catalyst solution was transferred via syringe into a 50-mL Pyrex reaction vessel containing **20** (296 mg, 1.50 mmol), and the reaction vessel was placed in a 300-mL stainless steel autoclave. The reaction was run at 125 °C and 2000 psi (CO/H_2 = 1) for 18 h with stirring. After the pressure was released from the autoclave, the solvent was removed. The reaction mixture was dissolved in 10% aqueous sodium carbonate and the solution extracted with ethyl acetate. Two layers were separated. The organic layer was dried over anhydrous $MgSO_4$, and then ethyl acetate was removed to give the crude product. The crude product was submitted to GLC and NMR analyses and then purified by column chromatography on silica gel (eluant CH_2Cl_2/methanol = 20) to give 2-carbethoxy-1-azabicyclo[4.3.0]nonan-9-one (**14**-OEt) as a colorless oil (169 mg, 50% yield). **14**-OEt (a mixture of diastereomers): ^1H NMR ($CDCl_3$) δ [1.01 (d, J = 6.9 Hz), 1.04 (d, J = 6.9 Hz)] (3 H), [1.28 (t, J = 6.9 Hz), 1.30 (d, J = 6.9 Hz)] (3 H), 1.4–2.6 (m, 5 H), 3.3–3.9 (m, 4 H), 3.94 (m, 1 H), 4.0–4.28 (m, 3 H); IR (neat, cm^{-1}) 1732 (ν_{CO}), 1698 (ν_{CO}); MS (m/e) 225 (1, M^+), 152 (100); HRMS (m/e) Calcd for $C_{12}H_{19}NO_3$ 225.1365, found 225.1355.

In the same manner, the reaction of **21** was carried out to give 2-carbethoxy-1-azabicyclo[4.4.0]decan-10-one (**15**-OEt) in 70% yield. **15**-OEt (a mixture of two diastereomers (1:1)): ^1H NMR ($CDCl_3$) δ [0.97 (d, J = 6.5 Hz), 1.00 (d, J = 6.7 Hz)] (3 H), 1.27 (t, J = 7.1 Hz, 3 H), 1.31–2.04 (m, 7 H), 2.34–2.46 (m, 2 H), 3.20–3.80 (m, 2 H), 3.52 (m, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.62 (m, 1 H); IR (neat, cm^{-1}) 1734 (ν_{CO}) 1641 (ν_{CO}); MS (m/e) 239 (1, M^+), 166 (100); HRMS (m/e) calcd for $C_{13}H_{21}NO_3$ 239.1512, found 239.1522.

Carbonylation of Bicyclic Hemiamidal 4 and its *O*-Ethyl Derivative 19 Catalyzed by $Co_2(CO)_8$. A 50-mL reaction vessel containing **4** (142 mg, 0.94 mmol) and $Co_2(CO)_8$ (32.1 mg, 0.094 mmol) in THF (2.4 mL) was placed in a 300-mL stainless steel autoclave. The reaction was run at 125 °C and 2000 psi (CO/H_2 = 1) for 18 h stirring. After the standard workup for amidocarbonylation (vide supra), the organic layer (ethyl acetate extract) was dried and concentrated in vacuo to the crude product. The GLC analysis of the crude product showed the formation of **16** in 31% yield. The aqueous layer was acidified and extracted with ethyl acetate and the extract dried, concentrated in vacuo, and dissolved in chloroform. The chloroform solution was treated with diazomethane in ether. The GLC analysis of the reaction mixture showed many peaks, but no trace of **13**-OMe was detected.

In a similar manner, the reaction of **19** was carried out under the same conditions as those used for the reaction of **4**. The GLC analysis of the reaction mixture showed the formation of **16** (24% yield) and its saturated derivative **16a** (15% yield) as the products. No trace of **13**-OEt was detected. **16a** (a mixture of two diastereomers): colorless oil; ^1H NMR ($CDCl_3$) δ 0.96 (d, J = 6.6 Hz, 3 H), 1.10–2.20 (m, 6 H), [2.58 (dd, J = 1.6, 14.5 Hz), 2.63 (dd, J = 1.6, 15.5 Hz)] (1 H), [3.08 (dd, J = 5.3, 14.5 Hz), 3.11 (dd, J = 5.0, 15.5 Hz)] (1 H), 3.71 (m, 1 H), 4.83 (m, 1 H); IR (neat, cm^{-1}) 1754 (ν_{CO}); HRMS (m/e) calcd for $C_8H_{13}NO$ 139.0997, found 139.0993.

Acknowledgment. This research has been supported by grants from the National Science Foundation, the National Institutes of Health (NIGMS), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Generous support from Mitsubishi Kasei Corp. is also gratefully acknowledged.

Hydrosilylation of 1-Hexyne Catalyzed by Rhodium and Cobalt–Rhodium Mixed-Metal Complexes. Mechanism of Apparent Trans Addition†

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Hydrosilylation of 1-hexyne with triethylsilane catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$ gives a mixture of *cis*-1-(triethylsilyl)-1-hexene (**1a**, major), its trans isomer (**2a**, minor), and its α-isomer (**3a**, minor) in excellent yield. Under optimum conditions, the yield of **1a** increases to 96%. The cis/trans ratio depends on the concentration of catalyst as well as the substituents of hydrosilane used. It is found that the lower catalyst concentration, the higher cis/trans ratio. Triethylsilane, dimethylphenylsilane, diethylmethylsilane, and ethyldimethylsilane give thermodynamically unfavorable cis isomers as the major products, whereas chlorodimethylsilane, dichloromethylsilane, and trimethoxysilane do not give cis isomers (**1**) at all under the usual conditions. A mechanism is proposed to accomodate the observed unique stereoselectivity. The proposed mechanism includes first a silicon shift to the acetylenic bond and the carbene-type zwitterionic rhodium complex as the key intermediate, which undergoes isomerization from a higher energy form (Z complex) to a lower energy form (E complex) followed by reductive elimination to give the cis isomer (**1**) as the kinetic product.

