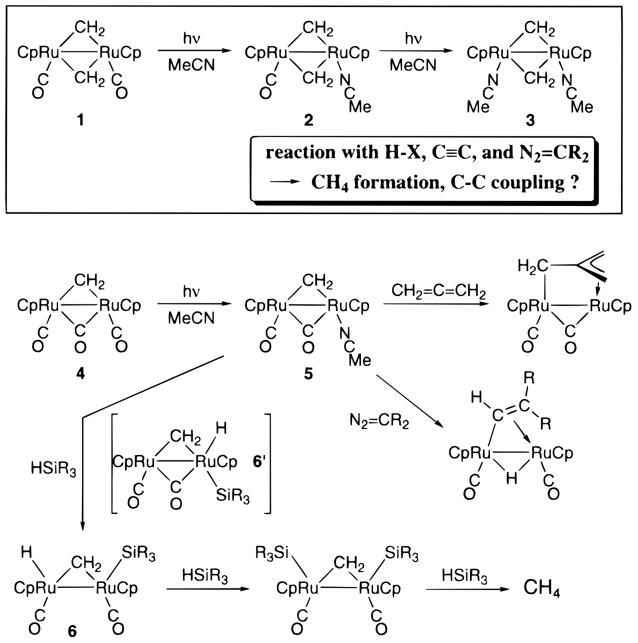
Scheme 2



with external, unsaturated hydrocarbons[7] and we recently reported C−C coupling of **5** with diazoalkane.[8] In the latter system, olefinic products, including the μ-alkenyl complexes $Cp_2Ru_2(\mu\text{-}CH{=}CR_2)(\mu\text{-}H)(CO)_2$, were obtained via efficient coupling between the methylene unit in **5** and the external alkylidene unit. In addition, the methylene ligand in **4** and **5** was found to be converted to methane upon treatment with hydrosilane, and the formation mechanism of methane was successfully analyzed by using **5**.[9]

As an extension of these studies, we report herein synthesis of the labile MeCN adduct of the bis(μ-methylene) complex **1**, $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ (**2**), and its reactivity toward various substrates (Scheme 2). Complex **2** has been subjected to reactions with H sources ($HSiR_3$, $HSnR_3$, and H_2) as a comparative study of our previous experiments of **5** mentioned above. Reactions with alkyne and diazoalkane have also been examined, but the expected multiple C−C coupling among the two methylene bridges and an external substrate has not been observed, as will be discussed below. The synthesis and reactivity of the bis(acetonitrile) species $Cp_2Ru_2(\mu\text{-}CH_2)_2(MeCN)_2$ (**3**) will also be described.

Results and Discussion

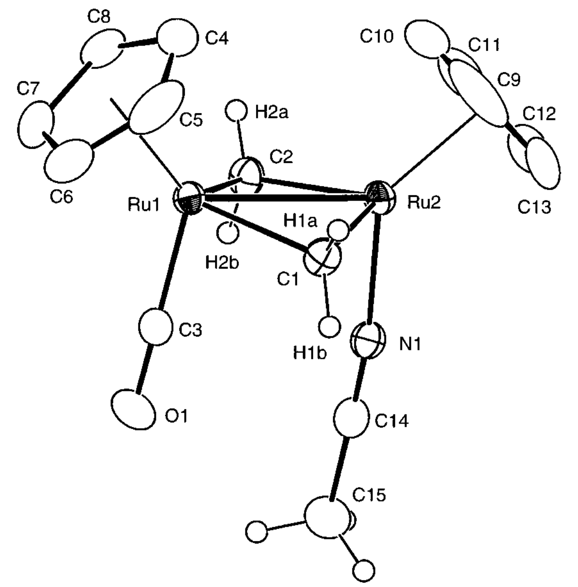


Figure 1. Molecular structure of **2** drawn at the 30% probability level.

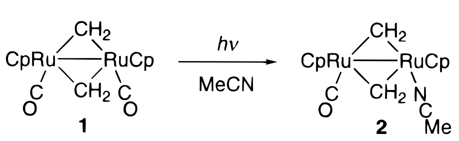
Table 1. Selected Structural Parameters for 2[a]

	Bond Lengths		
Ru1−Ru2	2.6682(9)	Ru1−C3	1.811(5)
Ru1−C1	2.083(5)	Ru2−N1	2.025(4)
Ru2−C1	2.032(5)	C3−O1	1.160(5)
Ru1−C2	2.078(5)	C14−N1	1.127(5)
Ru2−C2	2.045(5)	C14−C15	1.460(7)
	Bond Angles		
Ru2−Ru1−C1	48.7(1)	N1−Ru1−C1	85.3(2)
Ru2−Ru1−C2	49.1(1)	N1−Ru2−C2	83.3(2)
Ru2−Ru1−C3	98.8(1)	Ru2−N1−C14	173.1(4)
C1−Ru1−C2	96.0(2)	Ru1−C1−Ru2	80.8(2)
C1−Ru1−C3	87.1(2)	Ru1−C2−Ru2	80.6(2)
Ru1−Ru2−N1	92.9(1)	Ru1−C3−O1	178.7(5)
Ru1−Ru2−C1	50.4(1)	N1−C14−C15	178.1(5)
Ru1−Ru2−C2	50.2(1)		

[a] Bond lengths in Å and bond angles in deg.

Synthesis and Characterization of the MeCN Adduct of a Bis(μ-methylene) Species, $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ (2).

Irradiation (6 h) of an MeCN solution of an isomeric mixture of *cis*- and *trans*-$Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ (**1**) (ν(CO) 1961, 1923 cm^{-1} (in MeCN)) resulted in, at first, complete isomerization to the *cis* isomer (ν(CO) 1961 cm^{-1})[10] and then the formation of **2** (ν(CO) 1909 cm^{-1}), which was isolated in a quantitative yield after crystallization from CH_3CN (eq 1). The spectral features of **2** ((1) ^1H NMR spectrum containing an MeCN signal (δ 0.82) in addition to two Cp signals (δ 4.59 and 4.91) and a pair of μ-CH_2 signals (δ 7.28 (s, 2H), 8.86 (s, 2H)); (2) absence of a bridging CO stretching vibration) support its formulation as $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ (**2**), and a molecular structure with the *cis* configuration has been confirmed by X-ray crystallography (Figure 1). The structural parameters listed in Table 1 are quite similar to those of the starting compound **1**,[4] and the MeCN ligand is coordinated to Ru2 in an essentially linear fashion (Ru2−N1−C14, 173.1(4)°; N1−C14−C15, 178.1(5)°). Complex **2** is found to be more stable than the mono(μ-methylene) species **5**.



(1)

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(7) (a) Fildes, M. J.; Knox, S. A. R.; Orpen, A. G.; Turner, M. L.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1680. (b) Howard, J. K.; Knox, S. A. R.; Terril, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 640. (c) Adams, P. Q.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem Soc., Chem. Commun.* **1983**, 222. (d) Colborn, R. E.; Dyke, A. F.; Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Mead, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1990**, 761.

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(9) (a) Akita, M.; Oku, T.; Hua, R.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 1670. (b) Akita, M.; Hua, R.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1996**, *15*, 4162.

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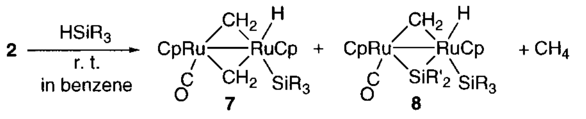
Reaction of 2 with Hydrosilanes: Oxidative Addition of the H−Si Bond and Formation of μ-Methylene-μ-silylene Complexes 8 Accompanied by Elimination of CH_4. Reaction of the mono(μ-methylene) derivative **5** with hydrosilane resulted in H−Si oxidative addition to give the hydrido−silyl−μ-methylene species $Cp_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2$ (**6**) (Scheme 2).[9] As for the bis(μ-methylene) species **2**, two types of reactions ((1) oxidative addition of the H−Si bond giving $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(H)(SiR_3)$ (**7**) and (2) formation of μ-methylene-μ-silylene complexes $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiR_2)(CO)(H)(SiR_3)$ (**8**)) have been observed (eq 2). The reaction of dihydrosilane will be described at first, because the reaction of trialkylhydrosilane is sluggish.



(2)

HSiR3			
H_2SiEt_2 (**a** series)	36 %	60 % (R'_2= Et_2)	67 %
H_2SiPh_2 (**b** series)	not isolated	38 % (R'_2= Ph_2)	45 %
$HSiMe_3$ (**c** series)	58 %	not detected	0 %
$HSiEt_3$ (**d** series)		no reaction at r. t.	
$HSiMe_2Ph$ (**e** series)	not isolated	73 % (R'_2= Me_2)	64 % [+ C_6H_6 (100 %)]
$HSiPh_3$ (**f** series)	not isolated	26% (R'_2= Ph_2)	26 % [+ C_6H_6 (30 %)]

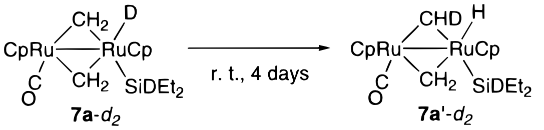
(i) Reaction with Dihydrosilanes. Treatment of **2** with H_2SiEt_2 in benzene afforded the two hydride complexes **7a** (36% yield) and **8a** (60% yield) after TLC separation (eq 2). The minor product **7a** has been assigned to the oxidative-addition product $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(H)(SiHEt_2)$ on the basis of its ^1H NMR data containing two μ-CH_2 and hydride signals (δ_H 8.05, 7.07 (2H × 2, s × 2, (μ-CH_2)$_2$), 4.79, 4.67 (5H × 2, s × 2, Cp_2), 3.25 (1H, m, SiH), 1.46−0.94 (10H, m, $SiEt_2$), −15.1 (1H, s, RuH)), which are similar to those for the $HSnPh_3$ adduct **9b** characterized crystallographically (see below). Complex **7** is analogous to **6′**, the undetectable intermediate assumed for formation of **6** (Scheme 2), and its isolation supports the viability of **6′**. The other product **8a** has been characterized as the μ-methylene−μ-silylene complex $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiEt_2)(CO)(H)(SiHEt_2)$ on the basis of its ^1H NMR spectrum indicating loss of one of the two μ-methylene ligands and incorporation of the two $SiEt_2$ units (δ_H 8.03, 5.93 (1H × 2, d × 2, J = 3.0 Hz, μ-CH_2), 4.64, 4.46 (5H × 2, s × 2, Cp_2), 4.04 (1H, m, SiH), 1.46−1.02 (20H, m, $SiEt_2$), −15.4 (1H, s, RuH)). The spectroscopic features are similar to those of the derivative **8e** obtained from $HSiMe_2Ph$ and characterized crystallographically (see below). The lost methylene part was converted into methane, as revealed by GLC analysis of the gas phase, and the yield of CH_4 (67%) was found to be comparable to the yield of **8a** (60%) (eq 2). It is notable that the adducts **7** and **8** belong to a rare class of high-valent organoruthenium complexes (Ru(III)−Ru(V))[11] and that, to our knowledge, **8** is the first example of a complex containing both methylene and silylene bridges.

The structure of **8a** and formation of methane suggest that **8a** may arise from interaction of **7a** with H_2SiEt_2. Actually, treatment of an isolated sample of **7a** with H_2SiEt_2 led to the quantitative formation of **8a** (eq 3). Thus

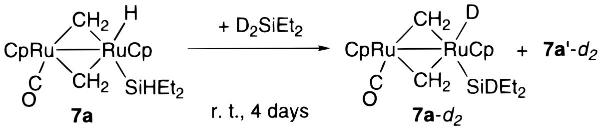
$$\mathbf{7a} \xrightarrow[C_6D_6]{H_2SiEt_2} \mathbf{8a}\ \text{(quant.)} \qquad (3)$$

it has been confirmed that reaction of **2** with H_2SiEt_2 produces **7a**, which is then converted to **8a** through interaction with excess H_2SiEt_2 with concomitant elimination of an equimolar amount of methane. However, because a considerable amount of **8a** was formed even at an early stage of the reaction, selective synthesis of **7a** was unsuccessful.

