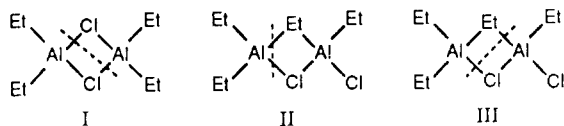


tances observed in the cation (1.968 (6) Å) are shorter than those reported for [EtAl-SALEN] (2.013 (6) and 2.027 (6) Å), while the Al-O bond distances observed for the cation (1.955 (6) Å) are longer than those reported for the Schiff base complex (1.800 (5) and 1.829 (5) Å).

It is interesting to consider an unusual disproportionation of diethylaluminum chloride wherein Et_2Al^+ and EtAlCl_2^- contribute to the formation of the title compound. While the symmetric bridge cleavage of dihalo-bridged dimers of alkylaluminum halides (I) is commonplace, the



asymmetric bridge cleavage of mixed chloro-alkyl-bridged dimers is much less often encountered. Asymmetric cleavage of the mixed chloro-ethyl-bridged dimer of diethylaluminum chloride (II) would readily result in Et_2Al^+ and $\text{Et}_2\text{AlCl}_2^-$. It is reasonable that reaction of Et_2Al^+ with the aza crown could afford the $[(\text{EtAl})_2\text{dianza-18-crown-6}]^{2+}$ cation. Symmetrical cleavage of the mixed chloro-ethyl-bridged dimer of diethylaluminum chloride (III) would result in Et_3Al and EtAlCl_2 . One could envisage the EtAlCl_3^- anion of $[(\text{EtAl})_2\text{dianza-18-crown-6}]^{2+}$ resulting from reaction of $\text{Et}_2\text{AlCl}_2^-$ with EtAlCl_2 .

There is precedence for aluminum moieties behaving in this manner, as asymmetric bridge cleavage of aluminum-chloro dimers was previously reported by Atwood et al. in the generation of the Cl_2Al^+ cation.¹² Disproportionation

(12) (a) Means, N. C.; Means, C. M.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* 1987, 26, 1466. (b) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* 1985, 107, 1796.

of alkylaluminum halides resulting in mixed alkyl-halo-bridged dimers has been observed in this laboratory.¹³ Moreover, Atwood et al. reported that the related Me_2Al^+ ion was stabilized by 18-crown-6 in the $[\text{Me}_2\text{Al}\cdot 18\text{-crown-6}]^+$ cation.¹⁴ Indeed, the same anion that was isolated in our system, $[\text{EtAlCl}_3]^-$, was isolated as the anion of $[\text{Cl}_2\text{Al}\cdot 18\text{-crown-6}]^+$.¹⁵

This study indicates that the chemistry of mixed-donor crown ethers differs substantially from that of non-mixed-donor crown ethers. Moreover, the coordination chemistry of aluminum in these systems is quite unpredictable. This study will be used as a bench mark as we continue to explore the organoaluminum chemistry of mixed-donor crown ethers.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (Grant No. RII-8520554).

Supplementary Material Available: A summary of data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (12 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(13) (a) Moise, F.; Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* 1990, 21, 129. (b) Sangokoya, S. A.; Moise, F.; Pennington, W. T.; Self, M. F.; Robinson, G. H. *Organometallics* 1989, 8, 2584. (c) Robinson, G. H.; Sangokoya, S. A. *Organometallics* 1988, 7, 1453.

(14) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 485.

(15) Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom.* 1984, 2, 367.

Silylformylation of 1-Hexyne Catalyzed by Rhodium-Cobalt Mixed-Metal Carbonyl Clusters

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Summary: Reactions of hydrosilanes with 1-hexyne catalyzed by $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ at 25 °C and atmospheric pressure-150 psi of carbon monoxide give (*Z*)-1-silyl-2-formyl-1-hexenes (**1**), which are the products of "silylformylation", and/or (*E*)-1-silyl-1-hexenes (**2**). The ratio of silylformylation vs hydrosilylation products depends on the electronic nature of hydrosilane used. Depending on the conditions, the reaction gives 2,4-di-*n*-butyl-3-silylcyclopent-2-en-1-one (**3**) as a major side product, which is a unique carbometalation-cyclization product. The novel Rh-Co mixed-metal complexes $(\text{PhMe}_2\text{Si})_2\text{Rh}(\text{CO})_n\text{Co}(\text{CO})_4$ ($n = 2, 3$); **6a** and $\text{RhCo}(n\text{-BuC}\equiv\text{CH})(\text{CO})_5$ (**7**) are found to be important catalyst species for silylformylation catalyzed by $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$. Possible catalytic cycles of silylformylation that can accommodate the observed results are proposed.

