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Deoxygenative Reduction of Diruthenium Carbonyl Complexes (η^5-$C_5H_4R)_2Ru_2(\mu$-$CO)_2(CO)_2$ with Hydrosilanes Leading to Bridging Methylene Complexes (η^5-$C_5H_4R)_2Ru_2(\mu$-$CH_2)_n(\mu$-$CO)_{2-n}(CO)_2$ (n = 1, 2; R = H, CH_3)

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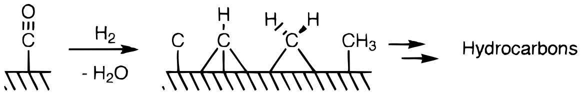
Reaction of diruthenium carbonyl complexes (η^5-$C_5H_4R)_2Ru_2(\mu$-$CO)_2(CO)_2$ (**1**) with di- or trihydrosilane $H_nSiR'_{4-n}$ (n = 2, 3) at 150 °C results in sequential formation of the mono-(η^5-$C_5H_4R)_2Ru_2(\mu$-$CH_2)(\mu$-$CO)(CO)_2$ (**2**) and di-μ-methylene complexes (η^5-$C_5H_4R)_2Ru_2(\mu$-$CH_2)_2$-$(CO)_2$ (**3**). Labeling experiments confirm that the C and H atoms in the resulting μ-CH_2 moieties come from CO attached to Ru and $\mathit{H}_nSiR'_{4-n}$, respectively, and that neither intermolecular CH_2 transfer nor H transfer between bridging ligands is involved in the present methylenation. The reduction mechanism of bridging carbonyl ligands has been assumed to be deoxygenative hydrosilation (a direct thermal reaction or a catalytic reaction effected by a ruthenium species present in a reaction mixture). Thus, the present system serves as a model system for formation of a bridging methylene species following Fischer−Tropsch mechanism. The molecular structures of the *cis*- and *trans*-isomers of **3a** (R = H) have been determined by X-ray crystallography.

Introduction

Transition metal bridging methylene (alkylidene) complexes[1] have been studied extensively as model compounds for a surface-bound methylene species, which is postulated as a crucial intermediate for catalytic conversions of carbon monoxide and hydrocarbons (Scheme 1).[2,3] Typical preparative methods involve transfer of a methylene unit from a diazoalkane or alkylidene phosphorane to a labile metal center,[4] metalation of a *gem*-dihaloalkane,[5] and functionalization of a hydrocarbyl ligand such as alkyl, alkylidyne, and alkenyl species.[6] However, transformation of CO into a bridging methylene group on a polymetallic system is rather limited,[7] though such a process is closely related to the reaction mechanism of catalytic CO hydrogenation.

Scheme 1



Our research interest has been focused on reduction of hydrocarbyl groups and *O*-containing functional groups attached to a transition metal center by employing hydrosilanes ($HSiR'_3$) as the equivalent of H_2.[8] It has been established that the reactivity of the H−Si bond is quite similar to that of the H−H bond as typically exemplified by oxidative addition to a low-valent metal center and catalyzed addition reactions to unsaturated organic compounds (hydrogenation vs hydrosilation).[9] In addition, the Si part exhibits high affinity toward the oxygen atom in a functional group. These advantageous features of hydrosilane lead to

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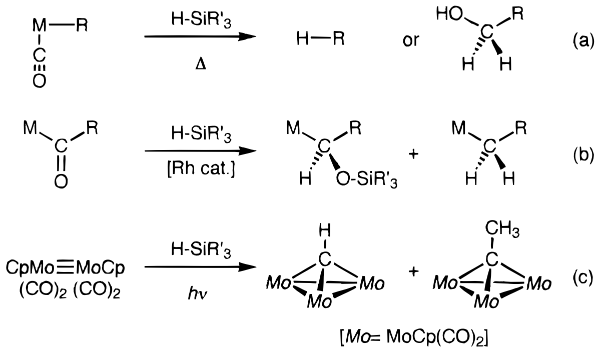
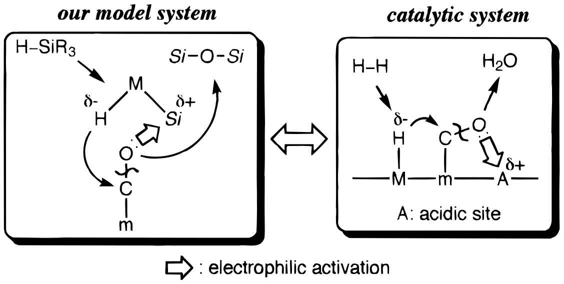
Scheme 2



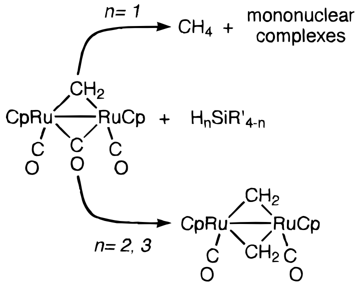
Scheme 3



successful reduction of the $CpFe(CO)_2-R$ type alkyliron complexes releasing alkane and/or alcohol (Scheme 2a)[8b,d] and deoxygenative reduction of acyl metal complexes $M-C(=O)-R$ giving the alkyl complex $M-CH_2-R$ (Scheme 2b).[8a,c] Combined with carbonylation, the latter system serves as a model reaction for the carbon-chain propagation step of the Pichler−Schulz mechanism. Recently, we also reported deoxygenative reduction of dimolybdenum carbonyl complexes leading to trinuclear μ_3-alkylidyne complexes (Scheme 2c).[8g,i] Thus the silyl moiety in a $M(H)(SiR'_3)$ species, resulting from oxidative addition of $HSiR'_3$, is expected to activate an *O*-containing functional group just like an acidic site on a catalyst surface so as to promote subsequent hydride transfer (Scheme 3).