The $HSiR_3$ adducts of the mono(μ-methylene) species (**6**; Scheme 1) exhibit complicated facile exchange processes, as we reported previously.[9] Similarly, the intramolecular H−D exchange between the hydride and methylene hydrogen atoms (eq 4) and the intermolecular exchange of the $(H)(SiHEt_2)$ parts with external hydrosilane (eq 5) were also observed for the bis(μ-methylene) complex **7a**. However, it took more than 4 days to attain an equilibrium. In the case of **6**, the intramolecular exchange corresponding to eq 4 was completed upon addition of $HSiR_3$ to **5**, and the intermolecular exchange equilibrium corresponding to eq 5 was attained after a couple of hours. Thus, **7a** has proved to be rather rigid, though it is anticipated that reductive elimination from a higher valent Ru(V) center may be a more facile process compared to that from a Ru(III) species (**6**). The exchange processes would follow pathways similar to those of the mono(μ-methylene) species **6**:[9] reversible reductive elimination and oxidative addition of the hydride and methylene groups (eq 4) and reductive elimination of H−$SiHEt_2$ followed by addition of external D_2SiEt_2 (eq 5).



(4)



(5)

Reaction of H_2SiPh_2 produced a mixture of three hydride complexes (δ_H −13.4, −13.7, −14.2), from which the μ-methylene−μ-silylene complex $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiPh_2)(CO)(H)(SiHPh_2)$ **7b** (δ_H −13.4) was isolated in 38% yield after TLC separation (eq 2). The other two products could not be isolated due to decomposition on TLC. In this case, too, formation of a comparable amount of CH_4 (45% yield) was observed.

(ii) Reaction with Monohydrosilane. The reaction with trialkylhydrosilanes such as $HSiMe_3$ and $HSiEt_3$ was sluggish (eq 2). The reaction product from $HSiMe_3$ was assigned to $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(H)(SiMe_3)$ (**7c**; $\delta_H(C_6D_6)$ 7.94, 6.00 (2H × 2, d × 2, J = 3.0 Hz, μ-CH_2), 4.62, 4.45 (Cp), −15.4 (hydride)) by comparison of its spectral data with those of **7a**. However, **7c** could not be isolated in pure form owing to its thermal instability. $HSiEt_3$ did not react with **2** at ambient temperature, in contrast to the high reactivity of **5**, but

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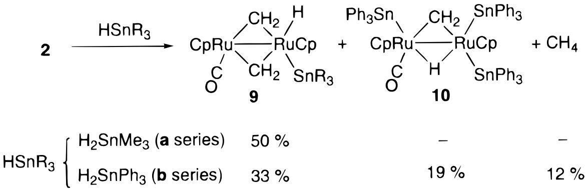
[11] Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, U.K., 1995; Vol. 7.

heating at 60 °C resulted in the formation of methane (95% yield) together with a mixture of unidentified organometallic products.

The reaction with monohydrosilane bearing an aryl group ($HSiMe_2Ph$ and $HSiPh_3$) afforded a mixture of three hydride complexes, from which μ-methylene–μ-silylene complexes $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiR_2)(CO)(H)(SiMe_3)$ (R_2= Me_2 (**8e**; 73%), Ph_2 (**8f**; 26%)) were isolated after TLC separation (eq 2). The other two products could not be isolated, owing to decomposition on TLC. Complexes **8e**,**f** should be formed via Si–Ph bond cleavage and loss of one of the two methylene ligands (see below), and the eliminated groups were converted to benzene and methane, as confirmed by GLC analysis of the mixture. The structure of **8e** has been confirmed by X-ray crystallography, though the quality of the crystal was not satisfactory.[12]

Reaction of 2 with Hydrostannanes: Formation of Oxidative-Addition Products 9 and 10. The reaction of **2** with $HSnMe_3$ in hexane occurred readily at room temperature to give the oxidative-addition product $Cp_2Ru_2(\mu\text{-}CH_2)_2(H)(SnR_3)(CO)$ (**9a**) as the sole isolable organometallic product in 50% yield (eq 6). In



(6)

the case of the reaction with $HSnPh_3$, the hydrido–tristannyl–μ-methylene complex $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}H)(SnPh_3)_3(CO)$ (**10**) was obtained in addition to **9b** after TLC separation.

The spectroscopic features of **9** are similar to those of the silyl analogues **7**, and the molecular structure of the stannyl–bis(μ-methylene) complex **9b** has been determined by X-ray crystallography (Figure 2 and Table 2). It is notable that the CH_2–Ru^V distances are longer than the CH_2–Ru^{III} distances by 0.06 Å. Although it has been established that alkyl-hydride complexes readily undergo reductive elimination,[13] **9** is stable and no dynamic behavior is observed at room temperature.[14] The structure of **10**, also characterized by X-ray crystallography (Figure 3 and Table 3), contains three $SnPh_3$

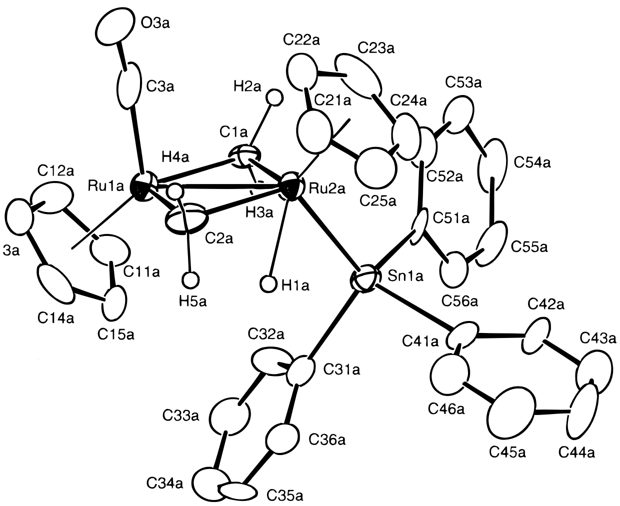


Figure 2. Molecular structure of **9b** (molecule 1) drawn at the 30% probability level.

Table 2. Selected Structural Parameters for 9b[a]

	Bond Lengths		
Sn1–Ru2	2.620(2)	Ru1–C3	1.90(2)
Ru1–Ru2	2.710(2)	Ru2–C1	2.12(1)
Ru1–C1	2.05(1)	Ru2–C2	2.11(2)
Ru1–C2	2.05(1)	C3–O3	1.12(2)
	Bond Angles		
Ru2–Ru1–C1	50.5(4)	Sn1–Ru2–C1	78.3(3)
Ru2–Ru1–C2	50.2(5)	Sn1–Ru2–C2	122.0(4)
Ru2–Ru1–C3	90.3(6)	Ru1–Ru2–C1	48.5(4)
C1–Ru1–C2	100.7(6	Ru1–Ru2–C2	48.5(4)
C1–Ru1–C3	93.3(7)	C1–Ru2–Ru1	97.0(6)
C2–Ru1–C3	88.4(7)		

[a] Bond lengths in Å and bond angles in deg for molecule 1 (a series).

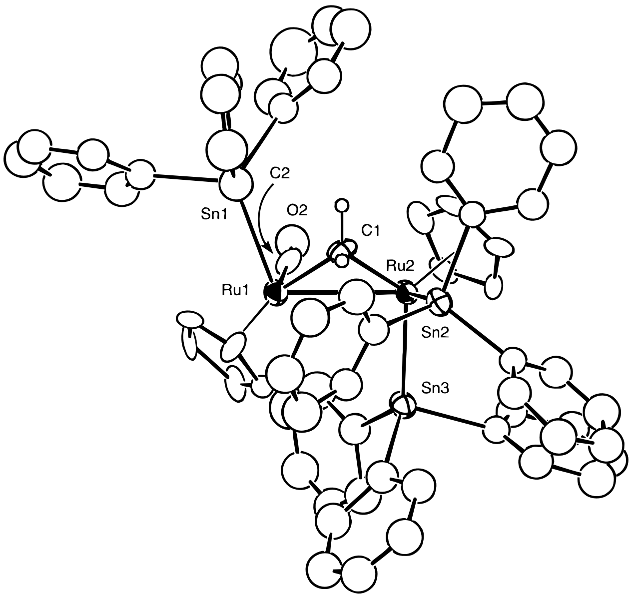


Figure 3. Molecular structure of **10** drawn at the 30% probability level.

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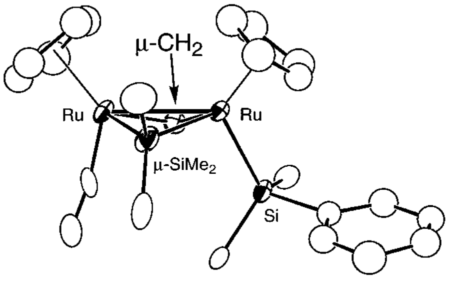
[12] Crystallographic data for **8e**: triclinic, space group $P\bar{1}$, a = 15.489(8) Å, b = 16.071(8) Å, c = 10.374(5) Å, α = 93.15(4)°, β = 114.84(3)°, γ = 90.53(5)°, V = 2338(4) $Å^3$, Z = 4 (with two crystallographically independent molecules). The methylene and silylene ligands bridge the ruthenium centers in a symmetrical manner, and the configuration of the two Cp rings is found to be *cis*. The Ru–CH_2 and Ru–Si distances are comparable to those in related μ-methylene and μ-silylene complexes.



[13] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[14] Stable μ-methylene–hydride complexes such as $Cp_2Ta(\mu\text{-}CH_2)_2IrCp^*(H)$ and $Cp_2Ta(\mu\text{-}CH_2)_2M(H)_2(L)$ (M = Rh, Ir; L = CO, PPh_3) have been reported: (a) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743. (b) Butts, M. D.; Bergman, R. G. *Organometallics* **1994**, *13*, 2668.

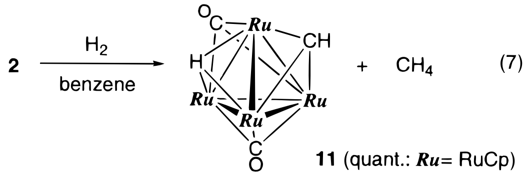
Table 3. Selected Structural Parameters for 10[a]

	Bond Lengths		
Sn1−Ru1	2.640(3)	Ru1−C2	1.75(4)
Sn2−Ru2	2.670(3)	Ru2−C1	2.02(3)
Ru1−Ru2	2.875(4)	C2−O2	1.19(3)
Ru1−C1	2.06(3)		
	Bond Angles		
Sn1−Ru1 Ru2	110.6(1)	Sn2−Ru2−Ru1	105.7(1)
Su1−Ru1−C1	75.9(7)	Sn2−Ru2−C1	72.0(8)
Sn1−Ru1−C2	80(1)	Sn3−Ru2−Ru1	88.2(1)
Ru2−Ru1−C1	44.7(7)	Sn3−Ru2−C1	127.8(8)
Ru2−Ru1−C2	81(1)	Ru1−Ru2−C1	45.8(8)
C1−Ru1−C2	102(1)	Ru1−C1−Ru2	90(1)
Sn2−Ru2−Sn3	108.1(1)	Ru1−C2−O2	174(3)

[a] Bond lengths in Å and bond angles in deg.

groups, and one of the two methylene ligands in **2** is found to be eliminated. In accord with this structure, formation of methane was detected by GLC analysis. Sn−Ph bond cleavage leading to a *μ*-methylene−*μ*-stannylene species analogous to **8** was not observed, although in the case of the reaction of **5** with $HSnPh_3$, Sn−Ph bond cleavage led to functionalization of the $SnPh_3$ moiety.[9]

Reaction of 2 with Hydrogen: Formation of the Tetranuclear μ_3-Methylidyne Complex 11 and Interconversion between Methylene and Methylidyne−Hydride Species on a Tetranuclear System.[15] When a benzene solution of **2** was stirred under H_2 (1 atm) overnight at room temperature, black precipitates **11** were obtained almost quantitatively and formation of CH_4 (104% yield based on **2**) was observed by GLC analysis (eq 7). A ^1H NMR spectrum of **11**



(7)

11 (quant.: *Ru*= RuCp)

contains three Cp resonances in a 5:10:5 ratio (δ_H-($CDCl_3$) 5.31, 5.00, 4.78) in addition to two singlets in very low and high field (δ_H15.0 (1H), −12.6 (1H)). Although a satisfactory ^{13}C NMR spectrum has not been obtained owing to the low solubility, the lower energy CO stretching vibration (1617 cm^{-1}) indicates the presence of face-capping CO ligands.

