Pergamon

Tetrahedron 55 (1999) 3937–3948

TETRAHEDRON

Michael Additions of Carbonucleophiles to Butenone Catalyzed by the Non-Hydride $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ Complex

Michel Picquet, Christian Bruneau, Pierre H. Dixneuf*

UMR 6509 : CNRS - Université de Rennes, Laboratoire de Chimie de Coordination et Catalyse, Campus de Beaulieu, F-35042 Rennes, France

Received 12 October 1998; accepted 1 February 1999

Abstract: $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ in acetonitrile is an efficient catalyst precursor for the Michael addition of soft carbonucleophiles to butenone. The utilization of terminal alkynes as donors makes possible the selective formation of γ,δ-ynones. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: ruthenium catalysis ; Michael addition ; ynones

INTRODUCTION

The creation of carbon-carbon bonds *via* C-H activation has a tremendous potential for organic synthesis provided that catalytic reactions under mild conditions and high selectivity are found. The Michael addition constitutes an efficient reaction to form carbon-carbon bonds with atom economy. It was initially carried out in the presence of strong bases,[1] however, the required alkaline conditions were not suitable for a variety of functional groups and have brought several limitations to its utilization in organic synthesis. Catalytic reactions under milder conditions were discovered using various transition metal precatalysts based on nickel,[2] copper,[3] cobalt,[4] rhodium,[5] iron[6] and lanthanide salts.[7] Recently, ruthenium complexes have shown their power to activate inert C-H bond of arenes[8] and conjugated alkenes,[9] to promote ene coupling reactions,[10] and catalyze the aldol[11,12] and Michael reactions[12-14] from stabilized carbonucleophiles, most of them with atom economy. Up to now, the ruthenium-catalyzed Michael reactions were performed under neutral conditions in the presence of non-basic hydridoruthenium complexes such as $RuH_2(PPh_3)_4$ or $(dppe)_2RuH(\eta^1\text{-acac})$,[12-14] which due to their

* E-mail: pierre.dixneuf@univ-rennes1.fr FAX: (33)2 99 28 69 39

0040-4020/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(99)00115-5

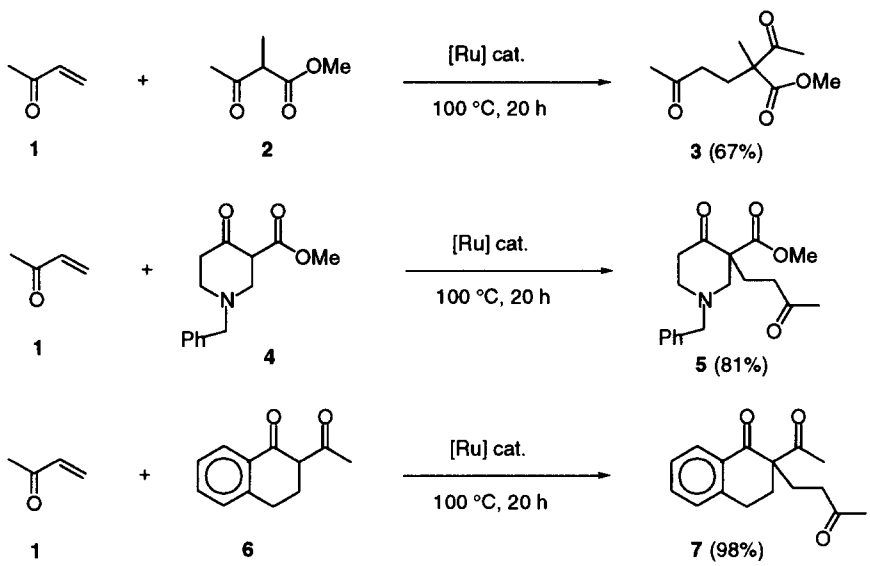
hydride character, were able to deprotonate pronucleophiles. We now report that a variety of carbonucleophiles can be added to butenone in acetonitrile in the presence of a non-hydride binuclear ruthenium catalyst of the type $[Ru(O_2CH)(CO)_2(PR_3)]_2$. Moreover, this catalytic system makes possible the first utilization of terminal alkynes as Michael donors to afford γ,δ-ynones.

RESULTS AND DISCUSSION

1. Addition of pronucleophiles RCH(Z¹)(Z²) to butenone

The reaction of 10 mmol of butenone **1** with 5 mmol of the ketoester **2** in acetonitrile at 100 °C for 20 h in the presence of 0.025 mmol of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ **I**[15] led to the complete conversion of the starting pronucleophile and the Michael adduct **3** was selectively formed and isolated in 67% yield (Scheme 1).

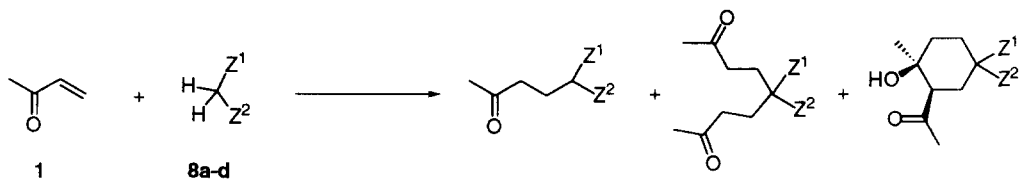
Scheme 1



Similarly, the functional piperidinone **4** and the aromatic diketone **6** were treated with butenone in the presence of **I** at 100 °C for 20 h to produce the addition compounds **5** and **7** in 81 and 98% yield, respectively. These experiments show that the Michael addition of carbopronucleophiles containing one labile proton to butenone can be selectively performed in acetonitrile in the presence of non-hydride ruthenium complexes of type **I**. The reaction of 5 mmol of butenone **1** with 5 mmol of diethylmalonate **8a** in acetonitrile at 80 °C for 20 h in the presence of 0.5 mol% of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ **I** led the complete conversion of the starting compound and the Michael adduct **9a** was highly selectively formed and isolated in 68% yield (Table 1). When the reaction was performed starting from 0.5 equivalent of the pronucleophile **8a**, besides **9a** (39%), the formation of the cyclic compound **11a** was observed (31%). It likely results from an intramolecular ruthenium-catalyzed aldol reaction of the dialkylated malonate intermediate **10a** *via in situ* generation of an enolate which reacts intramolecularly with the carbonyl group under the control of the metal centre to stereoselectively afford **11a** with the hydroxy cis to the acetyl group, as already reported.[14] The fact that no dialkylated compound **10a**

was observed shows that at 80 °C the cyclization is very fast and takes place as soon as the second Michael addition occurs. It was possible to selectively obtain **11a** in 59% isolated yield by performing the reaction at 100 °C with an excess of the acceptor **1**. The reaction of penta-2,4-dione **8b** with but-3-en-2-one at 100 °C in a 1:1 ratio afforded the monoalkylation product **9b** in 49% yield. The reaction of 0.5 equivalent of ethyl nitroacetate **8c** or cyanoacetate **8d**, containing more acidic methylene protons, with but-3-en-2-one promoted by catalyst **I** at 100 °C led to the dialkylation compounds, but the acyclic diketones **10c** (50%) and **10d** (57%) were isolated as the major products (Scheme 2 - Table 1).