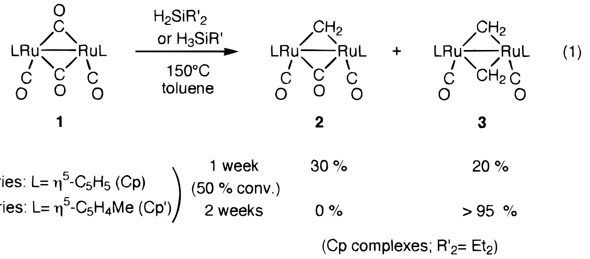
As an extension, we have studied reduction of hydrocarbyl species bridging two metal centers, and it has been found that reaction of a diruthenium bridging methylene complex $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2$ depends on the structure of the hydrosilane used. Treatment with monohydrosilane resulted in the formation of methane through reduction of μ-CH_2,[8f] whereas reaction with di- or trihydrosilane resulted in methylenation of the bridging CO ligand (Scheme 4).[10] We also found that a simple diruthenium carbonyl complex $Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2$ is susceptible to the methylenation. Herein we disclose details of the methylenation of bridging carbonyl ligands in diruthenium complexes $(\eta^5\text{-}C_5H_4R)_2Ru_2(\mu\text{-}CO)_2(CO)_2$ and $(\eta^5\text{-}C_5H_4R)_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2$ by the action of hydrosilanes.[10]

Scheme 4

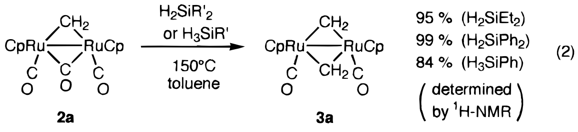


Results and Discussion

Thermolysis of a toluene solution of the simple diruthenium carbonyl complex $Cp_2Ru_2(\mu\text{-}CO)_2(CO)_2$ (**1a**) (Cp: η^5-C_5H_4R where R = H) at 150 °C in the presence of di- or trihydrosilane ($H_nSiR'_{4-n}$: $n = 2, 3$) produced a mixture of the mono- [$Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2$ (**2a**)] and di-μ-methylene complexes [$Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)_2$ (**3a**)] (eq 1). The reaction was very slow. After 1 week, only half of **1a** was converted to a 2:3 mixture of **2a** and **3a**, and it took 2 weeks for complete conversion of **1a** into **3a** (NMR experiments). However, the methylenation of an isolated sample of **2a** was complete within 2 days in an almost quantitative yield (eq 2). Therefore it was concluded that (i) **1a** was converted to **3a** in a stepwise manner (**1a** → **2a** → **3a**) and (ii) the initial methylenation was slower than the second step. The pseudo-first-order rate constants for the two consecutive steps at 150 °C were determined to be 6.7×10^{-3} h^{-1} (**1a** → **2a**) and 3.2×10^{-2} h^{-1} (**2a** → **3a**). In sharp contrast to the reaction with di- and trihydrosilanes leading to the methylenation, reaction of **1a** with monohydrosilane resulted in Ru−Ru bond cleavage to produce methane along with a mixture containing $CpRu(H)(SiR'_3)_2(CO)$ and $CpRu(CO)_2-SiR'_3$ (Scheme 4)[8f,j] and no trace of the μ-methylene complex **2a** was detected at all. As for the derivative of **1a**, the η^5-C_5H_4-Me (Cp′) complex **1b** (R = CH_3) was converted successfully to **2b** and **3b** in a manner similar to that for the Cp complexes (eq 1), whereas reaction of $(\eta^5\text{-}C_5Me_5)_2Ru_2(\mu\text{-}CO)_2(CO)_2$ with H_2SiEt_2 resulted in Ru−Ru bond cleavage to give $(\eta^5\text{-}C_5Me_5)Ru(CO)_2-SiHEt_2$.[11] Treatment of the μ-ethylidene complex $Cp_2Ru_2(\mu\text{-}CHMe)(\mu\text{-}$



(1)



(2)

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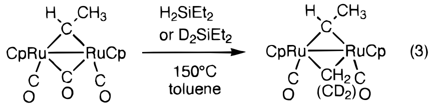
CO)(CO)$_2$ (**4**) with H_2SiEt_2 produced a mixed di-μ-alkylidene complex $Cp_2Ru_2(\mu\text{-CHMe})(\mu\text{-CH}_2)(CO)_2$ (**5**) (eq 3). By contrast, the reaction of the μ-vinylidene complex $Cp_2Ru_2(\mu\text{-C=CH}_2)(\mu\text{-CO})(CO)_2$[6d] afforded a complicated mixture of products arising from reduction of the μ-C=CH$_2$ moiety as judged by the disappearance of the μ-C=CH_2 signal.



