J. Am. Chem. Soc. **1998,** *120,* 6965−6979 6965

Mechanistic and Synthetic Studies of the Addition of Alkyl Aldehydes to Vinylsilanes Catalyzed by Co(I) Complexes

Christian P. Lenges, Peter S. White, and Maurice Brookhart*

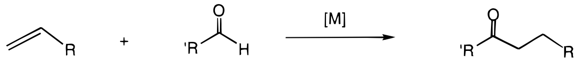
Contribution from the Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Received February 23, 1998

Abstract: The mechanistic details of the cobalt-catalyzed intermolecular hydroacylation reaction have been investigated using kinetic, spectroscopic, and crystallographic methods. The Co(I) bisolefin complex **1**, [$C_5Me_5Co(C_2H_3SiMe_3)_2$], was shown to catalyze the addition of a series of alkyl aldehydes (**2a−l**) to vinylsilanes to give the corresponding ketones with exclusive anti-Markovnikov selectivity under mild conditions. The catalytic cycle exhibits two resting states, complex **1** and a bisalkyl carbonyl complex, [$C_5Me_5Co(CO)(R)(R')$], **4a−l** which are in equilibrium. Kinetic investigations along with low-temperature NMR spectroscopy establish a sensitive balance between resting states during catalysis which is strongly dependent on substrate structure. The turnover-limiting step was established as the reductive elimination of ketone from intermediate **4**. Using ferrocenecarboxaldehyde (Fc-C(O)H), **2l**, as substrate, the intermediate **4l** [$C_5Me_5Co(CO)(Fc)(CH_2CH_2SiMe_3)$] was isolated at low temperatures and characterized by X-ray crystallography. Complex **4l** was used to study the carbon−carbon bond-forming step directly by thermolysis in the presence of a trapping ligand L ($P(OMe)_3$, PMe_3). Kinetic analysis showed competitive ligand dependent and ligand independent pathways for ketone formation. Deuterium scrambling, isomerization of aldehydes prior to ketone formation, and production of isomeric ketones in certain cases establish that complex isomerization processes occur prior to productive ketone elimination from **4**. A detailed mechanism accounting for all observations is proposed. Catalyst deactivation was shown to involve primarily decarbonylation to yield [$C_5Me_5Co(CO)]_2$ and [$C_5Me_5Co(CO)(C_2H_3SiMe_3)$]. When excess aldehyde is present, catalytic aldehyde dimerization occurs to give esters.

Introduction

The selective activation of a C−H bond by a transition metal complex followed by the functionalization of the activated substrate has been an area of intensive research. One of the few catalytic processes reported which successfully combines C−H bond activation with C−C bond formation[1−10] is the hydroacylation[11−27] of olefins to generate ketones.



The most thoroughly studied example of this reaction has been the intramolecular hydroacylation of 4-pentenals to generate cyclopentanones using a cationic Rh(I) catalyst described by Bosnich and co-workers.[28−33] The mechanism of intramo-

---

(1) Kim, Y. H.; Kang, J.-B.; Lim, Y.-G. *J. Chem. Soc., Chem. Commun.* **1994**, 2267.

(2) (a) Jones, W. D.; Duttweiler, R. P.; Feher, F. J. J.; Hessell, E. T. *New J. Chem.* **1989**, *13*, 725−736. (b) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047−5048.

(3) Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147−1150.

(4) Shul′pin, G. B.; Shilov, A. E. *Chem. Rev.* **1997**, *97*, 2879−2932.

(5) Jordan, R.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778.

(6) Murai, S.; Chatani, N.; Ie, Y.; Kakiuchi, F. *J. Org. Chem.* **1997**, *62*, 2604−2610.

(7) Murai, S.; Kakiuchi, F.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62−83.

(8) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature (London)* **1993**, *366*, 529.

(9) Murai, S.; Chatani, N.; Yamada, A.; Kakiuchi, N.; Fujii, N. *Chem. Lett.* **1997**, 425.

(10) Trost, B. M.; Imi, K.; Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371.

(11) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.

(12) Watanabe, Y.; Tsuji, Y.; Kondo, T. *Tetrahedron Lett.* **1987**, *28*, 6229−6230.

(13) Watanabe, Y.; Tsuji, Y.; Kondo, T.; Akazome, M. *J. Org. Chem.* **1990**, *55*, 1286−1291.

(14) Sneeden, R. P. A.; Denise, B.; Isnard, P. *J. Organomet. Chem.* **1982**, *240*, 285−288.

(15) Marder, T. B.; Roe, C. D.; Milstein, D. *Organometallics* **1988**, *7*, 1451−1453.

(16) Sakai, K.; Suemune, H.; Ichikawa, Y.; Xie, Z.-F. *Chem. Pharm. Bull.* **1987**, *35*, 1812−1816.

(17) Sakai, K.; Kawahara, T.; Suemune, H. *Chem. Pharm. Bull.* **1986**, *34*, 550−557.

(18) Sakai, K.; Oda, O. *Tetrahedron Lett.* **1972**, 4375−4376.

(19) Sakai, K.; Ide, J.; Oda, O.; Nakamura, N. *Tetrahedron Lett.* **1972**, 1287−1290.

(20) Miller, R. G.; Campbell, R. E.; Lochow, C. F.; Vora, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 5824−5830.

(21) Miller, R. G.; Lochow, C. F.; Krishnakant, P. V. *J. Organomet. Chem.* **1980**, *192*, 257−264.

(22) Miller, R. G.; Lochow, C. F. *J. Am. Chem. Soc.* **1976**, *98*, 1281−1283.

(23) Larock, R. C.; Potter, G. F.; Oertle, K. *J. Am. Chem. Soc.* **1980**, *102*, 190−197.

(24) James, B. R.; Young, C. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1215−1216.

(25) Gable, K. P.; Benz, G. A. *Tetrahedron Lett.* **1991**, *32*, 3473−3476.

(26) Vinogradov, M. G.; Tuzikov, A. B.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, *11*, 2557−2562.

(27) Vinogradov, M. G.; Tuzikov, A. B.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, *7*, 1686−1687.

(28) Bosnich, B.; Barnhart, R. W. *Organometallics* **1995**, *14*, 4343−4348.

(29) Bosnich, B.; Fairlie, D. P. *Organometallics* **1988**, *7*, 936−945.

(30) Bosnich, B.; Fairlie, D. P. *Organometallics* **1988**, *7*, 946−954.

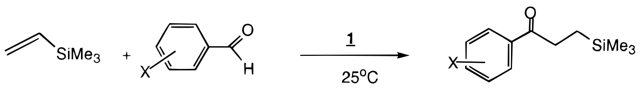
(31) Bosnich, B.; Whelan, J.; Bergens, S. H.; Noheda, P.; Wang, X.; Barnhart, R. W. *Tetrahedron* **1994**, *50*, 4335−4346.

(32) Bosnich, B.; Wang, X. *Organometallics* **1994**, *13*, 4131−4133.

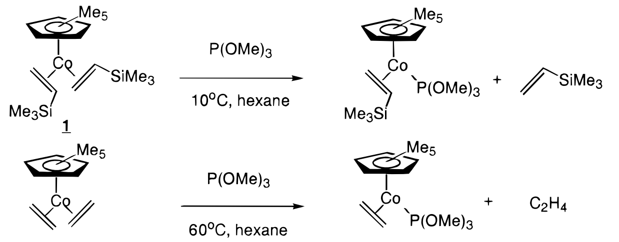
S0002-7863(98)00610-6 CCC: $15.00 © 1998 American Chemical Society
Published on Web 07/07/1998

lecular hydroacylation was investigated in detail for this system using labeling studies and product analysis. However, this catalyst system is quite specific for intramolecular hydroacylation and in this case for the formation of cyclopentanones. The intermolecular version of this reaction has been reported for only a few examples with, in general, reduced activity.[11−15,34] Marder, Milstein, and Roe[15] reported a system which involves use of the indenylrhodium ethylene complex $[(C_8H_7)Rh(C_2H_4)_2]$ as a catalyst for the addition of benzaldehyde to ethylene under quite severe conditions (1000 psi of C_2H_4, 100 °C, 12 h). About 5 TO were observed in the conversion of benzaldehyde to propiophenone with this system. Recently Jun et al. have reported a procedure using a Rh(I)−phosphine catalyst in combination with 2-aminopyridines to effect intermolecular hydroacylations. The intermediate formation of a pyridineimine is proposed to facilitate the catalysis; however, mechanistic details are scarce.[34]

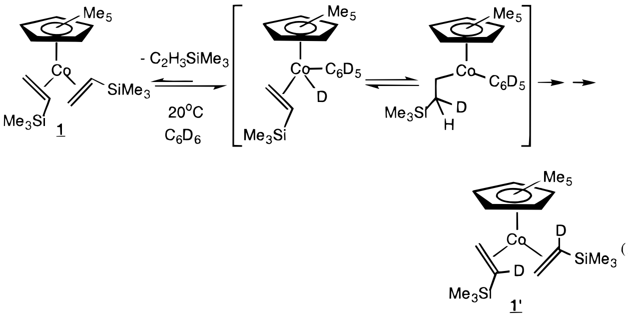
We have reported the intermolecular hydroacylation of vinylsilanes by aromatic aldehydes using a cobalt(I) bisolefin complex as catalyst.[35]



Key mechanistic features of this catalysis using cobalt complex **1** $[C_5Me_5Co(C_2H_3SiMe_3)_2]$ were investigated. Complex **1** is the resting state throughout catalysis; a first-order dependence of the turnover process on aldehyde concentration and an inverse first-order dependence on olefin concentration were discovered. Crucial for these catalytic hydroacylations was the lability of the bulky trimethylsilyl-substituted olefin.[36−38] For example, **1** reacts readily with $P(OMe)_3$ below room temperature to generate the monophosphite adduct.[39] The corresponding bisethylene complex, $[C_5Me_5Co(C_2H_4)_2]$, shows the same reactivity in the course of 1 h at 60 °C,[40] and attempts to carry out hydroacylations of ethylene or strongly binding olefins such as styrene were unsuccessful.

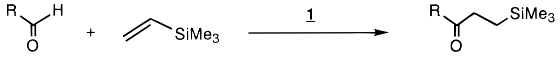


Due to the increased reactivity toward dissociative olefin loss, we were able to investigate the reactivity of the accessible 16-electron cobalt(I) system, $[C_5Me_5Co(C_2H_3SiMe_3)]$, toward other C−H bonds. Recently we reported that Co(I) complex **1** exhibits H/D exchange in C_6D_6 at room temperature via a Co(III) intermediate produced from oxidative addition of benzene to a Co(I) species (eq 1).[39]



(1)

In this paper we report the activity of **1** as a catalyst for the hydroacylation of vinyl silanes using a variety of aliphatic aldehydes (eq 2). Significant differences are observed in the hydroacylation of aliphatic aldehydes in comparison to aromatic aldehydes. On the basis of a kinetic analysis as well as in situ NMR spectroscopic studies and X-ray analysis of an intermediate during catalysis, the catalyst resting states have been identified. Kinetic results in combination with labeling experiments allow formulation of a mechanism for this complex transformation which can explain deactivation routes as well as the formation of isomeric products from certain substrates in this catalytic process.



(2)

2a-k **3a-k**

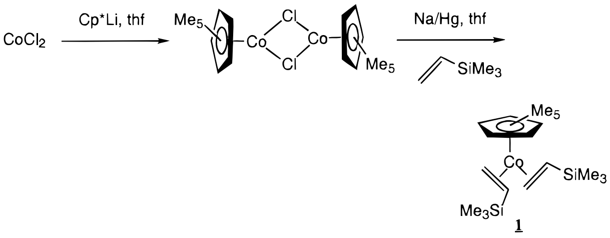
R =

a: -Et
b: -n-Pr
c: $-CH_2CHMe_2$
d: $-CH_2CHMePh$
e: $-CH_2CHMeCH_2CH{=}CMe_2$
f: $-CH_2CMe_3$
g: $-CHMe_2$
h: $-C_6H_{11}$
i: $-CMe_3$
k: $-CH_2CH_2SiMe_3$

Results and Discussion

A. Synthesis and Structure of $[C_5Me_5Co(C_2H_3SiMe_3)_2]$, 1.

The cobalt(I) complex **1** was prepared in a two-step synthesis (eq 3) starting from $CoCl_2$ using a modified procedure based on the reported synthesis of the parent Co(I)−bisethylene complex $[C_5Me_5Co(C_2H_4)_2]$.[41,42]



(3)

Suitable crystals for an X-ray structure determination were grown from an acetone solution of **1** at −78 °C. As shown in

---

(33) (a) Bosnich, B.; Whelan, J.; Bergens, S. H.; Noheda, P.; Wang, X.; Barnhart, R. W. *J. Am. Chem. Soc.* **1994**, *116*, 1821−1830. (b) Bosnich, B.; Barnhart, R. W.; McMorran, D. A. *Inorg. Chim. Acta* **1997**, *263*, 1−7.

(34) Jun, C.-H.; Lee, H.; Hong, J.-B. *J. Org. Chem.* **1997**, *62*, 1200. Aminopyridines are used in this Rh catalyst system as cocatalysts for intermolecular hydroacylation.

(35) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 3165.

(36) This notion is supported by the observation of Spencer[37] that the corresponding bispropene complex $[C_5Me_5Co(C_2H_3Me)_2]$ is only stable in the presence of excess propene in solution and highly reactive toward ligand substitution reactions: on the other hand, the parent bisethylene Co(I) complex $[C_5Me_5Co(C_2H_4)_2]$ is more resistant toward ligand substitution.

(37) Spencer, J. L.; Beevor, R. G.; Frith, S. A. *J. Organomet. Chem.* **1981**, *221*, C25−C27.

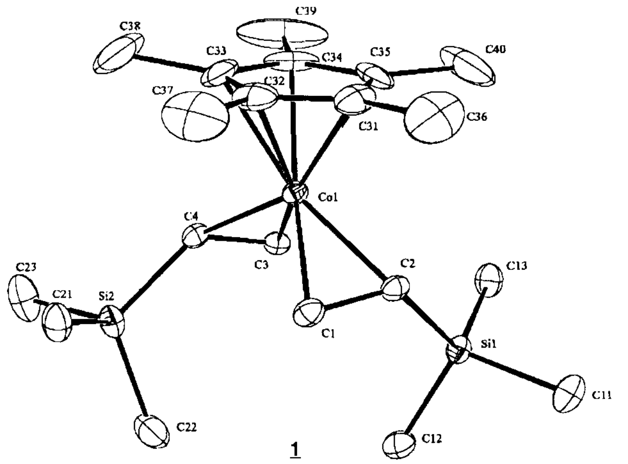
(38) (a) Boennemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (b) Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214−2221.