Scheme 2



a : $Z^1 = Z^2 = CO_2Et$
b : $Z^1 = Z^2 = COMe$
c : $Z^1 = NO_2$, $Z^2 = CO_2Et$
d : $Z^1 = CN$, $Z^2 = CO_2Et$

Table 1 : Michael addition of carbonucleophiles to butenone catalyzed by $[Ru(O_2CH)(CO)_2(PPh_3)]_2$

pronucleophile	**1/2** ratio	temp. (°C)	**9** (%)	**10** (%)	**11** (%)
8a	1	80	**9a** (68%)		
8a	2	80	**9a** (39%)		**11a** (31%)
8a	3	100			**11a** (59%)
8b	1	100	**9b** (49%)		
8c	2	100		**10c** (50%)	
8d	2	100		**10d** (57%)	**11d** (31%)

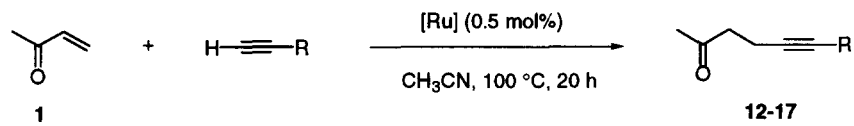
General conditions : pronucleophile **8** (5 mmol), complex **I** (0.025 mmol), acetonitrile (3 ml), 20 h, yield based on **8**.

It is noteworthy that the Michael addition of carbopronucleophiles to butenone in the presence of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ as catalyst precursor requires a higher temperature than the hydrido complexes $RuH_2(PPh_3)_4$[12,14] and $Ru(C_6H_4PPh_2)H(C_2H_4)(PPh_3)_2$,[12] but exhibit a similar behaviour as $(dppe)_2RuH(\eta^1\text{-acac})$ or $(dppe)_2RuH(\eta^1\text{-}O(MeO)C{=}CHCO_2Me)$[13] which proceed at 50-70 °C.

2. *Addition of terminal alkynes to butenone*

Terminal alkynes represent another class of potential carbonucleophiles. They are less acid compounds than the previous carbopronucleophiles and do not react at room temperature with Michael acceptors such as butenone and acrylonitrile in the presence of a ruthenium hydride catalyst precursor.[14] On the other hand, terminal alkynes are known to dimerize in the presence of such catalysts.[16] We have now found that the use of the binuclear catalyst **I** in acetonitrile at 100 °C selectively affords γ,δ-ynones resulting from Michael addition of terminal alkynes to butenone (Scheme 3).

Scheme 3



1 **12-17**

Table 2 : Ruthenium-catalyzed addition of terminal alkynes to butenone

R	ynone	Yield (%)[a]
C_6H_5	**12**	74[b]
p-NO_2-C_6H_4	**13**	34[b]
CH_2=C(Me-	**14**	42[b]
Me_3Si	**15**	46[c]
Bu^n	**16**	29[c]
Bu^t	**17**	20[c]

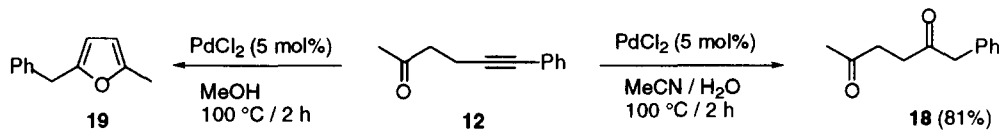
[a] Yield based on the terminal alkyne ; [b] $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**I**) used as catalyst ;[c] $[Ru(O_2CH)(CO)_2(PMe_3)]_2$ (**II**) used as catalyst

Thus, phenylacetylene cleanly reacts with butenone to give 6-phenylhex-5-yn-2-one **12** in 74% yield (Table 2). The presence of an attracting group in para-position of the phenyl ring favours the dimerization reaction from *p*-NO_2-C_6H_4-C≡C-H and 20% of 1,4-di(*p*-nitrophenyl)but-1-en-3-yne were isolated, decreasing the production of ynone **13** to 34% isolated yield. Thus, it appears that the complex **I** is much less active than hydridoruthenium complexes towards the dimerization of arylacetylenes[17] and makes possible the formation of the ynone in satisfactory yield. The addition of phenylacetylene to cyclohexenone was unsuccessful, which indicated that the ruthenium-catalyzed reaction was subject to steric hindrance. Aliphatic alkynes were less reactive, however the catalytic addition of 2-methylbut-1-en-3-yne to butenone gave 42% of the enynone **14**. On the other hand, saturated aliphatic alkynes such as n-hex-1-yne, *tert*-butylacetylene and trimethylsilylacetylene exhibited poor reactivity. The modification of the ruthenium catalyst **I** into **II** by changing PPh_3 to PMe_3 led to an improved catalytic activity and the corresponding ynone derivatives could be produced in 29% (**16**), 20% (**17**) and 46% (**15**) yield, respectively (Table 2). We have shown that no addition took place in the presence of PPh_3 alone, which confirmed that the reaction required the action of the ruthenium catalyst. This catalytic addition of terminal aliphatic alkynes to an activated olefin in the presence of the binuclear

$Ru^{(I)}$ catalyst precursor **I** or **II** contrasts with the formation of conjugated dienes catalyzed by Ru(cycloocta-1,5-diene)(cycloocta-1,3,5-triene) *via* oxidative coupling of the two unsaturated bonds at the Ru(0) centre.[18]

The γ,δ-acetylenic ketone **12** could be regioselectively hydrated[19] in the presence of $PdCl_2$ (5 mol%) at 100 °C in a $MeCN/H_2O$ mixture to give the 1,4-diketone **18** in 81% yield (Scheme 4). In the absence of water, the same ketone **12** was transformed with atom economy into the furan **19** at 100 °C in methanol *via* intramolecular addition of an enolate intermediate to the triple bond (Scheme 4).

