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Headline Articles

Catalytic Addition of Aromatic Carbon–Hydrogen Bonds to Olefins with the Aid of Ruthenium Complexes

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Ruthenium complexes, e.g., $Ru(H)_2(CO)(PPh_3)_3$, have been found to catalyze the addition of *ortho* C–H bonds of aromatic ketones to olefins with a high degree of efficiency and selectivity. 2′-Methylacetophenone reacts with various types of terminal olefins to give 1 : 1 coupling products in good to excellent yields. The C–C bond formation takes place exclusively at the terminal carbon atom of olefins except for styrene which affords a mixture of two regioisomers. Acetylnaphthalenes, cyclic aromatic ketones, and heteroaromatic ketones also react with triethoxyvinylsilane to give 1 : 1 addition products in virtually quantitative yields. From 2′-acetonaphthone or 3-acetylthiophene, in which two different reaction sites are available, only one out of four possible regioisomers is obtained. The importance of the coordination of the oxygen atom of the ketone to ruthenium and the intervention of a cyclometallation intermediate are suggested. A deuterium labeling experiment using acetophenone-d_5 and triethoxyvinylsilane shows that an H/D exchange between the aromatic and olefinic positions takes place to some extent, even prior to the formation of the product. This implies that the rate-determining step is not the C–H bond cleavage step, but the product forming step.

The cleavage of a C–H bond along with the formation of a new bond at that carbon center with the aid of transition-metal complexes has been a Holy Grail to chemists for thirty years, since it should provide an ideal synthetic operation. Encouraged by the first discoveries in the mid 1960's of the metal-mediated cleavage of otherwise unreactive C–H bonds, numerous studies have been carried out towards this goal, but only a few special cases have reached the level of efficiency required for useful organic transformations. This paper describes the details concerning the first example of a synthetically useful, highly efficient catalytic reaction involving the metal-mediated cleavage of C–H bonds that we have found recently.[1—3]

In 1963 the first, to the best of our knowledge, explicit example of C–H bond cleavage by transition-metals was reported by Kleiman and Dubeck, who observed the cleavage of an *ortho* C–H bond in azobenzene by the Cp_2Ni complex.[4] Chatt and Davidson reported in 1965 the first example of an oxidative addition of a β C–H bond in naphthalene to a Ru(0) complex.[5] These observations indicated the existence of a new possibility for direct functionalization at a C–H bond. Motivated by this hope, coupled with intrinsic interests in the novel chemistry, extensive studies have been performed and a number of reviews[6] and papers[7,8] dealing with *stoichiometric* reactions involving C–H bond cleavage with transition-metal complexes have been published.

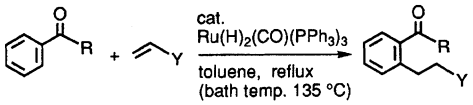
As for the *catalytic* reaction, progress has been very slow, and is still not sufficient from the viewpoint of synthetic organic chemistry. Early studies of $Co_2(CO)_8$-catalyzed carbonylation of azobenzene in 1955[9] and $RuCl_3$-catalyzed dimerization of acrylonitrile in 1966[10] and in 1967[11] could involve C–H bond cleavage by transition-metals. In 1978, Hong, Yamazaki, Sonogashira, and Hagihara reported that the addition of a C–H bond in benzene to diphenylketene could be brought about by using $Rh_4(CO)_{12}$ as a catalyst.[12] Although a number of examples of transition-metal-catalyzed functionalizations of C–H bonds, such as C–C multiple bond insertion,[13—15] carbon monoxide insertion,[16,17] isonitrile insertion,[18,19] and coupling with silanes,[20,21] are known today, most of these reactions suffer from significant drawbacks. In many cases, the use of a large excess amount of one of the reactants (often the solvent) is required to attain a reasonable catalyst turnover,[12,14—18,20,21] and/or photoirradiation is required.[15,17,18,21] Generally, the catalyst efficiencies

and the chemical yields of the products are not high. Recently, notable advances have been achieved by two research groups. In 1989, Jordan and Taylor reported that a cationic zirconium complex catalyzes the addition of the α C–H bond in 2-methylpyridine to propene in excellent yields.[13b,13c] In this reaction, the co-presence of dihydrogen was recommended to maintain a higher catalyst turnover, and, in turn, this causes the hydrogenation of propene as a side reaction. In 1992, Moore and co-workers reported on a coupling reaction of the α C–H bond in pyridines, carbon monoxide, and olefins by the use of ruthenium carbonyl, but using pyridine as a solvent.[16] In these two cases, the reactions seem to be applicable only to pyridine derivatives.

We have recently found a very efficient catalytic addition of a C–H bond in aromatic ketones to olefins with the aid of ruthenium complexes.[1—3] The details concerning the results are described below.

Results

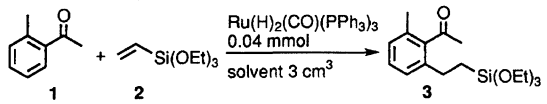
The new catalytic reaction permits the one-step addition of C–H bonds in aromatic ketones to terminal olefins. Ruthenium complexes are effective catalysts for the reaction. A new C–C bond is formed between the carbon atom at the *ortho* position of the carbonyl group and the terminal carbon atom of the olefin (Eq. 1). The chemical yields based on the aromatic ketones are very high, often close to quantitative. Even when equimolar amounts of the ketone and the olefin are employed, the yields also quantitative in many cases. The unprecedented degree of efficiency, selectivity, and generality are remarkable features of this new catalytic reaction.



(1)

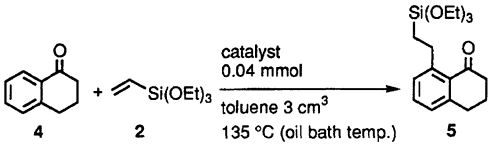
The present catalytic reaction is operationally simple: just mix and reflux. A typical experimental procedure is as follows. A mixture of an aromatic ketone (2 mmol), and olefin (2—10 mmol), hexadecane (internal standard for GC analysis) and $Ru(H)_2(CO)(PPh_3)_3$ (0.04—0.12 mmol) was dissolved in 3 cm^3 of toluene and then vigorously refluxed (oil bath temperature, 135 °C) for an appropriate period of time. The progress of the reaction was monitored by GC, which showed that the reaction generally proceeded without the formation of by-products. The isolation of the product was usually carried out by bulb-to-bulb distillation. The thus-isolated products were often already analytically pure.

The reaction temperature is important to obtain good results. When the reaction of 2′-methylacetophenone (**1**) with triethoxyvinylsilane (**2**) (Eq. 2) was conducted in toluene under vigorously refluxing conditions (oil bath temperature, 135 °C), the coupling product **3** was obtained in 93% yield after 2 h; at a lower reaction temperature (oil bath temperature, 120 °C), however, the yield was 7% after 2 h and 80% after 24 h. In refluxing benzene using an oil bath at 90 °C, the yield of **3** was 55% even after 24 h. Although the reason is not understood, the use of *o*-xylene as a solvent resulted in poor yields (7—10% at 120—160 °C) even after 24 h. All of the experiments described below were carried out in vigorously refluxing toluene using an oil bath heated to 135 °C.



(2)

Catalysts. Various transition-metal complexes have been examined for their catalytic activity using α-tetralone (**4**), which is one of the most reactive ketones (vide infra), with vinylsilane **2** under the reaction conditions shown in Eq. 3. Among those examined, only ruthenium complexes exhibited catalytic activity. The times required to complete of the reaction shown in Eq. 3 and give the product quantitatively were: 10 min for $Ru(H)_2(CO)(PPh_3)_3$,[22] 1 h for $Ru(CO)_2(PPh_3)_3$,[23] 2 h for $Ru(H)_2(PPh_3)_4$,[24] and 6.5 h for $Ru(CO)_3(PPh_3)_2$.[25] Some other ruthenium complexes such as $Ru(H)(Cl)(CO)(PPh_3)_3$,[22e] $RuCl(OAc)(CO)(PPh_3)_2$,[26] $Ru(Cl)_2(PPh_3)_3$, and $Ru_3(CO)_{12}$, were not effective as catalysts. Also, $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$,[27] $IrCl(CO)(PPh_3)_2$, and $[Ir(H)_2(acetone)_2(PPh_3)_2]BF_4$[28] showed no catalytic activity. In the literature, some of the complexes, e.g., $Ru(H)_2(PPh_3)_4$,[8a,8c] $RuCl(OAc)(CO)(PPh_3)_2$,[29] $Ru_3(CO)_{12}$,[16] $RhH(PPh_3)_4$,[30] $IrCl(CO)(PPh_3)_2$,[31] and $[Ir(H)_2(acetone)_2(PPh_3)_2]BF_4$,[32,33] have been shown to effect C–H bond cleavage. It should be noted that we have so far examined the effectiveness of the catalyst only under the reaction conditions shown in Eq. 3.



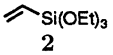
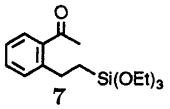
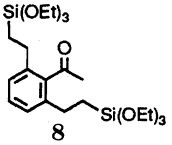
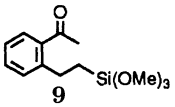
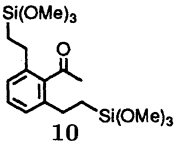
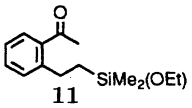
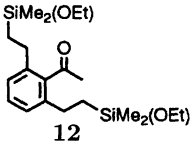
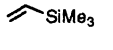
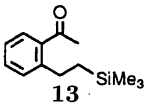
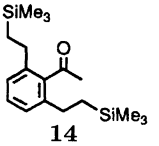
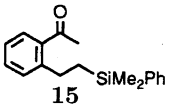
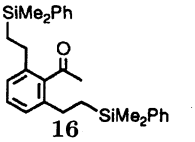
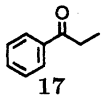
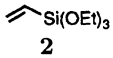
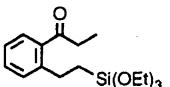
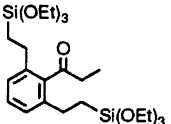
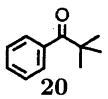
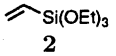
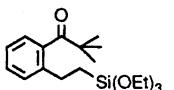
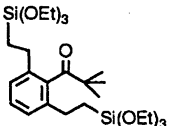
(3)

As will be shown later (Run 38 in Table 5), the reaction of Eq. 3 can be carried out using a smaller amount of olefin, which is recommended for synthetic purposes.

Reaction of Acetophenones with Vinylsilanes. The catalytic reaction of substituted acetophenones with various vinylsilanes was examined. The results of the coupling reactions are listed in Table 1 for phenyl alkyl ketones (**6**, **17**, and **20**) and in Table 2 for *o*-tolyl methyl ketone (**1**).

The reaction of acetophenone (**6**) with **2** was carried out in toluene (3 cm^3) at 135 °C (oil bath temperature) under a nitrogen atmosphere. Since acetophenone has

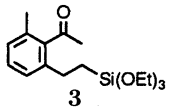
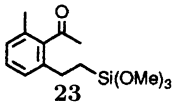
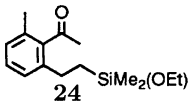
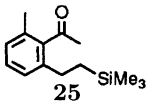
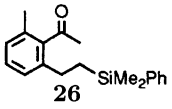
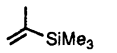
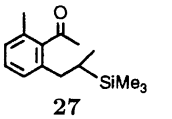
Table 1. Catalytic Reactions of Acetophenones with Vinylsilanes

Run	Ketone	Olefin	Ketone/Olefin/Catalyst / mmol	Time/h	Product and Yield/%[a,b]			
1	 **6**	 **2**	2/2/0.04	0.23	 **7**	75 (75)	 **8**	8 (16)
2			2/6/0.04	90	**7**	Trace	**8**	94
3			2/2/0.04	0.17	 **9**	67	 **10**	0
4			2/2/0.04	0.23	 **11**	60 (60)	 **12**	12 (24)
5			2/2/0.04	0.13	 **13**	29 (29)	 **14**	27 (54)
6			2/2/0.04	0.1	 **15**	25 (25)	 **16**	31 (62)
7	 **17**	 **2**	2/2/0.04	0.5	 **18**	87	 **19**	Trace
8			2/8/0.04	86	**18**	Trace	**19**	84[c]
9	 **20**	 **2**	2/2/0.04	0.5	 **21**	Quant.	 **22**	0
10			2/8/0.04	24	**21**	Quant.	**22**	0

a) GC yield based on the ketone. b) The values in parentheses are the yields based on the vinylsilane. c) Isolated yield based on the ketone.

two *ortho* C–H bonds, the reaction gave a mixture of the 1 : 1 and the 1 : 2 addition products (**7** and **8**) in 75 and 8% yields based on the ketone, respectively (Run 1). The total yield of **7** and **8** based on the vinylsilane was 91%, as shown in Table 1. Only the *ortho* C–H bonds were cleaved and the C–C bond formation occurred specifically at the terminal carbon atom of the olefin moiety. The 1 : 2 coupling product can be obtained as a sole product by the use of an excess amount of the vinylsilane (3 equiv) and a prolonged reaction time (Run 2). Reactions with trimethoxyvinylsilane and with ethoxydimethylvinylsilane also gave the corresponding 1 : 1 coupling product as a major product (Runs 3 and 4). The reaction with trimethylvinylsilane gave the 1 : 1 and the 1 : 2 coupling products in 29 and 27% yields (**13** and **14**, respectively) based on **6**. The yield of **14** (54% yield based on the vinylsilane) was rather high compared with that of **13** (29% yield based on the vinylsilane). This is discussed later. In the case of dimethylphenylvinylsilane, the 1 : 1 and the 1 : 2 coupling products were formed with a selectivity similar to that observe in Run 6.

Table 2. Catalytic Reactions of 2′-Methylacetophenone with Vinylsilanes

Run[a]	Ketone	Olefin	Ketone/Olefin/Catalyst mmol	Time/h	Product and Yield/%[b]
11	 **1**	 **2**	2/2/0.04	2	 **3** 93
12			2/2/0.04	4	 **23** 91
13			2/4/0.04	5	**23** Quant.
14			2/2/0.04	2	 **24** Quant.
15			2/2/0.04	4	 **25** 72
16			2/4/0.04	2	**25** 97
17			2/2/0.04	1	 **26** 90
18			2/10/0.12	33	 **27** 96

a) Continued from Table 1. b) GC yield based on the ketone.

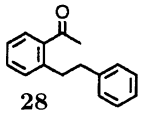
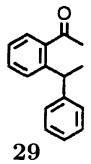
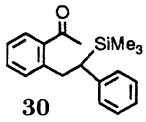
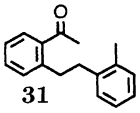
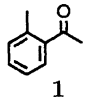
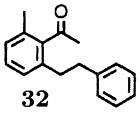
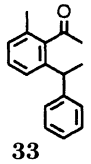
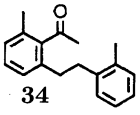
The alkyl group in phenyl alkyl ketones was varied from methyl to ethyl and *t*-butyl (Runs 1,2 and 7—10). The reaction of ethyl ketone **17** ceased in 0.5 h and the 1 : 1 coupling product **18** was obtained in 87% yield along with a trace amount of the 1 : 2 coupling product **19** (Run 7). The use of an excess amount of **2** and a longer reaction time afford **19** predominantly (Run 8). In the case of *t*-butyl ketone **20**, the 1 : 2 coupling product was not formed at all, even when a large excess amount of **2** was used (Run 10). The steric repulsion between the bulky *t*-butyl group and the silylethyl group introduced at the first *ortho* C–H bond probably prevented the ruthenium from positioning close to the second *ortho* C–H bond, as is discussed later.

The complexity arising from the formation of a mixture of the 1 : 1 and the 1 : 2 coupling products does not exist in the case of 2′-methylacetophenone (**1**), which has only one *ortho* hydrogen. The results of the reactions of **1** with several vinylsilanes are summarized in Table 2 (run numbers in Table 2 are continued from those in Table 1 for simplicity and this way of numbering is used in all the Tables in this paper).

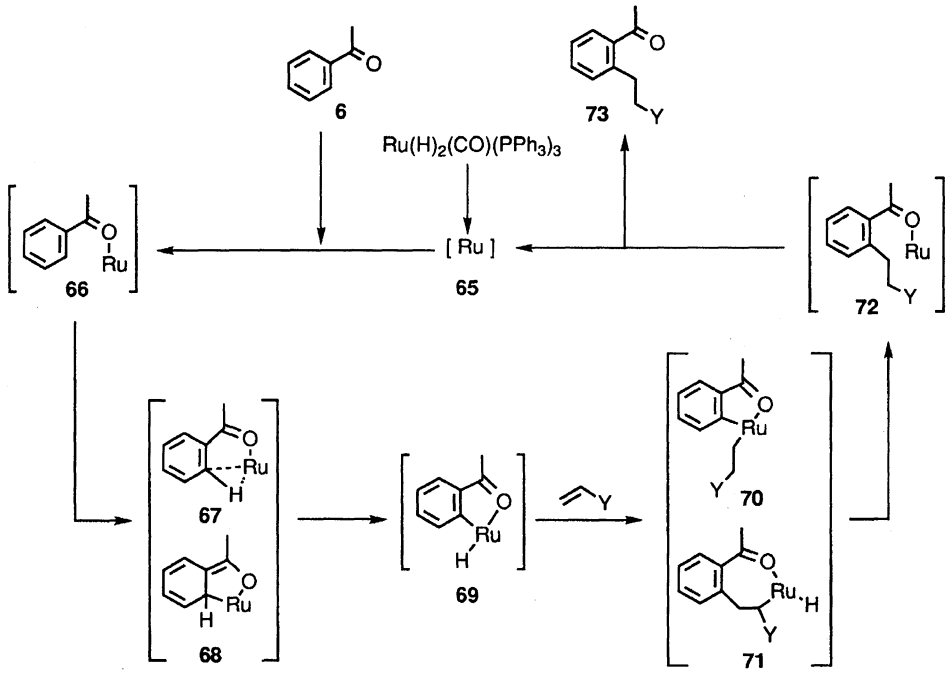
The coupling products were produced in close to quantitative yields based on **1** in many cases. In the reaction of **1**, a slightly longer reaction time was necessary than was used in the reaction of **6**. In Runs 11, 12, and 14, the coupling products were obtained in almost quantitative yields based on both the ketone and the vinylsilane. The use of excess vinylsilanes ensured virtually quantitative formations of the corresponding 1 : 1 coupling products in the cases of Runs 13 and 16. Interestingly, a 1,1-disubstituted olefin, i.e., isopropenyltrimethylsilane, also reacted with **1** to give **27** in 96% yield when somewhat forcing reaction conditions were employed (Run 18).