The silicon version of hydroformylation of olefins is known as "silylcarbonylation", discovered by Murai et al.,³ which is promoted by $\text{Co}_2(\text{CO})_8$ to give silyl enol ethers of homologous aldehydes. In Murai's silylcarbonylation, the silicon moiety always attaches to oxygen; viz., any silicon migration to the olefinic bond to form a silicon-carbon bond is not observed at all. As a part of our study on the catalysis of Co-Rh mixed-metal complexes such as $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{CoRh}(\text{CO})_7$,^{4,5} we have been investigating the reactions of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{CoRh}(\text{CO})_7$ with hydrosilanes in the presence and absence of carbon monoxide and/or substrates to determine the active sites of these Co-Rh mixed-metal catalyst systems by identifying active catalyst species as well as intermediates for catalytic cycles. In order to examine possible synergistic effects in the Co-Rh mixed systems, $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ have also been used as references.

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(3) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 837 and references cited therein.

(4) Ojima, I. *Chem. Rev.* 1988, 88, 1011 and references cited therein.

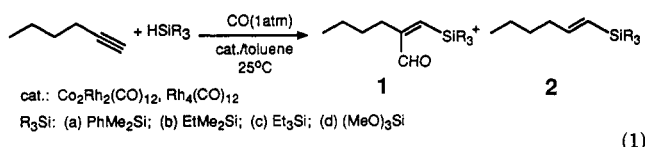
(5) Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horváth, I. T. *J. Am. Chem. Soc.* 1988, 110, 150.

Table I. Reactions of Hydrosilanes with 1-Hexyne Catalyzed by $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$ in the Presence of Carbon Monoxide^a

entry no.	catalyst	hydrosilane	condition ^b	yield, ^c %	product ratio ^d	
					1	2
1	$\text{Co}_2\text{Rh}_2(\text{CO})_{12}$	HSiMe_2Ph	A	72	100	
2			B	92	100	
3		HSiMe_2Et	A	48	60	40
4			B	84	100	
5	HSiEt_3	HSiEt_3	A	63	58	42
6			B	80	93	7
7		HSi(OMe)_3	A	86	20	80
8			B	95	38	62
9	$\text{Rh}_4(\text{CO})_{12}$	HSiMe_2Ph	A	72	100	
10			B	76	100	
11		HSiMe_2Et	A	61	65	35
12			B	80	91	9
13		HSiEt_3	A	65	65	35
14			B	77	86	14
15		HSi(OMe)_3	A	76		100
16			B	80		100

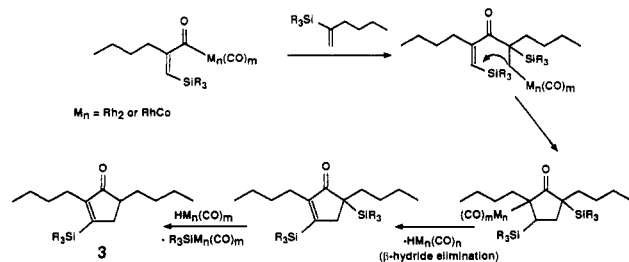
^aAll reactions were run with 5.0 mmol of 1-hexyne, 5.5 mmol of a hydrosilane, and 5.0×10^{-3} mmol of a catalyst in toluene (7.5 mL) at 25 °C for 24 h. ^bCondition A: reaction was carried out at ambient pressure of carbon monoxide in a Schlenk reactor. Condition B: reaction was carried out under 150 psi of carbon monoxide in a stainless steel autoclave with a Pyrex reaction vessel (50 mL). ^cYield was determined by GLC analysis based on 1-hexyne consumed. ^dDetermined by GLC analyses.