(39) Lenges, C. P.; Brookhart, M.; Grant, B. E. *J. Organomet. Chem.* **1997**, *528*, 199−203.

(40) Brookhart, M.; Grant, B.; Volpe, A. *Organometallics* **1992**, *11*, 3920−3922.

(41) Koelle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980−987.

(42) Koelle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131−132.



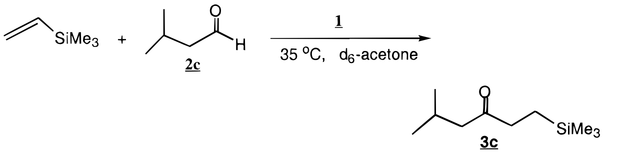
1

Figure 1. ORTEP view of $[C_5Me_5Co(C_2H_3SiMe_3)_2]$ (**1**). All atoms are drawn at 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): C1−C2 1.404(4); Co−C1 2.002(3); Co−C2 2.058(3); C2−Si1 1.865(3); C3−C4 1.414(4); Co−C3 2.018(3); Co−C4 2.065(3); C4−Si2 1.855(3); C1−Co−C2 40.43(12); C1−Co−C3 97.71(12); C1−Co−C4 95.20(12); C2−Co−C4 115.55(11); Si1−C2−C1 128.11(15).

the ORTEP diagram[43] (Figure 1), the arrangement of the coordinated trimethylvinylsilane ligands generates a C_2-symmetric structure which is consistent with the simple ^{1}H NMR spectrum of **1**.

The carbon−carbon double bond length of the coordinated olefin of 1.40 Å (C_1−C_2) is characteristic for a low-valent olefin complex in which back-bonding from filled metal d-orbitals is dominant in olefin binding.[44−47] The Co−C olefin distances are very similar; however, the length of Co−C_2, the carbon bearing the trimethylsilyl group, is slightly elongated, reflecting the steric influence of this substituent. The angles C1−Co−C3 (97.7°) and C2−Co−C4 (115.6°) indicate a twist in the coordinated olefin in support of this assignment. Other isomers with alternative orientations of the coordinated olefins are not observed.[48]

B. Hydroacylation of Isovaleraldehyde. Mechanistic Considerations. Complex **1** is an active catalyst for the hydroacylation of trimethylvinylsilane using a variety of simple alkyl aldehydes. Detailed kinetic studies of the turnover process have been carried out with isovaleraldehyde as a representative aldehyde. These studies are described in this section, followed in the next section by a survey of the reactivity of other alkyl aldehydes. A series of ^{1}H NMR experiments were performed in which the catalytic addition of isovaleraldehyde to trimethylvinylsilane to form ketone **3c** (eq 4) was followed with time.

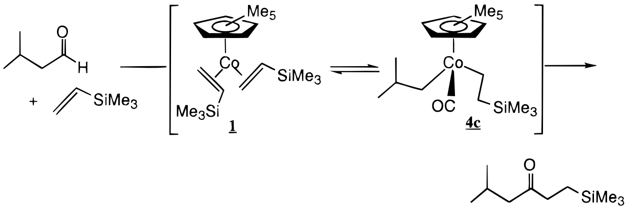


(4)

Table 1. Hydroacylation of Isovaleraldehyde with Vinyltrimethylsilane. Substrate Dependence of TOF and Ratio of Co Complexes **1** to **4c** during Catalysis

entry	aldehyde	olefin	ratio A:O	ratio **4c**:**1**	TOF [TO/h]	concn of **4c** [mol/L]
1	40	20	2	3.3	3.75	0.0162
2	40	20	2	3.4	3.75	0.0163
3	30	20	1.5	2.7	3.35	0.0154
4	40	40	1	1.8	3.00	0.0136
5	30	30	1	2.0	3.00	0.0141
6	20	20	1	2.3	2.80	0.0147
7	20	20	1	2.1	2.95	0.0143
8	20	30	0.75	1.5	2.60	0.0127
9	20	40	0.5	1.1	2.50	0.0111
10	20	50	0.4	1.0	1.70	0.0106
11	20	70	0.29	0.4	1.25	0.0060
12	10	40	0.25	0.5	1.20	0.0070

Complex **1** was employed as catalyst (1.27 × 10^{-5} M in d_6-acetone), and the ratio of substrate to catalyst was varied as well as the ratio of aldehyde to olefin. In addition to persistence of **1** during catalysis, ^{1}H NMR monitoring reveals the formation of a second Co-containing species which exhibits a ratio of Cp* to $SiMe_3$ groups of 1:1. Additional resonances in the aliphatic region are observed but are quite complex. This intermediate is assigned as the bisalkyl carbonyl cobalt(III) complex, **4c**, (eq 5); a more rigorous proof of its structure is given below.



(5)

The ratio of bisolefin complex **1** to the intermediate species **4c** is dependent on the ratio of aldehyde to olefin substrates. In a reaction with an aldehyde-to-olefin ratio of 1:1 and a 5 mol % catalyst load, the ratio of complex **4c** to **1** is 2:1 in the initial phase of catalysis. Increasing aldehyde concentration increases the ratio of **4c** to **1**, while increasing the olefin concentration decreases this ratio. The equilibrium between the two Co-containing species **1** and **4c** is rapidly established with respect to catalytic ketone formation. For example, addition of isovaleraldehyde to a d_6-acetone solution of **1** and trimethylvinylsilane at room temperature establishes the ratio of compounds **1** and **4c** in the course of minutes. Upon raising the temperature to 35 °C, catalysis with a turnover frequency of about 3 TO/h is observed and the ratio of **1** to **4c** is maintained. Table 1 summarizes the ratios of **4c** to **1** observed for various ratios of isovaleraldehyde to trimethylvinylsilane and at various absolute concentrations of these substrates. Initial turnover frequencies (TOFs) under these conditions are also listed. Several conclusions can be drawn from these data. Increasing the concentration of olefin in the reaction mixture results in decreased TOFs for ketone formation and a change in the ratio of **4c** to **1** which favors **1**. On the other hand, increasing aldehyde concentration increases the ratio of **4c** to **1** in favor of **4c** and increases the TOF. Addition of excess trimethylvinylsilane to a reaction mixture with a substrate ratio of 1:1 during catalysis and after 10% ketone formation changes the ratio of **4c** to **1** in favor of **1** and decreases the TOF. Even though a substrate dependent

---

(43) For complete structural data see the Supporting Information.

(44) Schmid, G.; Kilanowski, B.; Boese, R.; Blaeser, D. *Chem. Ber.* **1993**, *126*, 899−906.

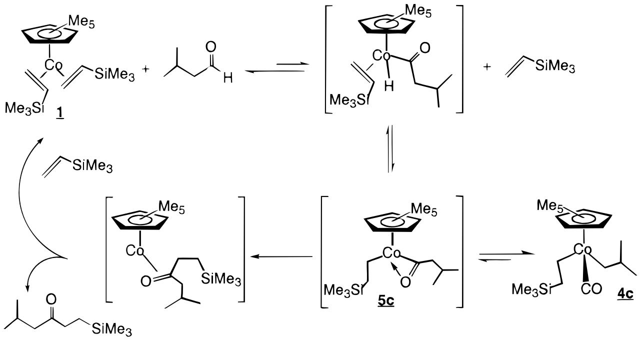
(45) Klein, H. F.; Lull, G.; Rodenhauser, B.; Cordier, G.; Paulus, H. *Z. Naturforsch.* **1988**, *43b*, 1256−1262.

(46) Lehmkuhl, H.; Naeser, J.; Mehler, G.; Keil, T.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G.; Krueger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 441−452.

(47) Kang, Y.; Kim, K.-i.; Kang, S.-O.; Ko, J.; Heaton, B. T.; Barkley, J. V. *J. Organomet. Chem.* **1997**, *532*, 79−82.

(48) For example, in the corresponding bisstyrene Co(I) complex, $[C_5Me_5Co(C_2H_3C_6H_5)_2]$, several isomers are observed in which the substituent on the olefin is directed either toward the other olefin substituent or toward the Cp* ligand. Brookhart, M.; Lenges, C. P. Unpublished results.

Scheme 1. Mechanism for Intermolecular Hydroacylation of Trimethylvinylsilane with Isovaleraldehyde Catalyzed by **1**



initial ratio of **4c** to **1** is reproducibly established initially and persists throughout ca. 80% of catalysis, a change in this ratio is apparant at high conversions. Using excess olefin, complex **1** is regenerated as the major species after nearly all aldehyde has been consumed and only olefin and ketone remain in solution. If aldehyde is the substrate in excess, hydroacylation terminates prior to complete consumption of olefin and deactivation and side products are observed, which will be discussed in more detail later.

The TOF is not dependent on absolute concentrations of substrates. In a series of experiments in which the ratio of aldehyde to olefin was constant at 1:1 and the amount of catalyst was varied from 5 to 3.3 and to 2.5 mol %, essentially complete conversion was observed in each case with a TOF of 3.0 TO/h at 35 °C. The initial TOF observed for a series of different substrate concentrations is roughly linearly dependent on the concentration of **4c** (see the Supporting Information for the plot). This indicates that **4c** is intimately involved in the catalytic cycle and not a result of a nonproductive side reaction.

Reaction of d_1-Isovaleraldehyde. To test reversibility of the oxidative addition of aldehyde, d_1-isovaleraldehyde, $(CH_3)_2CHCH_2C(O)D$, was examined. A reaction with 5 mol % catalyst **1** and a d_1-aldehyde-to-olefin ratio of 1:1 was followed by ^1H NMR spectroscopy at 35 °C. The aldehyde region showed no ^1H resonance after mixing of substrate and catalyst in d_6-acetone. After 2 h and 17 min, 20% of the aldehyde was converted to ketone, which corresponds to a TOF of 2.3 TO/h for catalytic ketone formation. At this point in the catalysis a 9.7 ppm triplet corresponding to h_1-isovaleraldehyde was observed. About 5% of all aldehyde present after 2 h is protioaldehyde. Analysis of the rate of appearance of protioaldehyde with time indicates that intermediate(s) **5c** and **4c** (see Scheme 1) return to complex **1** and aldehyde ca. $^1/_4$ of the time versus partitioning to product ca. $^3/_4$ of the time. Analysis of the reaction by ^{13}C NMR spectroscopy after complete ketone formation indicates that deuterium is selectively incorporated at the β-carbon of the ketone.

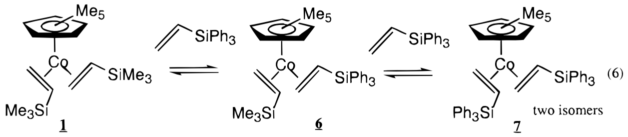
The mechanistic scheme presented in Scheme 1 is consistent with the data presented thus far.

Hydroacylation of Isovaleraldehyde with Triphenylvinylsilane. Intermolecular hydroacylation is also observed using triphenylvinylsilane. Several mechanistic features are considerably different from the trimethylvinylsilane case since the even bulkier triphenylvinylsilane is less strongly coordinated to the Co(I) center. Independent synthesis of a Co(I)−bis(triphenylvinylsilane) complex by sodium-amalgam reduction of the Co(II) precursor was not successful. However, if complex **1** is mixed with 16 equiv of triphenylvinylsilane in d_6-acetone, the formation of one major new species, the mixed olefin complex **6**, is observed by ^1H NMR spectroscopy.[49] Besides complex **6** and a small amount of remaining **1**, two new species with Cp* resonances at 1.38 and 1.42 ppm are observed. When all volatile materials in this reaction mixture are removed in vacuo, readdition of d_6-acetone allows the NMR spectroscopic characterization of what we believe are two isomers of a bis(triphenylvinylsilane)−Co(I) complex **7**. Solutions prepared in this manner feature the same characteristics in hydroacylation catalysis as the use of **1** in the presence of excess triphenylvinylsilane.

Table 2. Substrate Dependence of Hydroacylation of Triphenylvinylsilane with Isovaleraldehyde[a]

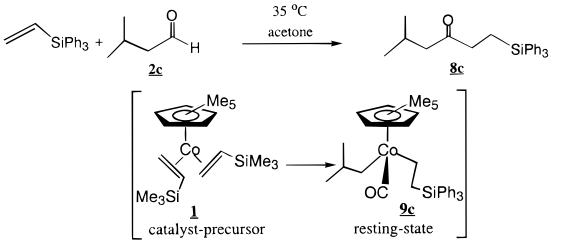
	equivalents of			
entry	aldehyde	olefin	ratio A:O	TOF [TO/h]
1	20	20	1	4.0
2	30	20	1.5	4.2
3	40	20	2	4.2
4	20	20	1	3.9
5	20	40	0.5	3.9
6	20	50	0.4	4.2
7	20	70	0.29	4.2
8	10	50	0.2	4.0
9	20	50	0.4	4.2
10	30	50	0.6	3.8

[a] Aldehyde: isovaleraldehyde. Olefin: triphenylvinylsilane. 1.27 × 10^{-5} mol of **1** in 0.6 mL of d_6-acetone at 35 °C, TOF over at least 50% conversion. Internal reference: ferrocene.



(6)

Triphenylvinylsilane reacts with isovaleraldehyde in acetone in the presence of catalytic amounts of **1** to give the β-$SiPh_3$-substituted ketone (eq 7).



(7)

A series of kinetic experiments was performed in which the substrate concentration of either olefin or aldehyde was varied and the initial turnover frequency for ketone formation was determined. Table 2 lists these results. First, the concentration of aldehyde was increased with constant olefin concentration (5 mol % catalyst load with respect to olefin, entries 1−4). In all cases initial formation of ketone is observed with similar TOFs; however, after 50−70% conversion considerable decrease in activity is observed and only about 70% of the olefin is converted to ketone. Deactivation of the catalyst occurs. Reactions in the presence of excess olefin (entries 5−10) are well-behaved and result in complete conversion of aldehyde. Throughout the range of substrate concentrations discussed here

---

(49) A characteristic of **6** is one Cp* resonance at 1.52 and one $-SiMe_3$ resonance at −0.21; several olefinic resonances in the region of 2.5−0.3 ppm support this assignment.