Reaction of 2′-Methylacetophenone with Styrenes. Acetophenones also underwent coupling with aromatic olefins. The results are shown in Table 3. In contrast to the reaction using vinylsilanes, the 1 : 2 coupling product was not obtained at all, even when an excess of the styrene was used. The reason for the absence of the 1 : 2 coupling product should be a steric one as in the reaction of the bulky ketone **20**. The reaction of **6** with styrene gave a mixture of regioisomers, **28** and **29**, in a 6 : 1 ratio, respectively (Run 19). However, ketones **6** and **1** also reacted with 2-methylstyrene (Runs 21, 23, and 24) to give only one regioisomer, where C–C bond formation occurred at only the terminal carbon atom

Table 3. Catalytic Reactions of Acetophenones with Styrenes

Run	Ketone	Olefin	Ketone/Olefin/Catalyst mmol	Time/h	Product and Yield/%[a]			
19	 **6**		2/4/0.04	1	 **28**	72	 **29**	12
20			2/4/0.04	44	 **30**	45[b]		
21			2/4/0.04	4	 **31**	89[b]		
22	 **1**		2/2/0.04	2	 **32**	59[b]	 **33**	14[b]
23			2/2/0.04	8	 **34**	54		
24			2/10/0.12	5	**34**	97		

a) GC yield based on the ketone. b) Isolated yield based on the ketone.

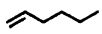
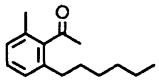
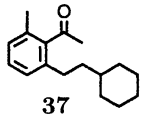
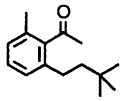
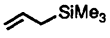
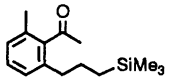
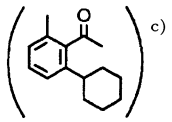
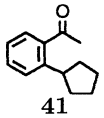
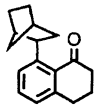


Scheme 1. The catalytic cycle with alternatives.

of the olefin. The improvement in the regioselectivity caused by a slight increase in the size of the olefin substituent is noteworthy, and is discussed latter in terms of a possible mechanism.

Reaction with Various Olefins. The present C–H/olefin coupling is applicable to various types of olefins. Selected results are listed in Table 4. The reaction of **1** with ethylene (6 kg cm^{-2}, initial pressure at 25 °C, in toluene) in an autoclave gave the coupling product in a quantitative yield (Run 25). In the cases

Table 4. Catalytic Reactions of Acetophenones with Various Olefins

Run	Ketone	Olefin	Ketone/Olefin/Catalyst mmol	Time/h	Product and Yield/%[a]
25	 **1**	=[b]	2/12/0.04 (6 kg cm^{-2})	24	 **35** Quant.
26			2/10/0.04	5	 **36** 23
27			2/2/0.04	24	 **37** 19
28			2/10/0.04	8	 **38** 99
29			2/10/0.12	4	 **39** Quant.
30			2/10/0.12	24	 [c] **40** Trace
31[d]	 **6**		2/10/0.12	48	 **41** 36
32	 **4**		2/4/0.04	1	 **42** 86

a) GC yield based on the ketone. b) The reaction was carried out in an autoclave at 135 °C (oil bath temp). c) The structure was not elucidated. d) Reaction was carried out in a stainless-steel pressure bottle.

of 1-hexene (Run 26) and vinylcyclohexane (Run 27), the coupling products were obtained in low yields due to the isomerization of the double bond to the internal ones. On the other hand, allyltrimethylsilane underwent coupling quantitatively without double bond isomerization (Run 29). While cyclohexene, an internal olefin, gave only a trace amount of the coupling product, cyclopentene gave the coupling product in moderate yield (Run 31). The addition of a C–H bond in **4** to norbornene took place smoothly, giving an *exo*-isomer **42** (Run 32). Other olefins which did not react are listed later.

Reaction of Aromatic and Heteroaromatic Ketones with Triethoxyvinylsilane. The new catalytic reaction is applicable to various types of ketones, the results are shown in Table 5.

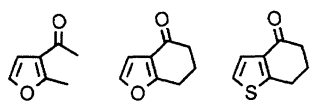
Using $Ru(H)_2(CO)(PPh_3)_3$ as the catalyst, the addition of a C–H bond in acetonaphthones **43** and **45** to **2** (Runs 33 and 34) took place to give the coupling products (**44** and **46**, respectively) in quantitative yields. Of the two different reaction sites in **45**, the C–H bond at the 1-position in the ring was cleaved exclusively. The

selectivity is noteworthy since the reaction gave only one out of four possible regioisomers, two from the different reaction sites of the C–H bond in the aromatic ketone and the other two from the regioisomers of the olefin. In the reaction of **47** with **2**, the 1:1 adduct **48** was obtained in 74% yield after 1 h (Run 35). By simply doubling the amount of the olefin **2**, the 1:2 adduct **49** was isolated in 99% yield as the sole product (Run 36). The ^{1}H and ^{13}C NMR spectra of **49** established its structure as shown in the Table as opposed to that having two 2-silylethyl groups on the same phenyl group. The reactivity of the cyclic ketones depends largely upon the ring size. The reaction of **4** afforded **5** in quantitative yield (Run 38). For a seven-membered ketone **51**, a considerably longer reaction time (20 h) than that of Run 38 (0.5 h) was required and the catalyst deactivation occurred before complete consumption of **51** (Run 39). Interestingly, 1-indanone (**50**), a five-membered ring ketone, did not undergo a coupling reaction at all (Run 37).

Five-membered heteroaromatic ketones also reacted with **2**. The reaction of 1-methyl-2-acetylpyrrole (**53**) gave the corresponding coupling product in almost quantitative yield, although a large amount of **2** was necessary to obtain this high yield. On the other hand, when 2-acetylfuran (**55**) and acetylthiophenes, **57** and **59**, were used as the ketones, the coupling products were obtained in quantitative yields based on both of the substrates (Runs 41—43). The catalytic reaction of **59** with **2** proceeded with perfect regioselection at the ring in a similar manner as that observed in Run 34. When the reactive site, e.g., the 2-position of **59**, was blocked with an alkyl group, such as in 3-acetyl-2-methylfuran (**62**), 6,7-dihydro-4(5*H*)-benzofuranone (**63**), and 6,7-dihydrobenzo[*b*]thiophene-4(5*H*)-one (**64**) (Fig. 1), the reaction did not proceed at all.

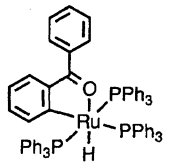
Discussion

Much work will be needed before drawing any conclusions about the details of the mechanism. However, some observations coupled with literature information allow us to suggest what is likely and what is not, even at this early stage of our study. The course of the catalytic reaction is outlined in Scheme 1 with important alternatives and with simplified structures; however, considerable equilibrium is not shown here (vide infra). The addition of an aromatic C–H bond to an olefin is energetically favorable by 16.1 kcal mol^{-1}, as pointed out by Jones,[34] thus ensuring that the catalytic reaction will take place.



62 **63** **64**

Fig. 1. Examples of unreactive ketones.

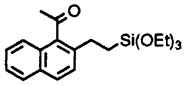
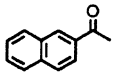
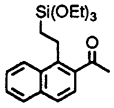
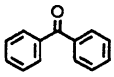
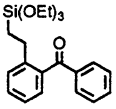
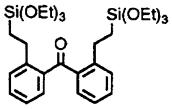
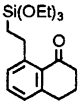
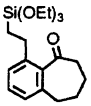
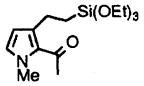
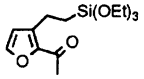
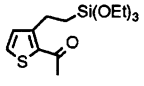
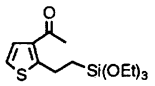
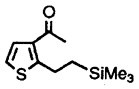


74

Fig. 2. A product from benzophenone.

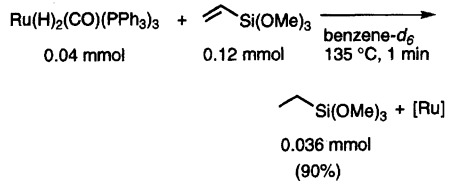
The most effective catalyst was $Ru(H)_2(CO)(PPh_3)_3$. Although $Ru(CO)_2(PPh_3)_3$, $Ru(H)_2(PPh_3)_4$, $Ru(CO)_3(PPh_3)_2$ were modestly effective with decreasing activity in this order, $Ru_3(CO)_{12}$ was not. This suggests that neither H nor CO is the necessary ligand and a zero valent ruthenium having at least two PPh_3 constitutes the essential part of the catalyst. From the structures of the effective catalyst precursors, the working catalyst is likely to be mononuclear. The catalytic reaction may begin with the formation of a 16-electron Ru(0) complex from $Ru(H)_2(CO)(PPh_3)_3$. There are three possibilities for the dehydrogenation at the initial step: 1) reductive elimination of dihydrogen, 2) reduction of the ketone, and 3) hydrogenation of the olefin. The first possibility seems unlikely since the reductive elimination of $Ru(H)_2(PMe_3)_4$ is known to proceed only at high temperature (>180 °C),[35] although it is suggested that $Ru(H)_2(dmpe)_2$ (dmpe=1,2-bis(dimethylphosphino)ethane) is labile at 140 °C.[19b,34] Indeed, in our case, when a benzene-d_6 solution of $Ru(H)_2(CO)(PPh_3)_3$ was heated at 120 °C in an NMR tube for 1.5 h, the hydride signals did not disappear. The possibility of the reduction of the ketone was suggested by Halpern and co-workers. They reported that the reaction of $Ru(H)_4(PPh_3)_3$ with benzophenone at 45 °C yielded cyclometallated complex **74**[36] (Fig. 2) and diphenylmethanol.[37] Their results show at the same time that a low-valent ruthenium complex generated by the reduction of the benzophenone with $Ru(H)_4(PPh_3)_3$ can cleave the C–H bond in an aromatic ketone. We have examined the stochiometric reaction of $Ru(H)_2(CO)(PPh_3)_3$ with acetophenone in toluene-d_8 at 135 °C for 2.5 h. The ^{1}H NMR spectrum of the reaction mixture showed that α-methylbenzyl alcohol was not produced at all. This experiment suggests that, in our catalytic reaction, the dehydrogenation of $Ru(H)_2(CO)(PPh_3)_3$ does not take place via a reduction of the ketone. The hydrogen atoms in $Ru(H)_2(CO)(PPh_3)_3$ are in fact transferred to the olefin as shown by the stoichiometric reaction of $Ru(H)_2(CO)(PPh_3)_3$ (0.04 mmol) with trimethoxyvinylsilane (0.12 mmol) (Eq. 4). After heating at 135 °C for 1 min, the ^{1}H NMR spectrum of the reaction mixture showed that the H–Ru signal disappeared and that the hydrogen atoms were completely transferred to the olefin. The structure of the ruthenium complex formed in this control experiment was not established, but is likely to be the corresponding olefin complex. Upon the addition of 0.08 mmol of a ketone **6** to this mixture,

Table 5. Catalytic Reactions of Various Ketones with Triethoxyvinylsilane

Run	Ketone	Olefin	Ketone/Olefin/Catalyst mmol	Time/h	Product and Yield/%[a]
33	 **43**	 **2**	2/2/0.04	6	 **44** Quant.
34	 **45**		2/2/0.04	6	 **46** Quant.
35	 **47**		2/2/0.04	1	 **48** 74[b,c]
36	**47**		2/4/0.04	4	 **49** 99[b]
37	 **50**		2/4/0.04	22	No reaction
38	 **4**		2/2/0.04	0.5	 **5** Quant.
39	 **51**		2/2/0.04	20	 **52** 88
40	 **53**		2/10/0.12	48	 **54** 99
41	 **55**		2/2/0.04	4	 **56** Quant.
42	 **57**		2/2/0.04	1	 **58** Quant.
43	 **59**		2/2/0.04	1	 **60** Quant.
44[d]	 **59**		2/2/0.04	24	 **61** 87

a) GC yield based on the ketone. b) Isolated yield based on the ketone. c) The product **49** was also obtained in 10% isolated yield based on **47**. d) Reaction was carried out in a stainless-steel pressure bottle.

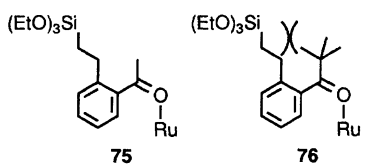
and heating for another 1 min at 135 °C, the ^{1}H NMR spectrum indicated complete conversion of the ketone to a 1 : 1 coupling product **9**. These experiments suggest that the effective catalyst **65** in Scheme 1 is produced by the hydrogenation of an olefin.



(4)

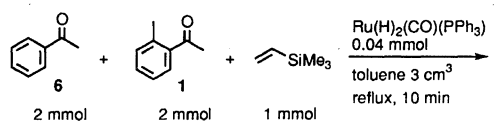
Several observations as well as related precedents suggest the importance of the coordination of the carbonyl group of ketones to the Ru atom in **66** and the formation of a cyclometallation intermediate **69**. The difference in the reactivities between **4** (Run 38) and **50** (Run 37) may be attributed to an unfavorable strain induced by chelation in the case of the five-membered ring ketone **50**. The ease of the incorporation of the second olefin molecule leading to a 1 : 2 coupling product **8** from **6** (Runs 1 and 2), contrasted with the difficulty of forming such 1 : 2 product in the case of *t*-butyl ketone **20** (Runs 9 and 10), can be explained by comparing the steric congestion in coordinated complexes **75** and **76** (Fig. 3). In the more stable conformational isomer (not shown) of complex **76**, the Ru is positioned far apart from the second C–H bond to be cleaved. Even under forcing conditions, no 1 : 2 coupling product was formed from the phenyl *t*-butyl ketone (Run 10).

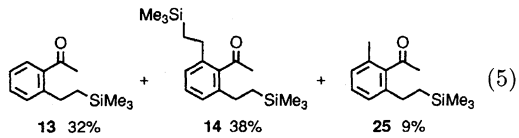
The importance of the coordination of the ketone carbonyl group to Ru is further demonstrated by an analysis of the product distribution shown in Eq. 5[2] Suppose that all of the dialkylated ketone **14** is formed only by further alkylation of monoalkyl ketone **13**, the yield of **14** (38%) is unusually large, since the related monoalkyl ketone **1** is alkylated to give **25** in only 9% yield in the same reaction. This implies the existence of an additional pathway leading to **14**. We suggest that the formation of **13** by decomplexation (Eq. 6) is in competition with C–C bond rotation in **77** (Eq. 7). A quantitative analysis (see Ref. 2 for details) suggests that the relative rate of the decomplexation vs. C–C bond rotation is 74 : 26. A surprisingly large portion (71/100) of **14** is formed without decomplexation of the carbonyl group from Ru throughout the reaction. Note that the Ru complex **77** at the junction of Eqs. 6 and 7 corresponds to **72** in Scheme 1.



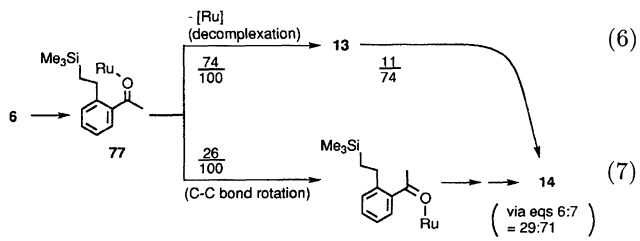
75 **76**

Fig. 3. Intermediates for second C–H bond cleavage.