When the hydrosilylation of 1-hexyne with triethylsilane catalyzed by $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ was carried out at 25 °C in the presence of carbon monoxide (ambient pressure) in toluene, we found that (*Z*)-1-(triethylsilyl)-2-formyl-1-hexene (**1c**) was formed in addition to the usual hydrosilylation product, (*E*)-1-(triethylsilyl)-1-hexene (**2c**; **1c**/**2c** = 53/47), and a small amount of 2,4-di-*n*-butyl-3-(triethylsilyl)-cyclopent-2-en-1-one (**3c**), a novel carbometalation-cyclization product.⁶ It was also found that dimethyl-



phenylsilane gave **1a** as the exclusive 1:1 product under the same reaction conditions, although the formation of small amounts of **3a**⁶ and hydrosilylation products of **1a** (**4a**, **5a**) were detected.⁷ This reaction yielding the com-

(6) The structure of **3** was unambiguously assigned on the basis of its ¹H and ¹³C NMR, 2D NMR (COSY, NOESY), FT-IR, and MS spectra and elemental analyses, e.g., **3c**: ¹H NMR (CDCl₃) δ 0.77 (m, 6 H), 0.82–1.02 (m, 15 H), 1.29 (m, 5 H), 1.39 (m, 2 H), 1.58 (m, 2 H), 1.78 (m, 1 H), 2.25 (dd, *J* = 2.9, 19.0 Hz, 1 H), 2.29 (m, 1 H), 2.48 (t, *J* = 7.5 Hz, 2 H), 2.76 (dd, *J* = 7.5, 19.0 Hz, 1 H); ¹³C NMR (CDCl₃) δ 3.5, 7.5, 14.0, 22.7, 23.0, 29.6, 30.8, 31.43, 34.0, 39.6, 46.5, 136.2 (=CSi), 189.2 (=CCO), 216.4 (CO); FT-IR (neat) 1688 (ν_{CO}), 1584 (ν_{C=C}) cm⁻¹; GCMS (*m/e*) 308 (M⁺, 1), 279 (M⁺ - 29, 100). Anal. C, H. A possible mechanism for the formation of **3** is



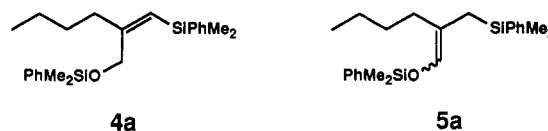
pound **1** from an alkyne is a new type of silylcarbonylation, i.e., "silylformylation", which is different from Murai's reaction. While our study was in progress,⁸ Matsuda et al. reported the discovery of silylformylation catalyzed specifically by $\text{Rh}_4(\text{CO})_{12}$ using a variety of alkynes and dimethylphenylsilane as the specific hydrosilane at 100 °C and 150–450 psi of carbon monoxide in the presence of triethylamine.⁹ We describe here our Co–Rh mixed-metal version of the silylformylation with a preliminary mechanistic study that unveiled the presence of $(\text{R}_3\text{Si})_2\text{Rh}(\text{CO})_n\text{Co}(\text{CO})_4$ (**6**; *n* = 2, 3) and $\text{RhCo}(\text{n-BuC}\equiv\text{CH})(\text{CO})_5$ (**7**) as key active catalyst species for the reaction.

We carried out the reactions of 1-hexyne with a variety of hydrosilanes in toluene at 25 °C and ambient pressure or 150 psi of carbon monoxide in the presence of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ (substrate/cat. = 1000) for 24 h; $\text{Rh}_4(\text{CO})_{12}$ was also employed for comparison purposes. Results are summarized in Table I.

As Table I shows, the structure of hydrosilane exerts a marked influence on the selectivity of the reaction, i.e., silylformylation vs hydrosilylation. Trimethoxysilane clearly favors hydrosilylation, whereas dimethylphenylsilane gives the silylformylation product exclusively, and trialkylsilanes give a ca. 40/60 mixture of the hydrosilylation and silylformylation products. At 25 °C and ambient pressure of carbon monoxide, the reaction catalyzed by $\text{Rh}_4(\text{CO})_{12}$ is substantially faster than that catalyzed by $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$, although the ratio of the hydrosilylation vs silylformylation is very similar. In both cases, considerable amounts of **3–5** are formed. At 25 °C and 150 psi of carbon monoxide, however, $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ acts as an excellent catalyst, giving the silylformylation product (**1**) with 93–100% selectivity (entries 2, 4, and 6), except the case with HSi(OMe)_3 (entry 8). The formation of **3–5** is also substantially decreased. Under the same conditions, the $\text{Rh}_4(\text{CO})_{12}$ -catalyzed reactions give a larger amount of **3–5** compared with the $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ -catalyzed ones, and HSi(OMe)_3 does not give any silylformylation product **1** (entry 16). As $\text{Co}_2(\text{CO})_8$ is found to be virtually inactive even under forced conditions, it is apparent that there is a synergistic effect in the Co–Rh mixed-metal system.