The structure was finally determined by X-ray crystallography, and one of the two independent molecules is reproduced in Figure 4 (bond distances and angles are given in Table 4). Complex **11** can be described as the tetraruthenium μ_3-methylidyne−μ_3-hydrido complex $Cp_4Ru_4(\mu_3\text{-}CH)(\mu_3\text{-}H)(\mu_3\text{-}CO)_2$, which is consistent with the FD-MS result (M^+ at *m/z* 734 for the ^{101}Ru isotopomer). The core structure of **11** consists of the tetrahedral Ru_4 array, and all the equilateral Ru_3 triangles with the averaged Ru−Ru distance of 2.7 Å are capped by the four μ_3 face-capping ligands (1 CH, 1 H, and 2 CO). Cluster **11** is an electron-precise tetrahedral cluster with 60 cluster valence electrons (CVE). All the above-mentioned spectral features are consistent with a mirror-symmetrical structure, and the highly deshielded ^1H NMR signal (δ_H 15.0) is assigned to the μ_3-CH ligand.[16]

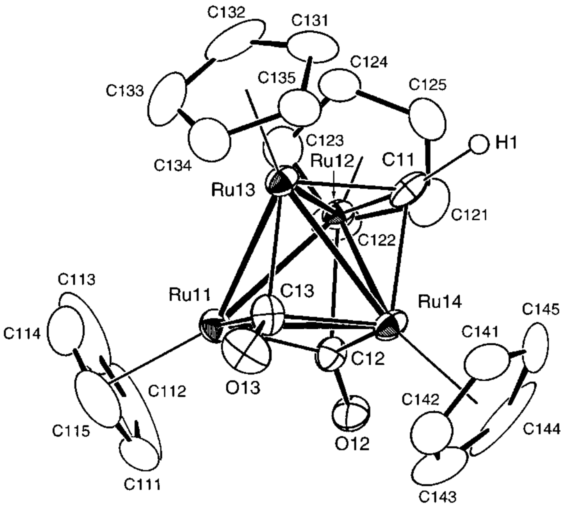


Figure 4. Molecular structure of **11** (molecule 1) drawn at the 30% probability level.

Table 4. Selected Structural Parameters for 11[a]

	Bond Lengths		
Ru11−Ru12	2.716(2)	Ru21−Ru22	2.727(5)
Ru11−Ru13	2.718(2)	Ru21−Ru23	2.727(4)
Ru11−Ru14	2.7073)	Ru21−Ru24	2.6893)
Ru11−C12	2.05(1)	Ru21−C22	2.00(1)
Ru11−C13	2.04(2)	Ru21−C23	2.03(1)
Ru12−Ru13	2.723(2)	Ru22−Ru23	2.720(2)
Ru12- Ru14	2.701(5)	Ru22−Ru24	2.695(2)
Ru12−C11	2.06(1)	Ru22−C21	2.16(1)
Ru12−C12	2.04(2)	Ru22−C22	1.99(1)
Ru13−C11	2.06(1)	Ru23−C21	2.15(1)
Ru13−C13	2.00(2)	Ru23−C23	2.00(2)
Ru14−C11	2.06(1)	Ru24−C21	2.16(2)
Ru14−C12	2.13(1)	Ru24−C22	2.06(1)
Ru14−C13	2.07(2)	Ru24−C23	2.10(1)
C12−O12	1.23(2)	C22−O22	1.27(2)
C13−O13	1.27(2)	C23−O23	1.26(2)
	Bond Angles		
Ru−Ru−Ru	59.75(9)−60.87(9)	Ru−C11, C21−O	127−133(1)
Ru−C11, C21−Ru	77.4−82.9(5)	Ru−C12, C22−O	127−133(1)
Ru−C12, C22−Ru	80.6−86.0(5)		

[a] Bond lengths in Å and bond angles in deg.

In order to confirm the distribution of the *μ*-CH_2 hydrogen atoms, $Cp_2Ru_2(\mu\text{-}CD_2)_2(CO)(MeCN)$ **2-d_4** (>95% deuterated) was treated with H_2. As a result, $Cp_4Ru_4(\mu_3\text{-}CD)(\mu_3\text{-}D)(\mu_3\text{-}CO)_2$ **11-d_2** was obtained, though the lower isotopic purity (ca. 60% as determined by ^1H NMR) indicated occurrence of H-D exchange processes to a considerable extent. The labeling experiments confirm that the C-H bond in the *μ*-CH_2 functional group is cleaved during formation of **11**.

The C−H cleavage process can be reversed by carbonylation. Stirring a benzene solution of **11** under a CO atmosphere (10 atm) at 80 °C afforded a mixture of the

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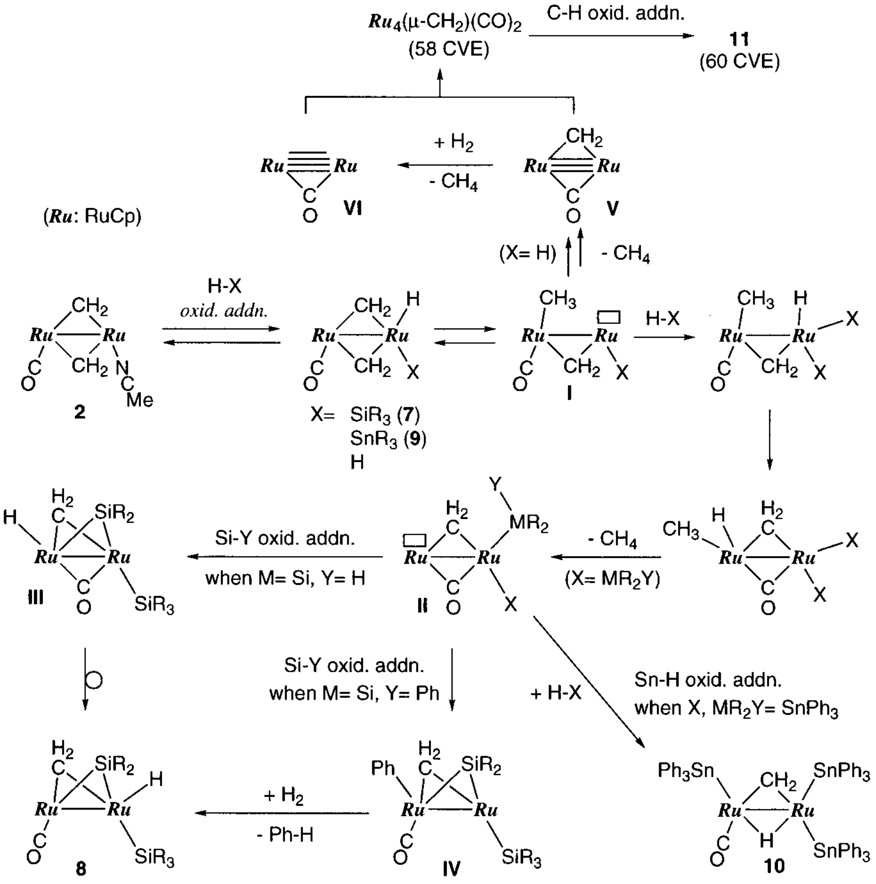
(15) A preliminary report has appeared. Akita, M.; Hua, R.; Moro-oka, Y. *J. Organomet. Chem.* **1997**, *539*, 205.

(16) (μ_3-CH)M_3 complexes: (a) M = Co: Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265. (b) M = Ru: Kakigano, T.; Suzuki, H.; Igarashi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192. (c) M = Os: Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140. (d) M = Ru: Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304. (e) M = Fe: Vites, J. C.; Jacobsen, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563. (f) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307. (g) M = Os: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225. (h) M = Rh: Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787. (i) Herrmann, W. A.; Plank, J.; Riedel, D.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (j) M_3 = Co, Cr, Mo, W, Ni: Duffy, D. N.; Kassis, M. M.; Rae, A. D. *J. Organomet. Chem.* **1993**, *460*, 97. (k) Schacht, H. T.; Vahrenkamp, H. *J. Organomet. Chem.* **1990**, *381*, 261. (l) Akita, M.; Noda, K.; Takahashi, Y.; Moro-oka, Y. *Organometallics* **1995**, *14*, 5209.

Scheme 3



mono(μ-methylene) complex **1** and the carbonyl complex $Cp_2Ru_2(CO)_4$ quantitatively. Thus, carbonylation induced recombination of the μ_3-CH and μ_3-H moieties associated with fragmentation of the tetranuclear core into two dinuclear species.

Plausible Mechanisms for Reaction of 2 with H−X (X = SiR₃, SnR₃, H). The reactions of **2** with H−X (X = SiR_3, SnR_3, H) can be interpreted in terms of the mechanisms summarized in Scheme 3, which are based on the structure of the products as well as the methane formation mechanism from **5** studied previously.[9]

The initial step should be oxidative addition of the H−X bond, giving the hydrido−bis(μ-methylene) intermediate. In some cases, the reaction is terminated at this stage to give the adduct **7** or **9**. Subsequent C−H reductive elimination produces the coordinatively unsaturated methyl intermediate **I**. The exchange processes of **7** (eqs 4 and 5) are viable, if the initial two steps are reversible. Oxidative addition of a second H−X molecule and reductive elimination of methane affords another coordinatively unsaturated intermediate, **II**. In the case of the reaction with H_2SiEt_2, Si−H bond cleavage gives the μ-silylene intermediate **III**, rearrangement of which leads to the final product **8**. Another mechanism involving a terminal silylene intermediate formed via intramolecular oxidative addition of the H−Si bond in **I** might be possible. On the other hand, the reaction with arylsilane should follow oxidative addition of the Ph−Si bond in **II**, giving the phenyl intermediate **IV**. Final hydrogenolysis may furnish **8** along with benzene, though the mechanism is not clear. A small amount of H_2 was actually detected in the gas phase of a reaction mixture. Finally, the formation of the tristannyl complex **10** should involve H−Sn oxidative addition to **II**.

The formation of the tetranuclear cluster **11** can be explained formally in terms of coupling of highly unsaturated intermediates **V** and **VI** resulting from hydrogenolysis of **2**. Because **11** is obtained in quantitative yield, **V** should be trapped by **VI** as soon as **V** is formed. The initial tetranuclear coupling product $Cp_4Ru_4(\mu\text{-}CH_2)(CO)_2$ is still a coordinatively unsaturated species with 58 CVE, and therefore, subsequent cleavage of the H−CH bond would lead to the electron-precise structure with 60 CVE. Similar oxidative addition of a μ-CH_2 ligand in **5** has a precedent as reported by Stone et al.[17] In this system, single and double C−H activation by $Pt(CH_2{=}CH_2)(PR_3)$ leads to the tetranuclear $Ru_2Pt_2(\mu_4\text{-}CH)(\mu\text{-}H)$ (methylidyne) and $Ru_2Pt_2(\mu_4\text{-}C)(\mu\text{-}H)_2$ (carbide) cluster compounds, respectively. Activation of a C−H bond in cluster compounds is a well-documented process, and interconversion of CH_x species on polymetallic systems has precedents.[13,18]

C−C Coupling of 2 with Alkynes Leading to Metallacyclic Products 12. Knox et al. reported the C−C coupling reaction of the mono(μ-methylene) species **5** with unsaturated hydrocarbons leading to metallacyclic products.[7] Then the bis(μ-methylene) species **2**

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(17) (a) Davies, D. L.; Jeffery, J. C.; Miguel, D.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1987**, 454. (b) Davies, D. L.; Jeffery, J. C.; Miguel, D.; Sherwood, P.; Stone, F. G. A. *J. Organomet. Chem.* **1990**, *383*, 463. See also: (c) Jeffery, J. C.; Parrot, M. J.; Stone, F. G. A. *J. Organomet. Chem.* **1990**, *382*, 225.