Scheme 4



19 **12** **18** (81%)

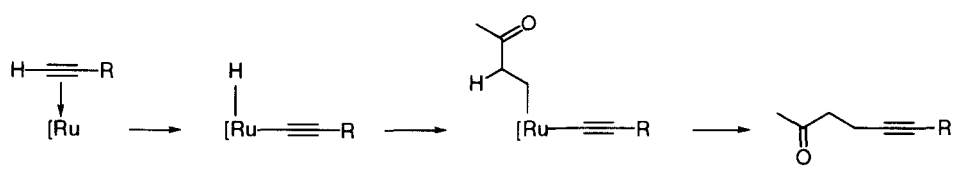
It is noteworthy that the two-step ruthenium-catalyzed Michael addition followed by palladium-catalyzed hydration affords the 1,4-diketone, while the direct three-component reaction of terminal alkyne, enone and water in the presence of (cyclopentadienyl)RuCl(cycloocta-1,5-diene))/NH_4PF_6 as catalyst precursor selectively gives the 1,5-diketone.[20]

3. Mechanism discussion

The mechanism of the addition of nucleophiles containing a coordinating functionality such as a nitrile or an ester group has been studied in details with Ru-H complexes.[12-14] It is assumed that the coordination of the functional group CO_2R or CN to the Lewis acid ruthenium centre provokes the labilization of the acidic proton and the generation of the enolate. The addition of the coordinated enolate to the Michael acceptor would then occur in the coordination sphere of the metal. It is noteworthy that among a variety of solvents tested for the reactions reported above involving either activated methylene derivatives or terminal alkynes, only the coordinating acetonitrile was a suitable solvent.

From terminal alkynes, the mechanism must be different. The η^2-coordination of the triple bond to the ruthenium centre followed by oxidative addition could be postulated. Then, the insertion of the double bond of the enone into the Ru-H bond, followed by reductive elimination would give the γ,δ-ynone (Scheme 5).

Scheme 5



In both cases, the starting ruthenium complex is recovered unchanged at the end of the catalytic reaction which shows that the complex is very robust and no ligand seems to be completely removed during the catalytic

cycle. This observation seems to indicate that the creation of vacant sites on the ruthenium centre is due to the hemilability of the formate assembling ligand.

CONCLUSION

The Michael addition of soft carbonucleophiles to butenone takes place in acetonitrile in the presence of $[Ru(O_2CH)(CO)_2(PR_3)]_2$ as catalyst, showing that the abstraction of proton does not require the presence of a preformed hydrido ruthenium precatalyst. However, the compounds and selectivities obtained with pronucleophiles containing one or two acidic protons are very similar to those obtained in the presence of hydrido ruthenium catalyst precursors. The predominant advantage of the binuclear complexes **I** and **II** is that they make possible the utilization of terminal alkynes as Michael donors and offer a new preparation of γ,δ-ynones from butenone. The resulting ynones have potential for selective access to 1,4-diketones or furans *via* palladium catalysis.

EXPERIMENTAL

All experiments were carried out in dry Schlenk tubes under an inert atmosphere of nitrogen. Acetonitrile (HPLC grade) was used without purification. Diethyl ether, pentane and dichloromethane were distillated over sodium/benzophenone, calcium hydride and phosphorus pentoxide, respectively. Flash column chromatography was performed over Merck silicagel 30-60 μm. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 200 at 200.130 and 50.32 MHz. IR spectra were recorded on a Nicolet 205 FTIR-spectrometer and GC-MS chromatography on a CE instruments GC 8000 Top (capillary column OV1 25 m x 0.32 mm, 0.1- 0.15 μm) coupled with an Automass II Finnigan Mat mass spectrometer operating under 75 eV. Elemental analyses were obtained from "Le Service de Microanalyses du C.N.R.S.", Vernaison, France.

Typical experiment for Michael additions catalysed by $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$: Butenone (1 to 3 eq.) was added to a mixture of pronucleophile (5 mmol), $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$[15] (0.025 mmol) and acetonitrile (3 ml). The mixture was stirred and heated at 80-100 °C for 20 hours. The crude mixture was evaporated and purified by column chromatography over silica gel or by distillation.

Methyl 2-acetyl-2-methyl-5-oxohexanoate (3). Obtained from methyl 3-methylacetylacetate **2** (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless oil (0.667 g, 67%) after a bulb-to-bulb distillation (Kugelrohr) at 110 °C under 1 mm Hg; IR ν/cm^{-1} 2993, 2954 (C-H), 1745 (C=O ester), 1714 (C=O ketone), 1258 (C-O); ^1H NMR δ (200 MHz, $CDCl_3$) 3.67 (s, 3 H, OMe), 2.50-2.29 (m, 2 H, CH_2), 2.09 (s, 3 H, COMe), 2.08 (s, 3 H, COMe), 2.22-1.09 (m, 2 H, CH_2), 1.28 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) 207.30 (C=O), 205.28 (C=O), 173.08 (CO_2), 58.57 (C), 52.44 (OMe), 38.51 (CH_2CO), 29.87 (COMe), 28.34 (CH_2), 26.11 (COMe), 19.29 (Me); GC-MS (Relative Intensity) 158 ([M^+] - [CH_2CO], 20), 130 (8), 126 (20), 125 (19), 102 (7), 101 (86), 99 (18), 98

(95), 97 (17), 83 (12), 73 (13), 70 (10), 69 (32), 59 (20), 58 (39), 55 (23), 53 (8), 44 (11), 43 (100), 42 (9), 41 (28), 39 (16), 29 (14), 27 (19); Anal. calcd. for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.47; H, 8.22.