Introduction

Hydrosilylation of carbon–carbon multiple bonds has been one of the most important laboratory and industrial methods of forming silicon–carbon bonds. The reaction of alkenes has especially been studied extensively for decades, but less attention has been drawn to that of alkynes. Nevertheless, the reaction of alkynes provides the most convenient and direct route to vinylsilanes, which are very useful intermediates for cross-linked silicones as well as reagents in organic syntheses.[3] The hydrosilylation

† This paper is dedicated to late Professor John K. Stille for his outstanding achievement and contribution to the advancement of homogeneous catalysis and its application to organic synthesis and polymer science.

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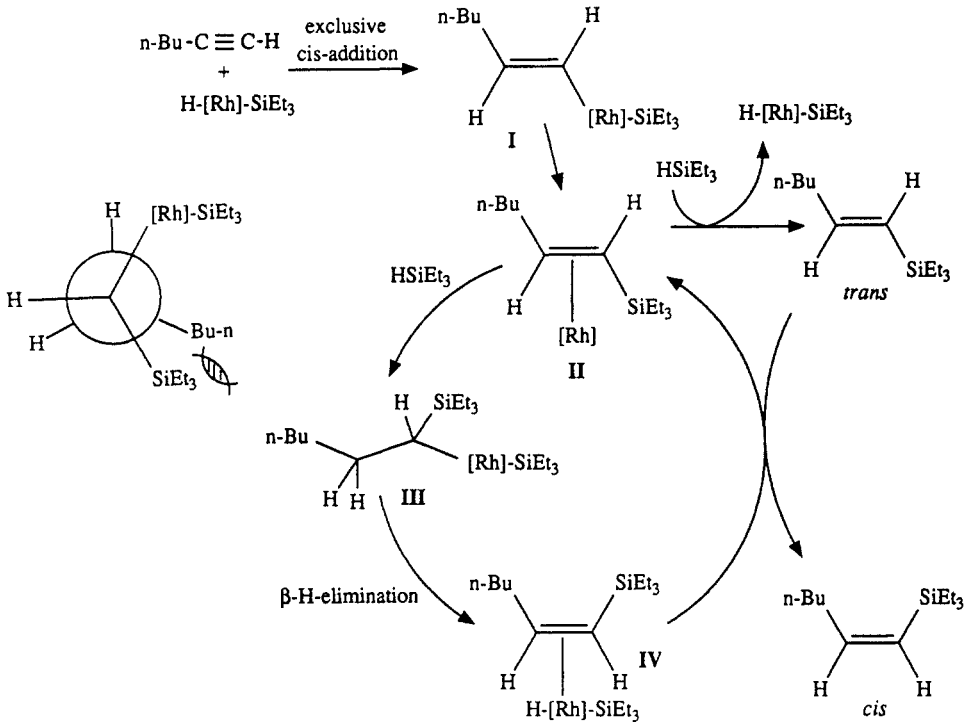
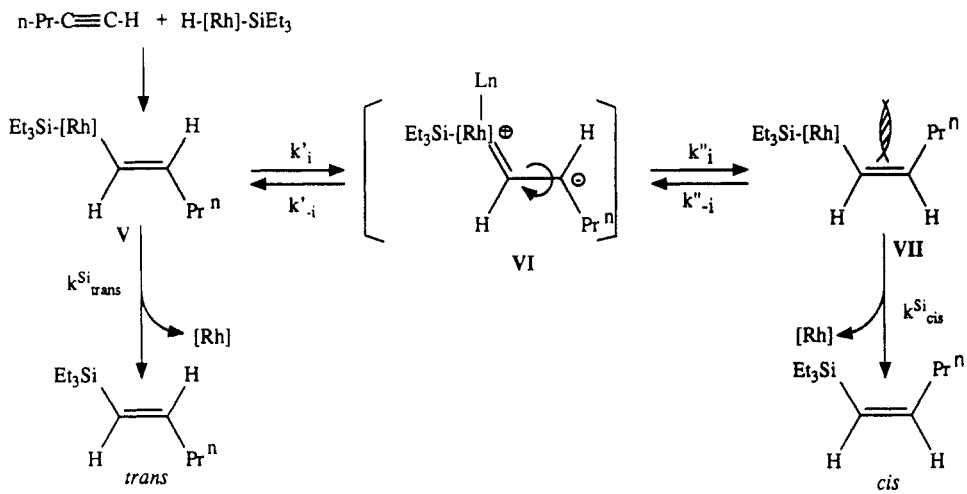
Scheme I. Haszeldine's Mechanism



Scheme II. Nile's Mechanism



of 1-alkynes can be promoted by a variety of catalysts, but radical initiators, chloroplatinic acid, and Wilkinson-type rhodium complexes have especially been studied.[3]

For the stereochemistry of the reaction giving 1-silylalkenes, it has been shown that the radical reaction gives the cis product predominantly via trans addition, whereas chloroplatinic acid gives the trans product via exclusive cis addition.[3,4] In rhodium complex catalyzed reactions, however, the formation of the cis product via an apparent trans addition was observed in most cases, and there have been controversy and dispute on this mysterious trans addition, which is very rare in transition-metal-catalyzed addition reactions to alkynes.[3]

In 1974, Ojima et al.[5] published the first report on the hydrosilylation of 1-alkynes with monohydrosilanes catalyzed by $RhCl(PPh_3)_3$, in which *cis*-1-silylalkenes were formed via trans addition as the major products. This result was rather surprising, since it had been generally accepted that a transition metal or metal complex catalyzed hydrosilylation of alkenes and alkynes proceeded through exclusive cis addition. Since the stereochemistry observed in this reaction resembles that obtained in the radical-initiator-promoted reaction of trichlorosilane with alkynes, Ojima suggested a mechanism involving a radical-like species as an intermediate or transition state.[5] In 1977, Watanabe et al.[6] reported the hydrosilylation of phenylacetylene with dimethylphenylsilane catalyzed by $RhCl(PPh_3)_3$, in which the cis/trans product ratio was found to depend on reaction conditions and the isomerization of cis product to trans product was observed. It was

(3) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 25, pp 1479–1526, and references cited therein. (b) Ojima, I.; Kogure, T. *Rev. Silicon, Germanium, Tin Lead Compd.* **1981**, *5*, 7–66 and references cited therein.