(18) Shriver, D. F.; Kaesz, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Complexes*; VCH: New York, 1990.

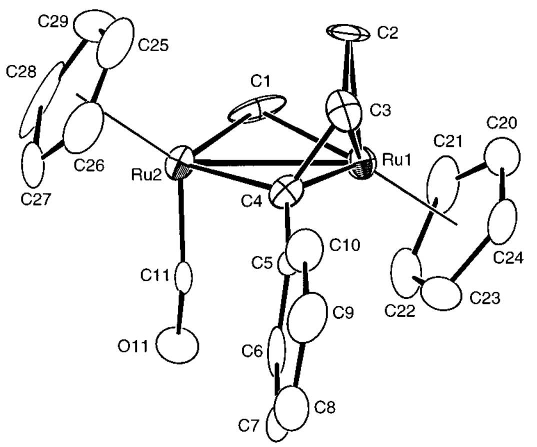
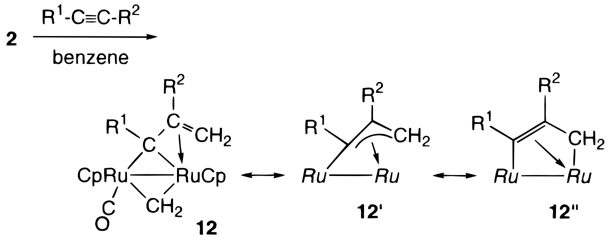


Figure 5. Molecular structure of **12a** (molecule 1) drawn at the 30% probability level.

was also subjected to reaction with unsaturated hydrocarbons.

Treatment of **2** with 1-alkyne (RC≡CH: R = Ph, Me_3Si) in benzene at ambient temperature afforded the adduct $Cp_2Ru_2(\mu\text{-}CH_2)[\mu\text{-}C(R)\text{-}CH{=}CH_2](CO)$ (**12**) (eq 8). The ^1H NMR spectrum indicates the presence of a vinyl functional group (three dd signals: **12a**, $\delta_H(CDCl_3)$ 4.87 (1H, dd, $J = 6.4$ and 7.8 Hz, α-CH=), 2.70 (1H, d, $J = 6.4$Hz, CH_2), −0.12 (1H, d, $J = 7.8$ Hz, CH_2); **12b**, $\delta_H(CDCl_3)$ 4.58 (1H, dd, $J = 4.7$ and 6.6 Hz, α-CH=), 2.70 (1H, dd, $J = 1.2$ and 6.4 Hz, CH_2), −0.12 (1H, dd, $J = 1.2$ and 4.4 Hz, CH_2)) in addition to one μ-methylene ligand left unreacted (**12a**, δ_H 9.07 (1H, s), 8.32 (1H, s); **12b**, δ_H 8.97 (1H, s), 8.42 (1H, s)). The vinyl group should be a part of the $C(R)CH{=}CH_2$ linkage arising from coupling of one of the two methylene ligands with 1-alkyne. It is notable that no other isomer has been detected and the insertion of 1-alkyne proceeds in a specific manner. As established for the Ph derivative **12a** by X-ray crystallography (Figure 5 (one of the two independent molecules) and Table 5), the vinylphenylalkylidene part interacts with the diruthenium core in a $\mu\text{-}\eta^1{:}\eta^3$-fashion and contribution of the allylic structure **12′** and the metallacyclopentene structure **12″** is evident from the three similar C−Ru1 distances (Ru1−C2, 2.18(2) Å; Ru1−C3, 2.18(2) Å; Ru1−C4, 2.13(2) Å).



(8)

12a (R_1= Ph, R_2= H; quant)
12b (R_1= $SiMe_3$, R_2= H; 74 %)
12c (R_1= R_2= Ph; 74 %)

Diphenylacetylene also readily reacted with **2** to afford the adduct $Cp_2Ru_2(\mu\text{-}CH_2)[\mu\text{-}C(Ph)C(Ph){=}CH_2](CO)$ (**12c**) in 74% yield (eq 8). The same compound was already prepared via an alternative route,[7d] which is a reversed version of the present synthesis, that is, addition of a methylene unit ($CH_2{=}N_2$) to the μ-acetylene species, $Cp_2Ru_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC{\equiv}CPh)(\mu\text{-}CO)$. Ethyne (HC≡CH) also readily reacted with **2**, but a complicated mixture was obtained.

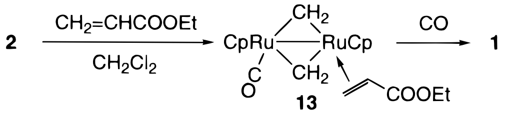
Table 5. Selected Structural Parameters for 12a[a]

Bond Lengths			
Ru1−Ru2	2.693(2)	Ru3−Ru4	2.696(2)
Ru1−C1	2.08(2)	Ru3−C31	1.96(3)
Ru1−C2	2.18(2)	Ru3−C32	2.22(2)
Ru1−C3	2.18(2)	Ru3−C33	2.16(2)
Ru1−C4	2.14(2)	Ru3−C34	2.07(2)
Ru2−C1	2.10(2)	Ru4−C31	2.05(2)
Ru2−C4	2.13(2)	Ru4−C34	2.03(2)
Ru2−C11	1.85(2)	Ru4−C41	1.86(2)
C11−O11	1.15(2)	C41−O41	1.11(2)
C2−C3	1.51(3)	C32−C33	1.40(3)
C3−C4	1.47(3)	C33−C34	1.48(3)
C4 -C5	1.37(3)	C34−C35	1.54(3)
Bond Angles			
Ru2−Ru1−C1	50.1(7)	Ru4−Ru3−C31	49.3(5)
Ru2−Ru1−C2	80.9(6)	Ru4−Ru3−C32	81.0(7)
Ru2−Ru1−C3	75.2(5)	Ru4−Ru3−C33	76.3(6)
Ru2−Ru1−C4	50.7(5)	Ru4−Ru3−C34	48.3(6)
C1−Ru1−C2	82.8(8)	C31−Ru3−C32	84.7(9)
C1−Ru1−C3	107.8(8)	C31−Ru3−C33	107.7(8)
C1−Ru1−C4	99.7(8)	C31−Ru3−C34	96.1(8)
C2−Ru1−C3	40.5(8)	C32−Ru3−C33	37.3(7)
C2−Ru1−C4	74.3(8)	C32−Ru3−C34	70.6(8)
C3−Ru1−C4	39.9(7)	C33−Ru3−C34	40.8(7)
Ru1−Ru2−C1	49.5(6)	Ru3−Ru4−C31	46.4(7)
Ru1−Ru2−C4	51.0(5)	Ru3−Ru4−C34	49.7(5)
Ru1−Ru2−C11	85.0(6)	Ru3−Ru4−C41	83.5(9)
C1−Ru2−C4	99.4(8)	C31−Ru4−C34	94.6(9)
C1−Ru2−C11	91.2(8)	C31−Ru4−C41	89.2(9)
C4−Ru2−C11	93.7(8)	C34−Ru4−C41	95(1)
Ru1−C1−Ru2	80.4(7)	Ru3−C31−Ru2	84.3(9)
Ru1−C2−C3	69(1)	Ru3−C32−C33	69(1)
Ru1−C3−C2	69(1)	Ru3−C33−C32	73(1)
Ru1−C3−C4	68(1)	Ru3−C33−C34	66(1)
C2−C3−C4	122(1)	C32−C33−C34	119(2)
Ru1−C4−Ru2	78.3(6)	Ru3−C34−Ru4	82.0(8)
Ru1−C4−C3	71(1)	Ru3−C34−C33	72(1)
Ru2−C4−C3	111(1)	Ru4−C34−C33	118(1)

[a] Bond lengths in Å and bond angles in deg.

The formation of **12** is explained in terms of insertion of the C≡C bond into the $Ru{-}CH_2$ bond followed by rearrangement of the σ- and π-bonds. Thus, single C−C coupling of the μ-methylene ligand with the external substrate was observed. Attempted double C−C coupling by addition of a 2e-donor (CO, PR_3) was unsuccessful, although it was reported that heating **12c** in refluxing xylene resulted in the formation of a C_4 product.[7d]

Reaction of **2** with olefinic substrates was also examined to see if C−C bond formation took place or not. However, ethene and α-methylstyrene left **2** unreacted, even when the mixture was heated at 50 °C. On the other hand, reaction with ethyl acrylate, bearing an electron-withdrawing substituent, resulted in simple ligand replacement to give an isomeric mixture (5:1) of the η^2-coordinated complex $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(\eta^2\text{-}CH_2{=}CH\text{-}COOEt)$ (**13**; 56% yield) (eq 9), which was



(9)

analogous to the structurally characterized mono(μ-methylene) derivative $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(\eta^2\text{-}CH_2{=}CH\text{-}COOMe)$.[6] Attempted C−C coupling under thermal conditions was unsuccessful, and instead decomposition was observed. Upon treatment with CO, **13** reverted to the carbonyl complex $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$.

C−C Coupling of 2 with Diazoalkanes To Give Vinylidene Complex 14. Recently we reported that

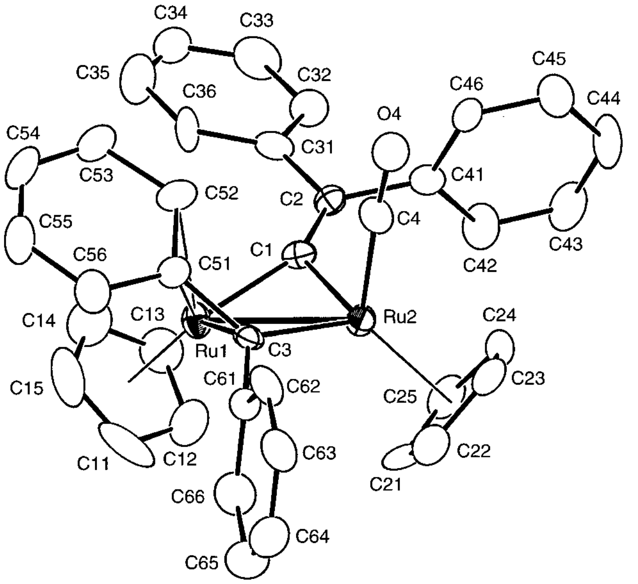


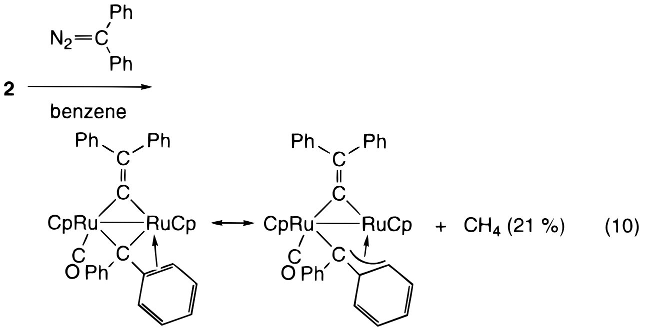
Figure 6. Molecular structure of **14** drawn at the 30% probability level.