Methyl 1-benzyl-4-oxo-3-(3-oxobutyl)-3-piperidine carboxylate (5). Obtained from methyl 1-benzyl-4-oxo-3-piperidine carboxylate **4** (4.6 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 21 h at 100 °C as a colorless viscous oil (1.19 g, 81%) after column chromatography using ether/pentane (3:1) as eluent: IR ν/cm^{-1} 3039 (arom. CH), 2959, 2923, 2813 (alkyl CH), 1749 (C=O ester), 1709 (C=O ketone), 1636 (C=C), 1215 (C-O); ^{1}H NMR δ (200 MHz, $CDCl_3$)) (attribution based on ^{1}H-^{13}C 2D experiment) 7.36-7.15 (m, 5 H, Ph), 3.66 (s, 3 H, OMe), 3.52 (d, 2 H, J = 2.1 Hz, $N\underline{CH_2}CH_2$), 3.28 (dd, 1 H, J = 11.5 and 2.5 Hz, $N\underline{CH_2}C$), 3.03-2.88 (m, 1 H, $N\underline{CH_2}Ph$), 2.87-2.73 (m, 1 H, $NCH_2\underline{CH_2}CO$), 2.60 (ddd, 1 H, J = 17.4, 10.4 and 4.9 Hz, $\underline{CH_2}CO$), 2.48-2.29 (m, 2 H, $N\underline{CH_2}Ph$ + $NCH_2\underline{CH_2}CO$), 2.29-2.05 (m, 2 H, $N\underline{CH_2}CH_2$ + $\underline{CH_2}CO$), 2.03 (s, 3 H, COMe), 1.95 (dd, 1 H, J = 10.2 and 4.9 Hz, $\underline{CH_2}CH_2CO$), 1.70 (m, 1 H, $\underline{CH_2}CH_2CO$); ^{13}C NMR (50 MHz, $CDCl_3$) 207.41 ($CH_2\underline{C}OC$), 206.27 (C=O), 172.03 (C=O ester), 137.79 (C ipso Ph), 128.87, 128.28, 127.43 (CH Ph), 61.69 ($N\underline{C}H_2C$), 61.18 ($N\underline{C}H_2CH_2$), 60.39 (C), 53.65 ($N\underline{C}H_2Ph$), 52.29 ($CO_2\underline{Me}$), 40.45 ($NCH_2\underline{C}H_2CO$), 38.82 ($\underline{C}H_2CO$), 29.89 ($CO\underline{Me}$), 25.67 (CH_2); Anal. calcd. for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30. Found: C, 67.98; H, 7.38.

2-Acetyl-2-(3-oxobutyl)-1-tetralone (7). Obtained from 2-acetyl-1-tetralone **6** (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless oil (1.27 g, 98%) after column chromatography using ether/pentane (1:1) as eluent: IR ν/cm^{-1} 3050, 3025 (arom. CH), 2933 (alkyl CH), 1712 (C=O), 1676 (C=O), 1600 (C=C); ^{1}H NMR δ (200 MHz, $CDCl_3$)) (attribution based on ^{1}H-^{13}C 2D experiment) 8.09 (dd, 1 H, ^{3}J = 7.8 Hz, ^{4}J = 1.0 Hz, arom. CH), 7.54 (dt, 1 H, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, arom. CH), 7.37 (dt, 1 H, ^{3}J = 7.8 Hz, ^{4}J = 1.3 Hz, arom. CH), 7.27 (d, 1 H, ^{3}J = 7.6 Hz, arom. CH), 3.05 (m, 2 H, Ar-CH_2), 2.63 (m, 2 H, $ArCH_2\ \underline{CH_2}$), 2.60-2.47 (m, 2 H, CH_2CO), 2.23 (t, 2 H, ^{3}J = 7.5 Hz, CH_2CH_2CO), 2.18 (s, 6 H, 2 COMe), 2.02 (m, 1 H, $ArCH_2\ \underline{CH_2}$); ^{13}C NMR (50 MHz, $CDCl_3$) 207.56 (C=O), 206.27 (C=O), 197.57 ($Ar\underline{C}O$), 143.25 (C Ar), 134.01, 128.94, 127.81, 126.91 (arom. CH), 131.84 (C Ar), 62.75 ($CO\underline{C}CO$), 38.38 ($\underline{C}H_2CO$), 30.00 ($CO\underline{Me}$), 29.97 ($ArCH_2\underline{C}H_2$), 27.00 ($CO\underline{Me}$), 26.93 ($\underline{C}H_2CH_2CO$), 25.53 ($Ar\underline{C}H_2$); GC-MS (Relative Intensity) 258 ([M$^+$], 1), 222 (9), 216 (14), 215 (12), 198 (22), 197 (10), 188 (29), 183 (11), 173 (7), 160 (12), 159 (82), 158 (25), 157 (63), 155 (8), 146 (49), 145 (35), 141 (8), 132 (7), 131 (37), 130 (7), 129 (24), 128 (24), 127 (13), 118 (38), 117 (8), 116 (11), 115 (36), 103 (9), 91 (41), 90 (58), 89 (31), 77 (15), 65 (9), 63 (10), 55 (10), 51 (9), 43 (100), 39 (12), 27 (9); Anal. calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.60; H, 7.48.

Diethyl 2-(3-oxobutyl) malonate (9a). Obtained from diethylmalonate (5 mmol), butenone (5 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 80 °C as a colorless liquid (0.789 g, 68%) after a bulb-to-bulb distillation (Kugelrohr) at 112 °C under 1 mm Hg; IR ν/cm^{-1} 2960, 2930 (C-H), 1728 (C=O ketone + ester), 1254, 1231 (C-O); ^{1}H NMR δ (200 MHz, $CDCl_3$) 4.16 (q, 4 H, ^{3}J =

7.1 Hz, O<u>CH</u>$_2$), 3.35 (t, 1 H, ^{3}J = 7.2 Hz, CH), 2.51 (t, 2 H, ^{3}J = 7.2 Hz, CH-<u>CH</u>$_2$), 2.10 (s, 3 H, COMe), 2.25-2.05 (m, 2 H, J = 7.2 Hz, <u>CH</u>$_2$CO), 1.23 (t, 6 H, ^{3}J = 7.1 Hz, OCH$_2$<u>CH</u>$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) 207.08 (C=O), 169.03 (<u>C</u>O$_2$Et), 61.32 (O<u>C</u>H$_2$), 50.59 (CH), 40.35 (<u>C</u>H$_2$CO), 29.80 (CO<u>Me</u>), 22.38 (CH<u>C</u>H$_2$), 13.97 (<u>C</u>H$_3$CH$_2$O); GC-MS (Relative Intensity) 230 ([M$^+$], 1), 185 (14), 173 (7), 169 (8), 160 (32), 141 (7), 140 (5), 139 (52), 138 (7), 133 (18), 127 (18), 115 (9), 114 (13), 113 (9), 111 (26), 110 (9), 105 (7), 99 (15), 88 (16), 87 (9), 86 (26), 85 (11), 84 (12), 83 (7), 82 (11), 73 (9), 71 (10), 698 (13), 58 (9), 55 (43), 45(16), 44 (7), 43 (100), 42 (16), 41 (16), 39 (11), 29 (78), 27 (35); Anal. calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found : C, 57.15; H, 7.78.