4 **5** (3)

An SiHEt$_2$ signal (δ_H 4.85 in C_6D_6) was detected in addition to excess H_2SiEt_2 (δ_H 3.80) by ^{1}H-NMR monitoring of the reaction (eq 1). Combined with the EI GC–MS data (*m/e* 161 [O(SiHEt$_2$)$_2$ − Et]), the signal has been assigned to the siloxane $O(SiHEt_2)_2$ formed by deoxygenation.

The chemistry of diruthenium μ-alkylidene complexes has been studied extensively by Knox and co-workers, who reported the first synthesis of the mono-μ-methylene complex **2a** via methylene transfer from $CH_2=PPh_3$ to a labile diruthenium complex $Cp_2Ru_2[\mu\text{-C(=O)C}_2Ph_2](\mu\text{-CO})(CO)$.[4c] Later a convenient preparative method (**1** + $LiHBEt_3$) was developed by Bercaw et al.[7c] Knox et al. also reported the synthesis of a few examples of di-μ-alkylidene complexes such as $Cp_2Ru_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(CO)_2$,[14] but the parent complexes **3a**,**b** were first prepared in the present study. The nature of the new di-μ-methylene complex **3** is readily determined on the basis of (i) the characteristic deshielded ^{1}H- and ^{13}C-NMR signals of the CH$_2$ parts[1] similar to those of **2a** (see Experimental Section) and (ii) disappearance of signals assignable to bridging CO ligands (IR and ^{13}C-NMR). The methylene complexes **2** and **3** exist as a mixture of *cis*- and *trans*-isomers. Although isomerization of **2a** in solution is observed even at room temperature,[4c] **3a** is sufficiently rigid to be separated by TLC. Thermal isomerization of **3a** requires heating in tol-d_8 for 7 h above 200 °C.[12] The equilibrium ratio is ca. 1:1 (*cis*:*trans*). Both of the isomers have been further characterized by X-ray crystallography. The molecular structures of the *cis*- and *trans*-isomers have a crystallographic mirror plane and inversion center, respectively (Figures 1 and 2). Crystallographic data and selected structural parameters are listed in Tables 1 and 2. The structures differ only by the orientation of the CpRu(CO) units and are similar to those of the previously reported analogues as compared with *cis*-$Cp_2Ru_2(\mu\text{-CH}_2)(\mu\text{-CO})(CO)_2$ (**6**)[4c] and *trans*-$Cp_2Ru_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(CO)_2$ (**7**)[14] (Table 2).

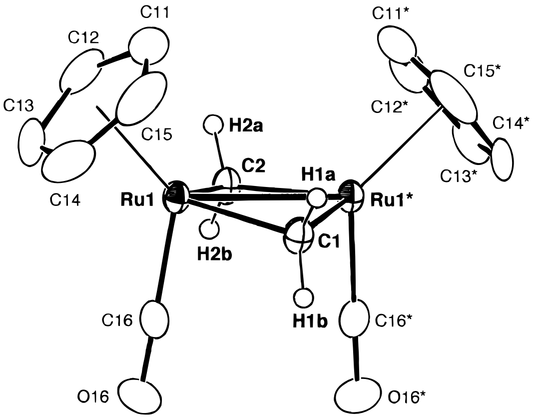


Figure 1. Molecular structure of *cis*-**3a** drawn at the 30% probability level.

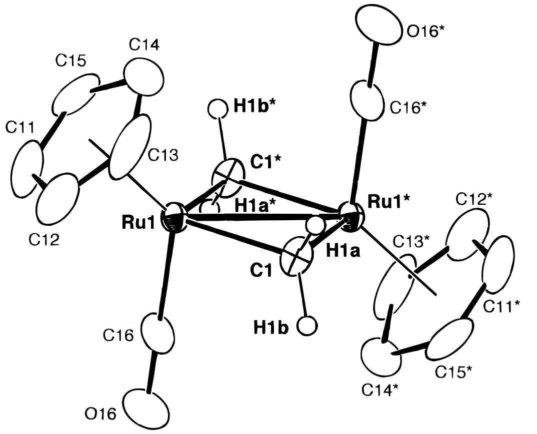


Figure 2. Molecular structure of *trans*-**3a** drawn at the 30% probability level.

Table 1. Crystallographic Data for *cis*-3a and *trans*-3a

complex	*cis*-**3a**	*trans*-**3a**
formula	$C_{14}H_{14}O_2Ru_2$	$C_{14}H_{14}O_2Ru_2$
fw	416.4	416.4
space group	*Pnma*	*P*2$_1$/*n*
a/Å	12.692(3)	7.5591(9)
b/Å	16.868(6)	7.6236(7)
c/Å	6.245(2)	11.601(2)
β/deg		94.82(1)
V/Å^3	1336.9(7)	666.2(1)
Z	4	2
d_{calcd}/g·cm^{-3}	2.07	2.08
μ/cm^{-1}	22.1	22.6
2θ/deg	5–50	5–50
no. of data collcd	1405	1367
no. of data with $I > 3\sigma(I)$	1030	871
no. of params refined	97	90
R	0.022	0.039
R_w	0.021	0.045