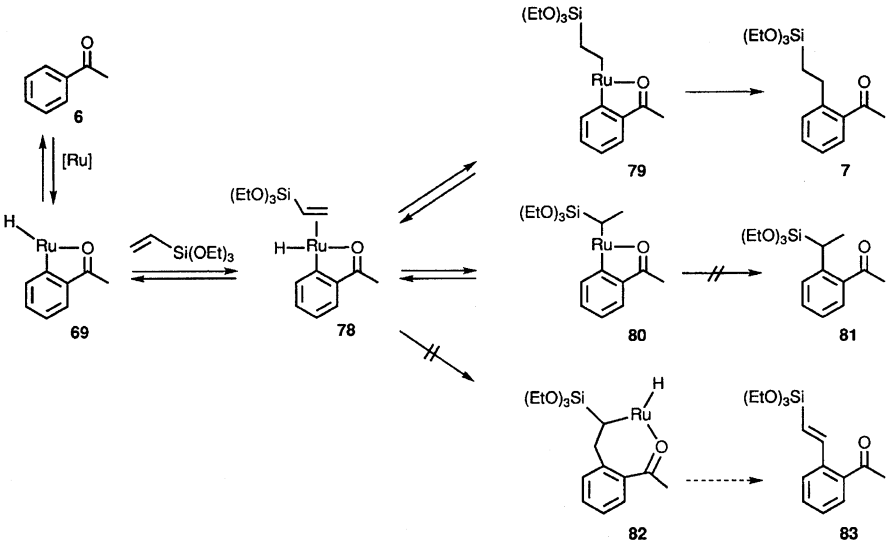
(5)



(6)

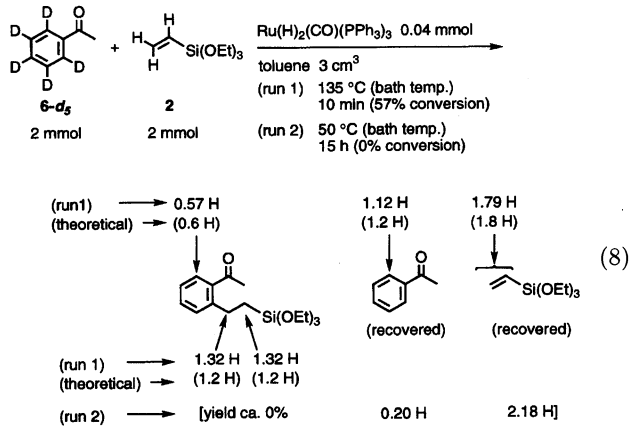
(7)

Very interestingly, rapid equilibria seem to exist among the intermediates involved in the steps from **6** to **70** (and less likely to **71**). This implies that C–H bond cleavage is not the rate-limiting step in the present catalytic reaction. The catalytic reactions of acetophenone-d_5 (**6**-d_5) with **2** were carried out at 135 °C for 10 min (57% conversion) and at 50 °C for 15 h (0% conversion). The results are shown in Eq. 8 as Runs 1 and 2, respectively. At higher temperature (Run 1), the two deuterium atoms at the *ortho* positions of the ketone scrambled completely over five positions (two *ortho* positions and three olefinic positions). The observed integrations in the ^{1}H NMR of Run 1 were very close to the theoretical value for the complete scrambling shown in parentheses in Eq. 8. At a lower temperature (50 °C), it was observed that the hydrogen exchange between aromatic and olefinic positions took place to some extent, even prior to the formation of the 1 : 1 coupling products (the yield of the coupling product was close to 0% at 50 °C). The equilibria that should exist in the catalytic process is shown in Scheme 2. The Ru inserts to the *ortho* C–H bond to give **69**. After the coordination of an olefin (intermediate **78**), hydrogen migration to the internal or terminal carbon atom of the olefinic bond affords intermediate **79** or **80**, respectively. The coupling product **7** is formed by a reductive elimination from **79**. Since the isomer **81** has not been obtained, the intermediate **80** does not undergo a reductive elimination. The observed H/D scrambling at the three olefinic hydrogen atoms indicates the presence of reverse reactions for both **79** and **80** to **78**, i.e., β-hydride elimination. The observation of H/D scrambling at the *ortho* position of **6**, even under conditions where the reaction does not afford any product (Run 2 in Eq. 8) implies 1), the existence of an equilibrium between **6**, **69**, **78**, **79**, and **80**, and 2) that these processes are faster than the product forming step of **79** to **7**. This is significant. Contrary to the widespread idea that C–H bond cleavage is difficult, it can be said that



Scheme 2. Equilibriums accounting for deuterium scrambling in the catalytic process.

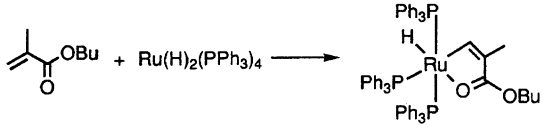
the cleavage of a C–H bond is facile compared with the product determining step or catalyst regeneration step at least in the catalytic reaction of acetophenone.[38]



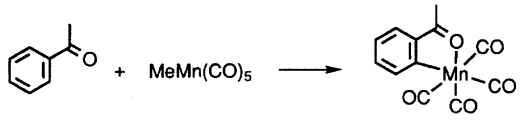
(8)

Two possibilities exist for the step leading to new bond formation (Scheme 1). The first is the insertion of the olefin into Ru–H bond in **69** to give **70**, i.e., a hydromatallation mechanism. The second is olefin insertion into the Ru–C bond in **69** leading to **71**, i.e., a carbometallation mechanism. Intermediates **70** and **71** in Scheme 1 correspond to **79** and **82** in Scheme 2, respectively. We prefer the former, hydrometallation mechanism, for the following reasons: 1) The formation of **82** in the rapid equilibrating system shown in Scheme 2 is unlikely, since **82**, if formed, should give **83** by β-hydride elimination as in the fast β-hydride elimination from **79** and **80** to **78**. The olefinic product **83**, however, was not detected. 2) The catalytic reaction gave a mixture of regioisomers **28** and **29** in the case of styrene (Run 19). This is understandable because the phenyl group may stabilize the internal ruthenation intermediate (corresponding to **80**) leading to **29**. From a slightly more crowded styrene, i.e., 2-methylstyrene, the branched isomer was not formed and only **31** with C–C bond formation at the terminal carbon of the olefin was produced (Run 21). This regioselection is compatible with the intermediary of **70**, but not **71**. 3) From 1,1-disubstituted ethylenes, such as isopropenyltrimethylsilane (Run 18) and α-trimethylsilylstyrene (Run 20), the 1 : 1 addition products were obtained in good yields. If the carbometallation mechanism is operating, these results invoke the formation of a bond between a tertiary carbon center and the Ru in the stage corresponding to **71** in Scheme 1. Such a sterically crowded situation seems less likely.

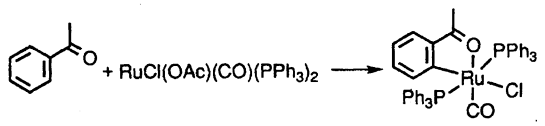
There have been ample precedents for cyclometallation[39] affording metal complexes similar to **69**. Closely related examples are shown in Eqs. 9,[8c] 10,[40] 11,[29] and 12.[41] In contrast to these, Tolman and coworkers reported that the reaction of acetophenone with $Fe(Me_2PCH_2CH_2PMe_2)_2$(2-naphthyl)(H) resulted in the oxidative addition of *meta* and *para* C–H bonds, but not the *ortho* C–H bond.[7i] Heys reported a highly *ortho*-selective hydrogen–deuterium exchange reaction of aromatic ketones with D_2 with the aid of $[Ir(H)_2(acetone)_2(PPh_3)_3]BF_4$.[32] Heys proposed that the regiospecificity of the deuterium exchange was consistent with the coordination of iridium with a carbonyl group adjacent to the phenyl ring.[42]



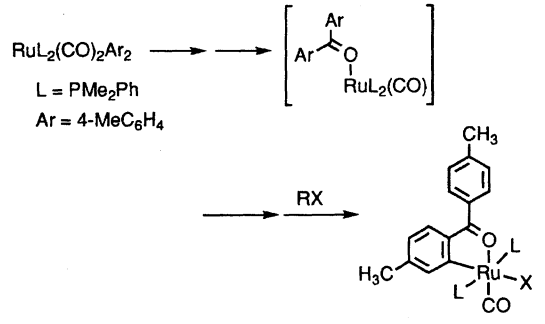
(9)



(10)



(11)



(12)

Interestingly enough, the cyclometallation mechanism has not been studied in detail. In these papers, comments concerning the mechanism have not been given, and/or the oxidative addition of the C–H bond to the metal (such as **66**, **69**) is suggested without evidence. In addition to the oxidative addition mechanism via **67**, we suggest the existence of an alternative mechanism involving **68**, i.e., a 1,2-hydrogen shift mechanism. Not closely related, but similar mechanisms have been postulated regarding the cleavage of the C–CH_3 bond by a Rh complex[30a] and in the C–H cleavage by a Pd complex.[43] The selective cleavage of one of two available C–H bonds in 2-acetonaphthone (**45**) to give **46** (Run 34) and also in 3-acetylthiophene (**59**) to give **60** (Run 43) may be explained by the idea that the reactions take place at the hydrogen atom attached to the double bond having the highest bond order. In other words, an aromatic ketone has behaved like an enone, and a 1,4-addition of Ru(0) to the enone moiety may lead to intermediate **68**. This idea is also compatible with the observations that the heteroaromatic ketones **62**—**64** (Fig. 1) did not undergo a catalytic reaction at all. However, it is not clear which mechanism (via **67** or **68**) is more likely or whether these two limiting mechanisms are separable in the present case.

Scope and Limitation

Examples of the direct cleavage of otherwise unreactive C–H bonds using stoichiometric amounts of transition-metal complexes are no longer exceptional today. However, catalytic reactions involving such a process are still rare. The present catalytic reaction may find use as a practical synthetic tool since it displays efficiency, selectivity, and generality.

The present reaction is highly efficient from a synthetic point of view because: 1) it is catalytic, 2) it offers a method to form C–C bonds directly from a C–H bond without sacrificing any extra functional groups, 3) it proceeds generally in very high yields based on at least one, and often both, starting materials. The catalytic C–H/olefin coupling shown in Eq. 3 can be carried out on a large scale (10 g of **4**) to give the addition product **5** in 95% isolated yield (22 g).

Aromatic ketones which are one of the starting materials for this reaction are readily available by Friedel–Crafts acylation and many other methods.[44] The products are also aromatic ketones. The ketone functionality is one of the most versatile functional groups, and can easily be transformed into alcohols and amines with and without additional C–C bond formation, and also into olefins.[44] It is also amenable to standard enolate chemistry.[44] It should be noted that the products obtained in the present reaction are difficult to obtain by conventional methods, because acylation of an alkylbenzene would give the *para*-isomer predominantly, and other techniques involving the electrophilic alkylation of benzenes could not be applied to electron-deficient acylbenzenes.[44] Indeed, all of the products reported in this paper have not been prepared previously. Thus, the present method opens up a new area of aromatic substitution chemistry.

As to the range of aromatic ketones as well as olefins that are suitable for this reaction, there is a significant limitation. Under the particular reaction conditions shown in Eq. 2 using $Ru(H)_2(CO)(PPh_3)_3$ as a catalyst, the following aromatic ketones did not undergo a coupling reaction with the vinylsilane **2**. These were 1-benzoylacetone, 2-chloroacetophenone, 2-acetylpyridine, acetylferrocene, benzil, 1,4-naphthoquinone, 2,2,2-trifluoroacetophenone, and benzylideneacetophenone.

The olefins that do not give any coupling products with 2′-methylacetophenone (**1**) fall into three categories: 1) those that do not react at all (shown in Chart 1), 2) those that undergo double bond isomerization (shown in Chart 2), and 3) those that undergo side reactions (see Chart 3). Unfortunately, olefins having electron-withdrawing groups or electron-donating groups do not react. Neither allyl alcohol derivatives nor dienes react. For the olefins shown in Chart 3, the reasons of the unsuccessful results seem to be different for each olefin. Ethyl acrylate seemed to have undergone a linear dimerization or a cyclic trimerization, as judged by the GCMS of the reaction mixtures. Diels–Alder dimerization seemed to be the side reaction of 1,3-dienes. The results of the catalytic reactions of allyl chloride and *N*-allylaniline were somewhat complicated giving several products which were not characterized.

It should be noted that these limitations are shown by experiments under the particular reaction conditions indicated. It is hoped that a deeper understanding of the mechanism and a modification of the catalyst may overcome these limitation in the future. In addition, Charts 1, 2, and 3 do not indicate the functional group compatibility. In separate experiments, it has been revealed that the presence of the oxygen- and nitrogen-containing functional groups do not interfere with the catalytic reactions, the results of which will be reported

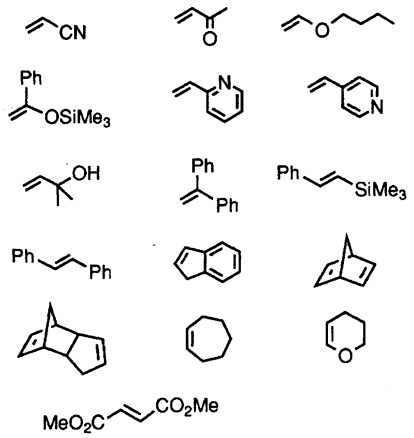


Chart 1. Olefins that do not react with **1**.

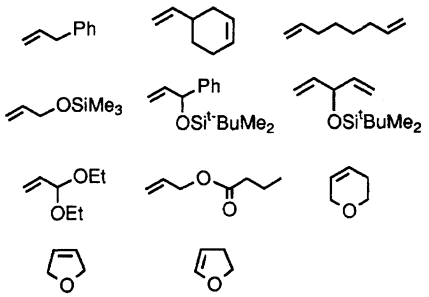


Chart 2. Olefins that do not react with **1** due to double bond isomerization.

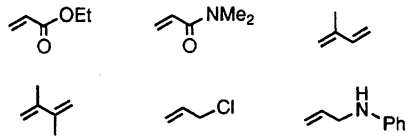


Chart 3. Olefins that do not react with **1** due to various reasons (see text).

in due course.

Conclusion

It has been shown that certain ruthenium phosphine complexes can bring about a catalytic addition of aromatic C–H bonds in aromatic ketones to olefins. The C–H/olefin coupling products were obtained in excellent yields in many cases. A wide rage of olefins and aromatic ketones can be employed in this C–H/olefin coupling reaction. The scope and limitation of the reaction under a certain set of reaction conditions are shown. The key to the success of this reaction is the coordination of the aromatic carbonyl group to the ruthenium, bringing the ruthenium center close to the *ortho* C–H bond to be cleaved. The mechanism involving cyclometallation is discussed. Deuterium labeling experiments show that C–H bond cleavage is not the rate-limiting step in the catalytic reaction of acetophenone.

For the future design of a new catalytic reaction involving C–H bond cleavage, two important points have been suggested by the present work. First, chelation assistance should be a powerful tool. Secondly, the step involving C–H bond cleavage may not be a difficult step in many cases.

As the immediate extension of the present work, we have been studying the catalytic addition of olefinic C–H bonds to olefins as well as the catalytic addition of aromatic and olefinic C–H bonds to acetylenes.[45]

Experimental

General Information. The ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. The chemical shift of ^{1}H NMR and ^{13}C NMR signals are quoted relative to internal $CHCl_3$ (δ=7.26 and 77.0) or tetramethylsilane. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, c=complex, br=broad), coupling constant (Hz), relative intensity, and interpretation. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ) and interpretation. IR spectra were measured on a Hitachi 270-50 infrared spectrometer. The GCMS analysis were measured on a Shimadzu GCMS-QP 1000 gas chromatography mass spectrometer.

GC Analysis. The conditions used for the GC analysis were as follows: Shimadzu GC-14A (equipped with CBP-20 25 m×0.2 mm); temperature program, 70 °C (0 min)→10/min→230 °C (30 min); injection temperature, 270 °C; detector temperature, 270 °C. The high-polarity capillary column (Shimadzu CBP-20) is suitable for quantification of the coupling products and the starting ketones using GC.

Solvents and Materials. Toluene, benzene, and *o*-xylene were distilled under nitrogen from CaH_2. Vinylsilanes were distilled from CaH_2. Acetophenone (**6**), 2′-methylacetophenone (**1**), and α-tetralone (**4**) were dried over $CaCO_3$ and were distilled under reduced pressure. 1-Methyl-2-acetylpyrrole (**53**) was synthesized according to a literature method.[46] Other aromatic ketones were used as commercial grade. Acetophenone-d_5 was purchased from Aldrich Chemical Co. and was distilled before use.

$Ru(H)_2(CO)(PPh_3)_3$. $Ru(H)_2(CO)(PPh_3)_3$ was prepared by a modified method from the literature.[22e] A 300-cm^3, four-necked, round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet, three 50-cm^3 pressure-equalizing dropping funnels, and a reflux condenser was flushed with nitrogen. The flask was charged with triphenylphosphine (3.14 g, 12 mmol), followed by 140 cm^3 of ethanol via a syringe. One dropping-funnel was charged with an ethanol (20 cm^3) solution of hydrated ruthenium trichloride (purchased from Aldrich Chemical Co.; 0.52 g, 2 mmol), aqueous formaldehyde (20 cm^3, 40% w/v solution), and ethanol (20 cm^3) solution of potassium hydroxide (85% content, 0.71 g, 10 mmol). The ethanol solution of the ruthenium chloride, the second one with aqueous formaldehyde, and the third one with the ethanol solution of potassium hydroxide were added quickly and successively to a boiling ethanol solution of triphenylphosphine. The solution was heated under reflux for 30 min and then cooled in an ice bath. The resultant gray precipitate was filtered using a glass filter, washed with successively with 30 cm^3 of ethanol, 50 cm^3 of deionized water, 30 cm^3 of ethanol, and 50 cm^3 of hexane, and

then dried in vacuo. The yield of the crude product was 1.3 g. After the crude product was dissolved in 30 cm^3 of warm benzene (about 50 °C), the solution was filtered to remove insoluble solids. The benzene solution was passed through a neutral alumina column (packing, Merck aluminum oxide 90 active, neutral activity I; eluent, benzene; 12 cm length×3 cm i.d.)(While, in the literature[22e] the crude ruthenium complex was purified through a neutral alumina column (27 cm length ×3 cm i.d.), the length (12 cm) was sufficient for the purification.). The elution of $Ru(H)_2(CO)(PPh_3)_3$ was monitored by UV. The benzene effluent (about 300 cm^3) was concentrated to about 100 cm^3 by rotary evaporation. To the concentrated solution was added 200 cm^3 of methanol; the solution was then concentrated to about 50 cm^3 until colorless solids precipitated. The concentrated liquid was cooled at 0 °C to enforce a precipitation of the solids. A colorless solid of pure $Ru(H)_2(CO)(PPh_3)_3$ was filtered using glass filter, washed with hexane, and dried in vacuo. The solids were used for the catalytic reaction without further purification.