*Diethyl 3-acetyl-4-hydroxy-4-methylcyclohexane-1,1-dicarboxylate (**11a**).* Obtained from diethylmalonate (5 mmol), butenone (15 mmol) and [Ru(μ-O$_2$CH)(CO)$_2$(PR$_3$)]$_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless oil (0.887 g, 59%) after column chromatography using ether/pentane (1:2) as eluent; IR ν/cm^{-1} 3501 (OH), 2977-2937 (C-H), 1730 (C=O), 1700 (C=O); ^{1}H NMR δ (200 MHz, $CDCl_3$) (indexation based on ^{1}H-^{13}C 2D experiment) 4.33-4.05 (m, 4 H, O<u>CH</u>$_2$), 3.87 (d, 1 H, ^{4}J = 2.5 Hz, OH), 2.72 (dd, 1 H, ^{3}J = 13.1 and 3.3 Hz, H-3), 2.28 (ddd, 1 H, ^{3}J = 13.1, 3.3 and 2.0 Hz, H-2ax.), 2.21 (s, 3 H, COMe), 2.27-2.08 (m, 2 H, H-6ax. + H-6eq.), 1.98 (t, 1 H, J = 13.1 Hz, H-2ax.), 1.64 (ddd, 1 H, J = 14.5, 3.6 and 3.1 Hz, H-5eq.), 1.33-1.29 (m, 1 H, H-5ax.), 1.25 (t, 3 H, ^{3}J = 7.0 Hz, OCH$_2$<u>CH</u>$_3$), 1.19 (t, 3 H, ^{3}J = 7.0 Hz, OCH$_2$<u>CH</u>$_3$), 1.13 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) 214.84 (C=O), 171.21, 170.77 (CO$_2$), 68.62 (C-4), 61.61, 61.43 (O<u>CH</u>$_2$CH$_3$), 54.14 (C-1), 53.09 (<u>C</u>H), 35.38 (CH$_2$-5), 31.06 (Me), 29.47 (CH$_2$-6), 28.70 (CO<u>Me</u>), 25.96 (CH$_2$-2), 14.09, 14.00 (OCH$_2$<u>CH</u>$_3$); GC-MS (Relative Intensity) 282 ([M$^+$] - H$_2$O, 1), 230 (23), 184 (11), 173 (24), 167 (6), 160 (10), 156 (7), 139 (7), 138 (20), 137 (23), 127 (15), 123 (15), 111 (15), 110 (6), 99 (8), 95 (16), 93 (31), 85 (7), 82 (9), 71 (8), 55 (12), 43 (100), 41 (8), 29 (32), 27 (13); Anal. calcd. for $C_{15}H_{24}O_6$: C, 59.99; H, 8.05. Found : C, 59.76; H, 7.95.

*3-Acetylhepta-2,6-dione (**9b**).* Obtained from acetylacetone (5 mmol), butenone (5 mmol) and [Ru(μ-O$_2$CH)(CO)$_2$(PR$_3$)]$_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100°C as a colorless oil (0.414 g, 49%) after a bulb-to-bulb distillation (Kugelrohr) at 109 °C under 1 mm Hg; IR ν/cm^{-1} 2964, 2927 (C-H), 1707 (C=O), 1421, 1362 (C-H); ^{1}H NMR δ (200 MHz, $CDCl_3$) 3.62 (t, 1 H, ^{3}J = 7.0 Hz, CH), 2.33 (t, 2 H, ^{3}J = 7.0 Hz, CH$_2$CO), 2.07 (s, 6 H, 2 COMe), 2.00 (s, 3 H, COMe), 2.05-1.87 (m, 2 H, CH$_2$); ^{13}C NMR (50 MHz, $CDCl_3$) (equilibrium between acetylacetonic form and enolic form) acetylacetonic form: 207.69 (C=O), 207.56 (C=O), 66.73 (CH), 40.46 (CH$_2$CO), 29.90 (CO<u>Me</u>), 28.87 (CO<u>Me</u>), 29.87 (CO<u>Me</u>), 21.40 (CH$_2$); enolic form: 191.13 (<u>C</u>OC=C(OH)Me), 43.85 (C(OH)=CCH$_2$<u>CH</u>$_2$CO), 22.87 (COC=C(OH)<u>Me</u>); GC-MS (Relative Intensity) 170 ([M$^+$], 1), 128 (29), 127 (9), 113 (17), 110 (31), 109 (8), 100 (8), 95 (49), 85 (42), 72 (8), 71 (98), 58 (45), 55 (18), 44 (13), 43 (100), 42 (10), 41 (11), 39 (12), 27 (14); Anal. calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.23; H, 8.42.

*Ethyl 2-nitro-2-(3-oxobutyl)-5-oxohexanoate (**10c**).* Obtained from ethyl nitroacetate (5 mmol), butenone (10 mmol) and [Ru(μ-O$_2$CH)(CO)$_2$(PR$_3$)]$_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless oil (0.680 g, 50%) after column chromatography using ether/pentane (1:3) as eluent : IR ν/cm^{-1}

1747 (C=O ester), 1719 (C=O ketone), 1553 (NO_2), 1360 (NO_2); ^{1}H NMR δ (200 MHz, $CDCl_3$) 4.22 (q, 2 H, ^{3}J = 7.2 Hz, $O\underline{CH_2}CH_3$), 2.41 (m, 8 H, 4 CH_2), 2.12 (s, 6 H, 2 COMe), 1.26 (t, 3 H, ^{3}J = 7.2 Hz, $OCH_2\underline{CH_3}$); ^{13}C NMR (50 MHz, $CDCl_3$) 205.67 (C=O), 166.27 (CO_2), 94.49 (C), 63.05 ($O\underline{C}H_2CH_3$), 37.60 ($\underline{C}H_2CO$), 29.92 (COMe), 28.30 (CH_2), 13.83 (CH_3); GC-MS (Relative Intensity) 181 ([M$^+$] - $CH_3CH_2COCH_3$, 16), 137 (16), 125 (16), 123 (42), 111 (11), 110 (9), 109 (8), 99 (10), 97 (13), 96 (9), 95 (31), 93 (7), 81 (13) , 67 (7), 58 (7), 55 (9), 53 (8), 44 (8), 43 (100), 41 (9), 39 (7), 30 (8), 29 (28), 27 (15); Anal. calcd. for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.87; H, 7.08; N, 5.19. The corresponding cyclised *ethyl 3-acetyl-4-hydroxy-4-methyl-1-nitrocyclohexane-1-carboxylate* and monoaddition product were isolated in mixture, respectively 14% and 6%.