In order to gain insight into the reaction mechanism additional experiments were carried out. At first, the source of the CH$_2$ moieties was investigated by labeling experiments. Reduction of **1a**-^{13}C with D_2SiEt_2 afforded **2a**-d_2,^{13}C and **3a**-d_4,^{13}C containing the deuterated *CD$_2$

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(11) (η^5-C$_5$Me$_5$)Ru(CO)$_2$–SiHEt$_2$ (colorless solid): δ_H (C_6D_6) 4.29 (1H, m, SiH), 1.60 (15H, s, η^5-C$_5$Me$_5$), 1.36–1.11 (10H, m, Et$_2$); δ_C 204.5 (s, CO), 99.0 (s, η^5-C_5Me$_5$), 11.2 (t, $J = 124$ Hz, CH_2CH_3), 9.9 (q, $J = 128$ Hz, η^5-C$_5$$Me_5$), 9.6 (q, $J. = 124$ Hz, CH$_2$$CH_3$); IR (CH$_2Cl_2$) ν(C≡O) 1991, 1931 cm^{-1}.

(12) Cotton and Knox reported *cis*–*trans* isomerization of $Cp_2Ru_2(\mu\text{-X})(\mu\text{-Y})(CO)_2$-type compounds as follows: X = Y = CO (**1a**),[13a] the Cp signals did not decoalesce at −100 °C ($\Delta G^\ddagger < 40$ kJ/mol). X = CMe$_2$, Y = CO,[13b] the Cp signals coalesced at 100 °C ($\Delta G^\ddagger \sim 85$ kJ/mol). X = CH$_2$, Y = CO (**2a**),[4c] the Cp signals did not coalesce at 150 °C, but the isomers interconverted in solution at rt. X = CMe$_2$, Y = CHMe (**7**),[14] The interconversion was not observed at 150 °C. Attempted determination of the activation parameters of **3a** was unsuccessful, because the isomerization at 150 °C was too slow to be measured and **3a** decomposed gradually at 200 °C before reaching the equilibrium. Thus we could not make a quantitative comparison of the activation parameters. However, it is evident that, as the number of the bridging alkylidene ligands increases, the *cis*–*trans* isomerization becomes a higher energy process.

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Table 2. Selected Structural Parameters for $Cp_2Ru_2(\mu\text{-}X)(\mu\text{-}Y)(CO)_2$[a]

	compound [(μ-X)(μ-Y)]			
	cis-**3a** [(μ-CH_2)(μ-CH_2)]	*trans*-**3a** [(μ-CH_2)(μ-CH_2)]	*cis*-**6** [(μ-CH_2)(μ-CO)][b]	*trans*-**7** [(μ-CHMe)(μ-CMe_2)][c]
		Bond Lengths		
Ru1−Ru1*	2.6813(6)	2.682(2)	2.707(1)	2.701(1)
Ru1−C1	2.074(5)	2.07(1)	2.077(6), 2.079(5)	2.073(3), 2.086(3)[d]
Ru1−C2	2.072(4)	2.071(1)[e]	2.019(4), 2.035(6)[f]	2.106(3), 2.108(3)[g]
Ru1−C11−15	2.229−2.297(5)	2.23−2.29(1)	2.219−2.290(6)	2.293[h]
Ru1−C16	1.823(4)	1.80(1)	1.852(6), 1.844(7)	1.835(3), 1.827(3)
C−C (Cp)	1.348−1.435(8)	1.32−1.43(2)	1.36−1.42(1)	1.370−1.444(6)
C16−O16	1.146(4)	1.18(1)	1.156(8), 1.153(9)	1.158(4), 1.158(3)
C1−H1A	0.96(5)	1.0(1)	1.02(6)	0.94(3)[d]
C1−H1B	0.92(5)	0.9(1)	0.84(7)	1.514(4)[d,i]
C2−H2A	1.04(5)			1.521(4)[g,i]
C2−H2B	0.97(5)			1.526(3)[g,i]
		Bond Angles		
Ru1*−Ru1−C1	49.7(1)	49.7(3)	49.3(2)	49.3(1)
Ru1*−Ru1−C2	49.7(1)	49.7(3)[j]	49.4(1)	50.1(1)
Ru1*−Ru1−C16	96.2(1)	91.1(4)	98.7(2), 96.5(2)	91.5(1)
C1−Ru1−C2	98.3(2)	99.2(4)[k]	97.8(2), 97.2(3)	*l*
C1−Ru1−C16	88.1(2)	90.4(5)	89.1(3), 85.0(2)	*l*
C2−Ru1−C16	88.7(2)	91.0(5)[m]	87.6(2), 88.9(3)[f]	*l*
Ru1−C1−Ru1*	80.5(2)	80.8(4)	81.3(2)	81.0(1)
Ru1−C2−Ru1*	80.7(2)		82.8(3)[f]	79.7(1)
Ru1−C16−O16	179.0(4)	179(1)	177.6(6), 178.6(4)	175.6(3), 175.7(3)

[a] Bond lengths in Å and bond angles in deg. [b] Reference 4c. [c] Reference 14. [d] Parameters for the μ-CHMe ligand. [e] Ru1−C1*. [f] Parameters for the μ-CO ligand. [g] Parameters for the μ-CMe_2 ligand. [h] Averaged value. [i] C−Me lengths. [j] Ru1−Ru1*−C1*. [k] C1−Ru1−C1*. [l] Not reported. [m] C1*−Ru1−C16.