(4) For radical reactions, see, e.g.: Benkeser, R. A. *Pure Appl. Chem.* **1966**, *13*, 133. For the reactions catalyzed by chloroplatinic acid, see e.g.: Benkeser, R. A.; Cunico, R. F.; Dunny, S.; Jones, P. R.; Nerlekar, P. G. *J. Org. Chem.* **1967**, *32*, 2634.

(5) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C14.

(6) Watanabe, H.; Kitahara, T.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1977**, *139*, 215.

Table I. Hydrosilylation of 1-Hexyne with Triethylsilane[a]

entry no.	Cat.	1-hexyne/Cat.	conditions	yield, %[b]	product ratio[c] 1a	2a	3a	1a/2a
1	$Rh_4(CO)_{12}$	1000	20 °C, 5 h	80	54	23	23	2.3
2		1000[d]	20 °C, 72 h	100	90	5	5	18.0
3		2000	20 °C, 23 h	100	80	9	11	8.9
4		10000	20 °C, 68 h	96	89	5	6	17.8
5		10000	55 °C, 5 h	85	84	8	8	10.5
6	$Co_2Rh_2(CO)^{12}$	1000	20 °C, 21 h	78	78	10	11	7.8
7		1000[d]	20 °C, 72 h	100	95	2.5	2.5	38
8		10000	55 °C, 8 h	93	89	6	5	14.8
9		20000[e]	20 °C, 68 h	48	98	1	1	98
10	$Co_3Rh(CO)_{12}$	1000[d]	20 °C, 72 h	100	96	2	2	48
11	$RhCl(PPh_3)_3$	1000	20 °C, 22 h	84	79	7	14	11.3
12		1000[f]	40 °C, 18 h	100	94	3	3	31.3
13		10000[g]	55 °C, 24 h	95	96	2	2	48
14	$Co_2(CO)_8$	125[h]	75 °C, 1 h	100	-	80	20	0

[a] Reactions were run with 2.00 mmol of 1-hexyne and 3.00 mmol of triethylsilane in 3.0 mL of benzene unless otherwise noted. [b] Determined by GLC analysis. The selectivity of the reaction giving hydrosilylation products is virtually 100% in each case; thus, this yield corresponds to the conversion of the reaction. [c] Determined by GLC analysis. [d] Reaction was run in 15 mL of toluene. [e] Reaction was run with 40.0 mmol of 1-hexyne and 4.0 mmol of triethylsilane in 15 mL of toluene; i.e., 1-hexyne/Cat. = 20000, hydrosilane/Cat. = 2000. [f] Reaction was run with 4.00 mmol of 1-hexyne and 8.00 mmol of triethylsilane in 15 mL of toluene. [g] Reaction was run with 2.00 mmol of 1-hexyne and 2.05 mmol of triethylsilane in 3.0 mL of toluene. [h] Reaction was run without solvent and with 5.00 mmol of 1-hexyne and 7.50 mmol of triethylsilane. No reaction took place under the standard conditions (see footnote *a*) with toluene or benzene as the solvent at 20–55 °C.

Table II. Substituent Effects on the Selectivity in the Hydrosilylation of 1-Hexyne Catalyzed by $Rh_4(CO)_{12}$[a]

entry no.	hydrosilane	conditions	conversion,[b] %	selectivity,[b] %	product ratio[b] 1	2	3
1	$HSiEt_3$	25 °C, 24 h	100	100	84	7	9
2	$HSiMe_2Ph$	25 °C, 36 h	100	93	60	27	13
3	$HSiMeEt_2$	0 °C, 12 h	100	100	62	31	7
4	$HSiMe_2Et$	25 °C, 5 days	100	100	42	37	21
5	$HSiMe_2Cl$	25 °C, 24 h	100	76		80	20
6		0 °C, 12 h	100	85		74	26
7	$HSiMeCl_2$	0 °C, 12 h	100	70		65	35
8	$HSi(OMe)_3$	0 °C, 12 h[c]	100	98		95	5
9		−15 °C, 3 h[c]	90	100		98	2

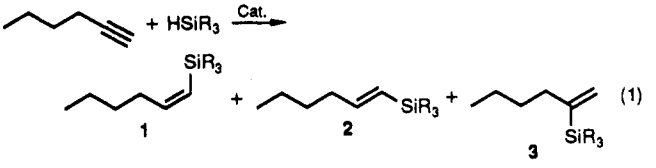
[a] All reactions were run with 2.00 mmol of 1-hexyne, 2.50 mmol of hydrosilane, and 2.00×10^{-3} mmol of $Rh_4(CO)_{12}$ in 5 mL of toluene unless otherwise noted. [b] Determined by GLC analysis. [c] Reaction was run without solvent.

also found that this cis to trans isomerization required the copresence of the catalyst and the hydrosilane. However, in 1978 Haszeldine and co-workers[7] reported a trans to cis isomerization in the hydrosilylation of 1-hexyne with triethylsilane catalyzed by $RhCl(PPh_3)_3$ and proposed a mechanism (Scheme I) including the first cis addition of the hydrosilane to 1-hexyne, giving the trans product followed by isomerization to the cis product. Nile and co-workers[8] studied the hydrosilylation of 1-pentyne with triethylsilane catalyzed by phosphine–rhodium(I) complexes formed in situ from $[Rh(C_8H_{14})_2Cl]_2$ and phosphines and found that good donor ligands gave the cis product while good acceptor ligands gave the trans product as the major species. On the basis of this finding, they proposed in 1981 another mechanism (Scheme II) in which the isomerization occurs via a zwitterionic carbene intermediate. Both proposed mechanisms, however, have serious shortcomings in rationalizing the occurrence of apparent trans addition.

In the course of our study on the homogeneous catalysis of cobalt–rhodium mixed-metal carbonyl clusters and related systems, we encountered this mysterious problem and found a clue to solve the problem. Also, we found that rhodium carbonyl, cobalt carbonyl, and cobalt–rhodium mixed-metal carbonyl complexes had not been used as catalysts for the hydrosilylation of alkynes before we started our research. Therefore, we describe here our study on the hydrosilylation of 1-hexyne catalyzed by $Co_2Rh_2(CO)_{12}$, $Rh_4(CO)_{12}$, and $Co_2(CO)_8$ as well as its mechanism.