Toluene can also be used as the eluent, though, a slightly larger volume of the eluent (two times as much) is necessary compared with in the case of benzene. The complex is stored in an ampul bottle (0.04 mmol in each) sealed under reduced pressure. The ruthenium complex is commercially available from Aldrich Chemical Co.. The purchased complex also works as a catalyst for the present reaction.

Catalysts. Catalysts, $Ru(CO)_2(PPh_3)_3$,[23] $Ru(H)_2(PPh_3)_4$,[24] $Ru(CO)_3(PPh_3)_2$,[25] $Ru(H)(Cl)(CO)(PPh_3)_3$,[22e] $RuCl(OAc)(CO)(PPh_3)_2$,[26] $RhH(PPh_3)_4$,[27] and $[Ir(H)_2(acetone)_2(PPh_3)_2]BF_4$,[28] were synthesized according to the published methods. Other catalyst, $Ru(Cl)_2(PPh_3)_3$, $Ru_3(CO)_{12}$, $RhCl(PPh_3)_3$, and $IrCl(CO)(PPh_3)_2$, were purchased from Aldrich Chemical Co..

A Typical Procedure. A 10-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. In the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (37 mg, 0.04 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, 2′-methylacetophenone (**1**) (268 mg, 2 mmol), triethoxyvinylsilane (**2**) (380 mg, 2 mmol), and hexadecane (200 mg, an internal standard for GC) using a syringe, in this order. The mixture was heated under vigorous reflux (at 135 °C, oil bath temperature) with stirring. The reaction was monitored by GC. After heating for 2 h, the mixture was allowed to cool to room temperature, and toluene and **2** (if any) were removed by rotary evaporation (40 °C/5 mmHg, 1 mmHg=133.322 Pa). A dark-brown concentrate was passed through a short column of silica gel (9 cm length×3 cm i.d.) with hexane (200—300 cm^3 total volume) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (150—200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg) and the product was isolated by bulb-to-bulb distillation.

2′-Methyl-6′-[2-(triethoxysilyl)ethyl]acetophenone (3). Bp=130 °C/2 mmHg; ^{1}H NMR δ=0.91—0.97 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.08 Hz, 9 H, CH_3), 2.24 (s, 3 H, $ArCH_3$), 2.49 (s, 3 H, $C(O)CH_3$), 2.57—2.63 (c, 2 H, CH_2), 3.82 (q, J=7.08 Hz, 6 H, OCH_2), 7.00—7.32 (m, 3 H, ArH); ^{13}C NMR δ=13.01 ($SiCH_2$), 18.23 (CH_3), 19.06 ($ArCH_3$), 26.23 ($C(O)CH_3$), 32.46 (CH_2), 58.37 (OCH_2), 126.06, 127.73, 128.62, 132.01, 139.34, 141.83 (Ar), 208.30 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS m/z (% rel intensity) 324 (M^+, 0.5), 279 (14), 278 (33), 163 (21), 145 (10), 144 (25), 135 (100), 129 (10), 119 (20), 107 (23), 91 (15), 79 (30), 63 (12). Found: C, 63.11; H, 8.70%. Calcd for $C_{17}H_{28}O_4Si$: C, 62.93; H, 8.70%.

8-[2-(Triethoxysilyl)ethyl]-α-tetralone (5). Product **5** was isolated by bulb-to-bulb distillation (bp=200 °C/2 mmHg) in 88% yield (588 mg). ^{1}H NMR δ=0.96—1.02 (c, 2 H, $SiCH_2$), 1.26 (t, J=7.02 Hz, 9 H, CH_3), 2.00—2.11 (m, 2 H, CH_2), 2.64 (t, J=6.84 Hz, 2 H, $ArCH_2$), 2.94 (t, J=6.10, 2 H, $C(O)CH_2$), 3.10—3.16 (c, 2 H, $SiCCH_2$), 3.89 (q, J=7.02 Hz, 6 H, OCH_2), 7.07—7.34 (m, 3 H, ArH); ^{13}C NMR δ=12.27 ($SiCH_2$), 18.26 (CH_3), 22.89 (CH_2), 28.58, 31.07 [($SiCCH_2$) and ($ArCH_2$)], 41.03 ($C(O)CH_2$), 58.27 (OCH_2), 126.77, 129.21, 130.45, 132.37, 145.76, 148.07 (Ar), 199.73 (C=O); IR (neat) ν(C=O) 1682 s cm^{-1}; MS m/z (% rel intensity) 336 (M^+, 1), 291 (30), 290 (100), 275 (12), 261 (11), 218 (10), 189 (10), 156 (12), 155 (10), 135 (26), 119 (11), 115 (12), 107 (12), 91 (11), 79 (25), 63 (12). Found: C, 64.00; H, 8.37%. Calcd for $C_{18}H_{28}O_4Si$: C, 64.25; H, 8.39%.

2′-[2-(Triethoxysilyl)ethyl]acetophenone (7) and 2′,6′-Bis[2-(triethoxysilyl)ethyl]acetophenone (8). The products were isolated by bulb-to-bulb distillation.

7: Bp=160 °C/5 mmHg. ^{1}H NMR δ=0.94—1.01 (c, 2 H, $SiCH_2$), 1.24 (t, J=7.02 Hz, 9 H, CH_3), 2.58 (s, 3 H, $C(O)CH_3$), 2.92—2.98 (c, 2 H, CH_2), 3.85 (q, J=7.02 Hz, 6 H, OCH_2), 7.22—7.31 (m, 2 H, ArH), 7.40 (t, J=7.29 Hz, 1 H, ArH), 7.62 (dd, J=1.48, 7.56 Hz, 1 H, ArH); ^{13}C NMR δ=12.90 ($SiCH_2$), 18.28 (CH_3), 27.26 ($C(O)CH_3$), 29.82 (CH_2), 58.34 (OCH_2), 125.64, 129.03, 130.62, 131.49, 137.51, 144.83 (Ar), 202.01 (C=O); IR (neat) 1692 s cm^{-1}; MS m/z (% rel intensity) 310 (M^+, 0.1), 265 (21), 264 (56), 192 (11), 177 (11), 163 (19), 136 (10), 135 (100), 131 (11), 130 (22), 129 (12), 119 (25), 107 (32), 91 (21), 79 (48), 77 (10), 63 (18). Found: C, 61.66; H, 8.64%. Calcd for $C_{16}H_{26}O_4Si$: C, 61.90; H, 8.44%.

8: Bp=220 °C/5 mmHg. ^{1}H NMR δ=0.90—0.96 (c, 4 H, $SiCH_2$), 1.22 (t, J=7.02 Hz, 18 H, CH_3), 2.50 (s, 3 H, $C(O)CH_3$), 2.55—2.62 (c, 4 H, CH_2), 3.81 (q, J=7.02 Hz, 12 H, OCH_2), 7.08 (d, J=7.56 Hz, 2 H, ArH), 7.21 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=12.96 ($SiCH_2$), 18.28 (CH_3), 26.24 ($C(O)CH_3$), 33.01 (CH_2), 58.40 (OCH_2), 126.11, 128.83, 139.24, 141.15 (Ar), 208.30 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS m/z (% rel intensity) 454 (16), 441 (14), 440 (35), 439 (100), 411 (16), 365 (11), 163 (63), 135 (16), 119 (36), 107 (17), 91 (16), 79 (41), 63 (14). Found: C, 57.43; H, 8.89%. Calcd for $C_{24}H_{44}O_7Si_2$: C, 57.56; H, 8.86%.

2′-[2-(Trimethoxysilyl)ethyl]acetophenone (9). A dark-brown residue was passed through a short column of silica-gel (10 cm length ×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on rotary evaporator (40 °C/5 mmHg). The product **9** was isolated by bulb-to-bulb distillation (150 °C/5 mmHg). ^{1}H NMR δ=0.96—1.03 (c, 2 H, $SiCH_2$), 2.52 (s, 3 H, CH_3), 2.92—2.98 (c, 2 H, CH_2), 3.59 (s, 9 H, OCH_3), 7.23—7.67 (m, 4 H, ArH); ^{13}C NMR δ=11.78 ($SiCH_2$), 27.19 (CH_3), 29.72 (CH_2), 50.51

(OCH_3), 125.74, 129.24, 130.69, 131.61, 137.29, 144.80 (Ar), 210.84 (C=O); IR (neat) ν(C=O) 1688 s cm^{-1}; MS *m/z* (% rel intensity) 268 (M^+, 0.1), 237 (12), 236 (59), 131 (11), 130 (34), 129 (17), 121 (47), 115 (14), 107 (100), 91 (56), 77 (22), 61 (20), 59 (19).

2′,6′-Bis[2-(trimethoxysilyl)ethyl]acetophenone (10). Product **10** was prepared by the following procedure. A toluene (3 cm^3) solution of acetophenone (240 mg, 2 mmol), trimethoxyvinylsilane (1475 mg, 10 mmol) and $Ru(H)_2(CO)(PPh_3)_3$ (110 mg, 0.12 mmol) was heated at 135 °C (oil bath temperature) for 90 h. The solvent and trimethoxyvinylsilane were removed by rotary evaporation (40 °C/5 mmHg). The residue was purified by bulb-to-bulb distillation (200 °C/3 mmHg). The product **10** was isolated in 48% yield (402 mg). ^{1}H NMR δ=0.96—1.03 (c, 4 H, $SiCH_2$), 2.56 (s, 3 H, CH_3), 2.59—2.66 (c, 4 H, CH_2), 3.61 (s, 18 H, OCH_3), 7.13 (d, J=7.6 Hz, 2 H, ArH), 7.29 (t, J=7.6 Hz, 1 H, ArH); ^{13}C NMR δ=11.72 ($SiCH_2$), 26.07 (CH_3), 33.01 (CH_2), 50.54 (OCH_3), 126.22, 128.91, 139.05, 142.20 (Ar), 200.60 (C=O); IR (neat) ν(C=O) 1697 s cm^{-1}. Found C, 51.92; H, 7.82%. Calcd for $C_{16}H_{26}O_4Si$: C, 51.89; H, 7.74%.

2′-[2-(Ethoxydimethylsilyl)ethyl]acetophenone (11) and 2′,6′-Bis[2-(ethoxydimethylsilyl)ethyl]acetophenone (12). 11: Bp=104 °C/4 mmHg. ^{1}H NMR δ=0.16 (s, 6 H, $SiCH_3$), 0.89—0.95 (c, 2 H, CH_2), 1.21 (t, J=7.02 Hz, 3 H, CH_3), 2.58 (s, 3 H, $C(O)CH_3$), 2.85—2.91 (c, 2 H, $ArCH_2$), 3.71 (q, J=7.02 Hz, 2 H, OCH_2), 7.22—7.29 (m, 2 H, ArH), 7.42 (t, J=7.56 Hz, 1 H, ArH), 7.65 (d, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=−2.13 ($SiCH_3$), 18.57 ($SiCH_2$), 19.03 (CH_3), 27.71 ($C(O)CH_3$), 29.82 (CH_2), 58.30 (OCH_2), 125.54, 129.21, 130.56, 131.55, 137.29, 145.50 (Ar), 202.01 (C=O); IR (neat) ν(C=O) 1690 s cm^{-1}; MS *m/z* (% rel intensity) 235 (10), 204 (23), 147 (12), 131 (14), 105 (24), 103 (59), 77 (27), 75 (100), 59 (20). Found: C, 66.96; H, 9.08%. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86%.

12: Bp=145 °C/4 mmHg. ^{1}H NMR δ=0.13 (s, 12 H, $SiCH_3$), 0.88—0.94 (c, 4 H, $SiCH_2$), 1.20 (t, J=7.02 Hz, 6 H, CH_3), 2.49—2.55 (c, 4 H, CH_2), 2.49 (s, 3 H $C(O)CH_3$), 3.67 (q, J=7.02 Hz, 4 H, OCH_2), 7.07 (d, J=7.56 Hz, 2 H, ArH), 7.22 (t, J=7.56 Hz, 1 H, Ar); ^{13}C NMR δ=−2.21 ($SiCH_3$), 18.54 (CH_3 or $SiCH_2$), 18.98 (CH_3 or $SiCH_2$), 18.98 (CH_3 or $SiCH_2$), 26.62 ($C(O)CH_3$), 33.04 (CH_2), 58.30 (OCH_2), 126.02, 128.81, 139.59, 140.99 (Ar), 208.35 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS *m/z* (% rel intensity) 319(26), 104 (10), 103 (100), 75 (64), 59 (31). Found: C, 62.86; H, 9.64%. Calcd for $C_{20}H_{36}O_3Si_2$: C, 63.10; H, 9.53%.

2′-[2-(Trimethylsilyl)ethyl]acetophenone (13) and 2′,6′-Bis[2-(trimethylsilyl)ethyl]acetophenone (14). The products were isolated by silica-gel column chromatography (Wakogel C-200; 30 mm i.d. ×180 mm length; 19:1, hexane:AcOEt).

13: Bp=97 °C/5 mmHg. ^{1}H NMR δ=0.04 (s, 9 H, $SiCH_3$), 0.78—0.84 (c, 2 H, $SiCH_2$), 2.58 (s, 3 H, CH_3), 2.80—2.87 (c, 2 H, CH_2), 7.2—7.4 (m, 3 H, ArH), 7.63 (d, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=−1.81 ($SiCH_3$), 19.44 ($SiCH_2$), 28.32 (CH_3), 29.86 (CH_2), 125. 42, 129.10, 130.48, 131.46, 137.39, 145.82 (Ar), 202.67 (C=O); IR (neat) ν(C=O) 1690 s cm^{-1}; MS *m/z*(% rel intemsity) 220 (M^+, 2.0), 205 (51), 131 (26), 129 (15), 115 (12), 75 (100), 73 (88). Found: C, 70.77; H, 9.31%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

14: Bp=140 °C/3 mmHg. ^{1}H NMR δ=0.06 (s, 18 H, $SiCH_3$), 0.78—0.85 (c, 4 H, $SiCH_2$), 2.48 (s, 1 H, CH_3), 2.43—2.50 (c, 4 H, CH_2), 7.06 (d, J=7.83 Hz, 2 H, ArH), 7.22 (t, J=7.83 Hz, 1 H, ArH); ^{13}C NMR δ=−1.95 ($SiCH_3$), 19.36 ($SiCH_2$), 27.36 (CH_3), 33.01 (CH_2), 125.94, 128.75, 139.92, 140.96 (Ar), 208.22 (C=O); IR (neat) ν(C=O) 1704 s cm^{-1}; MS *m/z* (% rel intensity) 320 (M^+, 0.8), 305 (18), 217 (12), 147 (12), 75 (16), 73 (100). Found: C, 67.33; H, 10.25%. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06%.

2′-[2-(Dimethylphenyl)silylethyl]acetophenone (15) and 2′,6′-Bis[2-(dimethylphenylsilyl)ethyl]acetophenone (16). The products were isolated by silica-gel column chromatography (Wakogel C-200, 30 mm. i.d. ×200 mm length; 10:1, hexane:AcOEt) followed by bulb-to-bulb distillation.

15: Bp=140 °C/4 mmHg. ^{1}H NMR δ=0.34 (s, 6 H, $SiCH_3$), 1.04—1.11 (c, 2 H, $SiCH_2$), 2.55 (s, 3 H, CH_3), 2.82—2.89 (c, 2 H, CH_2), 7.2—7.64 (m, 9 H, ArH); ^{13}C NMR δ=−3.16 ($SiCH_3$), 18.43 ($SiCH_2$), 28.40 (CH_3), 29.82 (CH_2), 125.53, 127.74, 128.86, 129.20, 130.54, 131.52, 133.61, 137.33, 139.17, 145.53 (Ar), 202.02 (C=O); IR (neat) ν(C=O) 1690 s cm^{-1}; MS *m/z* (% rel intensity) 268 (12), 267 (46), 205 (28), 147 (10), 137 (72), 136 (15), 135 (100), 131 (15), 130 (10), 129 (11), 107 (10), 105 (12), 91 (11), 75 (36). Found: C, 76.57; H, 7.94%. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85%.

16: Bp=194 °C/5 mmHg. ^{1}H NMR δ=0.29 (s, 12 H, $SiCH_3$), 1.02—1.08 (c, 4 H, $SiCH_2$), 2.26 (s, 3 H, CH_3), 2.41—2.47 (c, 4 H, CH_2), 7.01 (d, J=7.56 Hz, 2 H, ArH), 7.19 (t, J=7.56 Hz, 1 H, ArH), 7.34—7.37 (m, 6 H, ArH), 7.49—7.53 (m, 4 H, ArH); ^{13}C NMR δ=−3.31 ($SiCH_3$), 18.46 ($SiCH_2$), 27.33 (CH_3), 32.73 (CH_2), 126.02, 127.81, 128.75, 128.98, 133.57, 138.62, 139.66, 140.99 (Ar), 208.25 (C=O); IR (neat) ν(C=O) 1700 s cm^{-1}; MS *m/z* (% rel intensity) 351 (17), 231 (10), 207 (12), 137 (10), 136 (14), 135 (100), 75 (10). Found: C, 75.36; H, 8.18%. Calcd for $C_{28}H_{36}OSi_2$: C, 75.62; H, 8.16%.