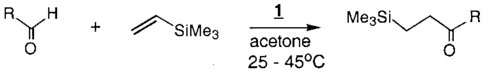
there is essentially no rate dependence on either aldehyde or olefin concentration; a constant turnover frequency of 4.0 [TO/h] at 35 °C for catalytic hydroacylation is observed.

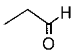
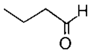
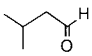
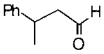
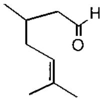
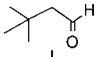
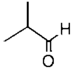
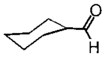
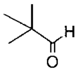
Investigating this catalytic process by ^{1}H NMR spectroscopy furnishes additional information. Addition of isovaleraldehyde to a mixture of excess triphenylvinylsilane (e.g., 20 equiv) and **1** in d_6-acetone (vide supra) results in the immediate formation of a single new species with a Cp* resonance at 1.50 ppm. This material accounts for all Co-containing species. In the TMS region only one singlet is observed which corresponds to uncoordinated trimethylvinylsilane along with the appropriate resonances in the olefinic region. Catalytic hydroacylation is not significant at this stage. In the concentration ranges of substrate investigated, the formation of one species with identical spectroscopic features was observed at all times. As in the case of trimethylvinylsilane, the new species observed is formulated as the Co(III)−bisalkyl−CO complex **9c** (see eq 7) on the basis of NMR and IR characterization (Experimental Section, Table 5). Following catalytic ketone formation at 35 °C by ^{1}H NMR spectroscopy shows that **9c** is the resting state throughout catalysis.

Reaction of d_1-Isovaleraldehyde. The hydroacylation of triphenylvinylsilane by d_1-isovaleraldehyde in the presence of catalyst **1** (5 mol %, 35 °C, d_6-acetone) was examined. Again, immediately upon mixing both substrates, the formation of the bisalkyl Co(III) species **9c** is observed exclusively. An initial TOF of 3.75 TO/h for the ketone formation is observed. Again, H/D exchange and formation of h_1-isovaleraldehyde occur during catalysis. An initial TOF for the appearance of protio-aldehyde of 3.4 [TO/h] was measured. This indicates that monodeuterated intermediate **9c** partitions about equally to product and back to unlabeled aldehyde. Consistent with these observations, the extent of H/D exchange reaches a steady state condition after about 3 h, whereas only about 55% of ketone has been formed (5 mol % catalyst, 1:1 ratio of substrates). Deuterium incorporation occurs selectively at the carbon β to the carbonyl group.

C. Hydroacylation of Various Alkyl Aldehydes. Cobalt(I) olefin complex **1** was also used in the catalytic hydroacylation of trimethylvinylsilane with a series of alkyl aldehydes. The efficiency of the catalyst is good. Essentially quantitative conversion with 1 mol % catalyst load and a ratio of olefin to aldehyde of 1:1 is observed. Catalytic reactions are also effective in neat trimethylvinylsilane. Catalyst loading can be reduced to 0.5 mol % with still nearly quantitative conversion for certain substrates (Table 3, entries a−c and e−f). Reactions employing a series of alkyl aldehydes (Table 3) were run under comparable conditions with increased catalyst load (5 mol %) either at 45 °C for 12 h or at room temperature for 48 h in acetone, benzene, or THF. Turnover frequencies in the initial stages of catalysis were obtained in reactions using 5 mol % catalyst load and an aldehyde-to-olefin ratio of 1:1 in d_6-acetone at 35 °C. Exclusive formation of the linear ketone with respect to olefin addition is observed in all cases. Reactions using 5 mol % catalyst load (1.27 × 10^{-5} mol) and an aldehyde-to-olefin ratio of 1:1 were more closely investigated by ^{1}H NMR spectroscopy at 35 °C in 0.6 mL of d_6-acetone for the same series of alkyl aldehydes. TOFs were extracted from the initially linear TON vs time plots. In all cases investigated, an intermediate Co complex was observed with spectroscopic features (Cp*:SiMe$_3$ of 1:1) analogous to those of the bisalkyl−CO−cobalt(III) complex in the isovaleraldehyde case, complex **4c**. The ratio of this intermediate **4** to **1** could be extracted from these experiments and remains constant during initial stages of catalysis (1−4 h on average). These two species account for all Co-containing material. Deviations at later times are due to deactivation processes. Results are listed in Table 3. Conversions to product were based on NMR analysis. Organic products were isolated and fully characterized.

Table 3. Hydroacylation of Trimethylvinylsilane with Alkyl Aldehydes



Entry	Aldehyde	TOF[1] [TO/h]	**4** / **1**[1]	Aldehyde : Olefin : Catalyst 20:20:1[2]	 40:40:1[2]
				in % conversion by NMR	
a		2.3	3.4	98	81
b		3.2	4.1	97	92
c		3.0	2.1	99	99
d		2.0	4.0[3]	75	76
e		2.2	1.9	99	98
f		4.0	0.1	98	97
g		2.4	4.0[4]	98	94
h		2.2	0.1	99	99
i		very slow	-	12	-

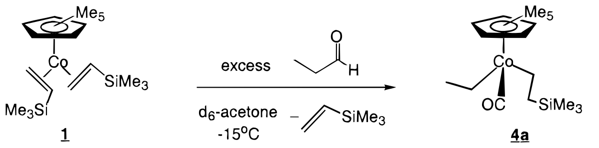
[a] [1] Initial stage of catalysis in a reaction with 5 mol % catalyst load and an aldehyde to olefin ratio of 1:1, by ^{1}H NMR at 35 °C in d_6-acetone, 1.27 × 10^{-5} mol of **1**. [2] Scaled up reactions in a total volume of 5 mL of acetone and 1.27 × 10^{-4} mol of **1** (0.05 g) for 24 h at 45 °C or 48 h at 25 °C. [3] Two diastereomeric complexes of **4d** and **4e** are observed. [4] The actual intermediate observed during catalysis is **4b** vide infra.

Aldehydes with one or two substituents at C$_\beta$ (entries b−e) show similar turnover frequencies and similar ratios of **4** to **1**, suggesting that rates of reductive eliminations from all these intermediates (**4b**−**e**) must be quite similar. In the case of the neopentyl aldehyde (entry f), with three C$_\beta$ substituents, the increased bulk at C$_\beta$ results in a somewhat higher TOF, yet a significantly smaller ratio of **4f** to **1** suggests that the lower percentage of **4f** present is compensated for by an increased rate of reductive elimination from the more crowded **4f**. Consistent with this observation is the fact that cyclohexanecarbaldehyde (entry h), with two C$_\alpha$ substituents, shows a reduced ratio of **4h** to **1** yet TOFs similar to those of aldehydes in entries a−e. For the highly crowded pivaldehyde system (entry i) no intermediate **4i** could be detected and the TOF was very small; product corresponding to only 2 TO could be detected after 24 h. While this system was not amenable to mechanistic investigation, it seems probable that the turnover-limiting step in the catalytic cycle may be altered. A reasonable proposal is that the initial oxidative addition of the aldehyde to the Co(I) center is turnover-limiting.

The importance of steric effects observed in this system is also illustrated in the reactivity of different alkyl aldehydes with triphenylvinylsilane. As discussed above, reactivity with isovaleraldehyde or cyclohexanecarbaldehyde is excellent and good turnovers are observed (>200 TO). On the other hand, if *n*-butyraldehyde (or propionaldehyde) is reacted in a 1:1 mixture with triphenylvinylsilane (5 mol % catalyst) only about 7 turnovers to form ketone are observed and rapid deactivation terminates catalysis early.

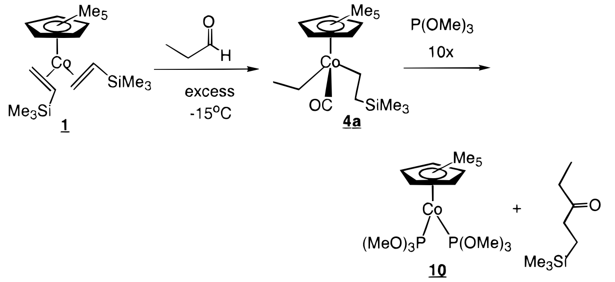
D. Spectroscopic Characterization of the Intermediates Formed during Catalytic Hydroacylation. A general method has been developed for generating intermediates **4** in high concentration at low temperature for spectroscopic observation. In a series of ^{1}H NMR experiments an excess of 10−20 equiv of the appropriate alkyl aldehyde was added to a d_6-acetone solution of complex **1** at −30 °C; no reaction is observed at this temperature. Controlled and slow warming of the NMR probe results in the formation of the intermediates **4** observed during catalysis. In addition to this, 1 equiv of uncoordinated trimethylvinylsilane is observed in solution, indicating that olefin substitution has occurred and 1 equiv of aldehyde has been incorporated into the new Co complex. With careful temperature adjustments these intermediates **4** can essentially be quantitatively generated without significant side reactions in most cases (for exceptions see below). The d_6-acetone solution has changed color at this stage from the red of **1** to yellow for **4**. Even at −10 °C slow hydroacylation is observed which eventually consumes all uncoordinated olefin to generate ketone. However, lifetimes were sufficiently long at −15 °C to allow characterization of these intermediates by ^{1}H and ^{13}C NMR spectroscopy. Since aliphatic aldehydes are used in excess and slow ketone formation is also observed, the new, complex resonances in the ^{1}H NMR spectrum which correspond to this intermediate were difficult to assign. Significant is the observation that the region downfield of ca. 2.2 ppm in the ^{1}H NMR spectrum contains only resonances for uncoordinated olefin and excess aldehyde.[50] After olefin consumption is observed at these temperatures, further reactivity in the presence of excess aldehyde results in side reactions and deactivation of the catalyst (aldehyde dimerization to esters is observed, vide infra) which complicate characterization of complexes **4**.

In the case of propionaldehyde we were able to isolate and characterize intermediate **4a** by NMR spectroscopy. Complex **1** was treated with excess propionaldehyde at −15 °C in d_6-acetone, and after 2 h the intermediate **4a** was generated (95%). All volatile materials were removed in vacuo at 0 °C from the NMR tube followed by readdition of d_6-acetone solvent through vacuum transfer. Characteristic NMR data for **4a** show singlets at 1.6 ppm (Cp*) and at −0.04 ppm (−SiMe$_3$) in the ratio of 15:9 and a methyl triplet at 0.91 ppm along with multiplets at 1.22, 1.33, 0.81, 0.62, and 0.90 ppm which correspond to the diastereotopic proton resonances of the aliphatic groups. The ^{13}C shifts for the two carbons bound to cobalt appear as broadened resonances at 14.2 and 15.3 ppm; the carbonyl carbon is not observed.[51,52] IR spectroscopy shows one band at 1970 cm^{-1}.



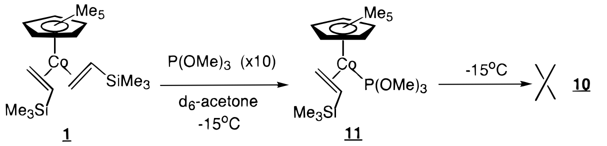
(8)

This Co(III)−CO−bisalkyl complex is extremly sensitive, and storage of the d_6-acetone solution of **4a** at −78 °C results in considerable decomposition after 24 h. Additional support for the formation of an intermediate with the structure of **4a** was gained from its reaction with P(OMe)$_3$ at −15 °C. Addition of P(OMe)$_3$ (10 equiv) to the solution of **4a** with remaining **1** (5%) in d_6-acetone resulted in slow formation of ketone and the bisphosphite complex [Cp*Co(P(OMe)$_3$)$_2$] (10) as the major species (95%) and the monophosphite−olefin adduct [Cp*CoP(OMe)$_3$(C$_2$H$_3$SiMe$_3$)] (**11**) as a minor species (5%).



(9)

Reaction of **1** at these temperatures with excess P(OMe)$_3$ results in the formation of only the monophosphite adduct [C$_5$Me$_5$Co(P(OMe)$_3$)(C$_2$H$_3$SiMe$_3$)] (**11**). Displacement of the second CH$_2$═CHSiMe$_3$ to give the bisphosphite adduct does not occur on these time scales.[39]



(10)

If intermediate **4a** were to be a simple aldehyde−olefin adduct, the displacement of aldehyde would be facile and the monophosphite adduct would be the expected major product. The formation of the bisphosphite adduct further supports the formulation of **4a** as the bisalkyl−CO−Co(III) complex since ketone formation removes all ligands at cobalt and allows direct conversion to the bisphosphite complex.[53] The minor olefin−phosphite adduct is generated from residual **1**.

To provide additional evidence for and to simplify the NMR assignment of a Co(III) dialkyl carbonyl complex, a system with higher symmetry was desired. Therefore, the aldehyde Me$_3$Si−CH$_2$−CH$_2$−C(O)H **2k**[54] was prepared and reacted in excess (10 equiv) with **1** at −15 °C in d_6-acetone. Over the course of 2 h the formation of only one new species was observed which featured ^{1}H NMR resonances for Cp* and −SiMe$_3$ groups in a ratio of 1:2 as expected at 1.61 (Cp*, 15, s) and −0.04 ppm (−SiMe$_3$, 18, s). Furthermore, a simplified ^{1}H NMR spectrum with three resonances centered at 1.33 (m, 2), 0.77 (m, 2), and 0.63 ppm (m, 4) for the eight −CH$_2$CH$_2$− protons was observed, confirming the structural assignment for **4k**. Convincing as well is the simple ^{13}C spectrum with

---

(50) Addition of trimethylvinylsilane to a reaction mixture prepared in this fashion allows entry into a typical catalytic hydroacylation cycle and regeneration of the equilibrium mixture of **1** and **4**.

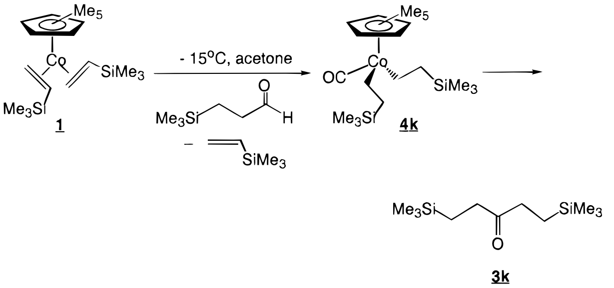
(51) The quadrupolar broadening effect of the ^{59}Co nucleus ($I = {}^7/_2$) is attributed in part to this effect. See: Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, 1971; p 61.