Results and Discussion

Hydrosilylation of 1-Hexyne. The hydrosilylation of 1-hexyne was carried out in benzene or toluene with triethylsilane in the presence of $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $RhCl(PPh_3)_3$, and $Co_2(CO)_8$ to examine the relative activity and selectivity of each catalyst and the effects of reaction conditions on the selectivity. Results are summarized in Table I. The reactions catalyzed by $Rh_4(CO)_{12}$ were also performed with other hydrosilanes, i.e., diethylmethylsilane, dimethylethylsilane, dimethylphenylsilane, chlorodimethylsilane, dichloromethylsilane, and trimethoxysilane, to look at the effects of hydrosilane structure on the selectivity. Results are summarized in Table II. In general, the reaction gave *cis*-1-silyl-1-hexene (**1**), *trans*-1-silyl-1-hexene (**2**), and 2-silyl-1-hexene (**3**) as the products (eq 1), accompanied by small amounts of higher molecular weight side products in some cases.



(1)

As Table I shows, the reactions catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$ gives *cis*-

(7) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91.
(8) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299.

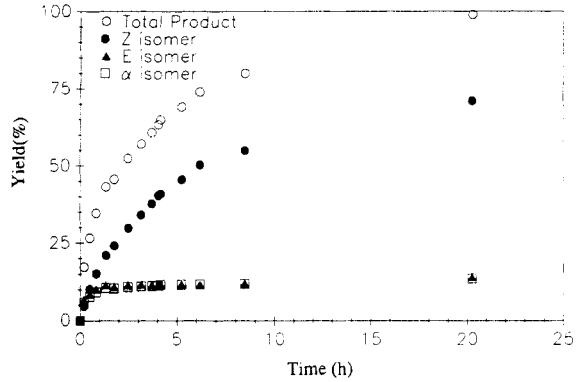


Figure 1. Reaction profile for the hydrosilylation of 1-hexyne catalyzed by $Rh_4(CO)_{12}$. The reaction was run with 2.00 mmol of 1-hexyne, 3.00 mmol of triethylsilane, and 2.00×10^{-3} mmol of $Rh_4(CO)_{12}$ in 3.0 mL of toluene at 20 °C.

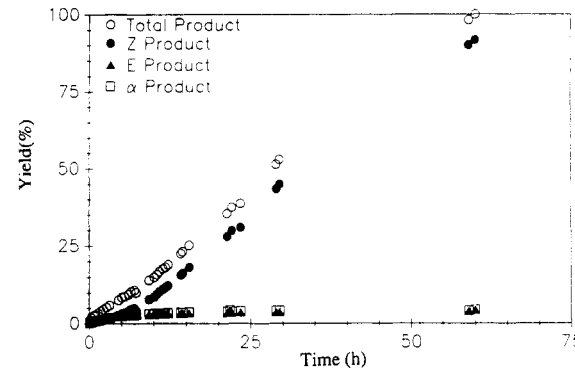


Figure 2. Reaction profile for the hydrosilylation of 1-hexyne catalyzed by $Co_2Rh_2(CO)_{12}$. The reaction was run with 4.00 mmol of 1-hexyne, 8.00 mmol of triethylsilane, and 2.00×10^{-3} mmol of $Co_2Rh_2(CO)_{12}$ in 15 mL of toluene at 20 °C.

1-(triethylsilyl)-1-hexene (**1a**, major), *trans*-1-(triethylsilyl)-1-hexene (**2a**, minor), and 2-(triethylsilyl)-1-hexene (**3a**, minor) as the products (entries 1–13), while the $Co_2(CO)_8$-catalyzed reaction gives only **2a** (major) and **3a** (minor) (entry 14).

On monitoring the reactions catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $RhCl(PPh_3)_3$, we observed a change in the trans/cis product ratio as the reaction proceeded; viz., at the very beginning of the reaction, the trans and α-products **2a** and **3a**, respectively, were major, whereas the cis product **1a** became predominant at the end of the reaction. This observation is somewhat unusual, since the possible isomerization of products, i.e., **1a** and **2a**, should take place in a way that the thermodynamically unfavorable cis isomer (**2a**) is converted to more the stable trans isomer (**1a**).

In order to make sure that the trans isomer (**2a**) is thermodynamically more favorable than the cis isomer, we carried out MM2 calculations using the program MACROMODEL[9] on both isomers and found that the trans isomer (**2a**) is indeed more favorable than the cis isomer (**1a**) by +2.26 kcal/mol. The result clearly indicates that, thermodynamically, the trans isomer (**2a**) is the favorable product. Therefore, it is obvious that the cis isomer (**1a**) *is produced under kinetic conditions.*

Accordingly, we looked at the reaction profile more carefully and found that *the trans isomer (**2a**) and the α-product (**3a**) were produced only in the beginning and both isomers virtually did not increase throughout the rest of the reaction!* The reaction profiles for the hydrosilylation of 1-hexyne with triethylsilane catalyzed by $Rh_4(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$ are shown in Figures 1 and 2 as typical examples. Both figures clearly show that the formation of **2a** and **3a** takes place only in the beginning. The observed phenomena are best explained by assuming the existence of two different catalyst species working in the reaction; viz., one of the two catalyst species gives **1a** exclusively (species A) and the other yields **2a** and **3a** selectively (species B).[10] At the beginning, both catalyst species are active in producing all three products, but later species B is deactivated (or disappears) or converted to species A and species A becomes the only active catalyst, giving **1a** exclusively. In connection with the assumed existence of species A and B, it is worth pointing out the fact that the use of a large excess (10 equiv) of 1-hexyne with triethylsilane remarkably suppresses the formation of **2a** and **3a** (Table I, entry 9) and the rate of the reaction is much slower than that under the standard reaction conditions, under which the triethylsilane/1-hexyne ratio is 1.5–2.0. This fact also strongly supports the above-mentioned hypothesis.