*Ethyl 2-cyano-2-(3-oxobutyl)-5-oxohexanoate (**10d**) and ethyl 3-acetyl-1-cyano-4-hydroxy-4-methylcyclohexane-1-carboxylate (**11d**).* Obtained from ethyl cyanoacetate (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as colorless oils after column chromatography using ether/pentane (1:3) as eluent :

(**10d**) (0.714 g, 57%) : IR ν/cm^{-1} 2983, 2942 (C-H), 2245 (C≡N), 1740 (C=O ester), 1718 (C=O ketone); ^{1}H NMR δ (200 MHz, $CDCl_3$) 4.18 (q, 2 H, ^{3}J = 7.2 Hz, $O\underline{CH_2}CH_3$), 2.75-2.40 (m, 4 H, 2 CH_2CO), 2.10 (s, 6 H, 2 COMe), 2.25-1.90 (m, 4 H, 2 CH_2), 1.25 (t, 3 H, ^{3}J = 7.2 Hz, $OCH_2\underline{CH_3}$); ^{13}C NMR (50 MHz, $CDCl_3$) 205.67 (C=O), 168.11 (CO_2), 118.43 (C≡N), 63.12 ($O\underline{C}H_2CH_3$), 47.94 (C), 39.04 ($\underline{C}H_2CO$), 30.50 (CH_2), 29.98 (CO$\underline{Me}$), 14.04 (CH_3); GC-MS (Relative Intensity) 183 ([M$^+$] - $CHCH_2COCH_3$, 10), 110 (10), 109 (7), 71 (30), 58 (38), 55 (13), 44 (7), 43 (100), 42 (7), 29 (21), 27 (12); Anal. calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.47; H, 7.64; N, 5.67.

(**11d**) (0.393 g, 31%) : IR ν/cm^{-1} 3480 (OH), 2980, 2940 (C-H), 2242 (C≡N), 1743 (C=O ester), 1700 (C=O ketone); ^{1}H NMR δ (200 MHz, $CDCl_3$) 4.25 (q, 2 H, ^{3}J = 7.1 Hz, $O\underline{CH_2}CH_3$), 3.81 (d, 1 H, ^{4}J = 2.5 Hz, OH), 2.86 (dd, 1 H, ^{3}J = 13.0 and 3.5 Hz , CH), 2.26 (s, 3 H, COMe), 2.40-2.12 (m, 2 H, CH_2), 2.12-1.87 (m, 2 H, CH_2), 1.85-1.53 (m, 2 H, CH_2), 1.29 (t, 3 H, ^{3}J = 7.0 Hz, $OCH_2\underline{CH_3}$), 1.22 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) 213.53 (C=O), 168.09 (CO_2), 118.60 (C≡N), 68.43 ($\underline{C}$-OH), 63.05 (OCH_2CH_3), 52.80 (CH), 44.98 (C), 35.02 (CH_2), 31.54 (C-$\underline{CH_3}$), 30.66 (CH_2), 28.39 (CO$\underline{Me}$), 28.08 (CH_2CO), 13.99 ($OCH_2\underline{CH_3}$); GC-MS (Relative Intensity) 183 ([M$^+$] - $CHCH_2COCH_3$, 7), 137 (7), 110 (11), 109 (9), 100 (7), 71 (57), 58 (28), 55 (7), 43 (100), 29 (16), 28 (7), 27 (10).; Anal. calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.62; H, 7.63; N, 5.58.

*6-Phenylhex-5-yn-2-one (**12**).* Obtained from phenylacetylene (20 mmol), butenone (40 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ (0.5 mol%, 0.1 mmol) in acetonitrile (10 ml) after 20 h at 100 °C as a colorless liquid (2.54 g, 74%) after a bulb-to-bulb distillation (Kugelrohr) at 125 °C under 1 mm Hg ; IR ν/cm^{-1} 3075 (arom. CH), 2900 (alkyl CH), 2232 (C≡C), 1718 (C=O), 1491, 1366 (C-H); ^{1}H NMR δ (200 MHz, $CDCl_3$) 7.41-7.28 (m, 2 H, Ph), 7.28-7.15 (m, 3 H, Ph), 2.61 (ddd, A_2B_2 system, 2 H, ^{2}J = 6.8 Hz, ^{3}J = 10.2 and 7.65 Hz, CH_2), 2.72 (ddd, A_2B_2 system, 2 H, ^{2}J = 6.8 Hz, ^{3}J = 10.2 and 7.65 Hz, CH_2), 2.16 (s, 3 H, CH_3);

^{13}C NMR (50 MHz, $CDCl_3$) 207.92 (C=O), 132.99, 129.68, 129.20 (CH Ph), 125.08 (C ipso Ph), 90.10, 82.38 (C≡C), 43.82 ($\underline{C}H_2CO$), 31.25 (CO$\underline{Me}$), 15.41 ($\underline{C}H_2C{\equiv}C$); GC-MS (Relative Intensity) 172 ([M$^+$], 29), 171 (31), 158 (11), 157 (75), 130 (8), 129 (68), 128 (85), 127 (37), 116 (8), 115 (64), 105 (7), 103 (11), 102 (27), 95 (14), 89 (15), 78 (7), 77 (23), 76 (8), 75 (10), 74 (9), 65 (8), 64 (7), 63 (23), 62 (8), 51 (23), 50 (9), 43 (100), 39 (13), 28 (7), 27 (7); Anal. calcd. for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.37; H, 7.09.