Table 6. Selected Structural Parameters for 14[a]

Bond Lengths			
Ru1−Ru2	2.680(2)	C2−C31	1.54(1)
Ru1−C1	1.97(1)	C2−C41	1.53(2)
Ru1−C3	2.12(1)	C3−C51	1.51(1)
Ru1−C51	2.21(1)	C3−C61	1.44(1)
Ru1−C52	2.31(1)	C51−C52	1.42(1)
Ru2−C1	2.06(1)	C51−C56	1.43(1)
Ru2−C3	2.03(1)	C52−C53	1.47(2)
Ru2−C4	1.82(1)	C53−C54	1.35(2)
C4−O4	1.15(1)	C54−C55	1.34(2)
C1−C2	1.33(1)	C55−C56	1.37(2)
Bond Angles			
C1−Ru2−C3	92.8(5)	C3−C51−C52	118(1)
C1−Ru2−C4	88.1(5)	C3−C51−C56	122(1)
C3−Ru2−C4	89.3(5)	C52−C51−C56	117(1)
Ru1−C1−C2	146(1)	Ru1−C52−C51	68.0(6)
Ru2−C1−C2	130.6(9)	Ru1−C52−C53	120.9(8)
Ru1−C3−Ru2	80.4(4)	C51−C52−C53	118(1)
Ru2−C4−O4	174(1)	C52−C53−C54	119(1)
Ru1−C51−C3	66.1(6)	C53−C54−C55	122(1)
Ru1−C51−C52	75.6(7)	C54−C55−C56	121(1)
Ru1−C51−C56	120.0(8)	C51−C56−C55	121(1)

[a] Bond lengths in Å and bond angles in deg.

the labile mono(μ-methylene) species **5** reacts with various diazoalkanes to give olefinic products through C−C coupling (Scheme 2).[8] Although the di(μ-methylene) species **2** was also found to readily react with diazoalkanes, the reaction was generally complicated (N_2CH_2, N_2CHPh, $N_2CHCOOEt$) and a clean reaction was observed only for the reaction with diphenyldiazomethane ($N_2{=}CPh_2$) (eq 10). Although the simple ^1H NMR spectrum of the product $Cp_2Ru_2(\mu\text{-}C{=}CPh_2)(\mu\text{-}\eta^1{:}\eta^3\text{-}CPh_2)(CO)$ (**14**) containing Cp and Ph signals



14 (34 %) (π-benzyl structure **14'**)

(δ_H 7.9−6.5 (Ph), 4.35, 4.05 (Cp_2)) along with small signals around 2.6 ppm suggested loss of the μ-CH_2 functional groups, the product could not be characterized by spectral data alone, and thus, **14** was subjected to an X-ray diffraction study. The molecular structure shown in Figure 6 (bond distances and angles are given in Table 6) contains the μ-diphenylvinylidene ligand in addition to the $\mu\text{-}\eta^1{:}\eta^3$-diphenylmethylene ligand, which interacts with Ru1 in a η^3-mode (π-benzyl structure **14′**: Ru1−C3, 2.12(1) Å; Ru1−C51, 2.21(1) Å; Ru1−C52, 2.31(1) Å). Upon coordination of the benzylic part the bond lengths of the C56−C51−C52−C53 part (1.42−1.47 Å) of the phenyl ring is slightly elongated compared to those of the C53−C54−C55−C56 part (1.34−1.37 Å) owing to partial localization of the aromatic π-electrons. In accord with this structure, the ^1H and ^{13}C NMR signals of the C52−H moiety are observed at considerably higher field (δ_H 2.66 (dd, 5.9 and 1.5 Hz), δ_C 72.9 (d, $J = 168$ Hz)), and C1 and C3 are located at δ_C 253.6 and 99.6, respectively. This type of coordination is rather usual, and $Cp_2Ru_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CPh_2)(CO)_2$[19] may be raised as a typical example. The structure of **14** suggests that disproportionation of the two μ-methylene ligands gives rise to the vinylidene quaternary carbon atom and methane ($2CH_2 \rightarrow C + CH_4$). As expected, methane was detected in the gas phase (21% yield).

A plausible formation mechanism of **14** is depicted in Scheme 4. The initial reaction may be similar to the C−C coupling of the mono(μ-methylene) species **5**. Successive incorporation of the CPh_2 group as an η^1-ligand, C−C coupling, and C−H oxidative addition afford the hydrido−μ-alkenyl intermediate **VII**. Subsequent reductive elimination of the H and μ-CH_2 parts gives the coordinatively unsaturated methyl intermediate **VIII**. Oxidative addition of the α-C−H bond and rearrangement give the μ-vinylidene−hydrido−methyl intermediate **IX**. Final reductive elimination of methane followed by coordination of a second molecule of diazoalkane furnishes **14**. According to the scheme, multiple C−C coupling is hampered by the reductive elimination (**VII** → **VIII**), resulting in the loss of the CH_2 functional group.

Synthesis and Reaction of Bis(μ-methylene) Bis(acetonitrile) Species 3. Irradiation of an MeCN solution of **1** produced **2** as described above. Further irradiation (ca. 20 h) caused disappearance of the ν(CO) vibration. The resulting species, formulated as the bis(μ-methylene) bis(acetonitrile) species $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ (**3**), decomposed to a considerable extent after evaporation of the solvent and, therefore, was characterized on the basis of the following experiments (Scheme 5).

The ^1H NMR experiment in CD_3CN indicated the formation of the single, symmetrical species **3** containing a single Cp resonance at δ 5.23. Treatment of **3** with 2e-donors (CO, cyclohexyl isocyanide (NCCy)) gave adducts (**1** and **15**) incorporating the 2e-donor at each

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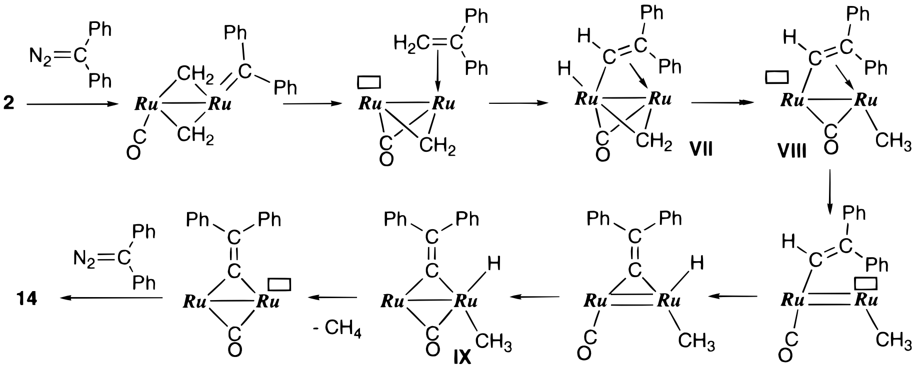
(19) (a) Davis, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293. See also: (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789. (c) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Razay, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1563.

Scheme 4



(*Ru*= RuCp)

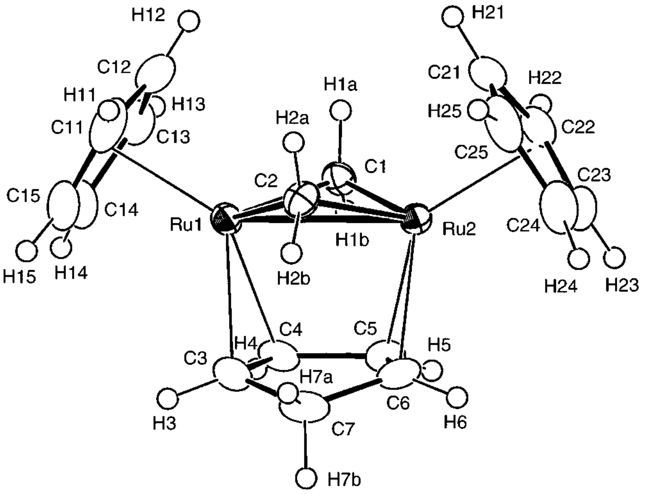
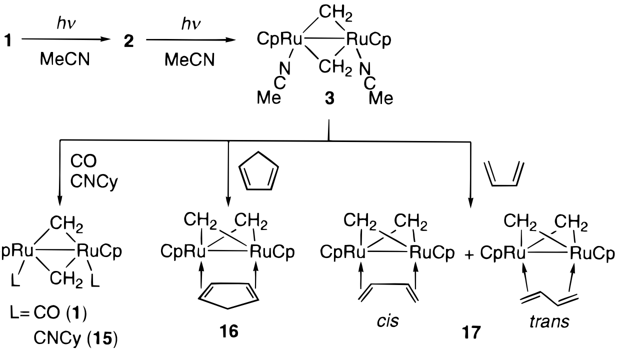


Figure 7. Molecular structure of **16** drawn at the 30% probability level.

Scheme 5



ruthenium center in quantitative yields. Although olefins did not react with **3** at all, conjugated dienes produces 1:1 adducts. Cyclopentadiene afforded complex **16** as a single product, whereas butadiene gave a mixture of *s-cis-* and *s-trans-*η^4-diene isomers, which interconverted with each other upon heating at 120 °C. The X-ray structure (Figure 7 and Table 7) indicates that cyclopentadiene is coordinated to each Ru center as an η^2-olefin ligand, as judged by the C4−C5 distance (1.492(6) Å) being comparable to the C(sp^2)−C(sp^2) single-bond length (1.48 Å).

We also examined the reaction of **3** with HSiR$_3$, HSnR$_3$, alkynes, and diazoalkanes; however, complicated mixtures of products were merely obtained.

Conclusions. Reactivity of the diruthenium complex Cp$_2$Ru$_2$(μ-CH$_2$)$_2$(CO)(NCMe) (**2**), containing two methylene bridges, has been examined with the emphasis on (1) reduction with H-X (X= SiR$_3$, SnR$_3$, H) and (2) C−C coupling with alkynes and diazoalkanes, and the results are summarized in Scheme 6.

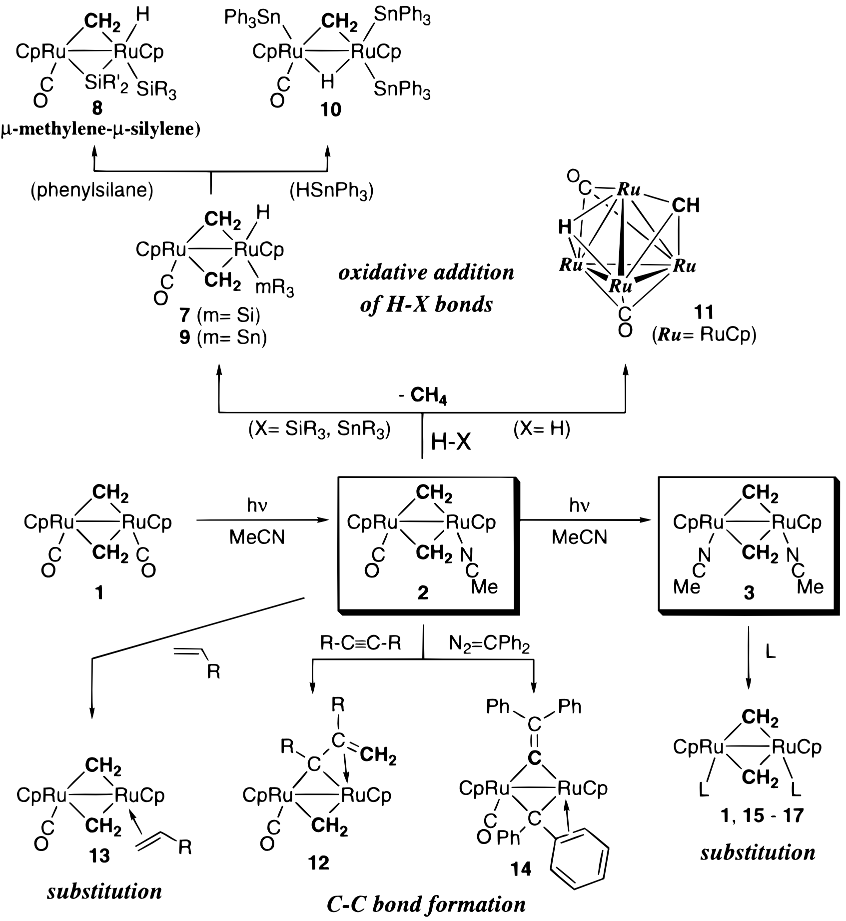
Table 7. Selected Structural Parameters for 16[a]