(52) In an analogous experiment using CH$_3$(CH$_2$)$_3$^{13}C(O)H, an intermediate of type **4** was generated in a low-temperature NMR experiment after addition of excess [^{13}C]pentanal to a d_6-acetone solution of **1**. NMR characteristics of the solutions obtained are quite complex, but ^{13}C{^{1}H} NMR analysis of the resulting reaction mixture showed a broad resonance at 210 ppm ($\nu_{1/2} \simeq 45$ Hz) which corresponds to a Co−CO.

(53) The formation of a Co(III) species of type [C$_5$Me$_5$Co(R)(−C(O)R)P(OMe)$_3$] was not observed in this reaction, vide infra.

(54) Sarkar, T. K.; Gosh, S. K.; Satapathi, T. K. *Tetrahedron* **1990**, *46*, 1885−1898.

resonances for Cp* (8.33 and 97.98 ppm) and $-SiMe_3$ (-1.85 ppm) and two resonances at 15.5 (broad) and 22.81 ppm for the CH_2 groups; the carbonyl resonance was not observed (ν_{CO} $= 1969$ cm^{-1}).

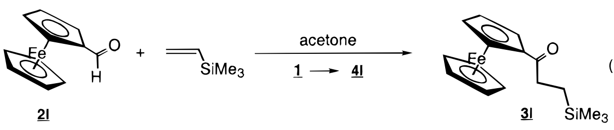


(11)

Warming the solution results in ketone formation and decomposition products.[55] This reaction was repeated under catalytic conditions (5 mol % **1**, ratio of aldehyde to trimethylvinylsilane of 1:1), and the same intermediate, **4k**, together with **1** was observed during catalytic ketone formation. Complex **4k** was also prepared directly and characterized by low-temperature NMR spectroscopy.

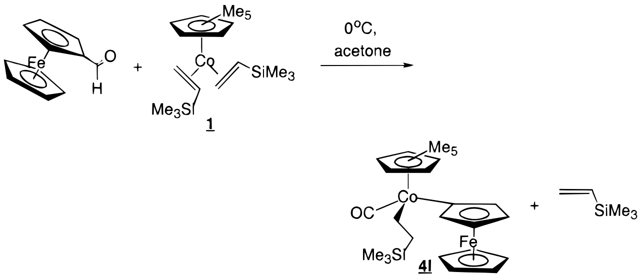
For essentially all aldehydes listed in Table 3 the formation of the intermediate Co(III) species **4** was observed. Even though the ratio of **1** to **4** is quite substrate dependent during catalysis with the turnover frequency for ketone formation similar in the listed series of aldehydes, the low-temperature NMR techniques described above allowed the characterization of these complexes by in situ NMR spectroscopy under conditions where side reactions and deactivation processes are slow. A trend in the IR data for complexes **4** substantiates the proposed difference in reactivity of complexes **4** in ketone formation. Complexes formed from linear aldehyes (**4a**,**b**,**k**) have a similar ν_{CO} at 1970 cm^{-1}. Complexes **4f** and **4h** which build up only to a small extend during catalysis show a ν_{CO} at 1962 cm^{-1}, indicating a more electron rich metal center. NMR and IR data for additional selected examples are summarized in the Experimental Section.[56] The low-temperature generation of the intermediates with aldehydes **2e** and **2d** of Table 3 results in the observation of two diastereomeric Co(III) bisalkyl CO complexes for both **4e** and **4d**. In the reaction of excess racemic 3-phenylbutanal (entry d) with **1** at -15 °C, two diastereomeric Co(III) complexes, **4d**, were generated in a 1.8:1 ratio which remains constant at -15 °C. With this substrate a corresponding observation is made during catalysis; the ratio of diastereomers remains constant at 1.8:1 throughout catalysis.

E. Isolation, Characterization, and Reactivity of an Intermediate Co(III) [$C_5Me_5Co(R)(R')(CO)$] Complex. Isolation of species of type **4** on a preparative scale using alkyl aldehydes was not successful. For example, **1** was reacted in acetone with excess propanal (10 equiv) at -20 °C and slowly warmed to 0 °C. After removal of all volatiles a yellow oil was isolated which showed the desired compound as the major species by NMR analysis (90%). This compound is thermally quite sensitive, and attempts to crystallize it or purify it by chromatography were unsuccessful. With the goal of isolating a Co(III) intermediate in this catalytic process ferrocenecarbaldehyde, **2l**, was investigated. In a reaction using 10 mol % catalyst and a substrate ratio of ferrocenecarbaldehyde to trimethylvinylsilane of 1:1, the formation of a new species with a ratio of Cp* to $-SiMe_3$ groups of 1:1 was observed together with complex **1**. However, the hydroacylation using this substrate is considerably slower than for alkyl aldehydes; comparable turnover frequencies are observed only at temperatures of 50 °C to generate ketone **3l** (eq 12). Catalytic solutions prepared in this manner contain 95% **4l** with 5% of **1** remaining throughout the reaction.



(12)

A direct synthesis of **4l** was now successful. Three equivalents of ferrocenecarbaldehyde were added to an acetone solution of **1** at 0 °C. After 4 h, the reaction mixture was cooled to -79 °C and yellow crystalline material was obtained. ^{1}H NMR analysis (-15 °C, d_6-acetone) of this material indicates the presence of a substituted ferrocene unit (3.96 (s, 5, C_5H_5); 3.51 (m, 1, $C_5H_3\mathit{H}$); 3.87 (m, 1, $C_5H_3\mathit{H}$); 4.09 (m, 2, $C_5H_2\mathit{H}_2$)) and a Cp* resonance (1.52 ppm, s, 15H) along with a $-SiMe_3$ resonance (0.09 ppm, s, 9H). Several more complex multiplet patterns are observed in the alkyl region integrating for 4 protons. The ^{13}C NMR spectrum features five resonances for the Co-substituted Cp ligand; significant is the resonance of the Co-bound carbon at 98.6 ppm. With a concentrated sample a resonance for the CO-carbon could be observed (broad signal, $\nu_{1/2} \approx 37$ Hz, at 208 ppm). The IR spectrum shows a CO stretch at 1983 cm^{-1} (compare with **4a**: $\nu_{CO} = 1970$ cm^{-1}). This indicates that the ferrocenyl substituent is effective in removing electron density from cobalt compared to the bisalkyl complexes and explains the slower reductive elimination of **4l**.



It was possible to characterize complex **4l** by X-ray crystallography. The ORTEP diagram is shown in Figure 2. Selected bond lengths and angles are summarized in Table 4. This complex is clearly a [$C_5Me_5Co(R)(R')(CO)$] type species with a direct Co−ferrocene bond and provides further proof that all of the intermediates **4** are complexes of this type. The arrangement of ligands generates an octahedral coordination environment at cobalt. In addition to facial coordination of the Cp* spectator ligand, angles between the Co and each of the two alkyl (ferrocenyl) and the CO ligands are very close to 90°. The Co−C_1, Co−C_2, and Co−C_{24} bond distances reflect the nature of the attached carbon in terms of hybridization. The large angles C_2−C_3−Si and Co−C_2−C_3 reflect the steric impact of the bulky trimethylsilyl substituent in the anti-periplanar configuration with respect to C_2−C_3, supporting again the effect of the $-SiMe_3$ group in directing the exclusive anti-Markovnikov addition reaction. The inter-carbon distances in the Co-coordinated Cp ring are quite similar; however, a considerable impact on the Fe−C_5H_4 distances is observed. The C_{24} to Fe

---

[55] The stability of aldehydes with β-silyl substituents has been discussed. See: Hoveyda, A. H.; Young, D. G. J.; Hale, M. R. *Tetrahedron Lett.* **1996**, *37*, 827−830.

[56] In comparison to other Co(III)−CO complexes the series of complexes of type **4** show relatively low CO bands. See for example: Dahl, L. F.; Nagaki, D. A.; Olson, W. L. *Organometallics* **1986**, *5*, 630−634.

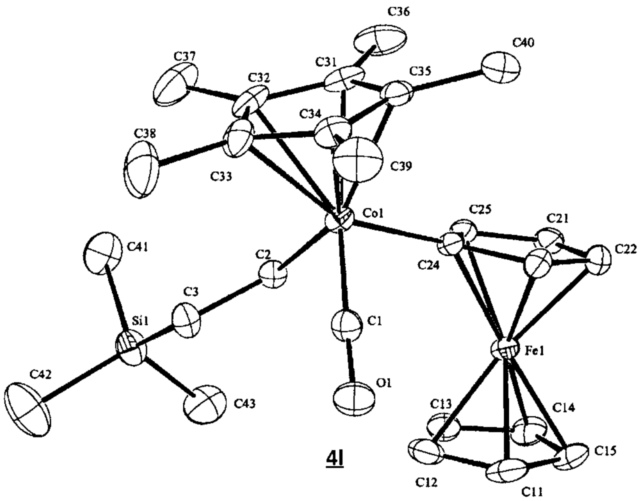


Figure 2. ORTEP view of **4l**. All atoms are drawn at 50% probability ellipsoids.

Table 4. Selected Bond Lengths and Bond Angles for **4l** (Å and deg)

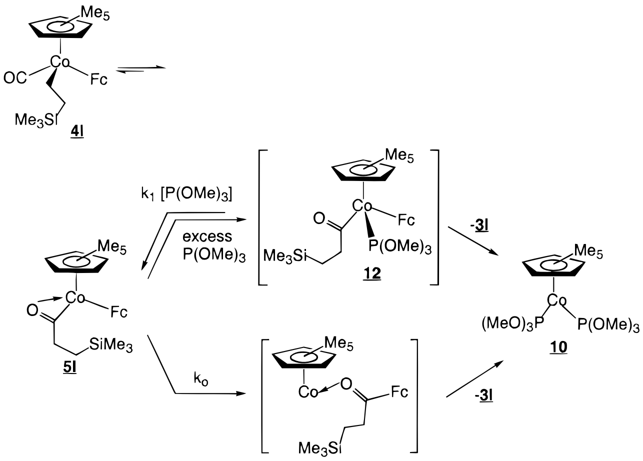
C1−O1	1.143(5)	C3−Si	1.876(5)	Fe−C24	2.091(3)
Co−C1	1.726(4)	Fe−C21	1.026(4)	C21−C25	1.413(6)
Co−C2	2.034(3)	Fe−C23	2.036(3)	C24−C25	1.430(5)
Co−C24	1.962(3)	Fe−C25	2.043(3)	C24−C23	1.418(5)
C2−C3	1.516(5)	Fe−C22	2.029(4)	C21−C22	1.407(6)

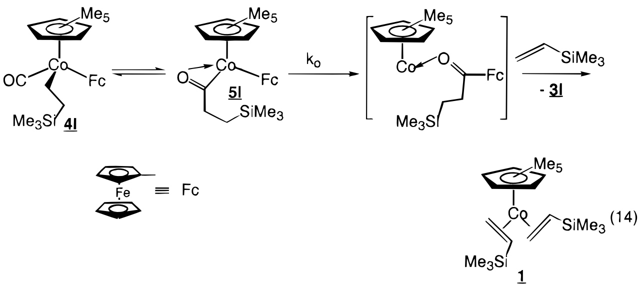
C11−Fe−C23	108.19(17)	C22−C21−C25	108.1(3)
C12−Fe−C24	109.85(15)	C21−C22−C23	107.2(3)
C13−Fe−C25	109.44(16)	C22−C23−C24	109.8(3)
C14−Fe−C21	106.20(17)	C23−C24−C25	105.5(3)
C15−Fe−C22	105.17(17)	C21−C25−C24	109.4(3)
C1−Co−C2	90.35(16)	Co−C2−C3	116.34(24)
C1−Co−C24	90.38(16)	Si−C3−C2	113.2(3)
Co−C1−O	178.1(3)	Co−C24−C23	125.8(3)
		C2−Co−C24	89.39(14)

distance is elongated with respect to the four remaining carbons in the top ring, with the shortest distances being C_{22}−Fe and C_{21}−Fe. Essentially Fe has moved from the centroid of the top ring away from C_{24}.[43]

The availability of compound **4l** now allows direct study of the C−C bond-forming step in catalytic hydroacylation. Insertion of CO into either Co−C bond generates an alkyl acyl intermediate which can undergo reductive elimination to form the corresponding ketone. In a series of kinetic experiments, compound **4l** was treated at 35 °C in d_6-acetone with excess trimethylvinylsilane. The bisolefin complex **1** was formed together with the corresponding ferrocene-coupled ketone, **3l**. The pseudo-first-order rate constant for this process was determined by monitoring the disappearing Cp* resonance of **4l**. Essentially no significant variation in rate was observed for different olefin concentrations ($k_{obs} = 2 \times 10^{-5}$ s^{-1}, 18 equiv; 2×10^{-5} s^{-1}, 25 equiv; 4×10^{-5} s^{-1}, 30 equiv; 3×10^{-5} s^{-1}, 50 equiv). This indicates that reductive elimination is not assisted by olefin under these conditions and occurs from a 16-electron, possibly solvated intermediate or, perhaps more likely, from an 18-electron η^2-acyl intermediate. In an additional reaction, **4l** was treated with 13 equiv of triethylvinylsilane in d_6-acetone and a pseudo-first-order rate ($k_{obs} = 4 \times 10^{-5}$ s^{-1}) was observed for ketone formation.[57] The observed pseudo-first-order rate constant is similar to that of the series with trimethylvinylsilane, supporting the substrate independent pathway. This was also repeated with triphenylvinylsilane which gave a rate constant of 4×10^{-5} s^{-1} (10 equiv) for this process.