Looking into the factors affecting the trans/cis ratio, we found a clear increase in the formation of the cis product (**1a**) at lower catalyst concentrations in all cases examined (entries 1–13), and this increase is especially dramatic for $Rh_4(CO)_{12}$, i.e., from 54% (**2a**/**1a** = 2.3; at 80% conversion)[11] at 7.0×10^{-4} M catalyst concentration (entry 1) to 89% (**1a**/**2a** = 17.8; at 96% conversion)[11] at 7.0×10^{-5} M catalyst amount (entry 4).

As Table II shows, the structure of the hydrosilane exerts a marked influence on the selectivity. It is noteworthy that the reactions with chlorodimethylsilane, dichloromethylsilane, and trimethoxysilane do not give any cis product (**2**); i.e., the reactions proceed exclusively through cis addition (entries 5–9). The results clearly indicate that the electronic nature of the hydrosilane is a crucial factor in the trans/cis stereoselectivity of the reaction. The same trend was observed when $Co_2Rh_2(CO)_{12}$ and $RhCl(PPh_3)_3$ were used as the catalysts for the reaction; i.e., the reactions with trimethoxysilane and chlorodimethylsilane did not give any cis product (**1**), consistent with the results obtained for $Rh_4(CO)_{12}$.

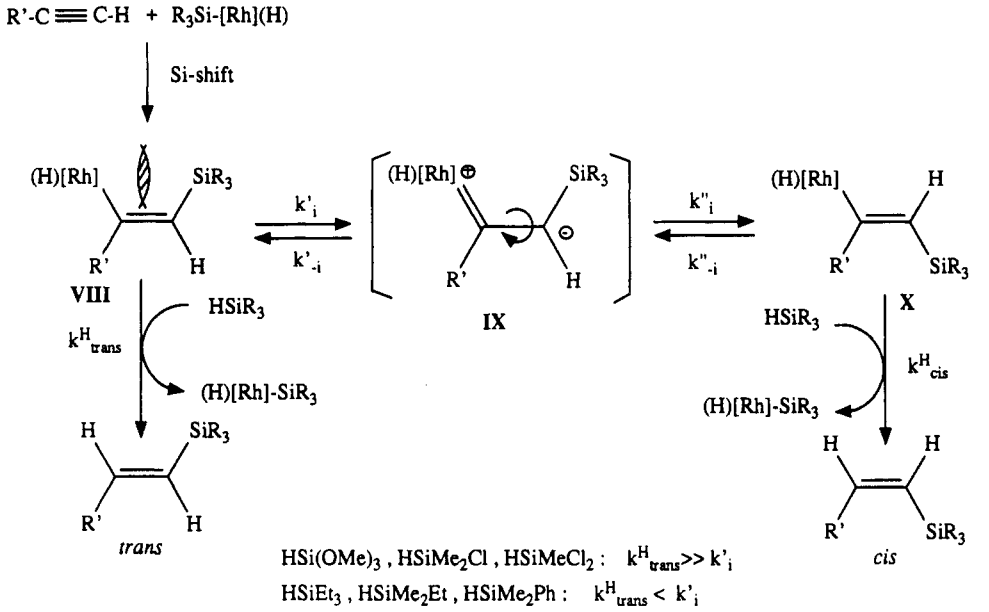
Mechanism of the Hydrosilylation of 1-Hexyne Catalyzed by Rhodium Complexes. As for the mechanism of the apparent trans addition of a hydrosilane across the carbon–carbon triple bond, the previously proposed mechanisms cannot accomodate our results mentioned above. In the mechanism proposed by Haszeldine et al. (Scheme I),[7] the formation of the cis product through β-hydride elimination of the 1-Et_3Si-hexyl-$Rh(SiEt_3)$ species (III) is not favorable since there is a serious steric conflict between the silyl and the butyl groups in the transition state (see the Newman projection). Also, it is unreasonable to assume that the sterically more demanding trans product selectively substitutes the cis product from the intermediate IV. Overall, it is against thermodynamics to assume isomerization of the more stable trans product to the less stable cis product. In the mechanism proposed by Nile et al. (Scheme II),[8] the proposed rotation of the

(9) MACROMODEL: a molecular modeling program developed by Professor W. C. Still, Department of Chemistry, Columbia University.

(10) It is reasonable to assume that species B catalyzes the hydrosilylation with low regioselectivity, giving the α-product (**3a**) and the trans product (and possibly some cis product as well). In fact, the formation of **3a** against that of **2a** + **1a** in the beginning stage increases when the reaction is carried out at higher temperature (40–60 °C).

(11) When the conversion of the reaction is not 100%, it is quite likely that the remaining substrate is converted to the cis isomer (**1**) virtually exclusively as demonstrated in Figures 1 and 2. Accordingly, the cis/trans ratio should be higher at 100% conversion. Nevertheless, the observed marked influence of catalyst concentration on the cis/trans ratio is obvious.

Scheme III. Proposed Mechanism for the Apparent Trans Addition



single bond in the zwitterionic carbene intermediate VI to give the sterically much more hindered *cis*-1-pentenyl-Rh(SiR_3) complex (VII) is very unfavorable. Also, the *n*-propyl group would destabilize the negative charge developing on C-2 of VII. Thus, this mechanism is not plausible either.