2′-[2-(Triethoxysilyl)ethyl]propiophenone (18). Product **18** was isolated by bulb-to-bulb distillation (155 °C/2 mmHg) in 74% yield (479 mg). ^{1}H NMR δ=0.94—1.01 (c, 2 H, $SiCH_2$), 1.19 (t, J=7.33 Hz, 3 H, CH_3), 1.24 (t, J=7.08 Hz, 9 H, $OCCH_3$), 2.85—2.91 (c, 2 H, CH_2), 2.90 (q, J=7.33 Hz, 2 H, $C(O)CH_2$), 3.84 (q, J=7.08 Hz, 6 H, OCH_2), 7.20—7.40 (m, 3 H, ArH), 7.51 (d, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=8.39 ($SiCH_2$), 13.01 (CH_3), 18.25 ($OCCH_3$), 26.97 (CH_2), 35.26 ($C(O)CH_2$), 58.33 (OCH_2), 125.56, 127.71, 130.31, 130.85, 138.36, 143.97 (Ar), 205.69 (C=O); IR (neat) ν(C=O) 1694 s cm^{-1}; MS *m/z* (% rel intensity) 279 (19), 278 (50), 163 (22), 144 (11), 135 (100), 129 (12), 119 (29), 107 (30), 97 (20), 91 (18), 79 (46), 77 (10), 63 (17). Found: C, 62.81; H, 8.90%. Calcd for $C_{17}H_{28}O_4Si$: C, 62.93; H, 8.70%.

2′,6′-Bis[2-(triethoxysilyl)ethyl]propiophenone (19). Product **19** was isolated by bulb-to-bulb distillation (210 °C/2 mmHg) in 84% yield (869 mg). ^{1}H NMR δ=0.90—0.97 (c, 4 H, $SiCH_2$), 1.20 (t, J=7.29 Hz, 3 H, CH_3), 1.22 (t, J=7.02 Hz, 18 H, $OCCH_3$), 2.50—2.57 (c, 4 H, CH_2), 2.75 (q, J=7.29 Hz, 2 H, $C(O)CH_2$), 3.81 (q, J=7.02 Hz, 12 H, OCH_2), 7.09 (d, J=7.57 Hz, 2 H, ArH), 7.24 (d, J=7.57 Hz, 1 H, ArH); ^{13}C NMR δ=7.48 ($SiCH_2$), 13.01 (CH_3), 18.23 ($OCCH_3$), 26.56 (CH_2), 38.71 ($C(O)CH_2$), 58.36 (OCH_2), 125.97, 128.72, 139.42, 141.02 (Ar), 210.94

(C=O); IR (neat) ν(C=O) 1704 s cm^{-1}; MS *m/z* (% rel intensity) 441 (14), 440 (37), 439 (100), 411 (25), 367 (14), 365 (14), 349 (12), 339 (11), 337 (11), 321 (16), 293 (11), 277 (17), 164 (10), 163 (76), 135 (24), 119 (61), 107 (30), 91 (25), 79 (57), 63 (19), 57 (13). Found: C, 58.41; H, 9.08%. Calcd for $C_{25}H_{46}O_7Si_2$: C, 58.33; H, 9.01%.

2′-[2-(Triethoxysilyl)ethyl]-2,2-dimethylpropiophenone (21). Product **21** was isolated by bulb-to-bulb distillation (150 °C/2 mmHg) in 85% isolated yield (596 mg). ^{1}H NMR δ=0.94—1.00 (c, 2 H, $SiCH_2$), 1.23 (t, J=7.02 Hz, 9 H, CH_3), 1.25 (s, 9 H, $C(CH_3)$), 2.53—2.59 (c, 2 H, CH_2), 3.83 (q, J=7.02 Hz, 6 H, OCH_2), 7.10—7.30 (m, 4 H, ArH); ^{13}C NMR δ=12.93 ($SiCH_2$), 18.28 (CH_3), 26.91 (CH_2), 27.40 ($C(CH_3)$), 44.82 ($C(CH_3)$), 58.37 (OCH_2), 124.38, 124.87, 128.72, 128.95, 140.21, 140.86 (Ar), 215.01 (C=O); IR (neat) ν(C=O) 1692 s cm^{-1}; MS *m/z* (% rel intensity) 307 (11), 306 (10), 296 (17), 295 (70), 164 (12), 163 (100), 135 (54), 119 (58), 117 (36), 107 (26), 91 (19), 79 (50), 63 (17), 57 (15). Found: C, 64.98; H, 9.17%. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15%.

2′-Methyl-6′-[2-(trimethoxysilyl)ethyl]acetophenone (23). A dark-brown residue was passed through a short column of silica gel (10 cm length ×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). The product **23** was isolated by bulb-to-bulb distillation (150 °C/5 mmHg). ^{1}H NMR δ=0.92—0.99 (c, 2 H, $SiCH_2$), 2.25 (s, 3 H, CH_3), 2.49 (s, 3 H, $C(O)CH_3$), 2.56—2.62 (c, 2 H, CH_2), 3.56 (s, 9 H, OCH_3), 7.02 (d, J=7.3 Hz, 1 H, ArH), 7.08 (d, J=7.8 Hz, 1 H, ArH), 7.20 (t, J=7.6 Hz, 1 H, ArH); ^{13}C NMR δ=11.77 ($SiCH_2$), 19.12 (CH_3), 26.08 ($C(O)CH_3$), 32.49 (CH_2), 50.50 (OCH_3), 126.09, 127.87, 128.70, 132.09, 139.09, 141.87 (Ar), 208.32 (C=O); IR (neat) ν(C=O) 1696 s cm^{-1}; MS *m/z* (% rel intensity) 282 (M^+, 2.2), 250 (35), 239 (11), 235 (11), 145 (12), 144 (42), 129 (25), 121 (74), 107 (100), 91 (61), 77 (15), 61 (19), 59 (14). Found: C, 59.82; H, 7.91%. Calcd for $C_{14}H_{18}O_4Si$: C, 59.54; H, 7.85%.

2′-[2-(Ethoxydimethylsilyl)ethyl]-6′-methylacetophenone (24). Product **24** was isolated by bulb-to-bulb distillation (110 °C/4 mmHg). ^{1}H NMR δ=0.12 (s, 6 H, $SiCH_3$), 0.88—0.94 (c, 2 H, $SiCH_2$), 1.20 (t, J=7.02 Hz, 3 H, CH_3), 2.24 (s, 3 H, $ArCH_3$), 2.48 (s, 3 H, $C(O)CH_3$), 2.50—2.56 (c, 2 H, CH_2), 3.67 (q, J=7.02 Hz, 1 H, OCH_2), 7.01 (d, J=7.56 Hz, 1 H, ArH), 7.08 (d, J=7.56 Hz, 1 H, ArH), 7.19 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=−2.23 ($SiCH_3$), 18.54 ($SiCH_2$), 19.01 ($OCCH_3$ or CH_3), 19.12 ($OCCH_3$ or CH_3), 26.61 ($C(O)CH_3$) 32.54 (CH_2), 58.30 (OCH_2), 126.08, 127.68, 128.65, 132.07, 139.69, 141.77 (Ar), 208.42 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS *m/z* (% rel intensity) 264 (M^+, 0.2), 249 (19), 218 (15), 145 (19), 144 (12), 129 (13), 105 (32), 103 (81), 77 (22), 75 (100), 59 (20). Found: C, 68.26; H, 9.30%. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15%.

2′-Methyl-6′-[2-(trimethylsilyl)ethyl]acetophenone (25). Product **25** was obtained in 97% GC yield, and was isolated by bulb-to-bulb distillation (100 °C/3 mmHg) in 74% yield (445 mg). ^{1}H NMR δ=0.02 (s, 9 H $SiCH_3$), 0.80—0.87 (c, 2 H, $SiCH_2$), 2.24 (s, 3 H, CH_3), 2.47 (s, 3 H, $C(O)CH_3$), 2.47—2.53 (c, 2 H, CH_2), 6.99 (d, J=7.56 Hz, 1 H, ArH), 7.07 (d, J=7.56 Hz, 1 H, ArH), 7.18 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=−2.04 ($SiCH_3$), 18.95 ($SiCH_2$), 19.27 (CH_3), 27.22 ($C(O)CH_2$), 32.32 (CH_2), 125.97, 127.45, 128.46, 131.84, 139.85, 141.63 (Ar), 207.95 (C=O); IR (neat) ν(C=O) 1704 s cm^{-1}; MS *m/z* (% rel intensity) 220 (14), 219 (69), 145 (35), 129 (16), 75 (81), 74 (11), 73 (100), 59 (11). Found: C, 71.85; H, 9.71%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

2′-[2-(Dimethylphenylsilyl)ethyl]-6′-methylacetophenone (26). A dark-brown residue was passed through a short column of silica gel (10 cm length ×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). The product **26** was isolated by bulb-to-bulb distillation (190 °C/4 mmHg) in 73% isolated yield (430 mg). ^{1}H NMR δ=0.30 (s, 6 H, $SiCH_3$), 1.04—1.10 (c, 2 H, $SiCH_2$), 2.23 (s, 3 H, CH_2), 2.38 (s, 3 H, $C(O)CH_3$), 2.44—2.51 (c, 2 H, CH_2), 7.00 (d, J=7.56 Hz, 1 H, ArH), 7.04 (d, J=7.56 Hz, 1 H, ArH), 7.18 (t, J=7.56 Hz, 1 H, ArH), 7.36—7.55 (m, 5 H, ArH); ^{13}C NMR δ=−3.30 ($SiCH_3$), 18.52 ($SiCH_2$), 19.11 (CH_3), 27.33 ($C(O)CH_3$), 32.38 (CH_2), 126.09, 127.67, 127.82, 128.63, 129.00, 132.07, 133.57, 138.59, 139.77, 141.77 (Ar), 208.38 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS *m/z* (% rel intensity) 281 (36), 219 (18), 145 (17), 137 (65), 136 (15), 135 (100), 129 (11), 107 (10), 105 (12), 75 (40). Found: C, 76.90; H, 8.27%. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16%.

2′-Methyl-6′-[2-(trimethylsilyl)propyl]acetophenone (27). Product **27** was isolated by Chromatotron chromatography (silica gel; 30 : 1, hexane : AcOEt) followed by bulb-to-bulb distillation (80 °C/8 mmHg). ^{1}H NMR δ=−0.01 (s, 9 H, $SiCH_3$), 0.79 (d, J=6.35 Hz, 3 H, CH_3), 0.83—0.97 (m, 1 H, CH_2CH), 2.11 (dd J=14.04 and 11.6 Hz, 1 H, C*H*H), 2.25 (s, 3 H, $ArCH_3$), 2.47 (s, 3 H, $C(O)CH_3$), 2.79 (dd, J=14.04 and 3.29 Hz, 1 H, CH*H*), 7.02 (d, J=7.57 Hz, 2 H, ArH), 7.21 (t, J=7.57 Hz, 1 H, ArH); ^{13}C NMR δ=−3.53 ($SiCH_3$), 13.33 (CH_3), 19.21 (CH_3), 21.60 (CH), 32.66 ($C(O)CH_3$), 34.72 (CH_2), 127.79, 127.74, 128.07, 132.10, 137.08, 142.69 (Ar), 208.42 (C=O); IR (neat) ν(C=O) 1701 s cm^{-1}; MS *m/z* (% rel intensity) 248 (M^+, 0.05), 233 (43), 159 (16), 143 (13), 75 (42), 73 (100). Found: C, 72.28; H, 9.89%. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

2′-(2-Phenylethyl)acetophenone (28) and 2′(1-Phenylethyl)acetophenone (29). Products **28** and **29** were isolated by bulb-to-bulb distillation (180 °C/3 mmHg) as a mixture.

28: ^{1}H NMR δ=2.54 (s, 3 H, CH_3), 2.86—2.92 (c, 2 H, CH_2), 3.13—3.20 (c, 2 H, CH_2), 7.1—7.7 (m, 9 H, Ar and Ph); ^{13}C NMR δ=29.54 (CH_3), 36.25 (CH_2), 38.11 (CH_2), 125.74, 125.80, 125.87, 128.13, 128.54, 129.17, 131.35, 131.38, 137.72, 141.80 (Ar), 201.75 (C=O); IR (neat, mixture) ν(C=O) 1691 s cm^{-1}; MS *m/z* (% rel intensity) 224 (M^+, 6), 210 (13), 209 (76), 133 (52), 131 (12), 105 (15), 103 (16), 91 (100), 90 (10), 89 (10), 79 (11), 77 (16), 65 (19), 51 (11). Found: C, 85.71; H, 7.18%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%.

29: ^{1}H NMR δ=1.62 (d, J=7.29 Hz, 3 H, CH_3), 2.37 (s, 3 H, $C(O)CH_3$), 4.88 (q, 3 H, CH), 7.1—7.7 (m, 9 H, Ar and Ph); ^{13}C NMR δ=21.86 (CH_3), 30.20 ($C(O)CH_3$), 39.41 (CH), 125.59, 127.55, 127.94, 130.76, 139.24, 145.03, 146.08 (Ar), 203.59 (C=O); MS *m/z* (% rel intensity) 225

(M+1$^+$, 6), 224 (M$^+$, 35), 210 (16), 209 (100), 207 (11), 206 (38), 195 (14), 194 (84), 191 (26), 181 (13), 178 (17), 166 (20), 165 (53), 146 (11), 145 (11), 133 (56), 131 (13), 115 (12), 105 (15), 103 (25), 97 (16), 91 (13), 89 (12), 83 (14), 82 (19), 78 (10), 77 (35), 76 (13), 63 (11), 51 (24).

2′-[2-Phenyl-2-(trimethylsilyl)ethyl]acetophenone (30). Product **30** was isolated by bulb-to-bulb distillation (150 °C/2 mmHg) in 45% yield (267 mg). ^{1}H NMR δ=0.01 (s, 9 H, SiCH$_3$), 2.32 (dd, J=11.88 and 3.78 Hz, 1 H, CH), 2.42 (s, 3 H, CH$_3$), 3.30 (dd, J=14.31 and 11.88 Hz, 1 H, C*H*H), 3.42 (dd, J=14.31 and 3.78, 1 H, CH*H*), 6.89—7.51 (m, 9 H, ArH); ^{13}C NMR δ=−2.79 (SiCH$_3$), 29.77 (CH), 32.95 (C(O)*C*H$_3$), 39.27 (CH$_2$), 124.38, 125.36, 127.93, 128.25, 128.62, 130.77, 131.24, 138.17, 142.23, 142.77 (Ar), 202.75 (C=O); IR (neat) ν(C=O) 1688 s cm^{-1}; MS m/z (% rel intensity) 282 (17), 281 (70), 91 (12), 75 (48), 73 (100). Found: C, 76.64; H, 8.26%. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16%.

2′-[2-(2-Methylphenyl)ethyl]acetophenone (31). A dark-brown residue was passed through a short column of silica gel (12 cm length×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). The product **31** was isolated by bulb-to-bulb distillation (175 °C/2 mmHg; mp=57—60 °C). ^{1}H NMR δ= 2.31 (s, 3 H, CH$_3$), 2.50 (s, 3 H, C(O)CH$_3$), 2.86—2.91 (c, 2 H, CH$_2$), 3.09—3.15 (c, 2 H, CH$_2$), 7.09—7.67 (m, 8 H, ArH); ^{13}C NMR δ=19.18 (CH$_3$), 29.63 (C(O)*C*H$_3$), 34.80 (CH$_2$), 35.52 (CH$_2$), 125.90, 126.00, 129.04, 129.32, 130.08, 131.43, 131.53, 136.10, 138.06, 139.54, 141.92 (Ar), 202.01 (C=O); IR (neat) ν(C=O) 1678 s cm^{-1}; MS m/z (% rel intensity) 238 (M$^+$, 1), 220 (21), 133 (14), 106 (10), 105 (100), 79 (14), 77 (15). Found: C, 85.67; H, 7.61%. Calcd for $C_{17}H_{18}O$: C, 85.47; H, 7.63%.

2′-Methyl-6′-(2-phenylethyl)acetophenone (32) and 2′-Methyl-6′-(1-phenylethyl)acetophenone (33). A dark-brown residue was passed through a short column of silica gel (10 cm length ×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). A mixture of **32** and **33** was isolated by bulb-to-bulb distillation (160 °C/5 mmHg).

32: ^{1}H NMR δ=2.35 (s, 3 H, CH$_3$), 2.49 (s, 3 H, C(O)-CH$_3$), 2.83—3.00 (c, 4 H, CH$_2$), 7.12—7.45 (m, 8 H, ArH); ^{13}C NMR δ=19.16 (CH$_3$), 32.38 (C(O)*C*H$_3$), 35.38 (CH$_2$), 38.01 (CH$_2$), 126.00, 126.79, 128.67, 128.37, 128.50, 132.11, 136.23, 141.40, 142.37 (Ar), 208.25 (C=O); IR (neat) ν(C=O) 1698 s cm^{-1}; MS m/z (% rel intensity) 238 (M$^+$, 0.3), 224 (18), 223 (100), 147 (49), 145 (19), 117 (22), 115 (10), 105 (10), 104 (12), 103 (14), 91 (97), 78 (11), 77 (17), 65 (24), 51 (14). Found: C, 85.57; H, 7.49%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

33: ^{1}H NMR δ=1.68 (d, J=7.06 Hz, 3 H, CH*C*H$_3$), 2.28 (s, 3 H, CH$_3$), 2.33 (s, 3 H, C(O)CH$_3$), 4.23 (q, J=7.02, 1 H, CH), 7.12—7.45 (m, 8 H, ArH); ^{13}C NMR δ=19.16 (CH$_3$), 22.30 (CH*C*H$_3$), 32.83 (C(O)*C*H$_3$), 40.95 (CH), 124.85, 126.11, 127.76, 128.12, 128.55, 131.91, 140.97, 142.27, 145.46 (Ar), 208.73 (C=O); MS m/z (% rel intensity) 239 (M+1$^+$, 12.8), 238 (M$^+$, 70), 237 (18), 224 (14), 223 (81), 220 (21), 209 (17), 208 (100), 205 (27), 195 (17), 180 (13), 179 (23), 178 (32), 166 (13), 165 (45), 160 (12), 152 (11), 147 (79), 145 (15), 117 (15), 115 (23), 105 (16), 104 (24), 103 (20), 91 (23), 89 (33), 77 (33), 76 (18), 65 (11), 63 (14), 51 (23).