Scheme 2. Reaction of **4l** with $P(OMe)_3$ in d_6-Acetone at 35 °C





To further characterize the reductive elimination step from **4l**, a series of reactions with excess $P(OMe)_3$ was performed and followed by ^{1}H NMR spectroscopy in d_6-acetone solution (Scheme 2). The formation of the ferrocene-coupled ketone is observed along with the clean formation of the known bisphosphite complex $[Cp^*Co(P(OMe)_3)_2]$ **10**.[58] Pseudo-first-order rate constants were determined for a series of reactions with different $P(OMe)_3$ concentrations. A linear increase in reductive elimination rate was observed with increasing phosphite concentration.[59] A general rate law of the type rate = ($k_o + k_1$[$P(OMe)_3$]) [**4l**] is observed which indicates that two pathways are viable for reductive elimination of ketone, a ligand independent pathway and a ligand accelerated pathway in which phosphite assists ketone formation. A plot of the data appears in the Supporting Information. The value of k_o determined from the intercept matches the rate observed in the reaction of **4l** with excess trimethylvinylsilane ($k_o = 0.3 \times 10^{-4}$ s^{-1}), and a second-order rate constant of $k_1 = 3.2 \times 10^{-4}$ s^{-1} (L/mol). At 0.4 M phosphite the rate of ligand-assisted ketone formation is ca. 6.5 times the rate of formation via the unassisted pathway. The presumed 18-electron Co(III) phosphite acyl alkyl complex (assigned structure **12**, vide infra) however has not been observed under these conditions.[60]

---

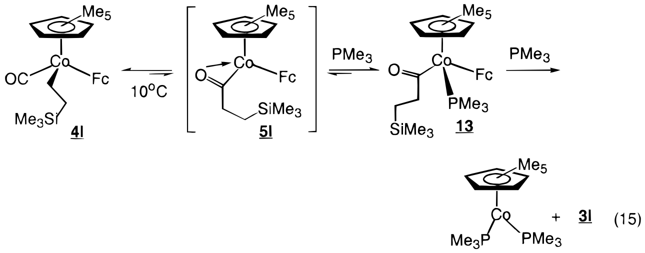
[57] In the reation of **4l** with triethylvinylsilane the formation of the bisolefin complex $[C_5Me_5Co(C_2H_3SiEt_3)_2]$ is observed.

[58] Werner, H.; Heiser, B.; Klingert, B.; Doefel, R. *J. Organomet. Chem.* **1982**, *240*, 179−190.

[59] The following pseudo-first-order rate constants were observed for the corresponding $P(OMe)_3$ concentration: 1.03×10^{-4} s^{-1}, 11 equiv; 1.18×10^{-4} s^{-1}, 16 equiv; 1.42×10^{-4} s^{-1}, 18 equiv; 1.52×10^{-4} s^{-1}, 24 equiv; 2.04×10^{-4} s^{-1}, 32 equiv; 2.91×10^{-4} s^{-1}, 44 equiv; 3.52×10^{-4} s^{-1}, 56 equiv.

[60] Kinetics are consistent with either rapid preequilibrium between **4l** and **12** favoring **4l** followed by reductive elimination or rate-determining trapping of **5l** followed by rapid reductive elimination.

We have investigated this reaction in more detail at lower temperatures using PMe_3, a more electron rich ligand which is expected to more effectively stabilize an intermediate of type **12**. Compound **4l** in d_6-acetone was treated with 20 equiv of PMe_3 at 0 °C, and the slow formation of a new Co complex was observed. At 10 °C compound **13** was generated during the course of 2 h. Compound **13** exhibits a 1:1:1 ratio for Cp* (1.54 ppm, d, 0.9 Hz) to $-SiMe_3$ (0.09 ppm, s) to PMe_3 (0.90 ppm, d, 9 Hz) groups. A series of complex resonances for the aliphatic hydrogens is observed which are shifted from the resonances for **4l**. Particularly informative is a multiplet at 3.21 ppm (ddd, 15.9, 11.9, 3.7 Hz, 1 proton), which is nearly 1 ppm downfield from a corresponding resonance of **4l**. In the ferrocene region five signals are observed for the substituted Cp unit.[61] Significant in the ^{13}C spectrum is the Co−acyl resonance at 270 ppm (d, 22.6 Hz) and a resonance at 49.9 ppm (d, 7 Hz) for the α-carbon of the Co−acyl, supporting the proposed regiochemistry of CO insertion. Even though compound **13** can be generated to nearly 90% in the reaction mixture at 10 °C, conversion to the bisphosphine complex $[C_5Me_5Co(PMe_3)_2]$[58] is eventually observed along with the formation of ketone **3l**.[62]

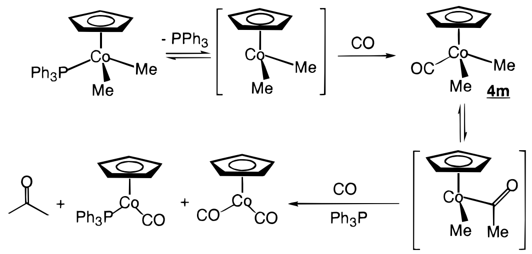


(15)

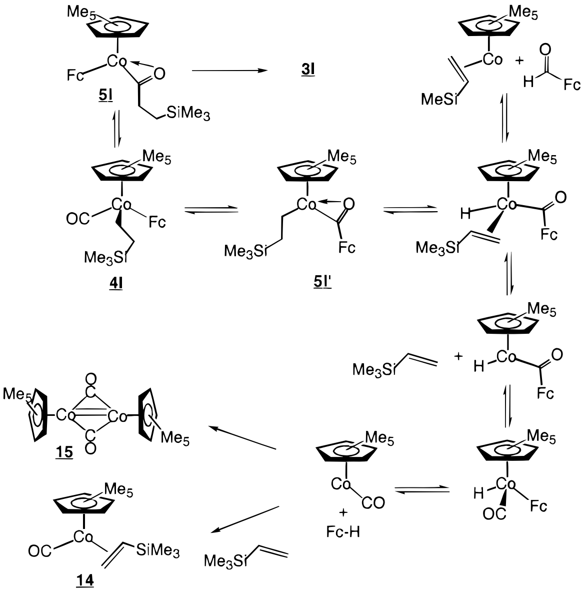
These trapping reactions show that the reductive elimination is more facile from an 18-electron system like **12** or **13** as opposed to a 16-electron Co(III)−alkyl−acyl species in which η^2-acyl coordination may assist reductive elimination as in **5l**.[63]

Bergman et al. have discussed a closely related reductive elimination reaction in which acetone was generated from a cobalt(III) complex. $[C_5H_5Co(PPh_3)Me_2]$ was treated with CO (1−5 atm), and besides the formation of acetone, the cobalt complexes $[C_5H_5Co(CO)_2]$ and $[C_5H_5Co(PPh_3)(CO)]$ were observed. The expected intermediacy of $[C_5H_5Co(CO)Me_2]$, **4m**, a Co(III) complex analogous to the complexes of type **4**, was confirmed by in situ NMR spectroscopy (1 atm of CO, THF, **4m** builds up to 8%, IR 1998 cm^{-1}); see Scheme 3.[64−66] The authors favored a transition state for reductive elimination which resembles a 16-electron species, possibly assisted by an η^2-acyl interaction; however, the assistance of excess CO was not excluded.[67,68] Such assistance seems likely in view of the above results. A significant feature of these reductive eliminations is that the eliminated ketone is capable of stabilizing an unsaturated species such as $[C_5Me_5Co]$ or $[C_5Me_5Co(L)]$. The reductive elimination of ketone to generate a metal−ketone complex has been directly observed by Suggs et al. in a Rh system.[69]

Scheme 3. Formation of Acetone through Carbonylation of a Cobalt Alkyl Complex



Scheme 4. Decomposition of **4l**



Compound **4l** is stable at 25 °C for short times in solution but decomposes over the course of several hours. For example, after 24 h at 22 °C in d_6-acetone the olefin CO complex **14** and the carbonyl-bridged dimer **15** are formed in a ratio of about 1:1 in addition to small amounts of unassigned organometallic products. Ferrocene, free trimethylvinylsilane, and a small amount of ketone **3l** (2%) are also present. The proposed decomposition pathway is shown in Scheme 4. The presence of excess trimethylvinylsilane in the catalytic system (and in the thermolyses described in eq 15) retards formation of **14** and **15**, thereby preventing catalyst deactivation.

F. Evidence for the Formation of Isomeric Ketones and Aldehydes during Hydroacylation. Catalytic Hydroacylation Using Butyraldehydes. An additional feature in intermolecular hydroacylation catalyzed by Co(I) complexes is illustrated in the reactivity of the isomeric butyraldehydes (*n*-butyraldehyde

---

[61] NMR data for **13** (d_6-acetone, −15 °C, 300 MHz): ^1H NMR δ 1.54 (d, 0.9 Hz, 15H, C_5Me_5), 0.90 (d, 9.0 Hz, 9H, $-PMe_3$), 0.09 (s, 9H, $-SiMe_3$), 0.77−0.94 (m, 2H, $-CH_2-$), 1.82 (m, 1H, $-CH_2-$), 3.21 (ddd, 15.9, 11.9, 3.7 Hz, 1H, $-CH_2-$), 3.33, 4.03, 4.12, 4.19 (m, 1H, $-C_5H_4$), 3.99 (s, 5H, C_5H_5); ^{13}C NMR δ 270.8 (d, 22.6 Hz, Co−C(O)-), 49.9 (6.8 Hz, $-C(O)$-CH_2-), 12.7 ($-CH_2SiMe_3$), −1.9 ($-SiMe_3$), 66.1, 66.5, 78.8 ($-CC_5H_4$), 79.9 (d, 6 Hz, $-CC_4H_5$), 67.9 (C_5H_5), 15.2 (d, 30 Hz, PMe_3), 10.2 (C_5Me_5), 95.7 (d, 3 Hz, (C_5Me_5).

[62] Repeated attempts to isolate **13** were not successful; decomposition to ketone **3l** and unassigned organometallic products are observed.

[63] Bunel, E. E.; Sheridan, R. E.; Roe, D. C. *J. Am. Chem. Soc.* **1994**, *116*, 1163−1164.

[64] Bergman, R. G.; Evitt, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 7003−7011.

[65] Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113−120.

[66] Bergman, R. G.; Bryndza, H. E.; Evitt, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 4948−4951.

[67] In a subsequent study Bergman et al. investigated a similar Co(III)−metallacyclopentanone system. Even at high temperatures the formation of cyclobutanone was not observed. See: (a) Bergman, R. G.; Theopold, K. H. *Organometallics* **1982**, *1*, 1571−1579. (b) Bergman, R. G.; Theopold, K. H.; Becker, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 5250−5252.

[68] Maitlis, P. M.; Saez, I. M., Fanizzi, F. P.; Sunley, G. J. *J. Organomet. Chem.* **1987**, *330*, C27−C30.

[69] Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101−1107.

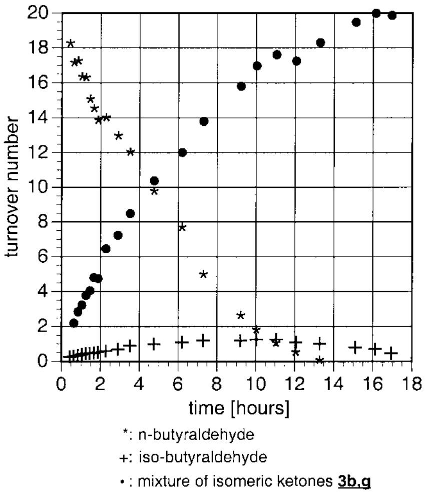
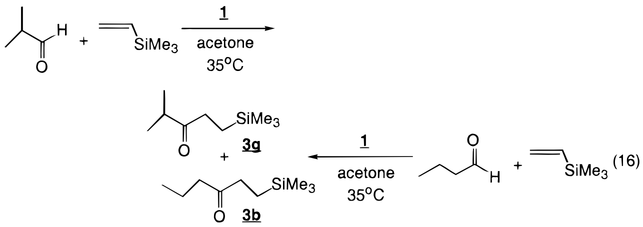


Figure 3. Conversion vs time plot for the hydroacylation of *n*-butyraldehyde.

and isobutyraldehyde, entries b and g, Table 3) with trimethylvinylsilane in the presence of **1**. In a typical reaction, a 1:1 mixture of olefin and aldehyde is treated at 35 °C in acetone with 5 mol % catalyst. Analysis of the reaction mixture after 10 h indicates that all aldehyde has been consumed (in either case this is observed) and that two isomeric ketones **3b** and **3g** are formed as sole organic products (eq 16).

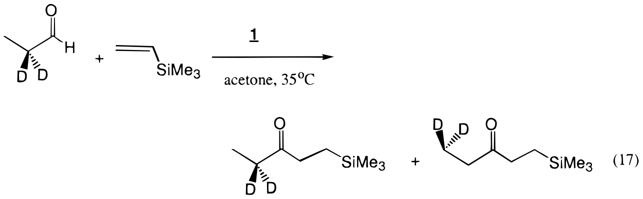


(16)

For example, reaction of *n*-butyraldehyde with trimethylvinylsilane and 5 mol % **1** in d_6-acetone at 35 °C results in 99% conversion to ketone, of which 67% is linear (*n*, **3b**) and 32% is branched (*iso*, **3g**). However, in a reaction of *n*-butyraldehyde with olefin at 25 °C after 2 days, 35% of aldehyde is converted to ketones, of which 58% corresponds to the branched ketone **3g**. This indicates that at lower temperatures isomerization is more extensive. In a reaction of isobutyraldehyde under the same conditions, 43% of the linear ketone (**3b**) is observed together with 56% of the branched product (**3g**). In a reaction of a 1:1 mixture of both aldehydes (5 mol % catalyst), complete conversion is also observed to a mixture of ketones (iso, 48%; *n*, 51%). A decrease in catalyst load to 3 or 1 mol % gives a similar result: complete conversion and 43% isopropyl vs 56% *n*-propyl ketone. Following this latter reaction by ^{1}H NMR spectroscopy in d_6-acetone at 35 °C shows that *n*-butyraldehyde is converted more rapidly to product than isobutyraldehyde (3.2 TO/h vs 2.4 TO/h). The catalytic conversion of *n*-butyraldehyde was followed by ^{1}H NMR spectroscopy and the individual TOFs for ketone formation extracted. Remarkably, during catalysis isobutyraldehyde is formed as evidenced by the appearance of a doublet at 9.62 ppm. This indicates that not only do isomerized products form but the isomerization process actually converts *n*-butyraldehyde to isobutyraldehyde during catalysis. The time course of the reaction is shown in Figure 3. As is evident, after conversion of ca. 16 equiv (out of 20), the ratio of isobutyraldehyde to *n*-butyraldehyde is about 1:1, and at longer times the concentration of the isobutyraldehyde exceeds that of the *n*-butyraldehyde. In the reaction of isobutyraldehyde with olefin only trace amounts of *n*-butyraldehyde are generated during catalysis; the isoaldehyde is converted to the mixture of isomeric ketones without considerable formation of *n*-butyraldehyde. The formation of small amounts of propene in the reactions of the isomeric butyraldehydes is also observed with ongoing catalysis; a trace amount of a third aldehyde is observed which we attribute to **2k**, $Me_3SiCH_2CH_2C(O)H$. When either butyraldehyde is treated with **1** in a low-temperature NMR experiment, the same intermediate is formed in each case which we assign to **4b**.[70] Characteristic for **4b** is a Cp*resonance at 1.62 ppm and a $-SiMe_3$ resonance at -0.05 ppm in a ratio of 15:9 along with a ν_{CO} at 1970 cm^{-1}.