We proposed a new mechanism that can accommodate all the observed results in Scheme III, which focuses on the extremely regio- and stereoselective catalyst species, species A, mentioned above. The proposed mechanism includes the insertion of an alkyne into the silicon–rhodium bond in the first place to form the (*Z*)-1-silyl-1-alken-2-yl–Rh intermediate (VIII), instead of the previously proposed insertion into the hydrogen–rhodium bond.[3,12] This is one of the most important steps in the whole mechanism. The intermediate VIII thus formed suffers from serious steric hindrance between the silyl group and the rhodium moiety, which are both bulky. Thus, VIII undergoes isomerization to the sterically more favorable (*E*)-1-silyl-1-alken-2-yl–Rh complex (X) via the zwitterionic carbene complex IX, which is somewhat similar to the one proposed by Nile et al.[8] (vide supra), but the silyl group is at C-1, i.e., β to the rhodium. From X, the cis product is formed through oxidative addition of another molecule of the hydrosilane and reductive elimination to regenerate the active catalyst species. However, if the oxidative addition of another molecule of the hydrosilane to VIII followed by reductive elimination is much faster than the isomerization ($k_{trans}{}^{H} \gg k'_i$), the trans product should be formed selectively. This mechanism explains well the fact that low catalyst concentration favors isomerization; viz., the isomerization process is intramolecular whereas the reductive elimination is a bimolecular process. The proposed mechanism also explains the fact that the reactions with hydrosilanes bearing electron-withdrawing substituents do not give any cis products arising from the isomerization of VIII to X. Namely, the hydrogen–silicon bonds in hydrosilanes bearing electron-withdrawing substituents, such as trimethoxysilane and dichloromethylsilane, are substantially weaker than those in the hydrosilanes bearing electron-releasing substituents, such as triethylsilane and dimethylethylsilane, and thus the oxidative addition of electron-deficient hydrosilanes to the rhodium catalyst is much faster that that of electron-rich hydrosilanes. Once the oxidative addition of another hydrosilane takes place,[13] the rhodium becomes higher in oxidation state, e.g., Rh(V), which makes the formation of the zwitterionic carbene species IX very difficult; hence, the reaction gives the trans product selectively. It is also well-known that a silyl group stabilizes an α-carbanion through a pπ–dπ interaction and a β-cation through σ–π interaction.[16] In the zwitterionic species IX, the α-anion stabilization effect may not be affected by the substitution pattern on the silicon since it has vacant d orbitals, but the β-cation stabilization effect would be substantially weakened when electron-withdrawing substituents are attached to the silicon. Consequently, the formation of IX is unfavorable with trimethoxysilane, chlorodimethylsilane, and dichloromethylsilane are used.

Although our proposed mechanism is for the rhodium complex catalyzed reactions, it is reasonable to assume that other transition-metal catalysts may have similar catalytic

(12) The insertion of carbonyl into the Rh–Si bond in preference to Rh–H in the rhodium complexes of the type Rh(H)(SiR_3)X has been proposed and established as the key aspect of the mechanism of rhodium complex catalyzed hydrosilylation of ketones and aldehydes; see, e.g.: (a) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. (b) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. (c) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211. (d) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (e) Ojima, I.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3722. On the other hand, it has generally been accepted that the selective insertion of carbon–carbon multiple bonds into the Rh–H bond is a key step in the hydrosilylation of alkenes and alkynes.

(13) The order of reactivity toward group VIII metal complexes for common hydrosilanes decreases in the following order: Cl_3SiH > Cl_2MeSiH > $ClMe_2SiH$ > $(MeO)_3SiH$ > $PhMe_2SiH$ > $EtMe_2SiH$ ≈ Et_3SiH.[3] It is well-known that trichlorosilane is much more reactive than other chloroalkylhydrosilanes, arylalkylhydrosilanes, and trialkylsilanes toward group VIII transition-metal complexes and forms stable oxidative adducts with Wilkinson-type complexes, which are usually too stable to react with substrates under mild conditions.[14]

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activity. In fact, Crabtree[16] has observed a similar selective cis-product formation in the hydrosilylation of 1-alkynes catalyzed by their iridium complex, which is stabilized by a unique O-donor ligand, and independently come to a conclusion essentially similar to ours.

Further detailed mechanistic studies, including precise kinetics and identification of active catalyst species for $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $RhCl(PPh_3)_3$, are currently actively underway, and results will be published elsewhere.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, and chloroform-*d* was used as the solvent. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer with a Hewlett-Packard HP 7470A plotter, using samples as neat liquids, Nujol mulls, or solutions. Mass spectra (GCMS) were obtained on a Spectros MS 30 mass spectrometer or a Hewlett-Packard HP 5980A mass spectrometer equipped with a HP 5710A gas chromatograph and a HP 5933A data system or a Hewlett-Packard HP 5971A mass spectrometer with a HP 5890 gas chromatograph and a HP Vecta QS/20 workstation at 70 eV. High-resolution mass spectra (HRMS) were measured with a Kratos MS-80RFA mass spectrometer with a Chrompack Carlo Erba/Kratos gas chromatograph and Data General Eclipse S/120 datat station. Analytical gas chromatography (GLC) was performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a HP 3396A integrator or a Perkin-Elmer 3920 gas chromatograph equipped with a Hewlett-Packard 3393A integrator, using columns packed with 3% OV-17 or 3% Dexsil-300. Column chromatography was performed on silica gel 60 (230–400 mesh) purchased from Brinkmann Instruments, Inc.

Materials. Toluene and benzene were dried over and distilled from calcium hydride. The complexes $RhCl_3{\cdot}3H_2O$ and $Co_2(CO)_8$ were obtained from Engelhard Industries KK and Strem Chemicals, Inc., respectively, and used as received. The rhodium complexes $Rh_4(CO)_{12}$,[18] $Co_2Rh_2(CO)_{12}$,[19,20] and $Co_3Rh(CO)_{12}$[19] were prepared according to the literature methods. 1-Hexyne and all hydrosilanes were purchased from Aldrich Chemical Co., Inc., distilled under nitrogen, and stored over molecular sieves. Wilkinson's catalyst, $RhCl(PPh_3)_3$, was obtained from Aldrich Chemical Co. and used as received.

Hydrosilylation of 1-Hexyne. General Procedure A (for Reactions Performed under Neat Conditions). To a dry Schlenk-type reaction vessel charged with the catalyst, evacuated and thoroughly flushed with nitrogen, is added a hydrosilane via a syringe. The mixture is stirred until the solution becomes homogeneous; the 1-hexyne is added dropwise via syringe. The reaction vessel is immersed in an oil bath or a cooling bath, which is kept at the required reaction temperature. The progress of the reaction is monitored by GLC, and when the substrate is totally consumed, the reaction mixture is submitted to a distillation under reduced pressure. The yield and the product ratio are determined by GLC analyses with *n*-hexadecane as the internal standard, and products are identified either by comparison with authentic samples in GLC experiments and/or by ^1H NMR analyses. The scale and specific conditions for each experiment are indicated in Tables I and II as footnotes.

General Procedure B (for Reactions Performed in Benzene or Toluene). A stock solution of the catalyst is freshly prepared, and the required amount is transferred with a syringe or a graduated pipet into a reaction vessel containing 1-hexyne in a solvent. A hydrosilane is then added dropwise via syringe, and the reaction mixture is stirred under proper reaction conditions. Subsequent steps are carried out in the same manner as described above in general procedure A. The scale and specific conditions for each experiment are indicated in Tables I and II as footnotes.