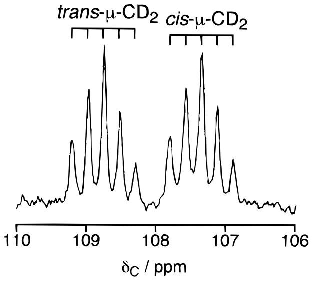
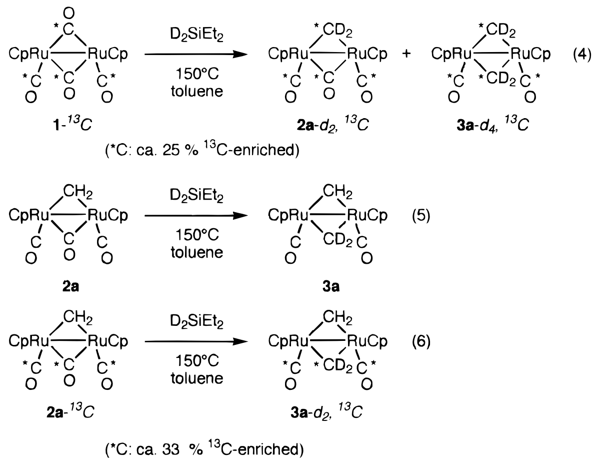
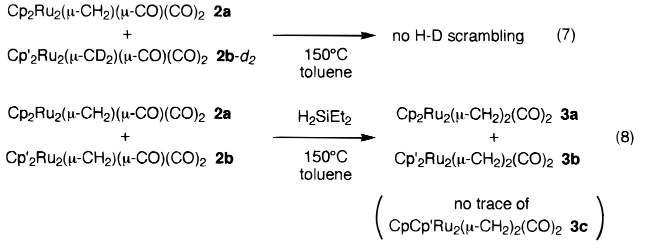


Figure 3. μ-*CD_2 signals (^{13}C-NMR) of *cis*- and *trans*-$Cp_2Ru_2(\mu\text{-}{*}CD_2)_2(CO)_2$ (**3a**-d_4,^{13}C) (observed in tol-d_8 at 100 MHz).

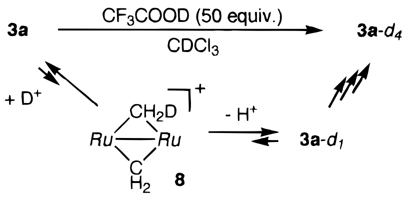
ligands (*C: ca. 25% ^{13}C-enriched) (eq 4). The μ-*CD_2 signals of **3a**-d_4,^{13}C is reproduced in Figure 3, which clearly indicates that two deuterium nuclei are bonded to the bridging carbon atom. The extent of deuteration was more than 95% as estimated by ^1H-NMR. D_2SiEt_2 reduction of **2a** afforded **3a**-d_2 as confirmed by analysis of distribution of the isotopomers (FD−MS) and the μ-CH_2:Cp_2 intensity ratio (2:10; ^1H-NMR) (eq 5). Treatment of **2a**-^{13}C (only the CO ligands were ca. 30% ^{13}C-enriched) with D_2SiEt_2 produced the (μ-CH_2)(μ-*CD_2) compound (**3a**-d_2,^{13}C) as the unique isotopomer as revealed by the absence of $^1J_{C-H}$ coupling of the *CD_2 signal (^{13}C-NMR: a spectrum similar to Figure 3 was obtained) and the ^1H-NMR coupling pattern of the CH_2 signals (*cis*-isomer, two doublets; *trans*-isomer, a singlet) (eq 6). The latter labeling experiment gave no trace of the μ-CHD and μ-*CHD isotopomers, suggesting the absence of intramolecular H transfer between the bridging ligands. Intermolecular processes such as CH_2 transfer and Ru−Ru bond cleavage are also eliminated on the basis of eq 6 as well as the scrambling experiments using the η^5-C_5H_4Me (Cp′) derivative where neither a μ-CHD complex resulting from H−D exchange (eq 7) nor crossover product $CpCp'Ru_2(\mu\text{-}CH_2)_2(CO)_2$ **3c** (eq 8) was detected. In accord with these results, reduction of the μ-ethylidene complex **4** with D_2SiEt_2 produced the (μ-$CHCH_3$)(μ-CD_2) complex **5**-d_2 in a specific manner (eq 3).