2′-Methyl-6′-[2-(2-methylphenyl)ethyl]acetophenone (34). Product **34** was isolated by bulb-to-bulb distillation (140 °C/7 mmHg). ^{1}H NMR δ=2.41 (s, 3 H, CH$_3$), 2.44 (s, 3 H, CH$_3$), 2.50 (s, 3 H, C(O)CH$_3$), 2.84—3.03 (m, 4 H, CH$_2$), 7.18—7.38 (m, 7 H, ArH); ^{13}C NMR δ=19.20 (*C*H$_3$), 32.47 (C(O)*C*H$_3$), 34.16 (CH$_2$), 35.56 (CH$_2$), 126.03, 126.20, 126.89, 128.10, 128.60, 128.91, 130.20, 132.16, 135.90, 136.49, 139.65, 142.35 (Ar), 208.36 (C=O); IR (neat) ν(C=O) 1699 s cm^{-1}; MS m/z (% rel intensity) 252 (M$^+$, 0.1), 238 (24), 235 (19), 147 (19), 105 (100), 79 (11), 77 (15). Found: C, 85.44; H, 7.95%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

2′-Ethyl-6′-methylacetophenone (35). In an oven-dried 50-cm^3 stainless-steel autoclave were placed Ru(H)$_2$(CO)(PPh$_3$)$_3$ (37 mg, 0.04 mmol), 3 cm^3 of toluene, 2′-methylacetophenone (268 mg, 2 mmol), and hexadecane (167 mg) under a flow of nitrogen. The system was flushed with 5 kg cm^{-2} of ethylene three times, and was finally pressurized to 6 kg cm^{-2}. The reaction mixture was vigorously stirred at 135 °C for 24 h. After the reaction mixture was allowed to cool to room temperature, any unreacted ethylene was carefully bled off. The contents were transferred to a 30-cm^3 round-bottom flask and 3 cm^3 of toluene was used rinse the autoclave three times. The combined solutions were evaporated by a rotary evaporator and the product **35** was isolated by bulb-to-bulb distillation (74 ° C/5 mmHg) in 88% yield (285 mg). ^{1}H NMR δ=1.21 (t, J=7.56, 3 H, CH$_2$*C*H$_3$), 2.25 (s, 3 H, CH$_3$), 2.49 (s, 3 H, C(O)CH$_3$), 2.54 (q, J=7.56 Hz, 2 H, CH$_2$), 7.02 (d, J=7.56 Hz, 1 H, ArH), 7.07 (d, J=7.56 Hz, 1 H, ArH). 7.21 (t, J=7.6 Hz, 1 H, ArH); ^{13}C NMR δ=15.80 (C*C*H$_3$), 19.07 (CH$_3$), 26.09 (C(O)*C*H$_3$), 32.49 (CH$_2$), 126.02, 127.74, 128.62, 131.96, 138.62, 142.08 (Ar), 208.45 (C=O); IR (neat) ν(C=O) 1700 s cm^{-1}; MS m/z (% rel intensity) 162 (M$^+$, 28), 148 (10), 147 (100), 119 (18), 117 (17), 91 (27), 77 (12), 51 (10). Found: C, 81.27; H, 8.75%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

2′-Hexyl-6′-methylacetophenone (36). Product **36** was isolated by Chromatotron (30:1, hexane:AcOEt) and then by bulb-to-bulb distillation (130 °C/5 mmHg). ^{1}H NMR δ=0.88 (t, J=6.7 Hz, 3 H, C*C*H$_3$), 1.2—1.4 (m, 6 H, CH$_2$), 1.57—1.73 (m, 2 H, ArC*C*H$_2$), 2.25 (s, 3 H, CH$_3$), 2.48 (s, 3 H, C(O)CH$_3$), 2.48 (t, J=7.32 Hz, 2 H, ArCH$_2$), 7.01 (d, J=7.56 Hz, 1 H, ArH), 7.04 (d, J=7.56 Hz, 1 H, ArH), 7.16 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ= 14.05 (C*C*H$_3$), 19.15 (CH$_3$), 22.56 (CH$_2$), 29.27 (C(O)*C*H$_3$), 31.60 (CH$_2$), 31.63 (CH$_2$), 32.60 (CH$_2$), 33.21 (CH$_2$), 126.66, 127.73, 128.46, 132.01, 137.40, 142.26 (Ar), 208.54 (C=O); IR (neat) ν(C=O) 1700 s cm^{-1}; MS m/z (% rel intensity) 218 (M$^+$, 6), 204 (14), 203 (100), 147 (16), 143 (24), 133 (24), 131 (21), 115 (10), 105 (37), 91 (16), 77 (12), 55 (15). Found: C, 82.60; H, 10.31%. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16%.

2′-(2-Cyclohexylethyl)-6′-methylacetophenone (37). Product **37** was isolated by silica-gel column chromatography (30 mm i.d. ×50 mm length: Wakogel C-200; eluent, 20:1, hexane:AcOEt) and then by bulb-to-bulb distillation (130 °C/8 mmHg) in 18% yield (88 mg). ^{1}H NMR δ=0.90—1.80 (c, 2 H, CH$_2$), 1.10—1.35 (m, 4 H, CHCH$_2$*C*H$_2$), 1.40—1.50 (c, 2 H, ArCCH$_2$), 1.6—1.8 (c, 5

H, $CHCH_2$), 2.24 (s, 3 H, CH_3), 2.48 (s, 3 H, $C(O)CH_3$), 2.46—2.52 (c, 2 H, $ArCH_2$), 7.01 (d, J=7.83 Hz, 1 H, ArH), 7.04 (d, J=7.83 Hz, 1 H, ArH), 7.18 (t, J=7.83 Hz, 1 H, ArH); ^{13}C NMR δ=19.14 (CH_3), 26.24 (CH_2), ($C(O)CH_3$), 30.56 ($ArCCH_2$), 32.57 26.59 (CH_2), 33.16 (CH_2), 37.69 (CH_2), 39.61 (CH), 126.64, 127.67, 128.48, 132.02, 137.72, 142.21 (Ar), 208.44 (C=O); IR (neat) ν(C=O) 1701 s cm^{-1}; MS m/z (% rel intensity) 244 (M^+, 4.4), 230 (12), 229 (61), 226 (13), 211 (13), 161 (12), 155 (12), 148 (19), 147 (36), 145 (11), 144 (18), 143 (15), 133 (100), 131 (19), 115 (10), 106 (12), 105 (46), 99 (15), 91 (15), 83 (13), 81 (18), 77 (12), 55 (52). Found: C, 83.36; H, 9.95%. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90%.

2′-(3,3-Dimethylbutyl)-6′-methylacetophenone (38). Product **38** was isolated by silica-gel column chromatography (30 mm i.d. ×100 mm length; Wakogel C-200; eluent, 20:1, hexane:AcOEt) and then by bulb-to-bulb distillation (140 °C/8 mmHg). ^1H NMR δ=0.93 (s, 9 H, $C(CH_3)$), 1.41—1.48 (c, 2 H, CH_2), 2.24 (s, 3 H, CH_3), 2.41—2.48 (c, 2 H, $ArCH_2$), 2.49 (s, 3 H, $C(O)CH_3$), 7.01 (d, J=7.56 Hz, 1 H, ArH), 7.03 (d, J=7.56 Hz, 1 H, ArH), 7.18 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=19.15 (CH_3), 28.49 ($C(O)CH_3$), 29.16 ($C(CH_3)$), 30.56 ($C(CH_3)$), 32.58 ($ArCH_2$), 46.58 (CH_2), 126.83, 127.67, 128.57, 132.10, 137.94 (Ar), 208.39 (C=O); IR (neat) ν(C=O) 1701 s cm^{-1}; MS m/z (% rel intensity) 218 (M^+, 21), 204 (14), 203 (87), 162 (13), 161 (100), 148 (11), 147 (88), 146 (15), 145 (61), 143 (26), 133 (35), 128 (13), 117 (14), 115 (16), 105 (29), 104 (11), 103 (15), 91 (24), 78 (12), 77 (18), 59 (28), 57 (73). Found: C, 82.47; H, 10.31%. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16%.

2′-Methyl-6′-[3-(trimethylsilyl)propyl]acetophenone (39). Product **39** was isolated by silica-gel column chromatography (30 mm i.d. ×150 mm length; Wakogel C-200; eluent, hexane:AcOEt, 10:1) and then by bulb-to-bulb distillation (150 °C/8 mmHg). ^1H NMR δ=−0.03 (s, 9 H, $SiCH_3$), 0.51—0.57 (c, 2 H, $SiCH_2$), 1.51—1.64 (c, 2 H, CH_2), 2.25 (s, 3 H, CH_3), 2.48 (s, 3 H, $C(O)CH_3$), 2.48—2.54 (c, 2 H, $ArCH_2$), 7.02 (d, J=7.56 Hz, 1 H, ArH), 7.05 (d, J=7.56 Hz, 1 H, ArH), 7.19 (t, J=7.56 Hz, 1 H, ArH); ^{13}C NMR δ=−1.74 ($SiCH_3$), 16.94 ($SiCH_2$), 19.18 (CH_3), 26.26 ($C(O)CH_3$), 32.61 (CH_2), 37.15 ($ArCH_2$), 126.72, 127.78, 128.46, 132.02, 137.28, 142.29 (Ar), 208.41 (C=O); IR (neat) ν(C=O) 1701 s cm^{-1}; MS m/z (% rel intensity) 248 (M^+, 0.9), 88 (11), 86 (63), 84 (100), 75 (16), 73 (18), 51 (64). Found: C, 72.60; H, 9.94%. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

2′-Cyclopentylacetophenone (41). The reaction of acetophenone (2 mmol) with cyclopentene (10 mmol) was carried out in the presence of 0.12 mmol of $Ru(H)_2(CO)(PPh_3)_3$ at 135 °C for 48 h in a stainless steel pressure bottle. Product **41** was obtained in 36% GC yield and was isolated by silica-gel column chromatography (Wakogel C-200, 30 mm i.d. ×100 mm length; eluent, 10:1, hexane:AcOEt) and then by bulb-to-bulb distillation (150 °C/2 mmHg), in 28% yield (105 mg). ^1H NMR δ=1.52—2.20 (c, 8 H, CH_2), 2.57 (s, 3 H, CH_3), 3.45 (m, 1 H, CH), 7.18—7.46 (m, 4 H, ArH); ^{13}C NMR δ=25.78 (CH_2), 30.67 ($C(O)CH_3$), 35.13 ($CHCH_2$), 41.49 (CH), 125.24, 127.06, 127.26, 130.86, 139.92, 145.21 (Ar), 203.98 (C=O); IR (neat) ν(C=O) 1692 s cm^{-1}; MS m/z (% rel intensity) 188 (M^+, 29.2), 174 (14), 173 (100), 171 (10), 170 (59), 156 (10), 155 (81), 154 (10), 153 (11), 146 (11), 145 (79), 143 (10), 142 (40), 141 (29), 132 (25), 131 (30), 130 (10), 129 (73), 128 (25), 127 (12), 117 (31), 116 (12), 115 (50), 105 (25), 104 (12), 103 (26), 91 (44), 89 (10), 78 (11), 77 (41), 65 (16), 63 (17), 51 (28). Found: C, 82.73; H, 8.63%. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%.

8-(*exo*-2-Norbornyl)-α-tetralone (42). Product **42** was isolated by bulb-to-bulb distillation (140 °C/2 mmHg) in 62% (300 mg) yield. ^1H NMR ($CDCl_3$) δ=1.23 (dq, J=9.5 and 0.6 Hz, 1 H, H(3)), 1.30—1.50 (m, 2 H, H(7)), 1.50—1.65 (m, 4 H, H(5) and H(6)), 1.94 (ddd, J=11.8, 8.8, and 3.0 Hz, H(3) *exo*), 2.05 (quint, J=6.4 Hz, 2 H, $C(O)CCH_2$), 2.31 (br s, 2 H, H(1) and H(4)), 2.64 (dt, J=0.8 and 5.9 Hz, 2 H, $C(O)CH_2$), 2.92 (t, J=6.8 Hz, 2 H, CH_2), 3.66 (dd, J=5.9 and 8.9 Hz, 1 H, H(2) *endo*), 7.03—7.34 (m, 3 H, ArH); ^{13}C NMR ($CDCl_3$) δ=28.45 ($C(O)CCH_2$), 30.82 ($ArCH_2$), 30.93 (CH_2), 33.66 (CH_2), 36.64 (CH_2), 36.71 (CH_2), 43.49 ($C(O)CH_2$), 44.15 (CH), 44.22 (CH), 123.02, 128.46, 142.17 (Ar), 209.83 (C=O); IR (neat) ν(C=O) 1678 s cm^{-1}; MS m/z (% rel intensity) 241 ($M+1^+$, 10), 240 (M^+, 52), 212 (18), 211 (14), 193 (13), 185 (12), 184 (29), 173 (17), 172 (17), 171 (100), 160 (17), 156 (10), 141 (12), 129 (16), 128 (21), 155 (26), 91 (11), 77 (11). Found: C, 84.99; H, 8.47%. Calcd for $C_{17}H_{20}O$: C, 85.00; H, 8.39%.

2′-[2-(Triethoxysilyl)ethyl]-1′-acetonaphtone (44). Product **44** was isolated by bulb-to-bulb distillation (210 °C/2 mmHg) in 67% yield (480 mg). ^1H NMR δ=0.99—1.06 (c, 2 H, $SiCH_2$), 1.25 (t, J=7.08 Hz, 9 H, CH_3), 2.65 (s, 3 H, $C(O)CH_3$), 2.74—2.81 (c, 2 H, CH_2), 3.85 (q, J=7.08 Hz, 6 H, OCH_2), 7.36—7.60 (m, 4 H, ArH), 7.78—7.83 (m, 2 H, ArH); ^{13}C NMR δ=13.24 ($SiCH_2$), 18.26 (CH_3), 26.65 ($C(O)CH_3$), 33.35 (CH_2), 58.45 (OCH_2), 124.02, 125.47, 126.78, 126.97, 128.20, 128.37, 128.54, 128.98, 131.76, 131.92, 131.99, 132.13, 136.94, 137.81, (Ar), 208.83 (C=O); IR (neat) ν(C=O) 1702 s cm^{-1}; MS m/z (% rel intensity) 360 (M^+, 9), 317 (17), 316 (13), 315 (28), 314 (65), 313 (22), 301 (13), 273 (31), 227 (16), 183 (12), 181 (28), 180 (100), 179 (20), 178 (11), 165 (22), 164 (11), 163 (74), 154 (10), 153 (15), 152 (18), 135 (77), 119 (35), 107 (30), 91 (17), 79 (47), 63 (20). Found: C, 66.36; H, 7.83%. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83%.

1′-[2-(Triethoxysilyl)ethyl]-2′-acetonaphthone (46). Product **46** was isolated by bulb-to-bulb distillation (220 °C/3 mmHg) in 88% yield (630 mg). ^1H NMR δ=1.09—1.15 (c, 2 H, $SiCH_2$), 1.29 (t, J=7.16 Hz, 9 H, CH_3), 2.65 (s, 3 H, $C(O)CH_3$), 3.26—3.33 (c, 2 H, CH_2), 3.92 (q, J=7.16 Hz, 6 H, OCH_2), 7.50—7.60 (m, 3 H, ArH), 7.73 (d, J=8.64 Hz, 1 H, ArH), 7.84 (dd, J=6.89 and 2.57 Hz, 1 H, ArH), 8.22 (d, J=8.37 Hz, 1 H, ArH); ^{13}C NMR δ=13.19 ($SiCH_2$), 18.36 (CH_3), 30.86($C(O)CH_3$), 22.48 (CH_2), 58.47 (OCH_2), 124.17, 125.32, 126.32, 126.71, 126.94, 128.65, 131.66, 134.62, 135.71, 140.87 (Ar), 203.69 (C=O); IR (neat) ν(C=O) 1692 s cm^{-1}; MS m/z (% rel intensity) 360 (M^+, 2), 315 (35), 314 (100), 313 (54), 181 (20), 180 (71), 179 (17), 178 (10), 165 (17), 163 (22), 153 (13), 152 (12), 135 (84), 119 (23), 107 (29), 91 (16), 79 (51), 63 (19). Found: C, 66.66; H, 7.97%. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83%.

2-[2-(Triethoxysilyl)ethyl]benzophenone (48). Product **48** was isolated by bulb-to-bulb distillation (200 °C/3 mmHg) in 74% yield (551 mg). ^1H NMR δ=0.89—0.96 (c, 2 H, $SiCH_2$), 1.15 (t, J=7.02 Hz, 9 H, CH_3), 2.70—2.77 (c, 2 H, CH_2), 3.72 (q, J=7.02 Hz, 6 H, OCH_2), 7.24—7.82

(m, 9 H, ArH); ^{13}C NMR δ=12.99 ($SiCH_2$), 18.17 (CH_3), 26.53 (CH_2), 58.27 (OCH_2), 125.16, 128.23, 128.36, 129.44, 130.11, 130.22, 133.11, 137.77, 138.18, 143.48 (Ar), 198.58 (C=O); IR (neat) ν(C=O) 1668 s cm^{-1}; MS *m/z* (% rel intensity) 372 (M^+, 12), 327 (28), 326 (55), 193 (13), 192 (48), 191 (20), 163 (16), 135 (100), 119 (22), 107 (24), 105 (13), 91 (17), 79 (38), 77 (24), 63 (14). Found: C, 67.33; H, 7.71%. Calcd for $C_{21}H_{28}O_4Si$: C, 67.71; H, 7.58%.