The regio- and stereochemistry of both silylformylation and hydrosilylation are worthy of mention. It is found that all silylformylation products **1** have a (*Z*)-1-silyl-2-formyl structure; i.e., the reaction is extremely regioselective as well as stereoselective. All hydrosilylation products **2** turn out to be (*E*)-isomers exclusively. This is in sharp contrast to the reported rhodium-complex-catalyzed hydrosilylation of 1-alkynes,¹⁰ which gives a mixture of the *Z* isomer

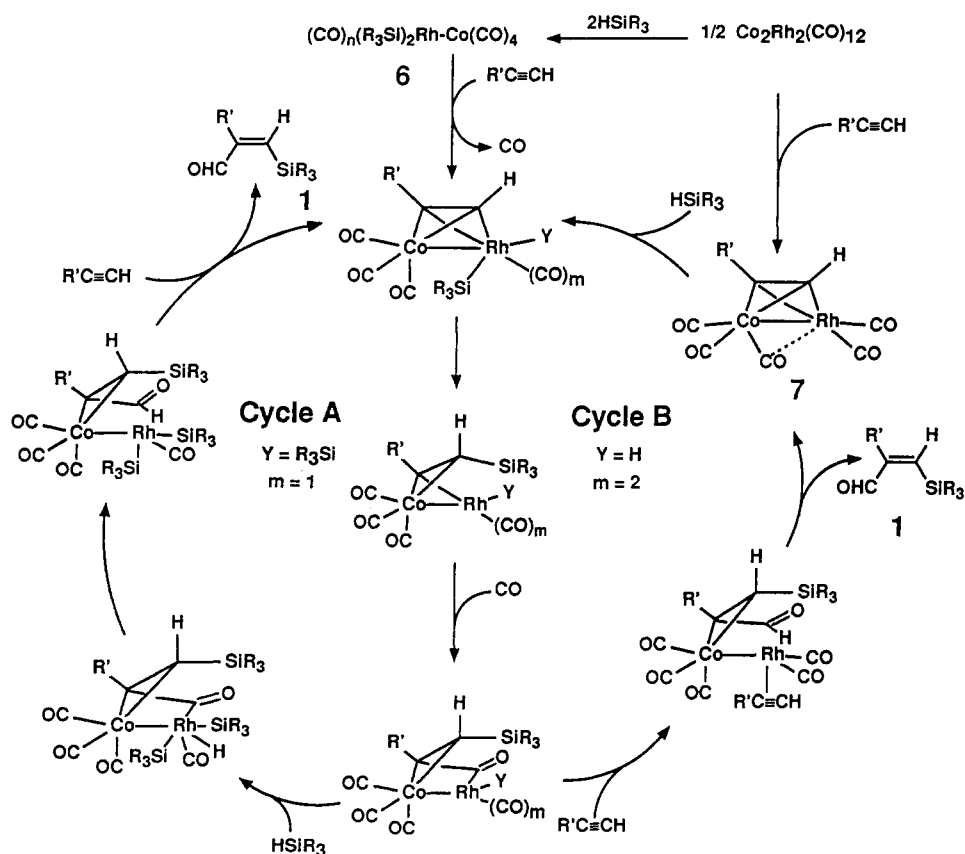
(7) There are two types of silylformylation–hydrosilylation products:



4a is formed via 1,2-addition of PhMe_2SiH to **1a**, while **5a** arises from 1,4-addition of the hydrosilane to **1a** as a mixture of *E* and *Z* isomers.