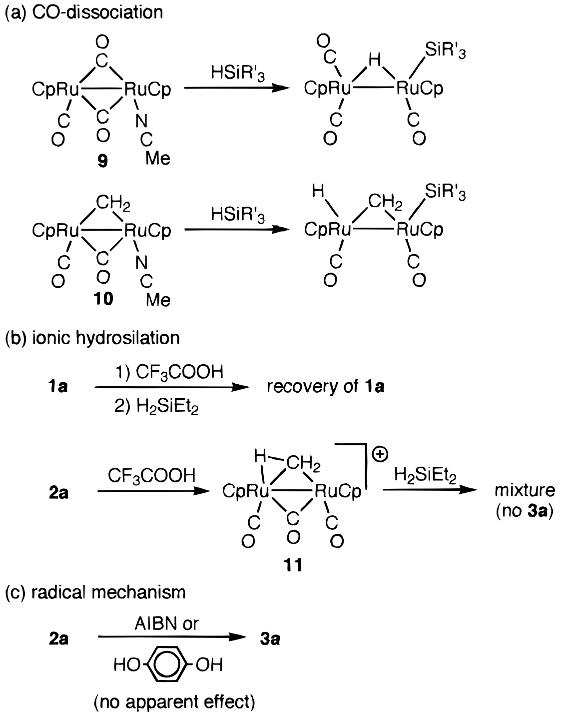


It is notable that H−D exchange of **3a** was observed during separation process. The labeling experiment using D_2SiEt_2 afforded **3a**-d_2 of high D content (>95%, eqs 4−6) as mentioned above. However, isolation of the product by preparative TLC (alumina) lowered the D content to ca. 50%. Therefore in the above-mentioned experiments the D content was determined on the reaction mixture or on a sample isolated by recrystallization. The H impurity may be incorporated by acid (alumina)-catalyzed protonation−deprotonation equilibrium by way of a cationic μ-CH_3 intermediate (**8**; see also **11** in Scheme 6). In fact, treatment of **3a** with CF_3COOD (1 equiv) at rt (room temperature) afforded an

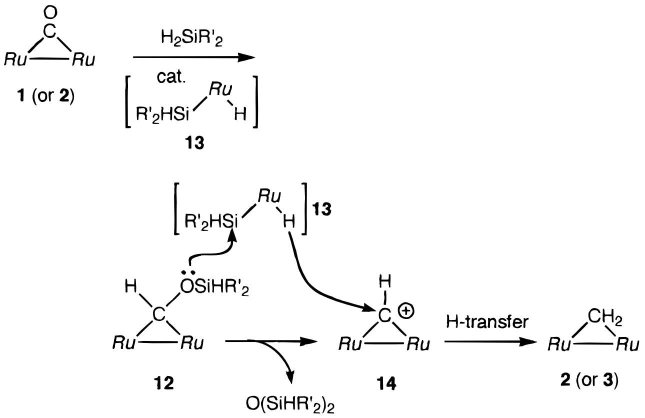
Scheme 5



Scheme 6

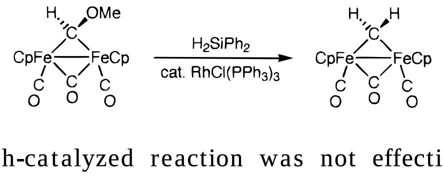


Scheme 7



equilibrated mixture of the deuterated isotopomers instantaneously, and addition of 50 equiv of the acid at rt caused disappearance of the μ-CH_2 signals (Scheme 5). But the protonated form of **3a** (with CF_3COOH and CF_3SO_3H) could not be detected by IR and ^1H-NMR.

The results of the above-mentioned labeling experiments clearly indicate that (i) the carbon and hydrogen atoms of the μ-CH_2 moieties come from CO and $H_2SiR'_2$, respectively, and (ii) the methylenation proceeds via stepwise reactions without H transfer between the bridging ligands. However, because the reaction is very clean and neither intermediates nor byproducts can be detected by NMR experiments, a clue to the reaction mechanism has not been obtained. A couple of possible mechanisms have been investigated as described below (Scheme 6). Many reactions of metal carbonyls are initiated by generation of a coordinatively unsaturated species via CO dissociation. Treatment of the labile MeCN adducts of coordinatively unsaturated species arising from decarbonylation, $Cp_2Ru_2(\mu\text{-}CO)_2(CO)(MeCN)$ (**9**)[15] and $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(MeCN)$ (**10**),[16] with hydrosilanes at ambient temperature resulted in oxidative addition of the H−Si bond to give hydridosilyl intermediates[17] instead of the μ-methylene complexes (Scheme 6a). Ionic hydrosilation, which has been applied to reduction of organic carbonyl compounds, was also examined (Scheme 6b).[18] Protonation of the mono-(μ-methylene) complex **2a** with CF_3COOH produced the μ-methyl intermediate $[Cp_2Ru_2(\mu\text{-}CH_3)(\mu\text{-}CO)(CO)]^+CF_3COO^-$ (**11**) as reported by Knox et al.[19] The cationic species reacted with H_2SiEt_2 with vigorous gas evolution, but an intractable mixture of products was obtained, which did not contain **3a**. Successive treatment of **1a** with CF_3COOH and H_2SiEt_2 resulted in recovery of **1a**. A radical mechanism is also excluded, because addition of the radical initator (AIBN) and the inhibitor (hydroquinone) did not cause any apparent effect on the yields and reaction rates (Scheme 6c). These control experiments do not provide us with any positive evidence for the reaction mechanism. One of the possible mechanisms is direct, thermal reduction of the bridging carbonyl group with $H_2SiR'_2$. Another plausible one is a deoxygenative hydrosilation catalyzed by an unknown ruthenium species arising from decomposition of **1** and **2** (Scheme 7). The bridging carbonyl moiety in **1** and **2** which can be viewed as a *dimetallaketone* may be susceptible to catalytic hydrosilation to give a μ-siloxymethylene intermediate **12** (cf. Scheme 2b).[8a,c] Subsequent electrophilic attack of a silyl−metal intermediate **13** at the siloxy group in **12** leads to the cationic methylidyne species **14** with elimination of siloxane. Final hydride transfer from **13** to **14** furnishes the μ-methylene complexes. The second step (**12** → **2**) is supported by our previous observation that the Rh-catalyzed hydrosilation of the methoxy−iron analogue of **12**, $Cp_2Fe_2(\mu\text{-}CHOMe)(\mu\text{-}CO)(CO)_2$, produced the μ-methylene complex, $Cp_2Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2$, with elimination of methoxysilane ($MeOSiHEt_2$) (eq 9),[8c] though the Rh-catalyzed reaction was not effective for the methylenation of **1** and **2**. The viability of **14** is also supported by the isolation of the phosphine-substituted derivative $[Cp_2Ru_2(\mu\text{-}CH)(\mu\text{-}CO)(dppm)]^{+}$ [19a] and the iron analogue $[Cp_2Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2]^+$.[5b,e]