Identification of Products. The following data were used for the identification of the hydrosilylation products.

***cis*-1-(Triethylsilyl)-1-hexene (1a):**[22] ^1H NMR δ 0.60 (q, J = 7.9 Hz, 6 H), 0.94 (m, J = 7.9 Hz, 12 H), 1.34 (m, 4 H), 2.09 (m, 2 H), 5.38 (d, J = 14.1 Hz, 1 H), 6.38 (dt, J = 14.1, 7.2 Hz, 1 H).

***trans*-1-(Triethylsilyl)-1-hexene (2a):**[21] ^1H NMR δ 0.54 (q, J = 7.8 Hz, 6 H), 0.93 (m, 12 H), 1.30–1.42 (m, 4 H), 2.13 (m, 2 H), 5.53 (d, J = 18.7 Hz, 1 H), 6.03 (dt, J = 18.7, 6.3 Hz, 1 H).

2-(Triethylsilyl)-1-hexene (3a):[21] ^1H NMR δ 0.56 (q, J = 7.8 Hz, 6 H), 0.94 (m, 12 H), 1.30–1.42 (m, 4 H), 2.12 (m, 2 H), 5.3 (m, 1 H), 5.6 (m, 1 H).

***cis*-1-(Dimethylphenylsilyl)-1-hexene (1b):**[22,23] ^1H NMR δ 0.40 (s, 6 H), 0.95 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.10 (m, 2 H), 5.8 (d, J = 8.1 Hz, 1 H), 6.47 (dt, J = 8.1, 6.9 Hz, 1 H), 7.30 (bs, 3 H), 7.70 (m, 2 H); MS (m/e, %) 220 (M^+ + 2, 0.3), 219 (M^+ + 1, 0.9), 218 (M^+, 5.5), 203 (46), 135 (76), 121 (100).

***trans*-1-(Dimethylphenylsilyl)-1-hexene (2b):**[22,23] ^1H NMR δ 0.375 (s, 6 H), 0.80 (t, J = 6.5 Hz, 3 H), 1.35 (m, 4 H), 2.30 (m, 2 H), 5.66 (d, J = 18.8 Hz, 1 H), 6.05 (dt, J = 18.8, 6.1 Hz, 1 H), 7.30 (bs, 3 H), 7.70 (m, 2 H); MS (m/e) 220 (M^+ + 2, 0.2), 219 (M^+ + 1, 0.3), 218 (M^+, 1.4), 203 (44.3), 161 (35), 135 (88), 121 (100).

2-(Dimethylphenylsilyl)-1-hexene (3b):[23] ^1H NMR δ 0.29 (s, 6 H), 0.90 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 1.95 (m, 2 H), 5.42 (d, J = 1.5 Hz, 1 H), 5.71 (d, J = 1.5 Hz, 1 H), 7.30 (bs, 3 H), 7.70 (m, 2 H); MS (m/e) 220 (M^+ + 2, 0.2), 219 (M^+ + 1, 1), 218 (M^+, 5.5), 203 (15), 161 (21), 135 (100), 121 (48).

***cis*-1-(Diethylmethylsilyl)-1-hexene (1c):**[24] ^1H NMR δ 0.07 (s, 3 H), 0.60 (m, 4 H), 1.00 (m, 9 H), 1.40 (m, 4 H), 2.10 (m, 2 H), 5.21 (d, J = 12.2 Hz, 1 H), 6.38 (dt, J = 12.2, 7.0 Hz, 1 H).

***trans*-1-(Diethylmethylsilyl)-1-hexene (2c):**[24] ^1H NMR δ −0.01 (s, 3 H), 0.55 (m, 4 H), 0.98 (m, 9 H), 1.40 (m, 4 H), 2.20 (m, 2 H), 5.60 (d, J = 6.0 Hz, 1 H), 6.05 (dt, J = 6.0, 6.2 Hz, 1 H).

2-(Diethylmethylsilyl)-1-hexene (3c):[23] ^1H NMR δ 0.03 (s, 3 H), 0.55 (m, 4 H), 1.0 (m, 9 H), 1.40 (m, 4 H), 2.10 (m, 2 H), 5.30 (s, 1 H), 5.35 (s, 1 H).

***cis*-1-(Dimethylethylsilyl)-1-hexene (1d):**[23,25] ^1H NMR δ 0.18 (s, 6 H), 0.62 (m, 2 H), 1.00 (m, 6 H), 1.40 (m, 4 H), 2.20 (m, 2 H), 5.52 (d, J = 14.0 Hz, 1 H), 6.40 (dt, J = 14.0, 7.2 Hz, 1 H); MS (m/e, %) 170 (M^+, 3.4), 155 (6.6), 141 (100).

***trans*-1-(Dimethylethylsilyl)-1-hexene (2d):**[23,25] ^1H NMR δ 0.16 (s, 6 H), 0.62 (m, 2 H), 1.00 (m, 6 H), 1.40 (m, 4 H), 2.30 (m, 2 H), 5.66 (d, J = 18.5 Hz, 1 H), 6.10 (dt, J = 18.5, 6.2 Hz, 1 H); MS (m/e, %) 171 (M^+ + 1, 0.5), 170 (M^+, 2.6), 155 (6.1), 141 (100).

2-(Dimethylethylsilyl)-1-hexene (3d):[25,26] ^1H NMR δ 0.10 (s, 6 H), 0.60 (q, J = 6.7 Hz, 2 H), 1.00 (m, 6 H), 1.40 (m, 4 H), 2.30 (t, J = 6.5 Hz, 2 H), 5.40 (d, J = 2.9 Hz, 1 H), 5.64 (d, J = 2.9 Hz, 1 H); MS (m/e) 170 (M^+, 1.4), 155 (6.7), 141 (100).