2,2′-Bis[2-(triethoxysilyl)ethyl]benzophenone (49). Product **49** was isolated by bulb-to-bulb distillation in 99% yield (1092 mg). ^{1}H NMR ($CDCl_3$) δ=0.98—1.04 (c, 4 H, $SiCH_2$), 1.20 (t, *J*=7.3 Hz, 18 H, CH_3), 2.87—2.93 (c, 4 H, CH_2), 3.80 (q, *J*=7.3 Hz, OCH_2), 7.14—7.40 (m, 8 H, ArH); ^{13}C NMR δ=12.92 ($SiCH_2$), 18.25 (CH_3), 26.97 (CH_2), 58.31 (OCH_2), 125.24, 130.04, 130.62, 131.14, 138.46, 145.24 (Ar), 200.31 (C=O).

3′-[2-(Triethoxysilyl)ethyl]-1,2-benzocyclohepten-3-one (52). Product **52** was isolated by bulb-to-bulb distillation (165 °C/2 mmHg) in 71% yield (494 mg). ^{1}H NMR δ=0.90—0.96 (c, 2 H, $SiCH_2$), 1.24 (t, *J*=7.02 Hz, 9 H, $OCCH_3$), 1.77—1.79 (m, 4 H, CH_2), 2.59—2.63 (m, 2 H, $ArCH_2$), 2.68—2.74 (m, 4 H, $SiCCH_2$ and $C(O)CH_2$), 3.83 (q, *J*=7.02 Hz, 6 H, OCH_2), 6.91 (d, *J*=7.02 Hz, 1 H, ArH), 7.14 (d, *J*=7.02 Hz, 1 H, ArH), 7.26 (t, *J*=7.02 Hz, 1 H, ArH); ^{13}C NMR δ=13.36 ($SiCH_2$), 18.25 (CH_3), 22.67 (CH_2), 25.66 (CH_2), 26.30 ($SiCCH_2$), 32.49 ($ArCH_2$), 42.38 ($C(O)CH_2$), 58.33 (OCH_2), 126.31, 127.71, 130.02, 137.65, 139.34, 142.28 (Ar), 210.90 (C=O); IR (neat) ν(C=O) 1692 s cm^{-1}; MS *m/z* (% rel intensity) 305 (25), 304 (65), 290 (10), 289 (17), 170 (31), 169 (11), 168 (29), 142 (11), 141 (18), 136 (11), 135 (100), 121 (14), 119 (14), 115 (11), 107 (22), 91 (17), 79 (32), 63 (16). Found: C, 65.25; H, 8.61%. Calcd for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.63%.

2-Acetyl-1-methyl-3-[2-(triethoxysilyl)ethyl]pyrrole (54). A dark-brown residue was passed through a short column of silica gel (10 cm length ×3 cm i.d.) with hexane (200 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). The product **54** was isolated by bulb-to-bulb distillation (170 °C/2 mmHg) in 56% yield (348 mg). ^{1}H NMR δ=0.97—1.03 (c, 2 H, $SiCH_2$), 1.24 (t, *J*=7.02 Hz, 9 H, CH_3), 2.47 (s, 3 H, $C(O)CH_3$), 2.83—2.90 (c, 2 H, CH_2), 3.84 (q, *J*=7.02 Hz, 6 H, OCH_2), 3.86 (s, 3 H, NCH_3), 6.05 (d, *J*=2.43 Hz, 1 H, pyrrolyl-H), 6.69 (d, *J*=2.43 Hz, 1 H, pyrrolyl-H); ^{13}C NMR δ=12.14 ($SiCH_2$), 18.31 (CH_3), 22.22 ($C(O)CH_3$), 30.29 (CH_2), 38.65 (NCH_3), 58.44 (OCH_2), 108.55, 128.36, 129.56, 130.67 (pyrrolyl), 189.05 (C=O); IR (neat) ν(C=O) 1644 s cm^{-1}; MS *m/z* (% rel intensity) 313 (M^+, 17), 271 (12), 270 (54), 268 (35), 267 (100), 266 (13), 254 (10), 252 (32), 227 (16), 226 (87), 198 (17), 195 (19), 180 (18), 166 (11), 164 (11), 163 (72), 152 (10), 150 (22), 136 (37), 135 (16), 134 (17), 133 (11), 132 (15), 120 (12), 119 (35), 108 (26), 107 (28), 106 (11), 94 (16), 91 (21), 90 (11), 84 (10), 83 (10), 79 (56), 77 (15), 63 (27). Found: C, 56.65; H, 8.69; N, 4.07%. Calcd for $C_{15}H_{27}NO_4Si$: C, 57.48: H, 8.68; N, 4.47%. HRMS Found: *m/z* 313.1702. Calcd for $C_{15}H_{27}NO_4Si$: M^+, 313.1709.

2-Acetyl-3-[2-(triethoxysilyl)ethyl]furan (56). Product **56** was isolated by bulb-to-bulb distillation (150 °C/3 mmHg) in 96% yield (576 mg). ^{1}H NMR δ=0.92—0.98 (c, 2 H, $SiCH_2$), 1.24 (t, *J*=7.02 Hz, 9 H, CH_3), 2.46 (s, 3 H, $C(O)CH_3$), 2.90—2.97 (c, 2 H, CH_2), 3.85 (q, *J*=7.02 Hz, 6 H, OCH_2), 6.47 (d, *J*=1.62 Hz, 1 H, furyl-H), 7.39 (d, *J*=1.62 Hz, 1 H, furyl-H); ^{13}C NMR δ=10.56 ($SiCH_2$), 18.25 (CH_3), 19.26 (CH_2), 26.97 ($C(O)CH_3$), 58.40 (OCH_2), 114.16, 137.13, 144.12, 147.87 (furyl), 188.74 (C=O); IR (neat) ν(C=O) 1676 s cm^{-1}; MS *m/z* (% rel intensity) 300 (M^+, 0.2), 256 (11), 255 (31), 254 (100), 182 (14), 163 (18), 135 (11), 119 (24), 107 (13), 91 (18), 79 (31), 63 (15). Found: C, 55.63; H, 7.97%. Calcd for $C_{14}H_{24}O_5Si$: C, 55.97; H, 8.05%.

2-Acetyl-3-[2-(triethoxysilyl)ethyl]thiophene (58). Product **58** was isolated by bulb-to-bulb distillation (145 °C/2 mmHg) in 93% yield (587 mg). ^{1}H NMR δ=0.97—1.03 (c, 2 H, $SiCH_2$), 1.25 (t, *J*=7.02 Hz, 9 H, CH_3), 2.53 (s, 3 H, $C(O)CH_3$), 3.07—3.13 (c, 2 H, CH_2), 3.86 (q, *J*=7.02 Hz, 6 H, OCH_2), 7.04 (d, *J*=5.13 Hz, 1 H, thienyl-H), 7.40 (d, *J*=5.13 Hz, 1 H, thienyl-H); ^{13}C NMR δ=11.27 ($SiCH_2$), 18.17 (CH_3), 23.46 (CH_2), 29.54 ($C(O)CH_3$), 58.28 (OCH_2), 129.61, 131.23, 135.00, 152.10 (thienyl), 190.71 (C=O); IR (neat) ν(C=O) 1670 s cm^{-1}; MS *m/z* (% rel intensity) 316 (M^+, 0.2), 272 (12), 271 (30), 270 (100), 198 (15), 183 (13), 163 (24), 135 (19), 119 (24), 107 (13), 91 (14), 79 (32), 63 (14). Found: C, 53.02; H, 7.83%. Calcd for $C_{14}H_{24}O_4SSi$: C, 53.13; H, 7.64%.

3-Acetyl-2-[2-(triethoxysilyl)ethyl]thiophene (60). Product **60** was isolated by bulb-to-bulb distillation (120 °C/4 mmHg) in 90% yield (574 mg). ^{1}H NMR δ=1.05—1.12 (c, 2 H, $SiCH_2$), 1.24 (t, *J*=7.02 Hz, 9 H, CH_3), 2.50 (s, 3 H, $C(O)CH_3$), 3.23—3.30 (c, 2 H, CH_2), 3.86 (q, *J*=7.02 Hz, 6 H, OCH_2), 7.03 (d, *J*=5.40 Hz, 1 H, thienyl-H), 7.34 (d, *J*=5.40 Hz, 1 H, thienyl-H); ^{13}C NMR δ=12.64 ($SiCH_2$), 18.26 (CH_3), 23.74 (CH_2), 29.88 ($C(O)CH_3$), 58.47 (OCH_2), 121.07, 129.12, 134.85, 158.15 (thienyl), 193.77 (C=O); IR (neat) ν(C=O) 1678 s cm^{-1}; MS *m/z* (% rel intensity) 316 (M^+, 0.3), 272 (12), 271 (28), 270 (100), 226 (15), 198 (18), 188 (11), 163 (13), 135 (17), 119 (22), 107 (16), 91 (16), 79 (45), 63 (21). Found: C, 53.29; H, 7.59; S, 10.05%. Calcd for $C_{14}H_{24}O_4Si$: C, 53.13; H, 7.64; S, 10.13%.

3-Acethyl-2-[2-(trimethylsilyl)ethyl]thiophene (61). The reaction of 3-acetylthiophene (2 mmol) with trimethylvinylsilane (2 mmol) was carried out in a stainless-steel pressure bottle at 135°C for 24 h. Product **61** was isolated by bulb-to-bulb distillation (120 °C/4 mmHg) in 76% yield (344 mg). ^{1}H NMR δ=0.06 (s, 9 H, $SiCH_3$), 0.93—0.99 (c, 2 H, $SiCH_2$), 2.50 (s, 3 H, $C(O)CH_3$), 3.14—3.20 (c, 2 H, CH_2), 7.03 (d, *J*=5.40 Hz, 1 H, thienyl-H), 7.35 (d, *J*=5.40 Hz, 1 H, thienyl-H); ^{13}C NMR δ=−1.84 ($SiCH_3$), 18.92 ($SiCH_2$), 24.74 (CH_2), 29.92 ($C(O)CH_3$), 120.90, 129.14, 134.64, 159.56 (thienyl), 193.89 (C=O); IR (neat) ν(C=O) 1678 s cm^{-1}; MS *m/z* (% rel intensity) 226 (M^+, 43), 212 (11), 211 (61), 197 (36), 153 (33), 137 (26), 135 (36), 85 (11), 75 (49), 74 (16), 73 (100), 59 (23). Found: C, 58.66; H, 7.98; S, 14.17%. Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01; S, 14.16%.

Reaction of 2′-Methylacetophenone (1) with Various Olefins. The reactions of **1** with various olefins shown in Charts 1, 2, and 3 were carried out under the following procedure. A 10-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with rubber septum, was flushed with dry nitrogen; the ap-

paratus was then flame dried under a flow of dry nitrogen. In the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (110 mg, 0.12 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, **1** (268 mg, 2 mmol), olefin (10 mmol), and hexadecane (an internal standard for GC) using a syringe, in this order. The mixture was heated under vigorous reflux conditions (oil bath temperature, 135 °C) with stirring. The reaction mixture was analyzed by GC.

Reaction of Various Ketones with Triethoxyvinylsilane (2). The reactions of ketones, e.g., 1-phenyl-1,3-butanedione, 2-chloroacetophenone, 2-acetylpyridine, acetylferrocene, benzil, 1,4-naphtoquinone, 2,2,2-trifluoroacetophenone, and benzylideneacetophenone, with **2** were carried out in a similar manner as described for the reaction of **1** with various olefins.

Stoichiometric Reaction of $Ru(H)_2(CO)(PPh_3)_3$ with Acetophenone. In an NMR tube was placed $Ru(H)_2(CO)(PPh_3)_3$ (36.7 mg, 0.04 mmol) and the tube was flushed with nitrogen. The tube was sealed with a rubber septum. After the complex $Ru(H)_2(CO)(PPh_3)_3$ was dissolved in 0.6 cm^3 of toluene-d_8, to the solution was added acetophenone (4.8 mg, 0.04 mmol). After the resulting mixture was heated at 135 °C for 2.5 h, the ^1H NMR spectrum of the reaction mixture was measured at room temperature. In the ^1H NMR spectrum of the reaction mixture, the hydride signals due to the ruthenium hydride complex were observed as the same signal patterns [$\delta=-8.47$ (ddt) and $\delta=-6.58$ (ddt)] as those observed before heating and a reduction product, α-methylbenzyl alcohol, was not detected at all.

Stoichiometric Reaction of $Ru(H)_2(CO)(PPh_3)_3$ with Trimethoxyvinylsilane and Acetophenone. In an NMR tube was placed $Ru(H)_2(CO)(PPh_3)_3$ (36.7 mg, 0.04 mmol) and the tube was flushed with nitrogen. The tube was sealed with a rubber septum. After the complex $Ru(H)_2(CO)(PPh_3)_3$ was dissolved in 0.6 cm^3 of benzene-d_6, to the solution was added trimethoxynylsilane (17.6 mg, 0.12 mmol). After the resulting mixture was heated at 135 °C for 1 min, the ^1H NMR spectrum of the reaction mixture was measured at room temperature. The ^1H NMR spectrum showed that ethyltrimethoxysilane was formed in 90% yield. To the reaction mixture was added acetophenone (9.6 mg, 0.08 mmol); the resulting mixture was heated at 135 °C for another 1 min. The ^1H NMR spectrum of the reaction mixture was measured at room temperature. The ^1H NMR spectrum showed that acetophenone was completely consumed and that the 1 : 1 coupling product **9** was formed in 98% yield. ^1H NMR data of ethyltrimethoxysilane (C_6D_6): $\delta=0.65$ (q, $J=7.2$ Hz, 2 H, $SiCH_2$), 1.05 (t, $J=7.2$ Hz, 3 H, CH_3), 3.43 (s, 9 H, OCH_3). ^1H NMR data of **9** (C_6D_6): $\delta=1.1$—1.2 (c, 2 H, $SiCH_2$), 2.12 (s, 3 H, CH_3), 3.13—3.25 (c, 2 H, CH_2).

Reaction of Acetophenone (6) and 2′-Methylacetophenone (1) with Trimethylvinylsilane. A 10-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen; the apparatus was then flame-dried under a flow of dry nitrogen. Into the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (37 mg, 0.04 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, **6** (240 mg, 2 mmol), **1** (268 mg, 2 mmol), trimethylvinylsilane (100 mg, 1 mmol), and hexadecane (231 mg, an internal standard for GC) using a syringe, in this order. The mixture was heated under vigorous reflux conditions (oil bath temperature, 135 °C) with stirring. After heating for 10 min, the reaction mixture was analyzed by GC. The products **13** (RRT=1.544), **14** (RRT=2.599), and **25** (RRT=1.603) were obtained in 32%, 38%, and 9% GC yields, respectively. RRT (relative retention time) is the retention time of the compound/retention time of the internal standard.

Reaction of Acetophenone-d_5 (6-d_5) with Triethoxyvinylsilane (2) at 135 °C. A 10-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen; the apparatus was then flame-dried under a flow of dry nitrogen. Into the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (37 mg, 0.04 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, **6-d_5** (250 mg, 2 mmol), **2** (380 mg, 2 mmol), and hexadecane (225 mg, an internal standard for GC) using a syringe, in this order. The mixture was heated under vigorous reflux (at 135 °C, oil bath temperature) with stirring. After heating for 10 min, the reaction mixture was cooled to room temperature and the reaction mixture was analyzed by GC. Toluene and the remaining **2** were transferred into a cold trap (liq. N_2) by vacuum distillation (25 °C/5 mmHg). Then, **2** was isolated by fractional distillation. A dark-brown residue was passed through a short column of silica-gel (10 cm length ×3 cm i.d.) with hexane (250 cm^3) to remove hexadecane and triphenylphosphine; the product was then eluted with ethyl acetate (200 cm^3). The ethyl acetate effluent was concentrated on a rotary evaporator (40 °C/5 mmHg). The acetophenone and the product were isolated by bulb-to-bulb distillation in 51% (318 mg) and 11% (27 mg) yields, respectively. The yields of the recovered starting materials and the product were determined by GC. The percentage of the deuterium incorporation into the vinylsilane and the product were determined based on the ^1H NMR spectrum. ^1H NMR data of the recovered acetophenone (CD_3CN): $\delta=2.55$ (s, 3 H, CH_3), 7.98 (s, 1.12 H, *ortho*-H). ^1H NMR data of the recovered triethoxyvinylsilane (CD_3CN): $\delta=1.16$—1.22 (m, 9.35 H, CH_3), 3.78—3.83 (m, 6.00 H, CH_2), 5.95 and 6.12 (br s, 1.79 H, $CH{=}CH_2$). ^1H NMR data of the coupling product (CD_3CN): $\delta=0.87$—0.93 (c, 1.32 H, $SiCH_2$), 1.22 (t, $J=7.0$ Hz, 9.05 H, CH_3), 2.55 (s, 3.00 H, $C(O)CH_3$), (c, 1.32 H, CH_2), 3.86 (q, $J=7.0$ Hz, 6.14 H, OCH_2), 7.70 (s, 0.57 H, *ortho*-H).