(8) (a) Ojima, I. 22nd Organosilicon Symposium, April 7–8, 1989, Philadelphia, PA; Abstracts, Plenary 7. (b) Ingallina, P.; Clos, N.; Ojima, I. 23rd Organosilicon Symposium, April 20–21, 1990, Midland, MI; Abstracts G2. (c) Ojima, I.; Ingallina, P.; Clos, N. Abstracts of Papers, 199th American Chemical Society National Meeting, April 22–27, 1990, Boston, MA; American Chemical Society: Washington, DC, 1990; INOR 206.

(9) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332.

Scheme I. Proposed Mechanisms for the $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ -Catalyzed Silylformylation and Hydrosilylation of 1-Alkynes

(major) and *E* and α -isomers (minor).

As for the mechanism of silylformylation, the following facts should be taken into account: silylformylation must include (a) a silicon shift from the catalyst metal to an alkyne to form a 2-silyl-1-alkenyl-RhCo complex, (b) subsequent formation of a 3-silyl-2-alkenyl-RhCo complex, (c) formation of a 3-silyl-2-alkenyl-RhCo hydride, and (d) reductive elimination to give the silylformylation product 1. In order to obtain structural information about active catalyst species in the silylformylation, first we looked at the reaction of hydrosilanes with $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$. It was found that the tetrametallic cluster (deep reddish brown) was converted to a Co-Rh mixed bimetallic complex (pale yellow) during the reaction.¹¹ When a hydrosilane (4 equiv) was allowed to react with $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ under a carbon monoxide atmosphere in organic solvent, e.g., chloroform-*d* and *n*-hexane, at ambient temperature for 1 h, novel $(\text{R}_3\text{Si})_2\text{Rh}(\text{CO})_n\text{-Co}(\text{CO})_4$ complexes (**6**) were quantitatively formed.¹² When the reaction was carried

out under nitrogen, **6-A** ($n = 2$) was selectively formed.¹² The bis(silyl)-RhCO structure of **6** is proposed on the basis of the following facts: (i) the number of silyl groups on the rhodium metal was unambiguously determined to be 2 by titration with ferrocene as the internal standard (¹H NMR), (ii) the ¹H NMR spectra of **6** ($\text{R}_3\text{Si} =$ (a) PhMe_2Si , (c) Et_3Si) do not show any Rh-H signals (δ 0 to -20 ppm) and the FT-IR spectra of **6a,c**, prepared from $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ with PhMe_2SiD and Et_3SiD , respectively, do not show any Rh-D stretching band at all in the expected region (1600–1450 cm^{-1}), and (iii) the silyl groups were replaced by RNC ($\text{R} = t\text{-Bu}$, cyclohexyl, 2,6-dimethylphenyl) to form $[(\text{RNC})_4\text{Rh}]^+[\text{Co}(\text{CO})_4]^-$.¹³ These results clearly indicate that **6** is generated through oxidative addition of two molecules of hydrosilanes to a rhodium followed by evolution of molecular hydrogen. These bis(silyl)-RhCo complexes **6** are stable in *n*-hexane under carbon monoxide for more than 1 week at ambient temperature but rather unstable under nitrogen and/or in chloroform, decomposing slowly.

We carried out the reaction of $(\text{PhMe}_2\text{Si})_2\text{Rh}(\text{CO})_n\text{-Co}(\text{CO})_4$ (**6a-A,B**) with 1 equiv of 1-hexyne at 25 °C and ambient pressure of carbon monoxide for 30 min (eq 2). The ¹H NMR monitoring of the reaction clearly demonstrated the formation of **1a** (with 5% *E* isomer) accompanied by a small amount of **6a-B** (**6a-A** disappeared) and a mixed-metal butterfly complex, $\text{Rh}_2\text{Co}_2(n\text{-BuC}\equiv\text{CH})(\text{CO})_{10}$ (**8**),¹⁴ which strongly suggests that **6a** is an active