	Bond Lengths		
Ru1−Ru2	2.6574(6)	Ru2−C5	2.159(4)
Ru1−C1	2.049(4)	Ru2−C6	2.186(4)
Ru1−C2	2.039(4)	C3−C4	1.410(6)
Ru1−C3	2.192(4)	C3−C7	1.494(6)
Ru1−C4	2.155(4)	C4−C5	1.492(6)
Ru2−C1	2.053(4)	C5−C6	1.405(6)
Ru2−C2	2.041(4)	C6−C7	1.507(6)
	Bond Angles		
Ru2−Ru1−C1	49.7(1)	C1−Ru2−C2	94.3(2)
Ru2−Ru1−C2	49.4(1)	C1−Ru2−C5	77.1(2)
Ru2−Ru1−C3	85.6(1)	C1−Ru2−C6	111.4(2)
Ru2−Ru1−C4	74.3(1)	C2−Ru2−C5	103.6(2)
C1−Ru1−C2	94.4(2)	C2−Ru2−C6	85.6(2)
C1−Ru1−C3	111.3(2)	C5−Ru2−C6	37.7(1)
C1−Ru1−C4	77.0(2)	Ru1−C1−Ru2	80.8(1)
C2−Ru1−C3	85.3(2)	Ru1−C2−Ru2	81.3(1)
C2−Ru1−C4	103.6(2)	C4−C3−C7	110.1(4)
C3−Ru1−C4	37.8(1)	C3−C4−C5	107.0(4)
Ru1−Ru2−C1	49.6(1)	C4−C5−C6	107.7(4)
Ru1−Ru2−C2	49.3(1)	C5−C6−C7	109.5(4)
Ru1−Ru2 C5	74.4(1)	C3−C7−C6	102.0(4)
Ru1−Ru2−C6	85.9(1)		

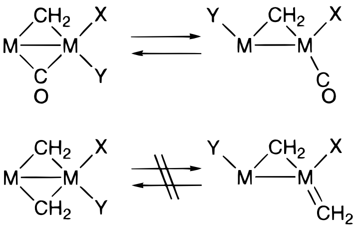
[a] Bond lengths in Å and bond angles in deg.

As for the first aspect, methane is evolved in moderate yields under milder conditions (at room temperature) compared to those for the mono(μ-methylene) derivative **5**.[9] The methane formation mechanism should be essentially similar to that discussed for **5**. However, the mechanism involving oxidative addition of H−X, Si−Ph, and C−H bonds is rather complicated as indicated by the dependence of the structure of the organometallic products (**8**, **10**, and **11**) on the structure of the reducing agent. In addition, only one of the two methylene ligands is converted to methane, and the other ligand remains as a supporting ligand. Possible origins of the dissimilar reactivity are (i) the nature of the other bridging ligand (μ-CH$_2$ (**2**) vs μ-CO (**5**)) and (ii) the oxidation state of the Ru centers (e.g. MeCN complexes: Cp$_2$Ru$^{III}_2$(μ-CH$_2$)$_2$(CO)(NCMe) (**2**) vs Cp$_2$Ru$^{II}_2$(μ-CH$_2$)(CO)$_2$(NCMe) (**5**)). CO can be coordinated to a metal center as a terminal as well as bridging ligand, whereas CH$_2$ can interact with a metal center only as a bridging ligand and a terminal methylene species (M=CH$_2$) should be a high-energy species owing to less effective back-donation from the metal center compared

Scheme 6



Scheme 7



to the dinuclear system ($M_2(\mu\text{-}CH_2)$) (Scheme 7).[20] A CO ligand with such flexible coordinating ability leads to stabilization of various structures compared to CH_2, which lacks flexibility in the coordination mode. As for the latter point, the oxidative addition increases the oxidation state of the Ru center up to +5 (**7**−**10**), which is a rather unusual one in organoruthenium chemistry.

It is also found that treatment of **2** with alkynes and diphenyldiazomethane induces C−C coupling, though the expected multiple C−C coupling has not been observed so far. The multiple C−C coupling is hampered by transformation of the μ-CH_2 functional group, namely reductive elimination with an η^1 ligand (in particular, hydride arising from oxidative addition of H−Si, H−Sn, H−H, and H−C bonds) leading to a methyl group. The expected reaction may be realized by designing a system which is not susceptible to methylene−hydride reductive elimination.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. Ether, hexanes, and toluene (Na−K alloy), CH_2Cl_2 (P_2O_5), and CH_3CN (CaH_2) were treated with appropriate drying agents, distilled, and stored under argon. Chromatography was performed on alumina (column, aluminum oxide, activity II-IV (Merck Art. 1097); preparative TLC, aluminum oxide 60PF$_{254}$ (Type E) (Merck Art. 1103)) or silica gel (preparative TLC, Kiesel gel 60 PF$_{254}$ (Merck 1.007747)). ^1H and ^{13}C NMR spectra were recorded on JEOL EX-90 (^1H, 90 MHz), GX-270 (^1H, 270 MHz; ^{13}C, 67 MHz), EX-400 (^1H, 400 MHz; ^{13}C, 100 MHz), and GX-500 spectrometers (^1H, 500 MHz; ^{13}C, 125 MHz). Solvents for NMR measurements containing 1% TMS were dried over molecular sieves, degassed, distilled under reduced pressure, and stored under Ar. IR and FD-MS spectra were obtained on a JASCO FT/IR 5300 spectrometer and a Hitachi M-80 spectrometer, respectively. Volatile products were quantified by GLC (methane (Porapak Q/FID); benzene (Silicone SE-30/FID); H_2 (molecular sieves 5A/TCD); Hitachi gas chromatograph 163).

Starting Materials. Diruthenium complexes $Cp_2Ru_2(CO)_4$,[21] **1**,[4] and **1**-d_4[4] were prepared according to the literature procedures. Most of the hydrosilanes and -stannanes were purchased and used as received. $HSiMe_3$, H_2SiEt_2, and $HSnMe_3$ were prepared by reduction of the corresponding chlorosilanes and bromostannane with $LiAlH_4$, and the deuteriosilane D_2SiEt_2 was prepared by treatment of Cl_2SiEt_2 with $LiAlD_4$. Diphenyldiazomethane was prepared by following the literature procedure.[22]

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[20] (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (c) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879.

[21] Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1989**, *26*, 259.

[22] Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1995; Collect. Vol. III, p 351.

Synthesis of $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(NCMe)$ (2). Irradiation of a saturated acetonitrile solution of **1** (ca. 2 mg/mL) with slow argon bubbling resulted in a color change of the reaction mixture from yellow to orange. The progress of the reaction was monitored by IR spectroscopy. After irradiation for 6 h, the acetonitrile complex **2** was obtained as yellow-orange crystals in a quantitative yield by crystallization from acetonitrile. **2**: δ_H (C_6D_6) 8.86, 7.28 (2H × 2, s × 2, CH_2 × 2), 4.90, 4.58 (5H × 2, s × 2, Cp_2), 0.82 (3H, s, CH_3CN); IR (CH_3CN) ν(C≡O) 1909 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NORu_2$: C, 41.91; H, 3.96; N, 3.26. Found: C, 41.75; H, 3.80; N, 3.32.

Reaction of 2 with H_2SiEt_2. A mixture of **2** (80.5 mg, 0.18 mmol) and H_2SiEt_2 (73 μL, 0.56 mmol) was stirred at room temperature overnight. After removal of the volatiles under reduced pressure, the residue was subjected to preparative TLC separation (silica gel, eluted with ether−hexane (1:10)). From two yellow bands, the bis(μ-methylene)−hydrido complex **7a** (30.0 mg, 0.063 mmol, 34% yield) and the μ-methylene−μ-silylene−hydrido complex **8a** (42.0 mg, 0.076 mmol, 41% yield) were obtained. **7a**: δ_H (C_6D_6) 8.05, 7.07 (2H × 2, s × 2, CH_2 × 2), 4.79, 4.67 (5H × 2, s × 2, Cp_2), 3.25 (1H, m, SiH), 1.36−1.08 (10H, m, C_2H_5), −15.1 (1H, s, RuH); δ_C (C_6D_6) 202.8 (s, CO), 118.8 (t, J = 141 Hz, μ-CH_2), 86.3, 85.6 (d × 2, J = 178 Hz, Cp_2), 13.2 (t, J = 119 Hz, $SiCH_2$), 10.6 (q, J = 126 Hz, CH_3); IR (CH_2Cl_2) ν(C≡O) 1920 cm^{-1}. Anal. Calcd for $C_{17}H_{26}ORu_2Si$: C, 42.85; H, 5.46. Found: C, 42.36; H, 5.49. **8a**: δ_H (C_6D_6) 8.03; 5.93 (1H × 2, d × 2, J = 2.9 Hz, CH_2), 4.64, 4.46 (5H × 2, s × 2, Cp_2), 4.04 (1H, m, SiH), 1.46−1.02 (20H, m, C_2H_5), −15.4 (1H, s, RuH); δ_C (C_6D_6) 203.8 (s, CO), 109.1 (t, J = 140 Hz, μ-CH_2), 86.0, 85.1 (d × 2, J = 176 Hz, Cp_2), 17.54 (t, J = 119 Hz, $SiCH_2$), 13.62 (t, J = 121 Hz, $SiCH_2$), 10.22 (q, J = 126 Hz, CH_3), 10.22 (q, J = 125 Hz, CH_3); IR (CH_2Cl_2) ν(C≡O) 1933 cm^{-1}. Anal. Calcd for $C_{20}H_{34}ORu_2Si_2$: C, 43.79; H, 6.20. Found: C, 44.04; H, 6.59.

Reaction of 2 with H_2SiPh_2. Stirring a mixture of **2** (83.0 mg, 0.19 mmol) and H_2SiPh_2 (110 μL, 0.6 mmol) in benzene (5 mL) for 48 h at room temperature afforded a yellow solution. After removal of volatiles under reduced pressure, the yellow μ-diphenylsilylene complex **8b** (62.0 mg, 0.084 mmol, 43% yield) was obtained by preparative TLC separation (silica gel, eluted with ether−hexane (1:10)). **8b**: δ_H (C_6D_6) 8.24 (1H, s, CH_2), 7.90−7.02 (m, Ph and CH_2), 5.32 (1H, s, SiH), 4.55, 4.46 (5H × 2, s × 2, Cp_2), −13.42 (1H, s, RuH); δ_C (C_6D_6) 202.9 (s, CO), 149.5 (s, ipso), 148.0 (s, ipso), 135.7, 135.6, 128.9, 128.8, 127.6, 127.4 (Ph signals), 114.3 (t, J = 147 Hz, μ-CH_2), 89.4 (d, J = 178 Hz, Cp), 87.5 (d, J = 178 Hz, Cp); IR (CH_2Cl_2) ν(C≡O) 1928 cm^{-1}. Anal. Calcd for $C_{36}H_{34}ORu_2Si_2$: C, 58.32; H, 4.59. Found: C, 58.58; H, 4.21.

Reaction of 2 with $HSiMe_3$. A mixture of **2** (21.4 mg, 0.05 mmol) and $HSiMe_3$ (30 μL, ca. 0.25 mmol) in benzene (0.5 mL) was stirred for 15 min at room temperature. The formation of the bis(μ-methylene)−hydrido−silyl complex **7c** (58% yield), which could not be isolated in pure form due to the thermal instability, was confirmed by a ^1H NMR spectrum of the reaction mixture. **7c**: δ_H (C_6D_6) 7.94, 6.00 (2H × 2, d × 2, J = 3.0 Hz, CH_2 × 2), 4.62, 4.45 (5H × 2, s × 2, Cp_2), −15.4 (1H, s, RuH).

Reaction of 2 with $HSiEt_3$. The reaction of **2** (13.7 mg, 0.032 mmol) with $HSiEt_3$ (26 μL, 0.16 mmol) did not occur at ambient temperature. Heating of this solution at 60 °C gave a mixture of unidentified organometallic products along with methane (95% yield), as revealed by GC analysis.