6-(p-Nitrophenyl)hex-5-yn-2-one (13). Obtained from *p*-nitrophenylacetylene (2.5 mmol), butenone (5 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ (0.52 mol%, 0.0129 mmol) in acetonitrile (2 ml) after 20 h at 100 °C as a brown powder (0.186 g, 34%) after column chromatography using dichloromethane/pentane (3:1) as eluent ; IR ν/cm^{-1} 3100 (arom. CH), 2922 (alkyl CH), 2224 (C≡C), 1712 (C=O), 1591 (NO_2), 1339 (NO_2); ^1H NMR δ (200 MHz, $CDCl_3$) 8.12 (d, 2 H, J = 8.7 Hz, C_6H_4), 7.47 (d, 2 H, J = 8.7 Hz, C_6H_4), 2.85-2.60 (m, 4 H, 2 CH_2), 2.19 (s, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) 206.11 (C=O), 146.76 (C ipso C_6H_4-NO_2), 132.35 (CH C_6H_4), 130.70 (C ipso C_6H_4), 123.52 (CH C_6H_4), 94.78, 79.51 (C≡C), 42.02 ($\underline{C}H_2CO$), 29.92 (CO$\underline{Me}$), 14.02 ($\underline{C}H_2C{\equiv}C$); GC-MS (Relative Intensity) 217 ([M$^+$], 10), 216 (7), 202 (18), 128 (25), 127 (9), 102 (12), 95 (10), 63 (9), 51 (7), 43 (100) ; Anal. calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.12; H, 5.20; N, 6.24.

7-Methyloct-7-en-5-yn-2-one (14). Obtained from isopropenylacetylene (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 61 h at 100 °C as an unstable colorless liquid (0.289 g, 42%) after a bulb-to-bulb distillation (Kugelrohr) at 65 °C under 1 mm Hg ; IR ν/cm^{-1} 2990, 2931, 2924 (alkyl CH), 2214 (C≡C), 1720 (C=O), 1674 (C=C), 1165 (C-O); ^1H NMR δ (200 MHz, $CDCl_3$) 5.15 (broad s, 1 H, C=CH), 5.10 (m, 1 H, J = 1.6 Hz, C=CH), 2.71-2.58 (m, 2 H, CH_2), 2.57-2.45 (m, 2 H, CH_2), 1.81 (m, 3 H, J = 1.2 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) 206.62 (C=O), 126.95 (CH_2=$\underline{C}$(Me)-), 120.75 ($\underline{C}H_2$=C(Me)-), 87.50, 82.16 (C≡C), 42.43 ($\underline{C}H_2CO$), 29.80 (CO$\underline{Me}$), 23.62 (CH_2=C($\underline{Me}$)-), 14.02 ($\underline{C}H_2C{\equiv}C$); GC-MS (Relative Intensity) 136 ([M$^+$], not seen), 123 (7), 96 (19), 95 (100), 67 (9), 53 (12), 51 (9), 43 (98), 41 (8), 39 (9), 27 (11).

6-Trimethylsilylhex-5-yn-2-one (15). Obtained from trimethylsilylacetylene (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PMe_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless liquid (0.384 g, 46%) after column chromatography using ether/pentane (1:2) as eluent ; IR ν/cm^{-1} 2960, 2920, 2910 (alkyl CH), 2177 (C≡C), 1719 (C=O), 1162 (C-O); ^1H NMR δ (200 MHz, $CDCl_3$) 2.67-2.57 (m, 2 H, CH_2), 2.45-2.35 (m, 2 H, CH_2), 2.10 (s, 3 H, CH_3), 0.15 (s, 9 H, $SiMe_3$); ^{13}C NMR (50 MHz, $CDCl_3$) 206.54 (C=O), 105.59 ($\underline{C}{\equiv}C$-$SiMe_3$), 85.05 (C≡$\underline{C}$-$SiMe_3$), 42.43 ($\underline{C}H_2CO$), 29.90 (CO$\underline{Me}$), 14.42 ($\underline{C}H_2C{\equiv}C$), 0.05 ($Si\underline{Me}_3$).

Decan-5-yn-2-one (16). Obtained from 1-hexyne (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PMe_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as a colorless liquid (0.120 g, 29%) after column chromatography using ether/pentane (1:3) as eluent ; IR ν/cm^{-1} 2959, 2933, 2873, 2863 (alkyl CH), 2213 (C≡C), 1719 (C=O), 1162 (C-O); ^{1}H NMR δ (200 MHz, $CDCl_3$) 2.65 (t, 2 H, J = 7.2 Hz, $\underline{CH_2}$-C≡C), 2.50-2.20 (m, 4 H, 2 CH_2), 2.10 (s, 3 H, CH_3), 1.60-1.10 (m, 4 H, 2 CH_2 ^{n}Bu), 0.85 (t, 3 H, J = 6.8 Hz, $\underline{CH_3}$ ^{n}Bu); ^{13}C NMR (50 MHz, $CDCl_3$) 207.28 (C=O), 80.91, 78.39 (C≡C), 43.03 ($\underline{C}H_2CO$), 31.08 ($CH_3\underline{C}H_2$), 29.72 (CO$\underline{Me}$), 21.92 ($CH_3CH_2\underline{C}H_2$), 18.38 ($CH_3(CH_2)_2\underline{C}H_2C$≡C), 13.62 ($\underline{C}H_3CH_2$), 13.5 (C≡C$CH_2\underline{C}H_2$-C=O).

7,7-Dimethyloctan-5-yn-2-one (17). Obtained from 3,3-dimethylbutyne (5 mmol), butenone (10 mmol) and $[Ru(\mu\text{-}O_2CH)(CO)_2(PMe_3)]_2$ (0.5 mol%, 0.025 mmol) in acetonitrile (3 ml) after 20 h at 100 °C as an colorless liquid (0.384 g, 46%) after a bulb-to-bulb distillation (Kugelrohr) at 75 °C under 2 mm Hg ; IR ν/cm^{-1} 2968 (alkyl CH), 2210 (C≡C), 1719 (C=O); ^{1}H NMR δ (200 MHz, $CDCl_3$) 2.70-2.30 (m, 4 H, 2 CH_2), 2.10 (s, 3 H, CH_3), 1.1 (s, 9 H, CMe_3); ^{13}C NMR (50 MHz, $CDCl_3$) 207.44 (C=O), 89.90, 76.80 (C≡C), 43.18 ($\underline{C}H_2CO$), 31.27 ($C\underline{Me}_3$), 30.01 (CO$\underline{Me}$), 27.29 ($\underline{C}Me_3$), 13.56 ($\underline{C}H_2C$≡C).