To support this assignment, we compare **4b** with **4h**, which serves as a model for a Co(III) complex bound to a secondary alkyl group as in **4g**, $[C_5Me_5Co(CO)(C_2H_4SiMe_3)(CHMe_2)]$. Complex **4h**, the Co−bisalkyl complex, which originates from the reaction of cyclohexanecarbaldehyde with **1**, has a Cp* resonance at 1.52 ppm and a ν_{CO} at 1962 cm^{-1}. Additional evidence was gained in an in situ IR experiment. Addition of 10 equiv of *n*-butyraldehyde to a toluene solution of **1** generated a yellow solution with a strong IR band at 1970 cm^{-1}; repeating this experiment with 10 equiv of isobutyraldehyde generated an essentially identical IR spectrum ($\nu_{CO} = 1970$ cm^{-1}). Addition of 10 equiv cyclohexanecarbaldehyde, **2h**, to a toluene solution of **1** resulted in a species with ν_{CO} at 1962 cm^{-1}.

As an additional experiment designed to probe isomerization, we have examined hydroacylation of 2,2-dideuteriopropionaldehyde. Following the catalysis in h_6-acetone by ^{2}H NMR spectroscopy shows clearly that deuterium is incorporated into both C_β and C_α sites of the ketone, which illustrates isomerization also occurs in the case of propionaldehyde (eq 17).[71]



(17)

On the basis of these observations and our kinetic investigations, we can propose an extended mechanistic scheme which accounts for the isomerized products and interconversion of isomeric aldehydes. This is illustrated in Scheme 5 for the butyraldehydes.

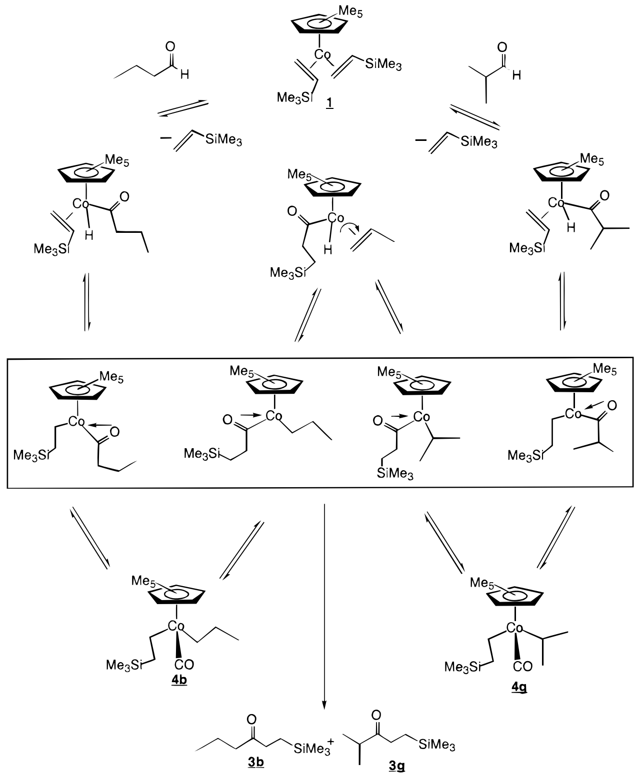
The consequence of the complete reversibility of all elementary steps in this process with the exception of the C−C bond-forming step is demonstrated in the formation of the mixture of isomeric ketones in the reaction of butyraldehyde. A Co(III) acyl olefin hydride species is proposed which is responsible for isomerization through insertion of propene with different regiochemistry after rotation.[47] This scheme also suggests that reductive elimination can occur from any of the four alkyl−

---

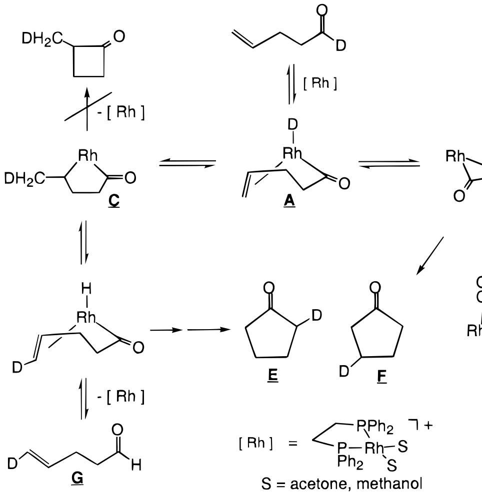
(70) In a reaction of **1** with 30 equiv of isobutyraldehyde in d_6-acetone at −15 °C the formation of one major intermediate assigned as **4b** was observed (Cp*: 1.62 ppm); at low temperature a second species builds up to about 5% with a Cp* resonance at 1.52 ppm and a $-SiMe_3$ resonance at −0.02 ppm (ratio 15:9). This intermediate is depleted quickly after warming to 0 °C, and only **4b** in addition to ***1*** remains; this species is tentatively assigned as **4g**.

(71) *n*-Hexanal was also reacted with trimethylvinylsilane and catalyst **1**. A mixture of two hydroacylation products is observed, the linear addition product (n-$C_5H_{11}C(O)C_2H_4SiMe_3$) and the methyl-branched addition product ($C_3H_7CH(Me)C(O)C_2H_4SiMe_3$); other products are not observed. During catalysis the formation of isomeric hexanals is observed as well.

Scheme 5. Catalytic Hydroacylation of Butyraldehydes. Formation of Isomeric Ketones **3b** and **3g**



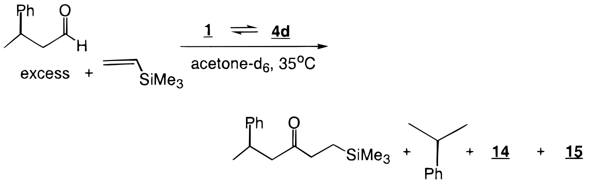
Scheme 6. Bosnich Mechanism for Intramolecular Hydroacylation of 4-Pentenals Catalyzed by Cationic Rh(I) Complexes[28−33]



acyl Co(III) intermediates since all isomers must be populated during catalysis (Scheme 5).

Bosnich[28−33] et al. have investigated the intramolecular hydroacylation of 4-pentenals using labeling studies. Their proposed mechanism is summarized in Scheme 6. A cationic Rh(I) bisphosphine system is applied as a catalyst; no discrete intermediates on the catalytic cycle build up in sufficient concentrations to be detected. Deuterium-labeling studies established the isomerization pathways also found in the Co system investigated in this study. Scrambling the deuterium label from the C_1-position to generate aldehyde **G** confirms that the aldehyde activation/olefin insertion sequence is faster than reductive elimination to generate ketone. The proposed dominant acyl alkyl Rh complex is a rhodacyclohexanone species (**B**) which is responsible for product formation (**E** and **F**). Isomerization to a rhodacyclopentanone complex (**C**) takes place as indicated by the labeling experiment, but reductive elimination to generate a cyclobutanone is not observed. On the basis of the results of additional labeling studies, a rhodacyclopentane−CO complex (**D**) was proposed but not detected.

F. Deactivation Processes. Catalyst deactivation and side reactions were investigated in more detail. In the presence of excess aldehyde, hydroacylation occurs and, depending on the structure of the aldehyde, olefin is converted to ketone in yields of 80−100%. The color of the reaction mixture changes during this process from orange-yellow to green. Analysis of the reaction mixture by NMR and IR spectroscopy reveals the formation of two CO-containing Co species which were mentioned above and have been described as products of decarbonylation reactions for aromatic aldehydes,[35] the olefin carbonyl complex $[C_5Me_5Co(CO)(C_2H_3SiMe_3)]$ **14** and the carbonyl-bridged dimer $[C_5Me_5Co(CO)]_2$ **15**. Both species are observed as final products during the decomposition of complex **4l** at room temperature as well. The ratio of **14** to **15** depends on substrate ratios used and on the nature of the aldehyde. This is illustrated in the case of 3-phenylbutanal **3d** (entry d, Table 3). Besides the cobalt−carbonyl complexes **14** (90%) and **15** (10%), the expected stoichiometric amount of isopropylbenzene is also observed after catalysis has stopped. These results are confirmed in a reaction of **1** with 15 equiv of 3-phenylbutanal at −15 °C. As described above the formation of the diastereomeric mixture of complexes **4d** is observed. If this sample is warmed to 25 °C, the ketone **3d** is formed along with the conversion of all organometallic material into complexes **14** and **15** now in a ratio of 1:1.



(18)

In the case of other aldehydes summarized in Table 3, deactivation reactions are more complex. Complexes **14** and **15** are observed; however, ^{1}H NMR integration shows that the material accounted for does not correspond to the amount of catalyst **1** introduced. Additional decomposition products were observed but could not be assigned.

Tishenko-Type Dimerization of Aldehyde. In the presence of excess aldehyde, an additional catalytic process is observed: dimerization of two molecules of aliphatic aldehyde to generate the corresponding alkyl ester. This type of intermolecular aldehyde disproportionation has a classic analogue in the base-catalyzed Tishenko reaction. Transition metal catalyzed versions of this reaction have also appeared.[72−76] For example, in a reaction of isovaleraldehyde (40 equiv) with trimethylvinylsilane (20 equiv) with **1** the formation of ketone **3c** is observed

---

(72) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 1346.

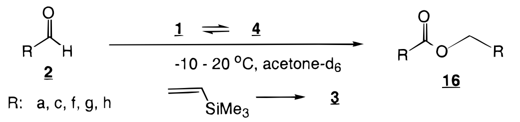
(73) SanFilippo, J.; Villacorta, G. M. *J. Org. Chem.* **1983**, *48*, 1151−1155.

(74) Takegami, Y.; Watanabe, Y.; Mitsudo, T.; Yamashita, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3597−3600.

(75) Yamamoto, A.; Koshiro, Y.; Horino, H.; Ito, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504−512.

(76) This reaction is observed with substrates without acidic α-protons to avoid competitive enolate-type transformations. The Tishenko analogue reaction reported here is curiously exclusive for alkyl aldehydes. Aromatic aldehydes show regular decarbonylation chemistry to **14** and **15** in the presence of excess aldehyde.

exclusively in the initial phase of catalysis. After 70% conversion to ketone, Tishenko-type ester begins to appear. During this process the resting states **1** and **4c** greatly diminish in intensity; uncharacterized Co species are formed. After complete conversion of aldehyde, all olefin had been converted to ketone and excess aldehyde was completely accounted for by ester formation.

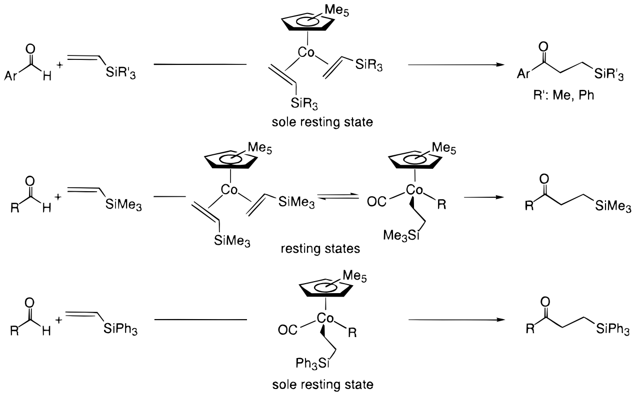


(19)

This reaction was also observed in the low-temperature NMR experiment described above used to generate intermediate **4c**. Even at low temperatures the formation of ketone was followed by the formation of ester. Careful adjustment of temperature was necessary to generate **4c** without ester and ketone formation. Depending on the aldehyde structure it was possible to cleanly generate intermediates of type **4** without contamination by ester (Table 3, entries a, b, d, f, and k). In other cases this was not possible (Table 3, entries c and h). For example, in the case of cyclohexanecarbaldehyde (entry h), intermediate **4h** was generated at −12 °C in d_6-acetone from **1** and 20 equiv of aldehyde. After 2 h complex **4h** was the major organometallic species observed (80%) with **1** as the minor species (20%); no other cobalt-containing complexes were observed at this stage (based on C_5Me_5 and $SiMe_3$ resonances). Besides small amounts of free trimethylvinylsilane and ketone **4h**, 60% of the cyclohexanecarbaldehyde had been converted to the ester. Isobutyraldehyde behaves in a similar manner. In the presence of excess olefin clean hydroacylation to ketones **3g** and **3b** is observed. On the other hand, in a reaction of 30 equiv of isobutyraldehyde **2g** with **1** at 0 °C in d_6-acetone, stoichiometric formation of **3g** was observed while formation of ester consumed all aldehyde.[77] The presence of esters added to the difficulties of characterizing intermediates **4** by NMR spectroscopy in these reaction mixtures.

G. Summary. The intermolecular hydroacylation of vinylsilanes with a variety of alkyl aldehydes using precatalyst **1** exhibits good turnover numbers under quite mild conditions. In a kinetic and spectroscopic study it was discovered that a sensitive interplay of binding affinity of olefin and reactivity of aldehyde determines the nature of the catalyst resting state(s) throughout catalysis. In our previous investigation of the hydroacylation of aromatic aldehydes we found that **1** was the sole resting state in catalysis;[35] in the reaction of alkyl aldehydes with complex **1**, an equilibrium between **1** and **4**, a Co(III) complex of the type $[C_5Me_5Co(CO)(C_2H_4SiR_3)(R')]$, is established during catalysis. Using the more bulky olefin, vinyltriphenylsilane, the bisolefin Co(I) species becomes unfavored and the Co(III)−bisalkyl−CO complex is observed as the sole resting state (Scheme 7).