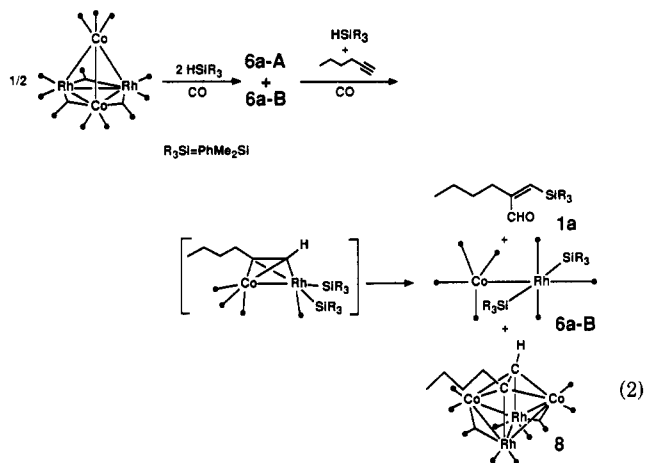
(10) E.g.: (a) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* 1974, 66, C14. (b) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *Ibid.* 1978, 161, 91. (c) Brady, K. A.; Nile, T. A. *Ibid.*, 1981, 206, 299. (d) Ojima, I.; Ingallina, P.; Clos, N.; Donovan, R. J. *Abstracts of Papers*, 199th American Chemical Society National Meeting, April 22–27, 1990, Boston, MA; American Chemical Society: Washington, DC, 1990; INOR 205.

(11) The reaction of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ with 1-alkynes in the absence of hydrosilane gave the corresponding purple butterfly cluster complexes $\text{Co}_2\text{Rh}_2(\text{CO})_{10}(\text{RC}\equiv\text{CH})$ ($\text{R} = n\text{-Bu}$, Ph, Me_2Si). The structure of a triphenylphosphine complex, $\text{Co}_2\text{Rh}_2(\text{CO})_9(n\text{-BuC}\equiv\text{CH})(\text{PPh}_3)$, was determined by X-ray crystallography: (a) Clos, N. Dissertation, State University of New York at Stony Brook, 1989. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. To be submitted for publication.

(12) **6a-A**: FT-IR (hexane) 2091 m, 2074 w, 2029 ms, 1997 vs cm^{-1} ; ¹H NMR (CDCl_3) δ 0.89 (s, 6 H), 7.40 (m, 3 H), 7.65 (m, 2 H). **6a-B**: FT-IR (hexane) 2100 m, 2047 m, 2015 s, 1997 vs cm^{-1} ; ¹H NMR (CDCl_3) δ 0.81 (s, 6 H), 7.40 (m, 3 H), 7.55 (m, 2 H). **6b-A**: FT-IR (hexane) 2090 m, 2074 w, 2028 ms, 1995 vs cm^{-1} . **6b-B**: FT-IR (hexane) 2100 m, 2045 m, 2013 s, 1995 vs cm^{-1} . **6c-A**: FT-IR (hexane) 2090 m, 2068 s, 2027 ms, 1995 vs cm^{-1} . **6c-B**: FT-IR (hexane) 2099 ms, 2044 m, 2013 s, 1995 vs cm^{-1} .

(13) Those complexes were fully characterized by spectroscopy as well as on the basis of satisfactory elemental analyses. One of the complexes ($\text{R} = 2,6\text{-dimethylphenyl}$) was also characterized by single-crystal X-ray analysis: Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. To be submitted for publication.

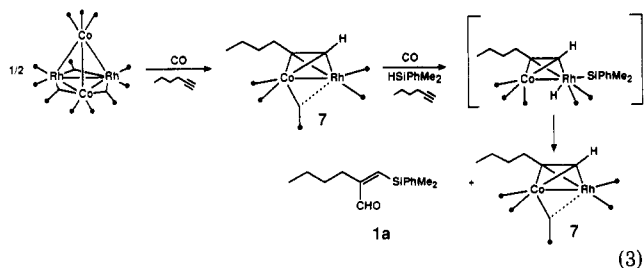
(14) Because of its characteristic bridgehead methine proton (δ 8.85 ppm) and propargylic methylene (δ 2.74 ppm), it is easy to identify the Rh-Co mixed-metal butterfly complex **8**.¹¹



catalyst species or its direct precursor.