Reaction of 2 with $HSiMe_2Ph$. A mixture of **2** (55.0 mg, 0.13 mmol) and $HSiMe_2Ph$ (60 μL, 0.39 mmol) in benzene (3 mL) was stirred for 48 h at room temperature. After removal of the volatiles, the μ-silylene complex **8e** (53.0 mg. 0.093 mmol, 73% yield) was obtained by preparative TLC separation (silica gel, eluted with ether−hexane (1:10)), and recrystallization from hexane afforded yellow crystals. **8e**: δ_H (C_6D_6) 7.95, 6.22 (1H × 2, d × 2, J = 2.9 Hz, CH_2), 7.75−7.15 (m, Ph signals), 4.65, 4.35 (5H × 2, s × 2, Cp_2), 1.13, 0.62 (3H, s × 2, μ-$SiMe_2$), 0.91, 0.90 (3H, s × 2, $SiMe_2$), −14.97 (1H, s, RuH); δ_C (C_6D_6) 204.3 (s, CO), 150.6 (s, ipso), 133.6, 127.6, 127.3 (Ph signals), 108.7 (t, J = 141 Hz, μ-CH_2), 86.7, 86.4 (d × 2, J = 176 Hz, Cp_2), 17.6, 14.6, 6.7, 6.5 (q × 4, J = 119 Hz, CH_3); IR (CH_2Cl_2) ν(C≡O) 1932 cm^{-1}. Anal. Calcd for $C_{22}H_{30}ORu_2Si_2$: C, 46.41; H, 5.27. Found: C, 46.41; H, 4.72.

Reaction of 2 with $HSiPh_3$. The reaction was carried out under the same conditions as described above. **8f**: δ_H (C_6D_6) 8.47 (1H, s, CH_2) 7.89−7.03 (m, CH_2 and Ph signals), 4.52, 4.17 (5H × 2, s × 2, Cp_2), −13.25 (1H, s, RuH); δ_C (C_6D_6) 203.1 (s, CO), 151−128 (Ph signals: some of them are overlapped with the C_6D_6 signals), 115.5 (t, J = 140 Hz, μ-CH_2), 90.2 (d, J = 178 Hz, Cp), 87.5 (d, J = 178 Hz, Cp); IR (CH_2Cl_2) ν(C≡O) 1928 cm^{-1}. Anal. Calcd for $C_{42}H_{38}ORu_2Si_2$: C, 61.76; H, 4.65. Found: C, 61.38; H, 4.38.

Reaction of 7a with H_2SiEt_2. A mixture of **7a** (36.0 mg, 0.076 mmol) and H_2SiEt_2 (20 μL, 0.15 mmol) in benzene (1 mL) was stirred at room temperature for 48 h, during which time **7a** was converted to **8a** in a nearly quantitative yield.

Reaction of 2 with $HSnMe_3$. To a suspension of **2** (68.0 mg, 0.16 mmol) in hexane (5 mL) was added $HSnMe_3$ (60 μL, 0.5 mmol). The resultant mixture was stirred for 30 min at room temperature. A yellow supernatant hexane solution was obtained by centrifugation. The bis(μ-methylene)−hydrido−stannyl complex **9a** (72.3 mg, 0.13 mmol, 83% yield) was obtained as a yellow precipitate by adding methanol to the hexane solution. **9a**: δ_H (C_6D_6) 8.25, 7.19 (2H × 2, s × 2, CH_2 × 2), 4.69, 4.45 (5H × 2, s × 2, Cp_2), 0.45 (9H, s, $SnMe_3$, $^2J_{Sn-Ru-H}$ = 23 Hz), −13.68 (1H, s, RuH, $^2J_{Sn-Ru-H}$ = 112 Hz); δ_C (C_6D_6) 202.4 (s, CO), 106.9 (dd, J = 137, 148 Hz, CH_2), 88.2, 85.4 (d × 2, J = 176 Hz, Cp), −3.16 (q, J = 126 Hz, $SnMe_3$); IR (CH_2Cl_2) ν(C≡O) 1936 cm^{-1}. Anal. Calcd for $C_{16}H_{24}ORu_2Sn$: C, 34.74; H, 4.34. Found: C, 34.71; H,4.54.

Reaction of 2 with $HSnPh_3$. A mixture of **2** (64.7 mg, 0.15 mmol) and $HSnPh_3$ (180.0 mg, 0.51 mmol) in benzene (3 mL) was stirred for 1 h at room temperature. After removal of the solvent under reduced pressure, the residue was subjected to preparative TLC separation (silica gel, eluted with ether−hexane (1:10)). Two bands were collected. From the higher band, the bis(μ-methylene)−hydrido−stannyl complex **9b** (54.0 mg, 0.073 mmol, 48% yield) was obtained as yellow crystals after recrystallization from ether−hexane. From the lower band, the tristannyl complex **10** (35.0 mg, 0.024 mmol, 15% yield) was obtained as pale yellow crystals after recrystallization from hot hexane. **9b**: δ_H (C_6D_6) 8.67, 8.51 (2H × 2, s × 2, CH_2 × 2), 7.80−6.98 (m, Ph signals), 4.68, 4.37 (5H × 2, s × 2, Cp_2), −12.74 (1H, s, RuH); δ_C (C_6D_6) 202.6 (s, CO), 145−128 (Ph signals: some of them are overlapped with the C_6D_6 signals), 111.5 (t, J = 139 Hz, μ-CH_2), 89.8 (d, J = 178 Hz, Cp), 87.9 (d, J = 178 Hz, Cp); IR (CH_2Cl_2) ν(C≡O) 1930 cm^{-1}. Anal. Calcd for $C_{31}H_{30}ORu_2Sn$: C, 50.32; H, 4.06. Found: C, 49.59; H, 4.24. **10**: δ_H (C_6D_6) 8.49, 7.58 (1H × 2, s × 2, μ-CH_2), 7.93−6.93 (m, Ph signals), 4.57, 4.49 (5H × 2, s × 2, Cp_2), −12.43 (1H, s, RuH); δ_C (C_6D_6) 200.5 (s, CO), 145.2 (s, ipso), 146−128 (Ph signals: some of them are overlapped with the C_6D_6 signals), 107.7 (t, J = 145 Hz, μ-CH_2), 88.4 (d, J = 176 Hz, Cp), 86.0 (d, J = 176 Hz, Cp); IR(CH_2Cl_2) ν(C≡O) 1904 cm^{-1}. Anal. Calcd for $C_{66}H_{59}ORu_2Sn_3$: C, 55.58; H, 4.14. Found: C, 55.58; H, 4.02.

Reaction of 2 with H_2. A benzene (20 mL) solution of **2** (30.2 mg, 0.07 mmol) in a glass autoclave under H_2 (1 atm) was stirred overnight at room temperature, and the black precipitate **11** (22.6 mg, 0.03 mmol, 86% yield) appeared gradually. Crystals of **11** were obtained by recrystallization from a saturated CH_2Cl_2 solution at room temperature. **11**: δ_H ($CDCl_3$) 15.0 (1H, s, μ_3-CH), 5.31 (5H, s, Cp), 5.00 (10H, s, Cp_2), 4.78 (5H, s, Cp), −12.6 (1H, s, μ_3-H); δ_C ($CDCl_3$) 91.8, 88.2, 85.3 (d × 3, J = 177 Hz, Cp); IR(KBr) ν(C≡O) 1617 cm^{-1}. FD-MS 734 (M^+ for the $^{101}Ru_4$ isotopomer). Anal. Calcd for $C_{23}H_{22}O_2Ru_4$: C, 37.60; H, 3.00. Found: C, 38.06; H, 3.21.

Reaction of 2 with PhC≡CH. Stirring a solution of **2** (42.0 mg, 0.098 mmol) and phenylacetylene (33.0 μL, 0.30 mmol) at room temperature for 15 min gave a red solution.

Table 8. Crystallographic Data

	2	**9b**	**10**·($^1/_2$hexane)	**11**·$^1/_4$(CH_2Cl_2)·$^1/_4$(H_2O)	**12a**	**14**	**16**
formula	$C_{15}H_{17}ONRu_2$	$C_{31}H_{30}OSnRu_2$	$C_{72}H_{72}OSn_3Ru_2$	$C_{23.5}H_{23}O_{2.25}$-$Cl_{0.5}Ru_4$	$C_{21}H_{20}ORu_2$	$C_{38}H_{30}ORu_2$	$C_{17}H_{20}ORu_2$
fw	429.5	739.4	1511.6	760.4	490.5	704.8	426.5
recryst solvent	CH_3CN	ether−hexanes	hexanes	CH_2Cl_2	ether−hexanes	methanol	THF−hexanes
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/a$	$P2_1/a$	$P\bar{1}$
a/Å	12.330(4)	43.404(8)	31.809(5)	36.10(2)	8.114(3)	16.709(5)	9.503(2)
b/Å	9.130(1)	10.629(2)	18.779(3)	9.530(6)	24.91(1)	19.871(7)	10.981(1)
c/Å	13.213(3)	18.486(2)	26.084(4)	30.05(2)	17.458(9)	9.0074()	7.560(1)
α/deg							94.71(1)
β/deg	100.77(2)	105.38(1)	123.76(1)	118.50(4)	90.46(3)	98.88(3)	113.00(1)
γ/deg							87.16(1)
V/Å^3	1461.2(6)	8222(3)	12954(3)	9084(19)	3527(4)	2954(3)	723.5(2)
Z	2	12	8	16	8	4	2
d_{calcd}/g cm^{-3}	1.95	1.79	1.55	2.61	1.85	1.58	1.96
μ/cm^{-1}	20.2	20.1	16.4	26.9	16.8	10.5	20.7
2θ/deg	5−50	5−40	5−45	3−50	3−48	5−50	5−55
no. of data collected	2883	7927	8973	8721	5880	5727	3527
no. of data with $I > 3\sigma(I)$	2206	2280	3731	5965	3606	2534	2665
no. of params refined	188	394	391	546	433	370	252
R	0.026	0.039	0.066	0.049	0.074	0.053	0.025
R_w	0.026	0.033	0.071	0.051	0.073	0.040	0.024

After removal of the volatiles under reduced pressure, the residue was subjected to preparative TLC separation (silica gel, eluted with ether−hexane (1:15)). A red-orange band was collected, from which **12a** (50.0 mg, 0.090 mmol, 92% yield) was obtained as red-orange crystals after recrystallization from ether−hexane. **12a**: δ_H ($CDCl_3$) 9.07, 8.32 (1H × 2, s × 2, μ-CH_2), 7.75−7.22 (5H, m, Ph), 4.87, 4.76 (5H × 2, s × 2, Cp_2), 4.87 (1H, dd, J = 6.4, 7.8 Hz, CH), 2.70 (1H, d, J = 6.3, CH_2), −0.12 (1H, d, J = 7.8 Hz, CH_2); δ_C ($CDCl_3$) 200.6 (s, CO), 175.7 (s, μ-C), 156.5 (s, ipso), 130.2 (t, J = 146 Hz, μ-CH_2), 128.4 (d, J = 157 Hz, Ph), 128.0 (d, J = 150 Hz, Ph), 125.7 (d, J = 159 Hz, Ph), 89.1 (d, J = 176 Hz, Cp), 83.9 (d, J = 184 Hz, Cp), 77.6 (d, J = 156 Hz, CH), 43.3 (t, J = 156 Hz, CH_2); IR(CH_2Cl_2) ν(C≡O) 1921 cm^{-1}. Anal. Calcd for $C_{21}H_{20}ORu_2$: C, 51.37; H, 4.08. Found: C, 51.69; H, 4.14.