(9)

In summary, deoxygenative reduction of dinuclear carbonyl complexes **1** and **2** induced by the action of

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[15] Complex **9** briefly mentioned in ref 6d was prepared in a manner analogous to the synthesis of **10** (irradiation of **1** in CH_3CN). **9**: δ_H (C_6D_6) 4.73, 4.30 (5H × 2, s × 2, Cp_2), 0.62 (3H, s, MeCN); IR (CH_2Cl_2) ν(C=O) 1936, 1737 cm^{-1}.

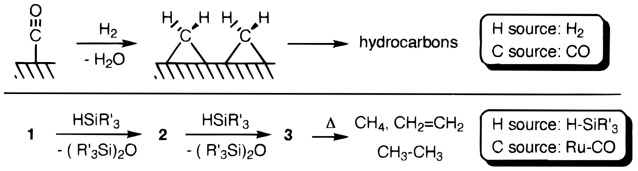
[16] Doherty, N. M.; Howard, J. A. K.; Knox, S. A. R.; Terril, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 638.

[17] (a) Reaction of **9**: unpublished results. (b) Reaction of **10**: see ref 8f,j.

[18] (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 21. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983; Chapter 17.

[19] (a) Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 841. Fe analogues: (b) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41.

Scheme 8



hydrosilane furnishes bridging methylene complexes **2** and **3**, respectively, where the C and H atoms come from CO attached to Ru and HSiR′3 used as the H_2 equivalent. Thermolysis of **3a** produces a low-yield mixture of methane, ethylene, and ethane[8e] in a manner similar to that for the di-μ-alkylidene complex, $Cp_2Ru_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(CO)_2$.[6d] Thus the present system serve as a good model system for production of ethylene via the Fischer−Tropsch mechanism (Scheme 8).[2]

Experimental Section

General Methods. All manipulations were carried out under an inert atmosphere by using standard Schlenk tube techniques. Ether, hexanes, and toluene (Na−K alloy), and CH_2Cl_2 and CH_3CN (P_2O_5) were treated with appropriate drying agents, distilled, and stored under argon. Complexes **1**,[20] **2**,[7c] **4**,[6d] **9**,[15] and **10**[16] were prepared according to the literature procedures. The ^{13}CO-labeled compounds **1a**-^{13}C and **2a**-^{13}C were obtained by carbonylation [^{13}CO (1−2 atm); >90% ^{13}C-enriched] of the corresponding MeCN complexes, **9** and **10**, in benzene at room temperature, respectively. The μ-CD_2 complex **2a**-d_2 was prepared by reaction between **1a** and $LiDBEt_3$.[7c] Hydrosilanes were prepared by reduction of corresponding chlorosilane with $LiAlH_4$, and deuteriosilane D_2SiEt_2 was prepared by treatment of Cl_2SiEt_2 with $LiAlD_4$. 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)]. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL EX-90 (^{1}H, 90 MHz), GX-270 (^{1}H, 270 MHz; ^{13}C, 67 MHz), EX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), and GX-500 spectrometers (^{1}H, 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 mass spectrometer, respectively.