Next, we looked at the reaction of $Co_2Rh_2(CO)_{12}$ with 1-hexyne under carbon monoxide. The reaction of $Co_2Rh_2(CO)_{12}$ with 2 equiv of 1-hexyne at 25 °C and 75 psi of carbon monoxide in hexane for 6 h gave a novel Rh-Co mixed bimetallic alkyne complex bearing a semibridging carbonyl (ν_{CO} 1935 cm^{-1}), $RhCo(n-Bu-C\equiv CH)(CO)_5$ (7), as the major product, which was isolated through column chromatography on silica gel under carbon monoxide as a reddish orange solid.¹⁵ Complex 7 was then allowed to react with 6 equiv of dimethylphenylsilane and 4 equiv of 1-hexyne at 25 °C and ambient pressure of carbon monoxide in chloroform for 1 h to give cleanly the silylformylation product 1a; viz., the 1H NMR spectrum of the reaction mixture only shows 1a, 7, and unreacted hydrosilane (eq 3). This result clearly indicates that 7 is an active catalyst species or its direct precursor.

Accordingly, there are two possible catalytic cycles for silylformylation at present, and either one or both catalytic cycles may be operative depending on the reaction conditions. Mechanisms for the silylformylation of 1-hexyne



with $Co_2Rh_2(CO)_{12}$ as the catalyst precursor, which can accommodate all the observations described above, are proposed in Scheme I.

It should be noted that the unique bis(silyl)-RhCO complex 6 and alkyne-RhCo complex 7 are identified as the key catalytic species for silylformylation of a 1-alkyne. Although the insertion of carbonyl compounds or imines into silicon-transition-metal bonds is known in rhodium-complex-catalyzed hydrosilylations, that of alkynes and alkenes in catalysis has not been reported under thermal reaction conditions.¹⁶ Our results present the first examples of such a process in catalysis by taking advantage of the unique properties of the Co-Rh mixed bimetallic system. Also, it is noteworthy that the silylformylation of alkynes catalyzed by Co-Rh mixed-metal systems is very likely to involve "homogeneous bimetallic catalysis".

Further study on the mechanism and applications of silylformylation promoted by Rh-Co mixed-metal catalysts is actively underway.

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

Supplementary Material Available: Typical procedures for eqs 1-3, identification data for silylformylation products 1, and 1H spectra of the reaction mixtures for eqs 2 and 3 (3 pages). Ordering information is given on any current masthead page.

(15) 7: orange solid; FT-IR (hexane) 2076 m, 2058 s, 2018 vs, 1934 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.95 (m, 3 H), 1.10-1.85 (m, 4 H), 2.38 (m, 1 H), 3.23 (m, 1 H), 5.64 (s, 1 H); ^{13}C NMR δ 13.8, 22.4, 34.1, 42.0, 93.4 (m, $\equiv CH$), 167.5 ($\equiv CBu^n$), 175.8 (d, $J = 32.7$ Hz, Rh-CO), 178.2 (d, $J = 83.9$ Hz, Rh-CO), 203 (br). Anal. C, H.

(16) Recently, we found the selective insertion of 1-alkynes into an Rh-Si bond in rhodium-complex-catalyzed hydrosilylation. See: Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics*, in press.

Ruthenium Amine and Amide η^5 -Cyclopentadienyl Complexes Having Monodentate Phosphines, Phosphites, or 1,2-Bis(dicyclohexylphosphino)ethane as Supporting Ligands

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Summary: Reacting $(\eta^5-cp)RuCl(PPh_3)_2$ with $Cy_2PCH_2CH_2PCy_2$ and then $AgCF_3SO_3$ and ammonia gives $[(\eta^5-cp)Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, which reacts with H^- to give $(\eta^5-cp)Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$. Similar synthetic strategies have been used to prepare $[(\eta^5-cp)Ru(NH_3)(PPh_3)_2]CF_3SO_3$, $[(\eta^5-cp)Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$, and $[(\eta^5-cp)Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, the first two of which have been confirmed by X-ray crystallography.

Monomeric organotransition-metal compounds containing a terminal unsubstituted NH_2 ligand are uncommon.¹ One reason for this scarcity is the ease with which such complexes undergo substitution oligomerization with

(1) For example see: Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* 1989, 95, 1-40. Bryndza, H. E.; Tam, W. *Chem. Rev.* 1988, 88, 1163-1188. Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* 1987, 26, 3972-3974. Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercau, J. E. *Organometallics* 1988, 7, 1309-1312.