REFERENCES

1. (a) Ballini R.; Bosica G. *Tetrahedron Lett.* **1996**, *37*, 8027-8030. (b) Konno M.; Nakae T.; Sakuyama S.; Imaki K.; Nakai H.; Hamanaka N. *Synlett* **1997**, 1472-1474.
2. (a) Nelson J. H.; Howells P. N.; DeLullo G. C.; Landen G. L.; Henry R. A. *J. Org. Chem.* **1980**, *45*, 1246-1249. (b) Irie K.; Miyazu K.; Watanabe K. *Chem. Lett.* **1980**, 353-354.
3. (a) Saegusa T.; Ito Y.; Tomita S.; Kinoshita H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 496-499. (b) Desimoni G.; Invernizzi A. G.; Quadrelli P.; Righetti P. P. *Gazz. Chim. Ital.* **1991**, *121*, 483-485.
4. Brunner H.; Hammer B. *Angew. Chem. Int. Ed. Engl.* **1984**, *32*, 312-313.
5. (a) Sawamura M.; Hamashima H.; Ito Y. *Tetrahedron* **1994**, *50*, 4439-4454. (b) Sawamura M.; Hamashima H.; Ito Y. *J. Am. Chem. Soc.* **1992**, *114*, 8295-8296.
6. (a) Christoffers J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3141-3149. (b) Christoffers J. *Eur. J. Org. Chem.* **1998**, 1259-1266.
7. (a) Keller E.; Feringa B. L. *Tetrahedron Lett.* **1996**, *37*, 1879-1882. (b) Keller E.; Feringa B. L. *Synlett* **1997**, 842-844. (c) Bonadies F.; Lattanzi A.; Orelli L. R.; Pesci S.; Scettri A. *Tetrahedron Lett.* **1993**, *34*, 7649-7650. (d) Soriente A.; Spinella A.; De Rosa M.; Giordano M.; Scettri A. *Tetrahedron Lett.* **1997**, *38*, 289-290. (e) Kotsuki H.; Arimura K. *Tetrahedron Lett.* **1997**, *38*, 7583-7586.
8. (a) Fujii N.; Kakiuchi F.; Yamada A.; Chatani N.; Murai S. *Bull. Soc. Chem. Jpn.* **1998**, *71*, 285-298. (b) Murai S.; Kakiuchi F.; Sekine S.; Tanaka Y.; Kamatani A.; Sonoda M.; Chatani N. *Nature* **1993**,

366, 529-531. (c) Kakiuchi F.; Yamauchi M.; Chatani N.; Murai S. *Chem. Lett.* **1996**, 111-112. (d) Kakiuchi F.; Yamamoto Y.; Chatani N.; Murai S. *Chem. Lett.* **1995**, 681-682.

9. (a) Kashiwagi K.; Sigise R.; Shimakawa T.; Matuura T.; Shirai M.; Kakiuchi F.; Murai S. *Organometallics* **1997**, *16*, 2233-2235. (b) Kakiuchi F.; Tanaka Y.; Sato T.; Chatani N.; Murai S. *Chem. Lett.* **1995**, 679-680. (c) Ohgomori Y.; Ichikawa S.; Sumitani N. *Organometallics* **1994**, *13*, 3758-3760. (d) Patzke B.; Sustmann R. *J. Organomet. Chem.* **1994**, *480*, 65-74. (e) Trost B. M.; Imi K.; Davies I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371-5372. (f) Mitsudo T.; Nakagawa Y.; Watanabe K.; Hori Y.; Misawa H.; Watanabe H.; Watanabe Y. *J. Org. Chem.* **1985**, *50*, 565-571.
10. (a) Ellis W. W.; Odenkirk W.; Bosnich B. *J. Chem. Soc., Chem. Commun.* **1998**, 1311-1312. (b) Trost B. M.; Müller T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985-4986.
11. Lin Y.; Zhu X.; Xiang M. *J. Organomet. Chem.* **1993**, *448*, 215-218.
12. (a) Naota T.; Taki H.; Mizuno M.; Murahashi S.-I. *J. Am. Chem. Soc.* **1989**, *111*, 5954-5955. (b) Murahashi S.-I.; Naota T.; Taki H.; Mizuno M.; Takaya H.; Komiya S.; Mizuho Y.; Oyasato N.; Hiraoka M.; Hirano M.; Fukuoka A. *J. Am. Chem. Soc.* **1995**, *117*, 12436-12451. (c) Murahashi S.-I.; Naota T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1805-1824.
13. Alvarez S. G.; Hasegawa S.; Hirano M.; Komiya S. *Tetrahedron Lett.* **1998**, *39*, 5209-5212.
14. Gomez-Bengoa E.; Cuerva J. M.; Mateo C.; Echavarren A. M. *J. Am. Chem. Soc.* **1996**, *118*, 8553-8565.
15. Seiller B.; Heins D.; Bruneau C.; Dixneuf P. H. *Tetrahedron* **1995**, *51*, 10901-10912.
16. (a) Yamazaki H. *J. Chem. Soc., Chem. Commun.* **1976**, 841-842. (b) Wakatsuki Y.; Yamazaki H. *J. Organomet. Chem.* **1995**, *500*, 349-362. (c) Bianchini C.; Frediani P.; Masi D.; Peruzzini M.; Zanobini F. *Organometallics* **1994**, *13*, 4616-4632. (d) Bianchini C.; Peruzzini M.; Zanobini F.; Frediani P.; Albinati A. *J. Am. Chem. Soc.* **1991**, *113*, 5453-5454. (e) Yi C. S.; Liu N. *Organometallics* **1996**, *15*, 3968-3971.
17. Mitsudo, T.; Nakagawa Y.; Watanabe H.; Watanabe K.; Misawa H.; Watanabe Y. *J. Chem. Soc., Chem. Commun.* **1981**, 496-497.
18. Mitsudo T.; Zhang S.-W.; Nagao M.; Watanabe Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598-599.
19. (a) Imi K.; Imai K.; Utimoto K. *Tetrahedron Lett.* **1987**, *28*, 3127-3130. (b) Fukuda Y.; Shiragami H.; Utimoto K.; Nozaki H. *J. Org. Chem.* **1991**, *56*, 5816-5819.
20. Trost B. M.; Portnoy M.; Kurihara H. *J. Am. Chem. Soc.* **1997**, *119*, 836-837.