***trans*-1-(Chlorodimethylsilyl)-1-hexene (2e):** ^1H NMR δ 0.05 (s, 6 H), 0.90 (t, J = 6.5 Hz, 3 H), 1.30 (m, 4 H), 2.10 (dt, J = 6.8, 5.9 Hz, 2 H), 5.60 (d, J = 19.0 Hz, 1 H), 6.10 (d, J = 19.0, 5.9 Hz, 1 H); MS (m/e, %) 176 (M^+, 1), 161 (8), 136 (12), 134 (33), 119 (12), 95 (40), 93 (100), 65 (11); HRMS (m/e) calcd for $C_8H_{17}ClSi$ 176.0788, found 176.0799.

2-(Chlorodimethylsilyl)-1-hexene (3e): ^1H NMR δ 0.10 (s, 6 H), 0.60 (t, J = 6.5 Hz, 3 H), 1.35 (m, 4 H), 2.13 (bt, J = 7.0 Hz, 2 H), 5.40 (s, 1 H), 5.65 (s, 1 H); MS (m/e, %) 176 (M^+, 0.5), 134 (4), 119 (14), 95 (40), 93 (100), 82 (20), 79 (8), 65 (9), 63 (8);

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HRMS (m/e) calcd for $C_8H_{17}ClSi$ 176.0788, found 176.0814; HRMS (m/e) calcd for $C_8H_{17}ClSi$ 177.0822, found 177.0801.

***trans*-1-(Dichloromethylsilyl)-1-hexene (2f)**: ^1H NMR δ 0.80 (s, 3 H), 0.95 (s, 3 H), 1.40 (m, 4 H), 2.20 (dt, J = 7.0, 5.7, Hz, 2 H), 5.75 (d, J = 19.0 Hz, 1 H), 6.51 (d, J = 19.0, 5.7 Hz, 1 H); MS (m/e, %) 198 (M^+ + 2, 0.6), 196 (M^+, 1), 183 (1.2), 181 (2.1), 169 (9), 167 (11), 156 (31), 154 (45), 115 (71), 113 (100).

2-(Dichloromethylsilyl)-1-hexene (3f): ^1H NMR δ 0.79 (s, 3 H), 0.94 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.20 (t, J = 7.0 Hz, 2 H), 5.71 (s, 1 H), 5.84 (s, 1 H); MS (m/e, %) 198 (M^+ + 2, 2), 196 (M^+, 4), 183 (2.7), 181 (3.9), 169 (9), 167 (12), 156 (10), 154 (15), 115 (71), 113 (100).

***trans*-1-(Trimethoxysilyl)-1-hexene (2g)**: ^1H NMR δ 0.95 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.18 (q, J = 7.0, 6.2 Hz, 2 H), 3.48 (s, 9 H), 5.38 (d, J = 18.9 Hz, 1 H), 6.43 (dt, J = 18.9, 6.2 Hz, 1 H); MS (m/e, %) 204 (M^+, 3), 172 (20), 143 (12), 121 (100), 91 (60); HRMS (m/e) calcd for $C_9H_{20}O_3Si$ 204.118, found 204.1192 (5).

2-(Trimethoxysilyl)-1-hexene (3g): ^1H NMR δ 0.95 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.20 (t, J = 7.0 Hz, 2 H), 3.48 (s, 9 H), 5.62 (bs, 1 H), 5.75 (bs, 1 H); MS (m/e, %), 204 (M^+, 10), 121 (100), 91 (65); HRMS (m/e) calcd for $C_9H_{20}O_3Si$ 204.118; found 204.1182 (5).

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Reactions of Fischer Carbene Complexes with Electron-Deficient Olefins: Scope and Limitations of This Route to Donor–Acceptor-Substituted Cyclopropanes[1]

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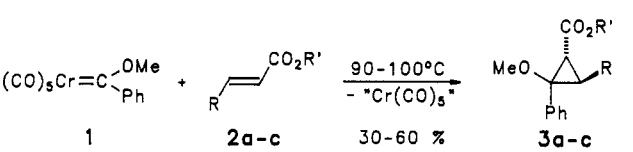
The Fischer carbene complex $[(CO)_5Cr{=}C(OMe)Ph]$ (**1**) is able to transfer its carbene ligand to a variety of electron-deficient olefins and provides donor–acceptor-substituted cyclopropanes in good yields. Apt activating groups with respect to the alkene are ester, amide, nitrile, sulfone, and dialkyl phosphonate functions. Methyl vinyl ketone (**19**) affords products in low yield that may arise from an intermediate cyclopropane derivative. Phenyl vinyl sulfoxide (**24**) mainly acts as an oxidizing agent, transforming **1** into methyl benzoate. For olefin **24** and α-(*N*-methylanilino)acrylonitrile we found products that should be formed on an olefin metathesis pathway. The methyl-substituted carbene complex **48** also affords the expected donor–acceptor-substituted cyclopropanes; however, acyclic isomers are formed in higher amounts. The molybdenum and tungsten complexes **55** and **56**, respectively, also furnish cyclopropane derivatives, but the yields are lower than with the chromium compound **1**. Disubstituted olefins and complex **1** still give the cyclopropanes in moderate yields, while all trisubstituted and most of the difunctionalized alkenes do not react with this Fischer carbene complex. The cyclopropanes synthesized can be deprotonated and alkylated or transformed into ring-opened products. These model reactions demonstrate the synthetic potentials of donor–acceptor-substituted cyclopropanes prepared via Fischer carbene complexes.

Introduction

Since the fundamental discovery of carbene complexes by Fischer and co-workers these novel organometallic compounds have found a number of highly interesting applications as building blocks for organic synthesis.[2] Among the very first reactions with the standard chromium carbene complex **1** were the formal [2 + 1] cycloadditions with electron-rich[3] and electron-deficient olefins,[4] which provide difunctional cyclopropanes. Thus, compound **1** and α,β-unsaturated esters **2a–c** furnish the corresponding donor–acceptor-substituted cyclopropanes **3a–c** in reasonable yields (eq 1).



1 **2a-c** 30-60 % **3a-c**

a R, R' = Me **b** R = Ph, R' = Me **c** R = CO_2Et, R' = Et (1)

Donor–acceptor-substituted cyclopropanes—usually prepared by alternative routes—have gained attention because of their high potential to serve as versatile intermediates.[5] They are precursors of a variety of heter-

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