Deoxygenative Reduction of the Ruthenium Carbonyl Complexes. (i) Conversion of the Carbonyl Complex 1 into Di-μ-methylene Complex 3. A toluene solution (4 mL) of **1a** (200 mg, 0.465 mmol) and H_2SiEt_2 (0.26 mL, 1.90 mmol) was heated at 150 °C in a glass autoclave. After consumption of **1a** was checked by TLC (~2 weeks),[11] the content was passed through an alumina plug. Then the volatiles were removed under reduced pressure and the residue was recrystallized from CH_2Cl_2−hexanes. The pale yellow di-μ-methylene complex **3a** (98 mg, 0.236 mmol, 51% isolated yield) was obtained as a mixture of *cis*- and *trans*-isomers, which were further separated by a preparative TLC plate. **3a** (*cis*-isomer): ^{1}H-NMR (C_6D_6) δ_H 8.08, 7.41 (1H × 2, d × 2, $J = 0.4$ Hz, μ-CH_2), 4.61 (10H, s, Cp_2); ^{13}C-NMR ($CDCl_3$) δ_C 202.0 (CO), 108.0 (dd, $J = 140$, 142 Hz, μ-CH_2), 88.0 (d, $J = 176$ Hz, Cp); IR (CH_2Cl_2) ν(C≡O) 1963 cm^{-1}. **3a** (*trans*-isomer) ^{1}H-NMR (C_6D_6) δ_H 8.03 (2H, s, μ-CH_2), 4.87 (10H, s, Cp_2); ^{13}C-NMR ($CDCl_3$) δ_C 201.8 (CO), 109.3 (t, $J = 148$ Hz, μ-CH_2), 90.1 (d, $J = 177$ Hz, Cp); IR (CH_2Cl_2) ν(C≡O) 1920 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2Ru_2$: C, 40.38; H, 3.39. Found (an isomeric mixture): C, 40.43; H, 3.35. Starting from **2a**, **3a** was isolated in more than 90% yield. The Cp′ complex **3b** was prepared in essentially the same method starting from **1b**. **3b** (pale yellow crystals; isomers were not separated): ^{1}H-NMR (tol-d_8) δ_H 8.41 (1H, s, *cis*-μ-CH_2), 8.26 (2H, s, *trans*-μ-CH_2), 8.41 (1H, s, *cis*-μ-CH_2), 4.93, 4.88, 4.74, 4.59, 4.29 (m, η^5-C_5H_4Me), 1.70, 1.75 (3H, s × 2, η^5-C_5H_4Me); ^{13}C-NMR (tol-d_8) δ_C 200.7, 200.6 (CO), 116.8 (t, $J = 141$ Hz, *trans*-μ-CH_2), 115.8 (dd, $J = 147$, 153 Hz, *cis*-μ-CH_2), 108.1, 111.2 (s, η^5-C_5H_4Me), 89.4, 89.1, 88.6, 88.5, 87.3, 86.9, 86.5 (d, η^5-C_5H_4Me), 13.0, 12.8 (q × 2, $J = 128$ Hz, η^5-C_5H_4Me); IR (CH_2Cl_2) ν(C≡O) 1965, 1920 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2Ru_2$: C, 43.24; H, 4.08. Found: C, 43.52; H, 4.13.

Labeling experiments were carried out by using the appropriate isotopomers.

NMR experiments were carried out in sealed NMR tubes [in tol-d_8; internal standard, the residual H of the solvent (H_2SiEt_2) and Cp_2Fe (H_2SiPh_2, H_3SiPh; added after the reaction)].

The pseudo-first-order rate constants at 150 °C were measured under the following conditions: initial [**1a**] = 5.3 × 10^{-2} mol/L, initial [H_2SiEt_2] = 7.2 × 10^{-1} mol/L (internal standard: the H residue of tol-d_8); initial [**2a**] = 4.1 × 10^{-2} mol/L, initial [H_2SiEt_2] = 6.2 × 10^{-1} mol/L (internal standard: the H residue of tol-d_8).

(ii) Conversion of 4 into 5. The μ-ethylidene complex **4** (32 mg) was converted to **5** (pale yellow crystals; *cis*-isomer, 8 mg, 27%; *trans*-isomer, 10 mg, 32%; separated by preparative TLC) in a manner similar to the above-mentioned methylenation of **1**. **5** (*cis*-isomer): ^{1}H-NMR ($CDCl_3$) δ_H 9.89 (1H, q, $J = 6.8$ Hz, μ-C*H*Me), 8.17, 7.06 (1H × 2, s × 2, μ-CH_2), 5.11 (10H, s, Cp_2); ^{13}C-NMR ($CDCl_3$) δ_C 201.9 (CO), 138.1 (d, μ-*C*HMe), 105.2 (t, $J = 139$ Hz, μ-CH_2), 88.4 (d, $J = 176$ Hz, Cp), 41.8 (q, $J = 125$ Hz, μ-CH*Me*). IR (CH_2Cl_2) ν(C≡O) 1956 cm^{-1}. **5** (*trans*-isomer): ^{1}H-NMR (C_6D_6) δ_H 9.51 (1H, q, $J = 7.3$ Hz, μ-C*H*Me), 7.93, 7.82 (1H × 2, s × 2, μ-CH_2), 4.86, 4.82 (5H × 2, s × 2, Cp_2), 2.84 (3H, d, $J = 7.3$ Hz, μ-CH*Me*); IR (CH_2Cl_2) ν(C≡O) 1919 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_2Ru_2$: C, 41.86; H, 3.72. Found: C, 41.40; H, 3.56.

Single-Crystal X-ray Crystallography. Single crystals of *cis*- and *trans*-**1a** were obtained by recrystallization from CH_2Cl_2−hexanes. Suitable crystals were mounted on a glass fiber. Diffraction measurements were made on a Rigaku AFC-5R automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 59$ Å). The unit cells were determined and refined by a least-squares method using 20 independent reflections ($2\theta \sim 20°$). Data were collected with the $\omega-2\theta$ scan technique. 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 at every 150 measurements. The data processing was performed on a micro vax II computer (data collection) and an IRIS Indigo computer (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.[21] In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction (ψ scan) were made.

The structures were solved by a combination of the direct methods and Fourier synthesis (SAPI91 and DIRDIF). All the non-hydrogen atoms were refined anisotropically. The μ-CH_2 hydrogen atoms were located by examination of the difference Fourier maps and were refined isotropically. The remaining hydrogen atoms were fixed at the calculated positions (C−H = 0.95 Å) and were not refined.

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Supporting Information Available: Tables of positional parameters and B_{eq} values, anisotropic thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

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