Scheme 7. Resting States during Catalytic Hydroacylation Using **1** as Catalyst Precursor



Further, it was established that the reductive elimination to generate the C−C bond is the turnover-limiting step in this process; as a consequence of this, isomerization processes can occur prior to reductive elimination which not only generate a mixture of isomeric ketones but also isomerize aldehydes during catalysis, e.g., *n*-butyraldehyde into isobutyraldehyde. It has been pointed out that acyl alkyl reductive elimination is especially facile,[28,64,69,78a,b] which might suggest that the hydroacylation of olefins is a specific example for a successful combination of C−H bond activation and C−C bond formation; the same catalyst system (complex **1**) will reversibly activate aromatic C−H bonds (eq 1), but olefin−arene coupling is not observed (eq 1).[78c] The C−H bond activation reaction, especially of aldehydes, has been well documented using Rh[79−82] or Ir[83] complexes. However, cobalt has been widely excluded from bond activation studies,[39,84,85] and the inability of the first-row cobalt system $[C_5H_5Co(CO)]$ to participate in such C_{sp^3}−H activation reactions has been discussed recently.[86,87] The system investigated here suggests that the oxidative addition of an aldehydic C−H bond to $[C_5Me_5Co(L)]$ is a facile process with a barrier well below the reductive elimination barriers discussed as the turnover-limiting step in hydroacylation catalysis.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled Vacuum Atmospheres drybox and, unless stated otherwise, were stored in the drybox at −20 °C. All coupling constants are reported in hertz. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H NMR signals and to the ^{13}C NMR signals of the deuterated solvents, respectively. NMR probe temperatures were measured using an anhydrous methanol sample. Elemental analyses were performed by Atlantic Microlabs, Inc., of Norcross, GA.

Materials. Toluene, pentane, tetrahydrofuran, and diethyl ether were distilled under nitrogen from sodium−benzophenone ketyl. d_6-Benzene was dried over potassium, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles and stored in the drybox. d_6-Acetone was dried over CaH_2, vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored in the drybox. $[C_5Me_5CoCl]_2$ was

---

(77) Turnover numbers on the order of 50−100 are observed for aldehydes such as isobutyraldehyde or cyclohexanecarbaldehyde at 10 °C with turnover frequencies of ~4 TO/h under these conditions. **4** persists to 90% conversion of aldehyde to ester; then deactivation is observed, and besides decarbonylation product **15** further unassigned organometallic complexes were observed.

(78) (a) Puddephatt, R. J.; Brown, M. P.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613−1618. (b) See also: Graham, W. A. G.; Gosh, C. K. *J. Am. Chem. Soc.* **1989**, *111*, 375−376. (c) Bergman, R. G.; McGhee, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 4246−4262.

(79) Suggs, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 640−641.

(80) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221−226.

(81) Bergman, R. G.; Luecke, H. F. *J. Am. Chem. Soc.* **1997**, *119*, 11538.

(82) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1357−1358.

(83) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045−1047.

(84) Wadepohl, H.; Borchert, T.; Buechner, H.; Pritzkow, H. *Chem. Ber.* **1993**, *126*, 1615−1618.

(85) Wadepohl, H.; Borchert, T.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1447−1448.

(86) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487−1496.

(87) Bergman, R. G.; Moore, B. C.; Bengali, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 3879−3880.

Table 5. NMR and IR Spectroscopic Data for Compounds **4a−l** and **9c**[a]

	^{1}H NMR, δ [ppm]			^{13}C NMR, δ [ppm]			IR [cm^{-1}]
compound	C_5Me_5	$-SiMe_3$	−R	C_5Me_5	$-SiMe_3$	−R	(C_7H_8, 20 °)
4a	1.60	−0.09	0.91 (t, 3, *J* = 7.5 Hz, $-CH_3$), 1.22, 1.34, 0.81, 0.90 (m, 1, −CH*H*), 0.62 (m, 2, $-CH_2-$)	8.8, 97.8	−1.80	14.2,, 15.3, 23.2 ($-CH_2-$), 19.3 ($-CH_3$, q, 113 Hz)	1970.3
4b	1.62	−0.05	na	8.8, 97.1	−1.78	14.6, 15.4, 23.2, 25.4, 29.0	1970.0
4c	1.61	−0.05	0.52, 0.65, 0.91, 1.28−1.71, 2.31 (m, 13H)	8.8, 97.5	−1.95	14.1, 17.3, 25.7 ($-CH_2-$), 34.5 (−*C*HMe$_2$), 27.6, 33.7 (−CH*Me*$_2$)	1968.2
4k	1.61	−0.04 (18H)	1.33, 0.77 m, 2H) 0.63 (m, 4H)	8.3, 98.0	−1.85	15.5 (Co−CH$_2$), 22.81 ($-CH_2-Si$)	1969.1
4f	1.61	−0.04	0.44, 1.43 (d, 1, 10 Hz), 0.68, 1.25 (m, 1H), 0.9−1.1 (m, 2H), 0.92 (s, 9H)	8.8, 97.8	−1.55	15.4, 24.0, 33.1, 34.3, 40.9	1961.8
4h	1.51	−0.01	na	8.2, 97.5	−1.72	na	1962.1
4d	1.62	−0.03	na	8.5, 97.2	−1.70	na	1968.1
	1.58	−0.03		8.7, 97.4	−1.70		
4l	1.52	0.09	1.50, 1.05, 1.82, 2.46 (m, 1, −CH*H*−), 3.51, 3.87, 4.09, 4.09 (m, 1, C_5H_4-), 3.96 (s, 5, C_5H_5)	8.9, 98.1	−1.83	20.0, 26.2, (Co−CH$_2$), 67.7, 67.8, 73.6, 77.4, 98.6, (C_5H_{4-}), 68.7, (C_5H_5)	1983.3
9c	1.57		na	8.8, 97.8		15.4, 18.8 (Co−CH$_2$), 26.0 ($-CH_2-Si$), 34.2 (−*C*HMe$_2$), 27.5, 33.8 (−CH*Me*$_2$); aromatics na	1966.0

[a] na = not assigned.

prepared according to the procedure of Koelle.[41] Alkyl aldehydes were distilled twice prior to use and vacuum-transferred, degassed by repeated freeze−pump−thaw cycles, and stored in the drybox. Trimethylvinylsilane (Aldrich) contained traces of tetrahydrofuran (∼5%) which were removed by stirring over $ZrCl_4$ followed by vacuum transfer. Triphenylvinylsilane (Celeste) was used as received without additional purification. Ferrocenecarbaldehyde (Aldrich) was used after recrystallization from acetone. The alkyl aldehydes used require utmost purity. If the corresponding carboxylic acid is added even in stoichiometric amounts, catalytic activity is extensively reduced and precipitation is observed. The aldehyde $Me_3SiCH_2CH_2C(O)H$ was prepared following a literature procedure[54] and stored at −30 °C, slow decomposition to unassigned products is observed.[88] *d*$_1$-Isovaleraldehyde was prepared from *d*$_2$-isoamyl alcohol by perruthenate (TPAP) oxidation (99%).[89,90] *d*$_2$-Propanal was prepared from a pyridine-catalyzed reaction of propanal in *d*$_2$-water.

[$C_5Me_5Co(C_2H_3SiMe_3)_2$] 1. The synthesis of the parent ethylene complex [$C_5Me_5Co(C_2H_4)_2$] has been reported in the literature. The trimethylvinylsilane complex **1** described here was prepared in a modification of that synthesis. [Cp*CoCl]$_2$ (2 g, 4.4×10^{-3} mol) was dissolved in 40 mL of tetrahydrofuran. Trimethylvinylsilane (4.4 g, 0.044 mol) was added via syringe, and the mixture was cannula transferred to a previously prepared amalgam mixture covered by 30 mL of tetrahydrofuran (1.0 g of Na, 100 g, 7.4 mL of Hg, 1 mol %). The amalgam reaction mixture was stirred for 1 h at room temperature. A color change from dark brown to dark red was observed. After filtration by cannula from the amalgam, the solvent was removed in vacuo, leaving a red solid, which was dissolved in pentane, filtered, and placed at −78 °C. Red crystals were isolated (1.3 g, 3.3×10^{-3} mol, 75%), and the compound was stored at −30 °C under an argon atmosphere. Crystals for X-ray analysis were grown from an acetone solution of **1** at −79 °C. NMR spectroscopic data for **1**: ^{1}H (400 MHz, *d*$_6$-acetone, 20 °C) δ 1.54 (s, 15, C_5Me_5), 0.09 (s, 18, SiMe$_3$), 0.28 (d, 2, *J* = 14.6 Hz, CH$_2$ syn), 1.82 (d, 2, *J* = 11.6 Hz, CH$_2$ anti), 0.87 (dd, 2, *J* = 14.6 Hz, *J* = 11.6 Hz, CHSi syn); ^{13}C{^{1}H} (75 MHz, C_6D_6, 20 °C) δ 2.43 (SiMe$_3$), 9.67 (C_5*Me*$_5$), 93.5 (*C*$_5$Me$_5$), 43.7 (CHSi), 47.4 (CH$_2$).

Turnover Frequency Determinations. A 5 mm NMR tube was charged with 0.005 g (1.27×10^{-5}mol) of **1**. *d*$_6$-Acetone (0.6 mL) was placed on top, and the appropriate amount of vinyltrimethylsilane was added via syringe by weight in the drybox. The NMR tube was sealed with a septum and removed from the drybox. After cooling to 0 °C, the corresponding amount of aldehyde was added by syringe. Shaking resulted in a homogeneous reaction mixture which was transferred to the temperature equilibrated probe of a Bruker AMX 300. Ketone formation was followed by ^{1}H NMR spectroscopy over time using an implemented kinetic routine. As internal standard during catalysis, either added ferrocene or the residual amount of tetrahydrofuran (2%)[35] present in the commercial vinyltrimethylsilane was used. Turnover frequencies are extracted from the slope of plots of turnover number (based on integration) over time for initial, linear segments (linear regression). At these low concentrations, the cobalt species are sensitive to impurities and accurate integration of resonances for **1** and **4c** in the presence of large excesses of substrates is difficult. Thus, substantial error limits apply to the TOFs in Table 1.

Table 6. Crystallographic Data and Refinement Details for **1** and **4l**

	1	**4l**
molecular formula	$CoSi_2C_{20}H_{39}$	$CoFeSiOC_{26}H_{37}$
FW	394.63	508.44
crystal dimensions (mm)	0.25 × 0.25 × 0.04	0.40 × 0.20 × 0.20
no. of reflections for cell determination	6261	8192
a (A)	17.7949(10)	10.2972(5)
b (A)	14.0181(7)	12.9968(7)
c (A)	18.9075(10)	19.050(10)
β (deg)	106.128(1)	91.433(1)
V (A^3)	4530.9(4)	2548.74(23)
space group	$P2_1/c$	$P2_1/n$
Z	8	4
μ (Mo, Kα, mm^{-1}	0.86	0.86
F(000)	1716.77	1075.62
T(°C)	−100	−100
no. of reflections	21778	8970
no. of unique reflections	7900	3610
no. of observations ($I > 2.5\sigma(I)$)	6261	3019
T_{min}, T_{max}	0.761, 0.888	0.695, 1.000
R, *R*^{w}	0.048, 0.043	0.039, 0.048
R (all data)	0.070	0.050
GOF	2.13	1.65

Reaction of 1 with Excess Aldehyde. To a solution of **1** in acetone at −5 °C (e.g., 0.1 g (2.5×10^{-4} mol) in 15 mL) was added by syringe the appropriate alkyl aldehyde (15−20 equiv). This mixture was stirred for several hours (1−4 h), keeping the solution at 0 °C. A characteristic color change from orange to yellow was observed and was used to estimate the reaction time. Removal of volatiles at low temperatures

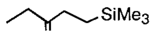
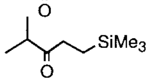
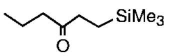
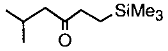
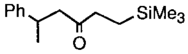
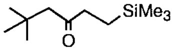
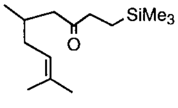
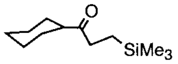
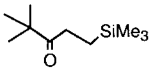
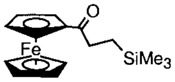
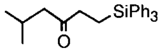
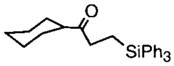
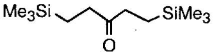
---

(88) Hoyeyda, A. H.; Young, D. G. J.; Hale, M. R. *Tetrahedron Lett.* **1996**, *37*, 827−830.

(89) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625−1627.

(90) Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 12−22.