Reaction of Acetophenone-d_5 (6-d_5) with Triethoxyvinylsilane (2) at 50 °C. A 10-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen; the apparatus was then flame-dried under a flow of dry nitrogen. Into the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (37 mg, 0.04 mmol) under a flow of nitrogen. To the flask were added 3 cm^3 of toluene, **6-d_5** (250 mg, 2 mmol) and **2** (380 mg, 2 mmol). The mixture was heated at 50 °C (oil bath temperature) with stirring. After heating 15 h, the reaction mixture was cooled to room temperature and the reaction mixture was analyzed by GC. No coupling product was detected within the accuracy of the GC analysis. Toluene and the remaining **2** were trans-

ferred into a cold trap (liq. N_2) by vacuum distillation (25 °C/5 mmHg). Then, **2** was isolated by fractional distillation. The acetophenone was isolated by bulb-to-bulb distillation. The percentage of the deuterium incorporation into the vinylsilane and the product were determined by the ^{1}H NMR spectrum. ^{1}H NMR data of the recovered acetophenone (CD_3CN): δ=2.55 (s, 3.00 H, CH_3), 7.98 (s, 0.20 H, *ortho*-H). ^{1}H NMR data of the recovered triethoxyvinylsilane (CD_3CN): δ=1.13—1.23 (m, 9.00 H, CH_3), 3.75—3.85 (m, 5.90 H, CH_2), 5.9—6.2 (m, 2.18 H, CH=CH_2).

A Large Scale Preparation. A 200-cm^3, two-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum, was flushed with dry nitrogen; the apparatus was then flame-dried under a flow of dry nitrogen. In the flask was placed $Ru(H)_2(CO)(PPh_3)_3$ (1.284 g, 1.4 mmol) under a flow of nitrogen. To the flask were added 105 cm^3 of toluene, α-tetralone (**4**) (10.22 g, 70 mmol) and triethoxyvinylsilane (13.30 g, 70 mmol). The mixture was heated at 135 °C for 0.5 h with stirring. The solution was allowed to cool to room temperature, and was then transferred into 200-cm^3 round-bottom flask. Toluene was removed by rotary evaporation (40 °C/5 mmHg). The product **5** was isolated by vacuum distillation (138—140 °C/1 mmHg) in 95% yield (22.40 g).

References

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

2) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, and N. Chatani, *Pure Appl. Chem.*, **66**, 1527 (1994).

3) For a first state of the art account: S. Murai, *J. Synth. Org. Chem. Soc., Jpn.*, **56**, 992 (1994).

4) J. P. Keiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).

5) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, **1965**, 843.

6) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970); G. W. Parchall, *CHEMTECH*, **4**, 445 (1974); G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975); D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977); E. L. Muetterties and J. R. Bleeke, *Acc. Chem. Res.*, **12**, 234 (1979); E. L. Muetterties, *Chem. Soc. Rev.*, **11**, 283 (1982); G. W. Parshall, D. L. Thorn, and T. H. Tulip, *CHEMTECH*, **12**, 571 (1982); G. W. Parshall, *CHEMTECH*, **14**, 628 (1984); R. G. Bergman, *Science*, **223**, 902 (1984); A. H. Janowicz, R. A. Periana, J. M. Bichanan, G. A. Kovac, J. M. Stryker, M. J. Wax, and R. G. Bergman, *Pure Appl. Chem.*, **56**, 13 (1984); A. E. Shilov, "Activation of Saturated Hydrocarbons by Transition Metal Complexes," D. Reidel, Dordrecht, Netherlands (1984); R. H. Crabtree, *Chem. Rev.*, **85**, 245 (1985); I. P. Rothwell, *Polyhedron*, **4**, 117 (1985); M. L. H. Green and D. O'Hare, *Pure Appl. Chem.*, **57**, 1897 (1985); J. Halpern, *Inorg. Chim. Acta*, **100**, 41 (1985); W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, **22**, 91 (1989); M. Tanaka, *CHEMTECH*, **19**, 59 (1989); "Activation and Functionalization of Alkanes," ed by C. L. Hill, John Wiley & Sons, Inc., New York (1989); A. D. Ryabov, *Chem. Rev.*, **90**, 403 (1990); A. E. Shilov and G. B. Shul'pin, *Russ. Chem. Rev.*, **9**, 853 (1990); R. G. Bergman, *J. Organomet. Chem.*, **400**, 273 (1990); "Selective Hydrocarbon Activation," ed by J. A. Davies, P. L. Watson, A. Greenberg, and J. F. Liebman, VCH Publisher, Inc., New York (1990); R. G. Bergman, *Adv. Chem. Ser.*, **230**, 211 (1992); M. Pfeffer, *Pure Appl. Chem.*, **64**, 335 (1992).

7) For the stiochiometric cleavage of aromatic C–H bond, see: a) M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, **1971**, 1508; b) C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, **1972**, 1114; c) U. Klabunde and G. W. Parshall, *J. Am. Chem. Soc.*, **94**, 9081 (1972); d) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, **1974**, 1415; e) K. L. T. Wong, J. L. Thomas, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **96**, 3694 (1974); f) S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, **98**, 6073 (1976); g) M. D. Rausch, R. G. Gastinger, S. A. Gardner, R. K. Brown, and J. S. Wood, *J. Am. Chem. Soc.*, **99**, 7870 (1977); h) C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 4080 (1978); i) C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, **101**, 1742 (1979); j) W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, **104**, 4240 (1982); k) P. L. Watson, *J. Chem. Soc., Chem. Commun.*, **1983**, 276; l) W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, **106**, 1650 (1984); m) W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, **108**, 4814 (1986); n) M. Hackett, J. A. Ibers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **110**, 1436 (1988); o) C. Bianchini, D. Masi, A. Meil, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, **110**, 6411 (1988); p) C. K. Ghosh and W. A. G. Graham, *J. Am. Chem. Soc.*, **111**, 375 (1989); q) R. F. Jordan and A. S. Guram, *Organometallics*, **9**, 2116 (1990); r) S. T. Belt, L. Dong, S. B. Duckett, W. D. Jones, M. G. Partridge, and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, **1991**, 266; s) R. M. Chin, L. Dong, S. B. Duckett, M. G. Partridge, W. D. Jones, and R. N. Perutz, *J. Am. Chem. Soc.*, **115**, 7685 (1993); t) E. Gutiérrez, A. Monge, M. C. Nicasio, M. L. Poveda, and E. Carmona, *J. Am. Chem. Soc.*, **116**, 791 (1994).

8) For the stichiometric cleavage of aliphatic C–H bond, see a) S. Komiya and A. Yamamoto, *Chem. Lett.*, **1975**, 475; b) J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 1056 (1976); c) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 3874 (1976); d) S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 7577 (1978); e) M. Berry, K. Elmitt, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, **1979**, 1950; f) J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, **104**, 3723 (1982); g) A. H. Janowicz and R. G Bergman, *J. Am. Chem. Soc.*, **105**, 3929 (1983); h) P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, **106**, 644 (1984); i) P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, **107**, 4581 (1985); j) J. M. Buchannan, J. M. Stryker, and R. G. Bergman, *J. Am. Chem. Soc.*, **108**, 1537 (1986); k) T. T. Wenzel and R. B. Bergman, *J. Am. Chem. Soc.*, **108**, 4856 (1986); l) C. Bianchini, D. Masi, A. Meli, M. Peruzzini, M. Sabat, and F. Zanobini, *Organometallics*, **5**, 2557 (1986); m) M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, **108**, 7433 (1986); n) M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, **108**, 7436 (1986); o) M. Hackett, J. A. Ibers, P. Jernakoff, and G. M. Whitesides, *J. Am. Chem. Soc.*, **108**, 8094 (1986); p) M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, **109**, 2825 (1987); q) C. Bianchini, M. Peruzzini, and F. Zanobini,

J. Organomet. Chem., **326**, C79 (1987); r) M. Hackett and G. M. Whitesides, *J. Am. Chem. Soc.*, **110**, 1449 (1988); s) P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, **110**, 5732 (1988); t) R. S. Shinomoto, P. J. Desrosiers, T. G. P. Harper, and T. C. Flood, *J. Am. Chem. Soc.*, **112**, 704 (1990); u) M. B. Sponsler, B. H. Weiller, P. O. Stoutland, and R. G. Bergman, *J. Am. Chem. Soc.*, **111**, 6841 (1989); v) J. Wu and R. G. Bergman, *J. Am. Chem. Soc.*, **111**, 7628 (1989); w) D. Rabinovich, R. Zelman, and G. Parkin, *J. Am. Chem. Soc.*, **112**, 9632 (1990); x) F. Neve, M. Ghedini, G. D. Munno, and A. Crispini., *Organometallics*, **10**, 1143 (1991); y) K. M. Doxsee, J. J. J. Juliette, K. Zietara, and G. Nieckarz, *J. Am. Chem. Soc.*, **116**, 2147 (1994).

9) S. Murahashi, *J. Am. Chem. Soc.*, **77**, 6430 (1955); S. Murahashi and S. Horiie, *J. Am. Chem. Soc.*, **78**, 4816 (1956); S. Horiie and S. Murahashi, *Bull. Chem. Soc., Jpn.*, **33**, 247 (1960).

10) A patent to Rhome-Paulenc, Netherland Patent 66603115 (1966); *Chem. Abstr.*, **66**, 85483 (1967).

11) A. Misono, Y. Uchida, M. Hidai, and H. Kanai, *J. Chem. Soc., Chem. Commun*, **1967**, 357.

12) P. Hong, H. Yamazaki K. Sonogashira, and N. Hagihara, *Chem. Lett.*, **1978**, 535.

13) a) Y. Lin, D. Ma, and X. Lu, *Tetrahedron Lett.*, **28**, 3249 (1987); b) R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, **111**, 778 (1989); c) S. Rodewald and R. F. Jordan, *J. Am. Chem. Soc.*, **116**, 4491 (1994).

14) S. E. Diamond, A. Szalkiewicz, and F. Mares, *J. Am. Chem. Soc.*, **101**, 490 (1979); P. Hong and H. Yamazaki, *Chem. Lett.*, **1979**, 1335; P. Hong, B.-R. Cho, and H. Yamazaki, *Chem. Lett.*, **1980**, 507; H. Yamazaki and P. Hong, *J. Mol. Catal.*, **21**, 133 (1983); P. Hong and H. Yamazaki, *J. Mol. Catal.*, **26**, 297 (1984); L. N. Lewis and J. F. Smith, *J. Am. Chem. Soc.*, **108**, 2728 (1986).

15) T. Sakakura, T. Sodeyama, and M. Yanaka, *Chem. Lett.*, **1988**, 683; K. Sasaki, T. Sakakura, Y. Tokunaga, K. Wada, and M. Tanaka, *Chem. Lett.*, **1988**, 685; Y. Tokunaga, T. Sakakura, and M. Tanaka, *J. Mol. Catal.*, **56**, 305 (1989).

16) E. J. Moore, W. R. Pretzer, T. J. O'Connell, J. Harris, L. LaBounty, L. Chou, and S. S. Grimmer, *J. Am. Chem. Soc.*, **114**, 5888 (1992). Examples employing nearly equimolecular amounts of the reactants are reported. E. J. Moore, C. Stream, and W. R. Pretzer, U. S. Patent 5081250 (1992); *Chem. Abstr.*, **116**, 174011 (1992).

17) B. J. Fisher and R. Eisenberg, *Organometallics*, **2**, 764 (1983); A. J. Kunin and R. Eisenberg, *J. Am. Chem. Soc.*, **108**, 535 (1986); T. Sakakura and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1987**, 758; T. Sakakura and M. Tanaka, *Chem. Lett.*, **1987**, 249; T. Sakakura, T. Hayashi, and M. Tanaka, *Chem. Lett.*, **1987**, 859; T. Sakakura and M. Tanaka, *Chem. Lett.*, **1987**, 1113; T. Sakakura, K. Sasaki, Y. Tokunaga, K. Wada, and M. Tanaka, *Chem. Lett.*, **1988**, 155; E. M. Gordon and R. Eisenberg, *J. Mol. Catal.*, **45**, 57 (1988); A. J. Kunin and R. Eisenberg, *Organometallics*, **7**, 2124 (1988); T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, and M. Tanaka, *J. Am. Chem. Soc.*, **112**, 7221 (1990); W. T. Boese and A. S. Goldman, *J. Am. Chem. Soc.*, **114**, 350 (1992).

18) M. Tanaka, T. Sakakura, Y. Tokunaga, and T. Sodeyama, *Chem. Lett.*, **1987**, 2373; W. D. Jones, G. P. Foster, and J. M. Putinas, *J. Am. Chem. Soc.*, **109**, 5047 (1987); W. D. Jones and E. T. Hessell, *Organometallics*, **9**, 718 (1990).

19) a) W. D. Jones and W. P. Kosar, *J. Am. Chem. Soc.*, **108**, 5640 (1986); b) G. C. Hsu, W. P. Kosar, and W. D. Jones, *Organometallics*, **13**, 385 (1994).

20) M. Ishikawa, S. Okazaki, A. Naka, and H. Sakamoto, *Organometallics*, **11**, 4135 (1992); Y. Uchimaru, A. M. M. E. Sayed, and M. Tanaka, *Organometallics*, **12**, 2065 (1993); M. Ishikawa, A. Naka, and J. Ohshita, *Organometallics*, **12**, 4987 (1993).

21) T. Sakakura, Y. Tokunaga, T. Sodeyama, and M. Tanaka, *Chem. Lett.*, **1987**, 2375.

22) Several synthetic methods are published, see: a) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, **1968**, 3143; b) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, **1970**, 2947; c) N. Ahmad, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, **1972**, 843; d) R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, **54**, 259 (1973); e) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 48 (1974); f) S. Cenini, A. Mantovani, A. Fus, and M. Keubler, *Gazz. Chim. Ital.*, **105**, 255 (1975). We synthesized the complex according to the procedure described in Ref. 22e.

23) T. R. Gaffney and J. A. Ibers, *Inorg. Chem.*, **21**, 2851 (1982).

24) R. Young and G. Wilkinson, *Inorg. Synth.*, **17**, 75 (1977).

25) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 50 (1974).

26) S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, **1973**, 478; A. Dobson, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **17**, 126 (1977).

27) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 58 (1974).

28) R. H. Crabtree, M. F. Mellea, and J. M. Mihekic, *Inorg. Synth.*, **26**, 22 (1989).

29) M. F. McGuiggan and L. H. Pignolet, *Inorg. Chem.*, **21**, 2523 (1982).

30) a) M. Gozin, A. Weisman, Y. Ben-Davis, and D. Milstein, *Nature*, **364**, 699 (1993); b) M. Gozin, M. Aizenberg. A.-Y., Liou, A. Weisman, Y. Ben-Davis, and D. Milstein, *Nature*, **370**, 42 (1994).

31) W. A. Gustavson, P. S. Epstein, and M. D. Curtis, *Organometallics*, **1**, 884 (1982).

32) R. Heys, *J. Chem. Soc., Chem. Commun.*, **1992**, 680.

33) R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. A. Parnell, J. M. Quirk, and G. E. Morrid, *J. Am. Chem. Soc.*, **104**, 6994 (1982); R. H. Crabtree, M. F. Mellea, F. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, **104**, 107 (1982).

34) W. D. Jones, "Selective Hydrocarbon Activation," ed by J. A. Davies, P. L. Watson, A. Greenberg, and J. F. Liebman, VCH Publisher, Inc., New York (1990), Chap.5.

35) J. F. Hartwig, R. A. Andersen, and R. G. Bergman, *J. Am. Chem. Soc.*, **113**, 6492 (1991); R. H. Heyn and K. G. Caulton, *J. Am. Chem. Soc.*, **115**, 3354 (1993).

36) The structure of **74** was determined by ^{1}H and ^{31}P NMR, and IR spectroscopy.

37) D. E. Linn, Jr., and J. Halpern, *J. Organomet. Chem.*, **330**, 155 (1987); J. Halpern, *Pure Appl. Chem.*, **59**, 173 (1987); See also: D. J. Cole-Hamilton and G. Wilkinson,

Nouv. J. Chim., **1**, 141 (1977).

38) Jones has also shown that the slow step in the catalytic insertion of isonitrile to a C–H bond is not the step of the C–H bond cleavage but the last step involving the reductive elimination.[19b)]

39) M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, **16**, 73 (1977); I. Omae, *Chem. Rev.*, **79**, 287 (1979); I. P. Rothwell, *Acc. Chem. Res.*, **21**, 153 (1985); A. D. Ryabov, *Synthesis*, **1985**, 233; G. R. Newkome, W. E. Puckett, V. K. Gupta, and G. E. Kiefer, *Chem. Rev.*, **86**, 451 (1986).

40) R. J. McKinney and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3066 (1975).

41) D. R. Saunders and R. J. Mawby, *J. Chem. Soc.*, **1984**, 2133. For the C–H bond cleavage of benzophenone, also see Ref. 37.

42) Similar *ortho* selective C–H bond cleavage was reported by several research groups. For recent examples of *ortho*-metallated aryl ketone complexes, see: D. Rabinovich, R. Zelman, and G. Parkin, *J. Am. Chem. Soc.*, **112**, 9632 (1990); R. C. Cambie, M. R. Metzler, P. S. Rutledge, and P. D. Woodgate, *J. Organomet. Chem.*, **429**, 41 (1992); R. C. Cambie, M. R. Metzler, P. S. Rutledge, and P. D. Woodgate, *J. Organomet. Chem.*, **429**, 59 (1992); N. P. Robinson, L. Main, and B. K. Nicholson, *J. Organomet. Chem.*, **430**, 79 (1992).

43) B. A. Markies, P. Wijkens, H. Kooijman, A. L. Spek, J. Boersma, and G. van Koten, *J. Chem. Soc., Chem. Commun.*, **1992**, 1420.

44) "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and C. H. Heathcock, Pergamon Press, Oxford, U. K. (1991).

45) The new catalytic reaction can also be extended to nitrogen analogues.[3)] See also, Y.-G. Lim, Y. H. Kim, and J.-B. Kang, *J. Chem. Soc., Chem. Commun.*, **1994**, 2267.

46) P. D. Croce, R. Ferraccioli, and A. Ritieni, *Synthesis*, **1990**, 212.