Reaction of 2 with $Me_3SiC≡CH$. The reaction was carried under the same conditions as described above. **12b** (79% yield): δ_H ($CDCl_3$) 8.97, 8.42 (1H × 2, s × 2, μ-CH_2), 4.65, 4.58 (5H × 2, s × 2, Cp_2), 4.58 (1H, dd, J = 4.7, 6.6 Hz, CH), 2.70 (1H, dd, J = 6.6, 1.4 Hz, CH_2), −0.12 (1H, dd, J = 4.7, 1.0 Hz, CH_2), 0.03 (9H, s, $SiMe_3$); IR (CH_2Cl_2) ν(C≡O) 1922 cm^{-1}. Anal. Calcd for $C_{18}H_{24}ORu_2Si$: C, 44.4; H, 4.94. Found: C, 44.0; H, 5.08.

Reaction of 2 with PhC≡CPh. The reaction was carried under the same conditions as described above. **12c** (74% yield) was characterized by comparison with the reported data.

Reaction of 2 with Ethyl Acrylate. A CH_2Cl_2 solution (3 mL) of **2** (120 mg, 0.28 mmol) and ethyl acrylate (40 μL, 0.37 mmol) was stirred overnight at room temperature. After removal of the volatiles under reduced pressure, **13** (76.5 mg, 0.16 mmol, 56% yield) was obtained by preparative TLC separation (silica gel, eluted with CH_2Cl_2−hexane (1:1)). **13**: δ_H ($CDCl_3$) 8.96, 8.75, 8.56, 8.43 (1H × 4, s × 4, μ-CH_2 × 2), 5.07, 4.83 (5H × 2, s × 2, Cp_2), 4.11 (2H, q, J = 7.3 Hz, C*H*$_2$-CH_3), 3.27 (1H, d, J = 10.7 Hz, C*H*$_2$=CH), 1.30 (3H, t, J = 7.3 Hz, CH_3), 1.16 (1H, dd, J = 10.7, 7.8 Hz, CH_2=CH), 0.91 (1H, d, J = 7.8 Hz, C*H*$_2$=CH); δ_C ($CDCl_3$) 202.2, (s, CO), 177.8 (s, COO), 126.4 (t, J = 145 Hz, μ-CH_2), 123.5 (t, J = 147 Hz, μ-CH_2), 90.3 (d, J = 178 Hz, Cp), 88.6 (d, J = 176 Hz, Cp), 59.4 (t, J = 147 Hz, *C*H_2CH_3), 49.03 (d, J = 160 Hz, CH), 42.6 (t, J = 158 Hz, CH_2=), 14.7 (q, J = 127 Hz, CH_2*C*H_3); IR (CH_2Cl_2) ν(C≡O) 1937, 1712 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_3Ru_2$: C, 44.26; H, 4.50. Found: C, 43.71; H, 4.45.

Reaction of 2 with Diphenyldiazomethane. Ph_2CN_2 (0.75 mmol; dissolved in 0.15 mL of CH_2Cl_2) was added to a solution of **2** (63.2 mg, 0.15 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred for 30 min. After removal of the volatiles, the residue was subjected to preparative TLC separation (alumina, eluted with ether−hexane (1:15)). An orange band was collected, from which **14** (38.0 mg, 0.054 mmol, 34% yield) was obtained after recrystallization from hot methanol. The formation of methane (21% yield) was observed by GLC analysis. δ_H ($CDCl_3$) 7.94−6.53 (m, Ph), 4.35, 4.05 (5H × 2, s × 2, Cp_2), 2.66 (1H, dd, J = 5.8, 1.5 Hz, Ph); δ_C ($CDCl_3$) 253.6 (s, μ-*C*=CPh_2), 205.8 (s, CO), 99.6 (s, μ-*C*Ph_2), 91.5 (d, J = 178 Hz, Cp), 160−120 (Ph signals), 85.6 (d, J = 178 Hz, Cp), 72.9 (d, J = 168 Hz, Ph); IR (CH_2Cl_2) ν(C≡O) 1941 cm^{-1}. Anal. Calcd for $C_{38}H_{30}ORu_2$: C, 64.77; H, 4.26. Found: C, 65.23; H,4.47.

Formation of 3. ^{1}H NMR Experiment. A CD_3CN solution (0.6 mL) of **1** (10.0 mg, 0.024 mmol; a mixture of *cis* and *trans* isomers) was irradiated by a high-pressure mercury lamp. Within 30 min complete isomerization to the *cis* isomer was observed, and then **1** gradually converted to **2**. Further irradiation produced **3** as the sole product.

Reaction of 3 with CNCy. An acetonitrile solution of 80 mL) of **1** (43.2 mg, 0.104 mmol) was irradiated by a high-pressure mercury lamp for 30 h, while a slow Ar bubbling was maintained. After the completion of the decarbonylation was checked by IR, cyclohexyl isocyanide (130 μL, 1.05 mmol) was added and the resulting mixture was stirred for 3 h at room temperature. Removal of the volatiles and TLC separation (silica gel; hexanes−ether (6:1)) gave **15** (30.2 mg, 0.052 mmol, 50% yield) as a yellow powder: δ_H (C_6D_6) 8.54 (2H, s, μ-CH_2), 7.07 (2H, s, μ-CH_2), 4.99 (10H, s, Cp_2), 3.26 (2H, s, CNCH), 1.2−1.4 (12H, m, Cy), 1.2−1.0 (8H, m, Cy); δ_C (C_6D_6) 176.3 (s, NC), 107.3 (dd, J = 147 and 136 Hz, μ-CH_2), 85.9 (d, 175 Hz, Cp), 54.4 (d, J = 142 Hz, CN*C*H), 34.7 (t, J = 129 Hz, Cy), 25.6 (t, J = 127 Hz, Cy), 23.3 (t, J = 127 Hz, Cy); IR (CH_2Cl_2) ν(NC) 2082, 2060 cm^{-1}. Anal. Calcd for $C_{26}H_{36}N_2Ru_2$: C, 53.96; H, 6.27; N, 4.84. Found: C, 53.64; H, 6.20; N, 4.86.

Treatment of an MeCN solution with CO gave Cp_2Ru_2(μ-CH_2)$_2$(CO)$_2$.

Reaction of 3 with Cyclopentadiene. An MeCN solution of **3** was prepared from **1** (50.0 mg, 0.120 mmol) as described above. Addition of cyclopentadiene (1 mL) followed by workup as described above gave **16** (20.5 mg, 0.048 mmol, 40% yield) as yellow crystals: δ_H (C_6D_6) 8.77 (1H, d, J = 2.4 Hz, μ-CH_2), 8.46 (1H, d, J = 1.2 Hz, μ-CH_2), 8.30 (1H, d, J = 2.4 Hz, μ-CH_2), 7.40 (1H, d, J = 1.2 Hz, μ-CH_2), 4.53 (10H, s, Cp_2), 3.71 (2H, d, J = 5.4 Hz, C=CH), 2.65 (2H, dd, J = 5.4 and 3.1 Hz, CH_2C*H*=), 2.50 (1H, d, J = 16.4 Hz, CH_2), 1.63 (1H, dt, J = 16.4 and 3.1 Hz, CH_2); δ_C (C_6D_6) 144.0 (t, J = 142 Hz, μ-CH_2), 122.8 (dd, J = 154 and 136 Hz, μ-CH_2), 85.8 (d, J = 177 Hz, Cp), 55.5 (d, J = 167 Hz, CH_2CH=*C*H), 47.1 (d, J = 160 Hz,

CH_2*C*H═CH), 27.7 (t, *J* = 132 Hz, CH_2). Anal. Calcd for $C_{15}H_{20}ORu_2$: C, 47.88; H, 4.73. Found: C, 47.78; H, 4.69.

Reaction of 3 with Butadiene. An MeCN solution of **3** was prepared from **1** (55.3 mg, 0.133 mmol) as described above. 1,3-Butadiene was introduced into the system from a balloon. Subsequent workup as described above gave an isomeric mixture of **17** (19.3 mg, 0.046 mmol, 35% yield) as yellow crystals. *s-cis* isomer: δ_H (C_6D_6) 8.92, 8.66, 8.65, 6.96 (1H × 4, s × 4, μ-CH_2), 4.51 (10H, s, Cp_2), 3.56 (2H, m, CH═), 1.87 (2H, d, *J* = 8.3 Hz, ═CH_2), 1.55 (2H, d, *J* = 9.7 Hz, ═CH_2); δ_C (C_6D_6) 132.4 (t, *J* = 141 Hz, μ-CH_2), 117.1 (dd, *J* = 156 and 136 Hz, μ-CH_2), 85.1 (d, *J* = 176 Hz, Cp), 56.8 (d, *J* = 160 Hz, ═CH), 37.5 (t, *J* = 158 Hz, ═CH_2). *s-trans* isomer: δ_H (C_6D_6) 8.64, 6.77 (2H × 2, s × 2, μ-CH_2), 4.51 (10H, s, Cp_2), 2.92 (2H, m, ═CH), 2.38 (2H, d, *J* = 9.8 Hz, ═CH_2), 2.32 (2H, d, *J* = 5.6 Hz, ═CH_2); δ_C (C_6D_6) 126.4 (dd, *J* = 145 and 136 Hz, μ-CH_2), 84.7 (d, *J* = 176 Hz, Cp), 63.0 (d, *J* = 158 Hz, ═CH), 46.3 (t, *J* = 154 Hz, ═CH_2). Anal. Calcd for $C_{16}H_{20}ORu_2$: C, 46.37, H, 4.86. Found: C, 46.14; H,4.45.

X-ray Crystallography. Suitable single crystals were obtained from recrystallization from the solvent described in Table 8 and mounted on glass fibers.

Diffraction measurement was made on Rigaku AFC-5R (**2**, **9**−**11**, **14**) and AFC-5S (**12a**) automated four-circle diffractometers by using graphite-monochromated Mo Kα radiation (λ = 0.710 59 Å). The unit cells were determined and refined by a least-squares method using 20 independent reflections ($2\theta \approx 20°$). Data were collected by $\omega-2\theta$ or ω scan techniques. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored every 150 measurements. The data processing was performed on a Micro Vax II computer (data collection) and IRIS Indigo and Indy computers (structure analysis) by using the teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.[23] In the reduction of data, Lorentz and polarization corrections were made. An empirical absorption correction (Ψ scan) was also made. Crystallographic data and the results of refinements are summarized in Table 8.

The structures were solved by a combination of direct methods (SAPI91 and MITHRIL87) and Fourier synthesis (DIRDIF). Unless otherwise stated, non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were fixed at calculated positions (C−H = 0.95 Å) and were not refined. Details of the structural analyses are as follows. **2**: the methylene hydrogen atoms (H1a,b and H2a,b) were refined isotropically. **9**: a unit cell contained two independent molecules, and one of them (molecule 2: b series) sits on a symmetrically imposed site. The non-hydrogen atoms of molecule 1 (a series) was refined with anisotropic thermal parameters. As for molecule 2, Sn1b, Ru1b, and Ru2b were refined anisotropically, O3b and C1−3b were refined isotropically, and the carbon atoms of the Cp and Ph parts were refined using rigid-group models. **10**: because of the limited number of the data, the Ph groups and the hexane molecule were refined isotropically. **11**: a unit cell contained two independent molecules. During the course of the refinement it was found that the μ_3 ligands were disordered. As for molecule 1, the minor component was not included in the refinement. As for molecule 2, the μ_3-CH and μ_3-CO ligands were considerably disordered and the occupancies of the oxygen atoms were refined as follows: O22, 0.757; O23, 0.724; O24, 0.519. **14**: All the hydrogen atoms were refined isotropically.

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Supporting Information Available: Tables of positional parameters and B_{eq} values, anisotropic thermal parameters, and bond lengths and angles and figures giving atomic numbering schemes for **9b** (molecule 2), the carbon atoms of the Ph and Cp groups and the hexane part of **10**·($^1/_2$hexane), (molecule 2), and the solvent parts of **11**·$^1/_4$(CH_2Cl_2)·$^1/_4$(H_2O), and **12a** (molecule 2) (48 pages). Ordering information is given on any current masthead page.

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(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.