Table 7. Spectroscopic and Analytical Data for Ketones Formed in Catalytic Hydroacylation

	Ketone	^1H NMR (ppm)	$^{13}C\{^1H\}$ NMR (ppm)	elemental analysis
3a		-0.04 (s, 9, -$SiMe_3$), 0.72 (m, 2, -CH_2), 0.91 (t, 3, -CH_3), 2.39 (m, 2, -CH_2), 2.44 (q, 2,-CH_2)	211.2 (CO); 36.9, 35.1 (-CH_2-), 10.6 (-CH_3), 8.1 (-CH_2-), -1.8 (-$SiMe_3$)	C: 59.63 (60.62) H: 10.91 (11.40)
3g		-0.03 (s, 9, -$SiMe_3$), 0.72 (m, 2, -CH_2), 1.05 (d, 6, -CH_3), 2.48 (m, 2, -CH_2), 2.65 (sp, 1,-CH)	214.0 (CO); 37.2 (-CH_2-), 40.3 (-CH), 18.7 (-CH_3), 10.3 (-CH_2-), -1.7 (-$SiMe_3$)	C: 62.55 (62.72) H: 11.20 (11.70)
3b		-0.03 (s, 9, -$SiMe_3$), 0.72 (m, 2, -CH_2), 0.88 (t, 3, -CH_3), 1.52 (qt, 2, -CH_2-), 2.38 (m, 2,-CH_2-), 2.40 (t, 2, -CH_2-)	210.5 (CO); 35.0 (-CH_2-), 44.1 (-CH_2-), 17.8 (-CH_2-), 13.8 (-CH_2-), 10.4 (-CH_3), -1.7 (-$SiMe_3$)	C: 62.55 (62.72) H: 11.20 (11.70)
3c		-0.03 (s, 9, -$SiMe_3$), 0.71 (m, 2, -CH_2), 0.85 (d, 6, -CH_3), 2.11 (m, -CH-), 2.31 (d, 2,-CH_2-), 2.38 (m, 2, -CH_2-)	213.7 (CO); 35.7 (-CH_2-), 50.9 (-CH_2-), 27.0 (-CH_3), 26.7 (-CH), 10.7 (-CH_2-), -1.75 (-$SiMe_3$)	C: 64.46 (64.45) H: 11.85 (11.90)
3d		-0.05 (s, 9, -$SiMe_3$), 0.65 (m, 2, -CH_2), 1.21 (d, 3, -CH_3), 2.33 (m,2, -CH_2-), 2.74 (m, 2,-CH_2-), 3.28 (m, 1, -CH-), 7.32 (m, 5, -Ph)	210.1 (CO); 36.5 (-CH_2-), 50.9 (-CH_2-), 22.8 (-CH_3), 38.4 (-CH), 10.7 (-CH_2-), -1.4 (-$SiMe_3$), 147.9, 129.5, 128.0, 127.2 (C_6H_5)	C: 72.42 (72.52) H: 9.08 (9.38)
3f		-0.01 (s, 9, -$SiMe_3$), 0.70 (m, 2, -CH_2), 0.98 (s, 9, -CMe_3), 2.38 (m,2, -CH_2-), 2.32 (s, 2,-CH_2-)	211.5 (CO); 40.0 (-CH_2-), 54.8 (-CH_2-), 30.5 (-$C\underline{Me}_3$), 31.6 (-$\underline{C}Me_3$), 10.9 (-CH_2-), -1.1 (-$SiMe_3$)	C: 65.93 (66.16) H: 12.07 (11.92)
3e		-0.01 (s, 9, -$SiMe_3$), 0.70 (m, 2, -CH_2), 0.82 (d, 3, -CH_3), 2.38 (m,2, -CH_2-), 2.32 (m, 2,-CH_2-), 2.05 (m,1, -CH), 1.98 (m, 2, -CH_2-),1.25 (m, 2, -CH_2-), 1.55 (s, 3, -CH_3), 1.65 (s, 3, -CH_3), 5.08 (m,1, -CH)	211.0 (CO); 38.1 (-CH_2-), 50.2 (-CH_2-), 26.4 (-CH_3), 26.6 (-CH), 20.6 (-CH_3), 29.9 (-CH_3), 18.2 (-CH_2-), 38.4 (-CH_2-),132.0 (=CH), 125.9 (=C), 11.0 (-CH_2-), -1.2 (-$SiMe_3$)	C: 70.10 (69.93) H: 11.67 (11.74)
3h		-0.01 (s, 9, -$SiMe_3$), 0.70 (m, 2, -CH_2), 1.30 (m, 4, -CH_2-), 1.78 (m,4, -CH_2-), 1.65 (m, 2,-CH_2-), 2.42 (m,1, -CH), 2.48 (m, 2, -CH_2-)	213.4 (CO); 50.5 (-CH_2-), 10.2 (-CH_2-), 35.2 (-CH), 25.9, 26.5, 26.2 (-CH_2-), -1.8 (-$SiMe_3$)	C: 68.00 (67.93) H: 11.11 (11.07)
3i		-0.02 (s, 9, -$SiMe_3$), 0.69 (m, 2, -CH_2), 1.10 (s, 9, -$C\underline{Me}_3$), 2.52 (m, 2, -CH_2-),	209.7 (CO); 44.5 (-CH_2-), 10.8 (-CH_2-), 31.3 (-$\underline{C}Me_3$), 28.0 (-$C\underline{Me}_3$), -1.5 (-$SiMe_3$)	MS (EI) m/z : 186.370 (M+)
3l		0.04 (s, 9, -$SiMe_3$), 0.84 (m, 2, -CH_2), 2.76 (m,2, -CH_2-), 4.19 (s, 5, C_5H_5), 4.49 (m, 2, Cp-), 4.79 (m, 2, Cp-)	202.5 (CO); 34.2 (-CH_2-), 10.1 (-CH_2-), 69.2, 71.5, 79.6 (-C_5H_4), 69.5 (-C_5H_5), -2.0 (-$SiMe_3$)	C: 61.11 (61.15) H: 7.06 (7.06)
8c		0.81 (d, 6, -CH_3), 1.65 (m, 2, -CH_2), 2.00 (m,1, -CH), 2.23 (d, 2, -CH_2-), 2.52 (m, 2, -CH_2-), 7.41, 7.53 (m,15, Ph_3)	210.2 (CO); 38.0 (-CH_2-), 51.4 (-CH_2-), 25.1 (-CH-), 22.8 (-CH_3), 6.9 (-CH_2-), 136.4, 135.6, 130.5, 128.9 (-$SiPh_3$)	C: 80.34 (80.59) H: 7.56 (7.59)
8h		1.21 (m, 2, -CH_2), 1.30 (m, 4, -CH_2-), 1.68 (m,6, -CH_2-), 2.32 (m, 1,-CH-), 2.61 (m,2, -CH_2), 7.38, 7.55 (m,15, Ph_3)	213.3 (CO); 51.1 (-CH_2-), 7.2 (-CH_2-), 35.8 (-$\underline{C}H$), 27.0, 26.7,29.7 (-$(CH_2)_2$-CH_2), 136.7, 136.0, 130.8, 129.3 (-$SiPh_3$)	C: 80.79 (81.35) H: 7.58 (7.59)
3k		0.72 (m, 2, -CH_2-), 2.43 (m, 2, -CH_2-), -0.02 (s,9, -$SiMe_3$),	212.0 (CO); 37.1 (-CH_2-),11.2 (-CH_2-), -1.3 (-$SiMe_3$)	MS (EI) m/z : 230.498 (M+)

furnishes a yellow solid material (or an oil in some cases). Characterization by ^1H NMR spectroscopy reveals the formation of complexes **4a**,**k**,**l** and is in agreement with the data found for the intermediates observed during catalysis or in direct NMR experiments as described. Additional resonances due to decomposition products or remaining **1** are often observed as well. Any attempt to purify the product by chromatography (−60 °C, alumina, pentane) or recrystallization resulted in extensive decomposition. Therefore, compounds **4a**,**k** were characterized by NMR and IR spectroscopy at this stage. Recrystallization was successful in the case of **4l**, and isolation on a larger scale was possible. Table 5 summarizes characteristic NMR and IR data for compounds **4** and **9c**. Complexes **4a**,**k**,**l** were isolated in the described manner, **4b**,**d** and **9c** were characterized under catalytic conditions at −20 °C, **4c**,**f**,**h** were generated in a reaction of excess aldehyde with **1** at low temperatures (vide supra) and characterized at −20 °C. All NMR data were obtained in d_6-acetone. IR spectra were obtained at 20 °C after addition of excess aldehyde to a toluene solution of **1** immediately after mixing.

[$C_5Me_5Co(CO)(C_2H_4SiMe_3)(C_5H_4FeC_5H_5)$] 4l. Complex **1** (0.2 g, 5 × 10^{-4} mol) and ferrocenecarbaldehyde (0.32 g, 15 × 10^{-4} mol) were combined in a drybox, and the flask was sealed and attached to a Schlenk line. After cooling to 0 °C, 15 mL of acetone was slowly added while the Schlenk flask was moved to ensure complete dissolution. The homogeneous solution was kept at 0 °C for 5−6 h, during which time the color changed to yellow. The reaction mixture was cannula filtered and the Schlenk flask placed at −78 °C for 24 h. Yellow crystalline material was isolated after the mother liquor was decanted (0.2 g, 77%). Compound **4l** is soluble in organic solvents such as pentane, ether, or toluene without decomposition; however, slow decay is observed in the course of hours at room temperature. The complex was stored at −20 °C under an Ar atmosphere. The material obtained this way was suitable for an X-ray structure determination. In repeated syntheses the coprecipitation of remaining **1** is frequently observed, and recrystallization results in largely reduced yields. NMR spectroscopic data for **4l**: ^1H (300 MHZ, d_6-acetone, −10 °C) δ 1.52 (s, 15, C_5Me_5), 0.09 (s, 9, $SiMe_3$), 1.05 (m, 1, $CH\mathit{H}-Si$), 1.50 (m, 1, $CH\mathit{H}-Si$) 1.81 (m, 1, $Co-CH\mathit{H}$), 2.46 (m, 1, $Co-C\mathit{H}H$), 3.51 (m, 1, $C_5H_3\mathit{H}$), 3.87 (m, 1, $C_5H_3\mathit{H}$), 4.09 (m, 2, $C_5H_2\mathit{H}_2$), 3.96 (s, 5, C_5H_5); $^{13}C\{^1H\}$ (d_6-acetone, −15°C) δ −1.83 ($SiMe_3$), 8.91 ($C_5\mathit{Me}_5$), 98.05 (C_5Me_5), 19.98, 26.18 ($-CH_2-$), 67.70, 67.82, 73.61, 77.35, 98.62 (C_5H_4-Co), 68.69 (C_5H_5); Anal. Calcd for $C_{26}H_{37}CoFeOSi$: C, 61.42; H, 7.33. Found: C, 60.92; H, 7.36; MS/EI 508 (m^+); IR (toluene, 20 °C) 1983 cm^{-1}.

[$C_5Me_5Co(CO)(C_2H_3SiMe_3)$] 14. This compound was synthesized independently in a reaction of **1** in pentane at 0 °C with CO (1.1 equiv). A solution of 0.2 g (5 × 10^{-4} mol) **1** in pentane (15 mL) was cooled to 0 °C, and 12.5 mL of CO gas was added slowly with vigorous stirring. Stirring was continued for 2 h at 0 °C. A green oil was isolated after filtration and evaporation of all volatiles. This compound is quite sensitive and is stored as a frozen C_6D_6 solution. The spectroscopic features of this complex are identical with the data for complex **14** characterized in situ after hydroacylation catalysis. NMR spectroscopic data for **14**: ^1H (300 MHZ, C_6D_6, 20 °C) δ d 1.52 (s, 15, C_5Me_5), 0.22 (s, 9, $SiMe_3$), 2.08 (d, 10.8 Hz, 1, CH_2 syn), 2.44 (d, 14.0 Hz, 1, CH_2 anti), 1.02 (dd, 14.0, 10.8 Hz, 1, CHSi syn); $^{13}C\{^1H\}$ (C_6D_6, 20 °C) δ d 0.32 ($SiMe_3$), 9.82 ($C_5\mathit{Me}_5$), 95.0 (C_5Me_5), 43.4 (CHSi), 44.2 (CH_2); IR (C_6D_6, 20 °C) 1944 cm^{-1}.

[$C_5Me_5Co(\mu$-$CO)]_2$ 15. This decarbonylation product of catalytic hydroacylation was isolated for example from a reaction using excess propanal and vinyltrimethylsilane; identical results were obtained in a reaction of other aldehydes with vinyltrimethylsilane. Complex **1**, (0.5 g, 1.27×10^{-3} mol) was dissolved in acetone (15 mL) with 20 equiv of vinyltrimethylsilane present (2.54 g, 0.025 mol). The orange solution was stirred, and 40 equiv of propanal (2.94 g, 0.05 mol) was added. This mixture was kept at 40 °C for 24 h, during which time the mixture changed color from yellow to green. The solution was cooled to −78 °C for 24 h. A dark-green, crystalline material was isolated after filtration (0.15 g, 53% for 100% decarbonylation to **15** (vide supra)): ^{1}H NMR (300 MHz, 20 °C, C_6D_6) δ 1.41 (C_5Me_5, s); ^{13}C NMR (20 °C, C_6D_6) δ 94.7 (C_5Me_5), 8.6 ($C_5\mathit{Me}_5$); MS (EI) *m/z* 444 (M^+), 135 (base, C_5Me_5); IR (hexane, 20 °C) 1758 cm^{-1}.[91−93]

X-ray Structure Determination of 1 and 4l. Data were collected on a Siemens SMART diffractometer, using the ω scans. The structures were solved by direct methods. Refinement was by full-matrix least squares with weights based on counter statistics. Hydrogen atoms were included in the final refinement using a riding model with thermal parameters derived from the atom to which they are bonded. Crystal data and experimental conditions are given in Table 6. All computations were performed using the NRCVAX suite of programs.[61,70]

General Procedure for Catalytic Hydroacylation. In a drybox under an argon atmosphere, a flask with a stir bar and with a Teflon screw cap (Kontes) was charged with catalyst **1**. A catalyst load of 0.05 g (1.27×10^{-4} mol) was usually used. The catalyst was dissolved in 2−3.5 mL of acetone to form a homogeneous solution. The olefin was added first, and then the appropriate amount of aldehyde was added. The reaction mixture was in all cases homogeneous. The ratio of aldehyde to olefin was in general 1:1 with a catalyst load of 2−5 mol %; in selected cases less catalyst was used (1 or 0.5 mol %). The flask was sealed with the Teflon screw-top and stirred for a period of 48 h at 25 °C or for 24 h at 45 °C. Conversion was based on ^{1}H NMR analysis of a sample of the reaction mixture after the reaction was stopped and opened to air. These reaction mixtures were filtered through silica or Celite plugs to separate the catalyst, and all volatiles were removed by aspirator vacuum. In selected examples (**3a**) the material isolated at this stage was pure by NMR analysis and elemental analysis. However, in most cases purification was accomplished by column chromatography on silica eluting with pentane/ether. Organic products (ketones **3a**−**l**; **8a**−**c**,**h**) were characterized by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy, elemental analysis, or mass spectroscopy (Table 7).

Acknowledgment is made to the National Institutes of Health (Grant GM 28938) for financial support. C.P.L. thanks the Fonds der Chemischen Industrie, Germany, for a Kekulé fellowship. We are indebted to Dan Tempel for providing a sample of [^{13}C]-pentanal. For additional crystallographic details, contact P.S.W.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **4l**, kinetic plots for ligand trapping reactions of **4l** with $P(OMe)_3$ and olefins, and plots for the substrate dependence of hydroacylation of isovaleraldehyde (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA980610N

---

[91] Brintzinger, H. H.; Lee, W.-S. *J. Organomet. Chem.* **1981**, *209*, 401−406.

[92] Dahl, L. F.; Ginsburg, R. E.; Cirjak, L. M. *Inorg. Chem.* **1982**, *21*, 940−957.

[93] Dahl, L. F.; Ginsburg, R. E.; Cirjak, L. M. *J. Chem. Soc., Chem. Commun.* **1979**, 468−472.